CIENCIA 14(2), 253 - 260, 2006
Maracaibo, Venezuela

Chemical characterization (C, H, N, and S) of size fractionated particles from a highway tunnel Caracas –Venezuela

Raiza Fernández*, Manuel Martinez and Federico Galarraga

Centro de Geoquímica, Instituto de Ciencias de la Tierra, Facultad de Ciencias, Universidad Central de Venezuela, Apartado 47325, Caracas 1041-Venezuela.

Recibido: 27-06-05 Aceptado: 24-05-06

Resumen

Se recolectaron partículas depositadas en el túnel El Paraíso, localizado al oeste de Caracas (Venezuela) y se separaron en cinco fracciones granulométricas correspondientes a 35, 60, 120, 230 y 325 mallas (500, 250, 125, 60 y 45 μm), estas fueron analizadas para determinar el porcentaje de carbono, hidrógeno, nitrógeno y azufre, adicionalmente fue determinado el contenido de azufre orgánico e inorgánico asociado a las mismas. El objetivo de este estudio es conocer el origen y la distribución de dichos elementos en este tipo de material. En este trabajo se presentan los resultados obtenidos para la fracción granulométrica de 45μm. Los análisis realizados indican la presencia de carbono y azufre en formas tanto orgánica como inorgánica. El azufre inorgánico está presente principalmente como sulfato y el carbono inorgánico corresponde a carbonato de calcio. Ambos elementos, C y S, están enriquecidos en la fracción de menor tamaño (45μm). En lo que respecta al elemento nitrógeno este podría estar principalmente asociado a la materia orgánica ya que este no fue detectado en fase acuosa mediante cromatografía iónica. Las relaciones H/C entre 1,0 y 1,5 sugieren que el elemento hidrógeno está íntimamente asociado a la materia orgánica, específicamente en compuestos tipo hidrocarburos saturados y aromáticos. Estos resultados sugieren que los elementos carbono, hidrógeno, nitrógeno y azufre asociados a la materia orgánica tienen un origen antrópico (emisiones vehiculares).

Palabras clave: Carbono; contaminación; partículas; Azufre; túneles.

Caracterización química (C, H, N, y S) de las fracciones granulométricas de partículas provenientes de un tunel, Caracas-Venezuela

Abstract

Settled particles collected in El Paraiso highway tunnel, located at the western Caracas (Venezuela) have been fractionated in five sizes 35, 60, 120, 230 and 325 meshes (500, 250, 125, 60 y 45 μm) and analyzed for carbon, hydrogen, nitrogen and sulphur; in addition, organic and inorganic content of sulphur were determined. The aim of this work is to gain some insight into elemental composition and distribution of these elements in this kind of material. The results indicated the presence of different organic and inorganic species for both, carbon and sul-

* Autor para la correspondencia. E-mail: raizadelvalle@yahoo.com.

phur elements. Inorganic sulphur is present mainly as sulphate; carbonate is the main chemical form for inorganic carbon. Carbon and sulphur elements were highly concentrated in the fine fraction (45 μm). Nitrogen might be mainly associated to the organic matter since it was no detected in aqueous phase by ionic chromatography. H/C ratio between 1.0-1.5 suggest that the hydrogen is strongly associated to the organic matter, specifically saturated and aromatic hydrocarbons. This result provides evidences of a common input for organic carbon and sulphur by fossil fuel combustion due to motor vehicle emissions.

Key words: Carbon, sulphur, particles, contamination, tunnels.

Introduction

Airborne particulate matter contains C, N, S and many other elements. The elements C, N and S are returned to terrestrial ecosystems and to the oceans by scavenging precipitation and by direct gas phase and particulate matter transfer at the earth surface (1).

Agriculture and industrial activities have changed the balances and quantities of input-output of nutrient elements in many ecosystems, which cause the ecosystems change according to their degree of resistance and adaptation. Human anthropogenic influence of the C, N and S cycles of terrestrial ecosystems is evident in most parts of the world. Humans undoubtedly provide the largest source of C, N and S by combustion of fossil fuel, mainly in automobile engines and power plants.

In urban places, the tunnels represent interesting places for sampling particulate matter, because usually the input of material transported by wind and rain is limited and the particles, rest of hydrocarbons, lubricant and gases, coming from motor vehicles emissions are accumulated.

