

CARBON AND NITROGEN ISOTOPES TO INVESTIGATE THE ORIGIN OF ATMOSPHERIC PARTICLES IN ANTHROPOGENIC AREAS

DOTSIKA E.^{1,2}, RACO B.¹, POUTOUKIS D.³, BATTAGLINI R.⁴, MINARDI I.⁴
and CHANTZI P.²

¹Institute of Geosciences and Earth Resources, Via G. Moruzzi 1, 56124 Pisa, Italy, ²Stable Isotope Unit, Institute of Nanoscience and Nanotechnology, National Centre for Scientific Research. "Demokritos", 153 10 Agia Paraskevi, Attica, Greece ³General Secretariat for Research and Technology, 14-18 Mesogion Ave., 115 10 Athens, Greece, ⁴Massa spin-off, Largo Guido Novello, Firenze, Italy
E-mail: p.chantzi@inn.demokritos.gr

ABSTRACT

To investigate the air pollution from aerosols in Piombino (Tuscany, Italy) bulk aerosol samples were collected to characterize carbonaceous, nitrogenous ionic species and carbon and nitrogen isotopes. Carbon and Nitrogen in atmospheric particles in an urban environment is the result of complex primary and secondary processes. The use of stable carbon and nitrogen-isotope compositions provides clear information on their sources.

Cluster analysis revealed three major sources/pathways for particles: a) industrial plant contribution (PO_4^{3-} , NO_3^- , Si), related to the combustion processes of carbon coke for produce steel, b) natural and anthropogenic origin (metal) and c) spray (Na^+ , Cl^- and SO_4^{2-}) marine aerosol transport. The presence of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ observed in aerosols of Piombino confirmed the origin from anthropogenic sources such as fossil fuel combustion, traffic emissions and industrial contribution.

1. Introduction

Carbonaceous aerosol species include elemental carbon (EC) and organic carbon (OC). Elemental carbon is a primary pollutant emitted directly from combustion sources, whereas organic carbon aerosol is generated from both anthropogenic and biogenic sources (Jacobson *et al.*, 2000). In addition to carbonaceous material, aerosols also include inorganic species that may also be emitted directly to the atmosphere in the particulate phase often as sulfate (SO_4^{2-}) and nitrate (NO_3^-). In this study, we report carbon and nitrogen concentration and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in emissions from different types of PM_{10} sources (road traffic and industry) in the atmosphere over Piombino (Tuscany Italy).

2. Sampling and Analysis of PM_{10}

Piombino (Tuscany) is a small but strongly industrialized city on the Tirreno Sea. The air quality is characterized by the presence of a steel plant and an energy plant. This study is focused on the definition of PM_{10} pollution in the nearness of a landfill mainly composed by inert waste and Conglomix, an industrial plant which transform blast furnace slag in concrete producing diffuse emission of particulate matter.

Sampling period started on November 29, 2010 and ended on December 2010. Low Volume Samplers (LVS) with sampling European Head for PM_{10} with operating flow rate of 2.3 mc/hr were used for collecting (24hr) aerosols samples on quartz fiber filters $\text{Ø}47$ mm of $\text{Ø} 0.4 \mu\text{m}$ equivalent porosity. Chemical (cations, anions, metals) and isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) analysis were carried out. Dionex Ion Chromatography system and optical ICP were used for chemical analysis, while Elemental Analyzer – mass spectrometer (Thermo Finnigan-Delta Plus) were also applied for isotopic determination, respectively. Carbon and nitrogen isotope ratios were calculated in per mil (‰) as follows: $\delta X = [(R \text{ sample}/R \text{ std}) - 1] * 1000$, $X = ^{13}\text{C}$ and $R = ^{13}\text{C}/^{12}\text{C}$ for carbon and $X = ^{15}\text{N}$ and $R = ^{15}\text{N}/^{14}\text{N}$ for nitrogen.