The studies about the settled particles characterization, especially from tunnels are scarce.

Hering (2) measuring the concentration of poliaromatic hydrocarbons (PAHs) and total carbon in particles from tunnels. Kirchstter et al (3) had done measurements of fine particle and nitrogen oxide emissions from light and heavy duty motor vehicle in order to characterize this kind of emissions.

In Venezuela, the information about carbon, hydrogen, nitrogen and sulphur in this kind of particles from tunnels is poor (4-10). Previous studies have been done in order to correlate the mineralogical and organic chemical composition with the origin (sources) of the C, N, S and H elements. Fernández and Galarraga (7) determine mineralogical composition of settled particles from several tunnels at the Caracas valley.The dominant mineral were quartz, calcite and plagioclase.

More recently Fernández et al. (10) conclude that the organic composition of these samples is dominated by saturated and poliaromatic hydrocarbons.

The aim of this work is to gain some insight into elemental composition and distribution of these elements (C, H, N, and S) in settled particles inside a main tunnel from an urban highway in the Caracas valley.

Results will contribute to an understanding about the processes controlling settled particles composition and human contribution, with emphasis on the particular environmental situation in the Caracas valley.

Experimental

Several composed samples of settled particles from the middle of *El Paraiso* tunnel (año 1998) in the metropolitan area of Caracas, were collected in sealed plastic bags. Dry samples (ambient temperature) were sieved through five sieves (35, 60, 120, 230 and 325 meshes). Determination of C, N and H for each fraction was made by using an elemental analyzer CARLO ERBA Model 1106 with interfaces ERBACARD and EA-

GER 2000 program. Sulphur content analysis was done in a LECO SC-432, with the following experimental conditions: oven temperature 1350°C; comparison level 1%; nominal time analysis, 5 minutes; sample weight 250-350 mg. Quantitative determination of inorganic-S (sulphate) was obtained by area integration under the obtained curve between 80 and 260 seconds in the pirogram against a standard (gypsum). The content of organic-S was obtained by difference from the total content of sulphur.

X-ray diffraction (XRD) analysis was done to determine mineralogical composition of these particles, using Phillips equipment with dust camera and Co anode.

T.A.Instrument TGA-51 was used for thermogravimetric analysis (TGA), in order to establish the different forms of carbon in the samples.

Samples were submitted to Soxhlet extraction and then analyzed by FID gas chromatography using PERKIN ELMER 8500 model equipment, with a SE-54 phase capillary column of 30 m x 0.25 mm internal diameter and 0.25 µm of film thickness. Experimental conditions were 80°C (4min) - 4°/min - 290°C (4min) (7-9, 11)

The identification and determination of organic compounds (saturated and aromatic) was realized using a Perkin-Elmer model Q-MASS 910, with SE-30 capillary column. The chromatographic condition was: initial temperature 80°C (4min)-4°/min-280°C.

Results and Discussion

C, N, H and S concentrations of settled samples

Table I shows the concentration values for total C, N, H and S in each grain size for the sampled tunnel. It can be observed that the largest concentrations values for each element correspond to the smallest grain size (<45µm). These facts suggest that organic matter is concentrated in this fraction.

Enrichment in carbon for the smallest size fraction is more than 50%, respect to the gross fraction (sieve fraction 500-250 µm). Similar enrichment is detected in hydrogen (21%), nitrogen (125%) and sulphur (49%).

Mineral contribution

The mineral phases detected in all fractions from the sample are: quartz (Qtz.30 %), calcite (Cal.20%), plagioclase (Pla.7%), muscovite (7%), chlorite (2%), and Fe-oxides (2%)**,** Figure 1 show the results for the smallest grain size <45µm. These values indicate that the total mineral contribution to the settled particles in the studied tunnel is approximately 68%. Therefore, the remaining 32% is mainly organic matter.

Inorganic composition revealed by XRD is a reflect of the main lithology in Caracas area: outcropping rocks, very near of the studied tunnel, are quartz-muscovite calcareous schists, strongly cutted by quartz and calcite veins (Formación *Las Mercedes).* Other lithologies in Caracas valley include marbles, quartz-feldspate and quartz-albite-epidote schists. Pyrite is a common accessory mineral in marbles and schists of the metamorphic suite around Caracas city (8).

Gypsum presence is inferred by sulphur analysis (see below), but XRD technique can not detected it, presumably due to the low content (< 2%).

Thermogravimetric analysis

The thermogravimetric analysis (Figure 2) illustrate four peaks at temperatures around 120°C, 300°C, 500 °C and 650 °C, associated to the loss of water (120°C), organic compounds (between 300°C - 500°C) and CO_2 from calcite decomposition (650°C). The loss of weight between 300°C - 500°C is derived from organic (saturated and aromatic) compounds of anthropogenic origin. The presence of different peaks in this range of temperature are probably due to the rupture of C-N,C-H,C-O bonds presents in this kind of organic compounds (12).

Table 2 shows that volatile organic matter content in the finest fraction (<45µm) is at least 18%. Carbonates are important constituents of the inorganic matrix of the settled particles (more than 12% CO_2 released in this fraction). The presence of

Table 1
Concentrations of total C, N, H and S in each grain size for the ***Paraiso*** tunnel

Tunnel	Sieve fraction (μm)	Carbon* (± 0.2)	Hydrogen* (± 0.1)	Nitrogen* (± 0.04)	Sulphur* (± 0.006)	Inorganic sulphur * (± 0.009)	Organic sulphur* (± 0.01)
El Paraiso	500-250	10.0	1.4	0.11	0.338	0.238 (70)**	0.10 (30)**
	250-125	9.8	1.4	0.13	0.304	0.226 (74)	0.08 (26)
	125-60	15.4	1.6	0.16	0.356	0.256 (72)	0.10 (28)
	60-45	13.3	1.5	0.20	0.371	0.345 (93)	0.03 (7)
	<45	15.4	1.7	0.25	0.451	0.351 (78)	0.10 (22)

* Expressed as % of the whole sample. ** Values between brackets correspond to percent of the total sulphur.

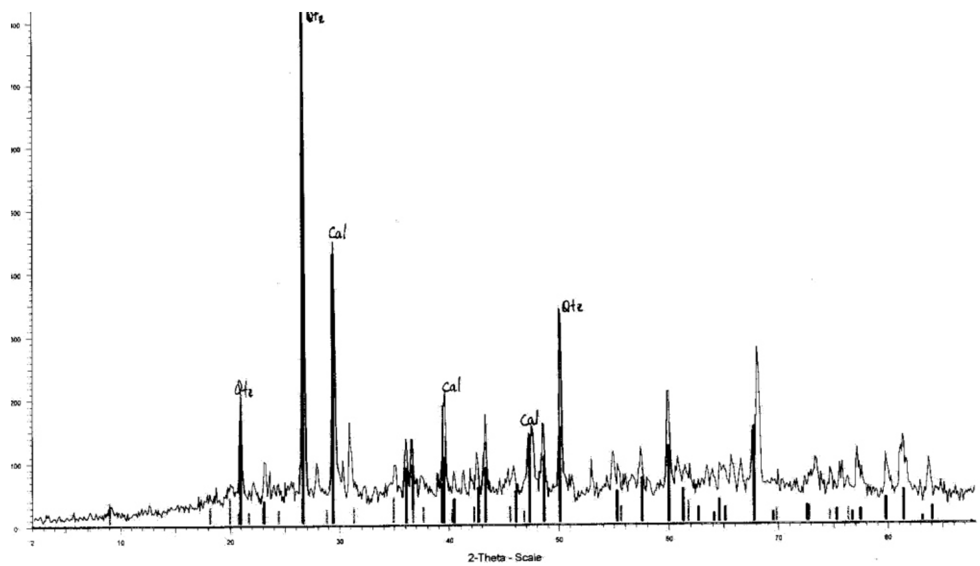

Figura 1. DRW for the fractio >45 μm of the El Paraiso Tunnel sample.

calcite can be deduced from stechiometric relationships, of 27.3% $CaCO_3$. This value is not in concordance with the semi-quantitative calcite determination by XRD (20%). The low confidence in results from XRD only allows establishing a similar magnitude in calcite for both techniques.

The residue from the thermogravimetric analysis is composed by mineral phases, calcium oxide derived from the decomposition of calcite, and refractory, non-volatile organic matter. By stechiometric assumption, it can be deduced that 15.1 % of the total residual is CaO; the remanent is composed by quartz, albite, Fe-oxides and micas (48%). At this moment, we take a good picture of the gross chemical composition of the fraction <45μm of the settled particles in the tunnel (Figure 3). The non-volatile, refractory organic matter must be less than 15%. This value plus the obtained for volatile organic matter by TGA (18%) gives a total of 33 % organic matter, in a very good agreement with the obtained value previously determined by XRD (32%).

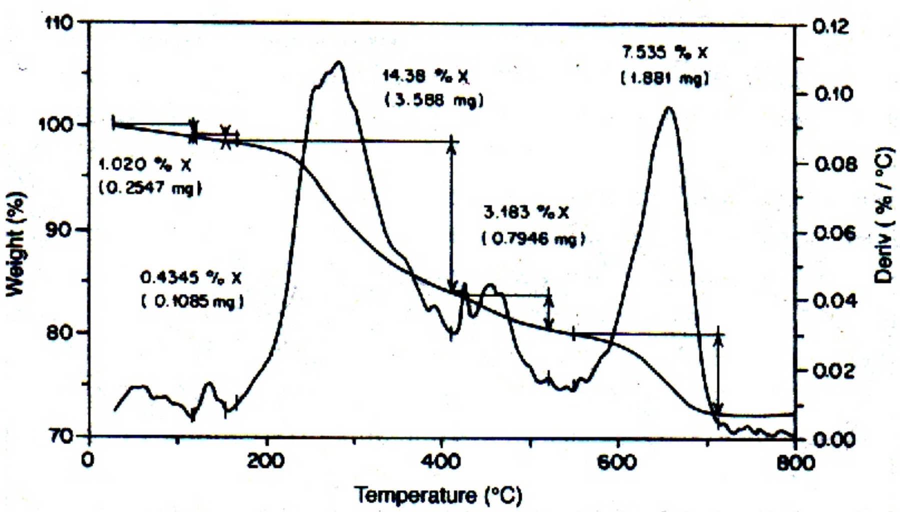

Figure 2. Thermogram from the fraction >45 μm of the El Paraiso Tunnel sample.

Table 2
Percent of different compound in the finest fraction (45m) of the samples.

Temperature	Class of compounds	Percent determined by lost weight (thermogravimetric)
100 °C	Moisture	1.2%
180-500 °C	Volatile organic matter	18.2%
500-700 °C	Carbonates decomposition (as CO_2)	12.1%
Residue	Refractory organic matter; CaO (derived from decomposition of calcite); mineral phases	68.5%

Sulphur content

The pirogram (Figure 4) shows the signals of different forms of sulphur.The first peak correspond to organic-S; while the second peak is associated to inorganic-S (sulphate).These assignation was corroborated using standards.

Table 1 shows the results of total sulphur and also in which forms it might be. The total sulphur values range between 0, 30-0,45 percent. The proportion of organic-S is essentially the same for each grain size.

Inorganic sulphur is firstly due to gypsum, derived from alteration of pyrite and other sources of sulphur. Gypsum estimates in the finest fraction (<45μm), from the inorganic sulphur content, is in the order of 1.9%.

Previous studies revealed that the sulphur in the particles settled inside the tunnel is present

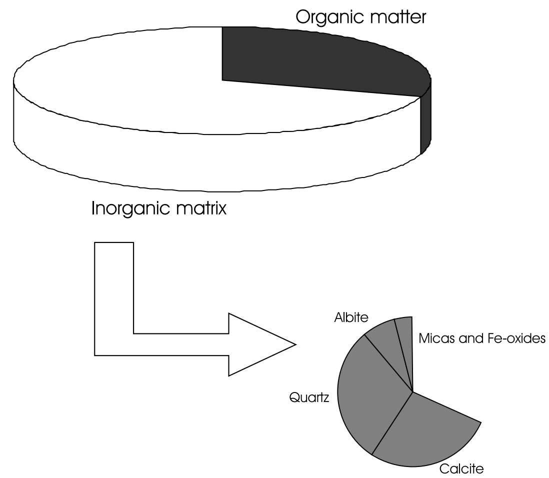

Figura 3. Gross mineralogical composition of the settled particles >45µm.

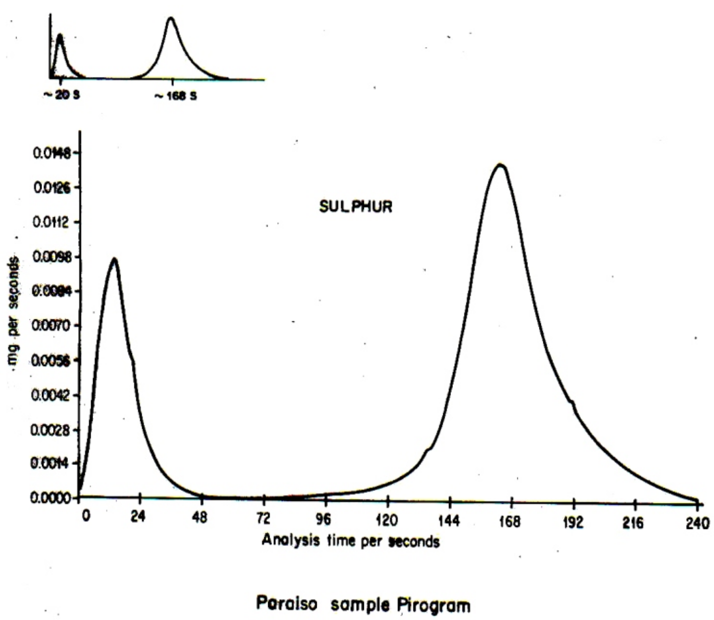

Figure 4. Pirogram obtained for the settled particles >45µm.

in two forms, inorganic-S as (SO_4^{2-}) and organic-S some as alkyl dibenzotiophenes (DBT) (7-11, 13).The results suggest sources from fossil fuel combustion.

Corrected elemental analysis

Table 3 summarizes corrections in the original elemental analysis performed on the finest grain size <45µm of the settled particles of the tunnel. These corrections included carbonate carbon, and hydrogen from water, allowing the elemental composition for the organic fraction of the sample. The most relevant information deduced from this correction is the H/C value: 1.6, typical value of aliphatic organic compounds; this result suggests that the organic matter pre-

Table 3
Corrected elemental analysis for the organic matter present in the settled particles 325 meshes (45m)*.

	Carbon* (± 0.2)	Hydrogen* (± 0.1)	Nitrogen* (± 0.04)	Organic sulfur* (± 0.01)	Elemental H/C
Elemental analysis for the whole sample	15.4	1.7	0.25	0.10	-
Elemental analysis of the organic fraction (ash and moisture free, and corrected by carbonate carbon)	38	5	0.8	0.3	1.6

* Corrections made included: subtraction of carbonate carbon; subtraction of hydrogen from moisture.

Table 4
Ratio of the different organic compounds for El Paraiso Tunnel.

Sample	El Paraiso Tunnel
C_{21}/C_{22}	1.33
C_{27}/C_{29}	2.80
C_{29}/C_{30}	1.20
$C_{23}/C_{23}+C_{30}$	1.20

(H) (m/z 191); C_{27},C_{29} : steranes 14 (H) , 17α (H) y 14 (H) 17β(H), (m/z 217); C_{21},C_{22} pregnane y methyl pregnane.

sent in the settled particles of the studied tunnel is mainly derived of lubricants and oil-derived products, and therefore, anthropogenic in origin (vehicles emissions). Table 4 summarized the molecular ratio for the different steranes and terpenes from the tunnel sample. The greatest ratio of C_{21}/C_{22} (1.33), C_{27}/C_{29} (2.80), C_{29}/C_{30} (1.20) and $C_{23}/C_{23}+C_{30}$ (1.20) indicates that these samples have been altered. This result was corroborated by GC/MS analysis (5-8).

Integration of results

The XRD and TGA information together with the results obtained for C, H, N and S analysis allow estimating a gross chemical composition of the settled particles. An inorganic matrix (~70% in weight) composed by quartz, plagioclase, micas and calcite, adsorbing a complex, organic mixture of oil-derived compounds (~30%), like lubricants, as determined by the geochemical fingerprinting. Regard nitrogen element it might be mainly associated to the organic matter since it was not detected in aqueous phase by ionic chromatography (6). The determination of nitrogenated hydrocarbons are under investigation.

Conclusions

Content of oil derived compounds in the settled particles of the studied tunnel is greatest in the smallest fraction (>45µm). Elemental carbon in this kind of samples is present as both carbonate form (calcite) and as organic carbon (mainly aliphatic structures). The organic matrix represents almost 30-32 % in weight of the smallest fraction (>45µm).

The oil associated to organic matter in the particles is composed by aliphatic hydrocarbons (H/C ~1.6), with a geochemical fingerprint pointing out lubricants and other oil-derived compounds; this anthropogenic material is adsorbed on the surface of the inorganic matrix, composed by quartz, calcite, micas, albite and Fe-oxihyroxides, derived of the metamorphic lithology (quartz-micaceous and calcareous schists) in the zone under study.

Regard nitrogen element it might be mainly associated to the organic matter since it was not detected in aqueous phase by ionic chromatography (6). The determination of nitrogenated hydrocarbons are under investigation.

Acknowledgement

We thank Dr. Armando Ramirez for his valuable suggestions and CDCH for economic support through the project 03-3000179-93-95.

References

1. FRENEY J.R., WILLIAMS C.H. Forms and amounts of sulphur in soils. In Sulphur in Australian (Ivanov and Nicolson editors): Camberra, Australian Academy of Sciences, New York (USA), pp. 170-175,1980.
2. HERING A., MIGUEL H., DOD L. ***The Science of the Total Environment*** 36: 39-45, 1984.
3. KIRCHSTTER T., HARLEY R., KREISBERG N., STOLZENBURG M., HERING S. ***Atmospheric Environment*** 33: 2955-2968, 1999.
4. FERNANDEZ R., RAMIREZ A. Analysis of the particles deposited in The Caracas Tunnels by ICP-AES***. Third Rio Symposium on Atomic Spectrometry*** Caracas (Venezuela), 1994.
5. FERNANDEZ R., GALARRAGA F., RAMIREZ A. Análisis de las Fracciones saturada y aromática en partículas depositadas en túneles del área metropolitana de Caracas. (Analysis of saturate and aromatic fraction in settled particles in highway tunnels from metropolitan area of Caracas). ***ASOVAC*** Caracas (Venezuela), pp. 313-315, 1995.
6. FERNANDEZ R., RAMIREZ A. Geoquímica de la Contaminación Urbana. IV ***Congreso Interamericano sobre Medio Ambiente CIMA'97 (Memorias del Congreso)***. Caracas, (Venezuela) pp. 116-120,1997.
7. FERNÁNDEZ R., GALARRAGA F. ***Environmental Geochemistry and Health*** 23: 17-25, 2001.
8. GONZALEZ DE JUANA C., AROZENA J., PICARD X. ***Geología de Venezuela y sus Cuencas Petrolíferas***. Tomo I. Ediciones FONINVES, Caracas (Venezuela), pp.407-408,1980.
9. FERNÁNDEZ R., GALARRAGA F. BENZO Z. ***Bull Env Cont and Tox*** 68: 525-531, 2002.
10. FERNÁNDEZ R., GAMBOA A., GALARRAGA F, BENZO Z., SALAS J. ***Revista de la Facultad de Ingeniería-UCV*** 2005 (in press).
11. FERNANDEZ R., GALARRAGA F., BENZO Z. ***Rev Sociedad Venezolana de Química*** 23: 3, 2000.
12. GALARRAGA F., FERNÁNDEZ R., RAMIREZ A. Aplicación de la Cromatografía de Gases en la Determinación de Compuestos Poliaromáticos y Organosulfurados. ***COLACRO VI.*** Caracas (Venezuela), 1996.
13. FERNÁNDEZ R., RAMIREZ A., MARTINEZ M. C, N, S, P in Atmospheric Particulate, Venezuela. ***XII ISEB 1995 International Symposium on Environmental Biogeochemistry*** (Brasil), 1995.