3. Results

3.1. Chemical analysis and Results

Chemical analysis of anions, cations and metals were carried out showing high concentration of calcium expressed in $\mu\text{g}/\text{m}^3$. The presence of furnace slug overlying the investigated area up to the 1 meter depth, which characterized by elevated Ca concentration, probably causes the enrichment of Ca in the investigated soil samples. High calcium concentration in PM_{10} associated to wind erosion action and transport from soil, so it can be a trace of "crustal contribution". High concentrations of phosphates have been measured and in general anions showed higher concentration with respect to cations (except for calcium). Our results concerning metals showed elements with concentration higher than $0.05 \mu\text{g}/\text{m}^3$ and heavy metals present in trace. The first group is mainly composed by silicon, aluminum and iron with concentration of the first group similar for each site, confirming that the cluster Al-Si-Fe represent natural contribution. Heavy metals group is composed by manganese, chromium, barium, nickel, arsenic and copper. "Enrichment Factor" for metals has been calculated according to Wedepohl, 1995. The method is based on the quantitative relations of metals at the top of the crust. Consequently, EF was calculated with the average abundances of continental crust elements. EF values less than 104 indicated that the analyzed metal has crustal origin and was defined as "element not enriched". On the contrary, higher values of 40-50 were indicative of anthropogenic source and were defined as "enhanced elements". Values between the two thresholds indicated mixed origin of the metal. EF value of iron and silicon are typical crustal components, while EF value of nickel and lead (values higher than 50-60) are considered as "enriched elements" associated to industrial activity. Manganese is derived from mixed sources, and the highest EF value is clearly representative of industrial impact on PM_{10} .

The analysis of Pearson matrix showed correlation among sulfate, chlorides, nitrates and phosphates. Moreover enrichment in nitrates with a depletion of chloride observed. This behaviour could be justified due to coastal industrial site of NaCl and nitrate which may react resulting in formation of sodium nitrate, sodium sulfate, sodium bisulphate and thus releasing hydrochloric acid in the gas phase. The following reaction: $\text{NaCl}(s) + \text{HNO}_3(g) = \text{NaNO}_3(s) + \text{HCl}(g)$ may explain the correlation between sodium–nitrate–magnesium (i.e., magnesium is associated to sea salt according the equation: $\text{Sea salt} = \text{Cl}^- + \text{ssNa}^+ + \text{ssSO}_4^{2-} + \text{ssMg}^{2+} + \text{ssCa}^{2+}$) and the reduction of the concentration of chlorine, which is dispersed in the gas phase. In ternary diagram samples collected during the same days, are illustrated with the same shape and colour. Thus, it is possible to observe how the sodium-chloride-nitrate ratio is similar for each site.

3.2. Characterization of pollution-source emissions- Carbon isotopes

Carbon concentrations from pollution sources showed large fluctuations (Widory 2006; Widory and Javoy 2003; Widory *et al.*, 2004), from 1 ‰ to 96 ‰, indicating the different pollution sources. Most of the sources cannot be segregated by their carbon concentrations. However, particles from fuel–oil, and diesel, both have a significantly different $\delta^{13}\text{C}$ from other sources, and at least 2 ‰ inferior to diesel emissions. In fact regular and unleaded fuel combustion particles have similar average $\delta^{13}\text{C}$, respectively -24.57‰ and -24.27‰ , while $\delta^{13}\text{C}$ of diesel particles is about -26.57‰ (Widory 2006; Widory and Javoy 2003; Widory *et al.*, 2004). Thus, the carbon-aerosols can be distinguished between diesel and fuel oil, as well as other sources (e.g., regular and unleaded petrol, coal and natural gas).

Stable isotope analysis of the studied samples of $\delta^{13}\text{C}$ ranged from -29‰ to -24‰ . The analytical results of $\delta^{13}\text{C}$ parameter showed a wider variability in sampling sites where the $\delta^{13}\text{C}$ parameter did not vary significantly. In fact, $\delta^{13}\text{C}$ values, showed a large range spanning over 5 ‰ indicating the probable influence of a multiple pollution source. The $\delta^{13}\text{C}$ in natural reserve is significantly negative ($\delta^{13}\text{C} = -28.5 \text{‰}$), while usually natural site shows values rather positive (3-4‰). This fact may be attributed to the impact of industrial chimney which causes high promoting PM_{10} long transport.

The isotopic values of samples with an isotopic signal between -26.5‰ and -25.0‰ indicated the contribution of traffic emissions. In fact, for most samples $\delta^{13}\text{C}$ is compatible with the range of isotopic compositions of emissions from both regular and unleaded fuel oil, central-heating

sources using domestic fuel oil, coal, and natural gas, as appeared from the above vehicles and heating sources contributed to PM₁₀ pollution.

The sample that had the lowest carbon isotope composition ($\delta^{13}\text{C} < -27$ ‰), indicated an industrial contribution. The position also of these samples in the figure (Fig.1) indicated the contribution of particles from other sources, with $\delta^{13}\text{C} < -29$ ‰, i.e., waste incinerators. In fact, the samples were originated from industrial and landfill area.

The study of $\delta^{13}\text{C}$ clearly identified vehicles, fuel oil emissions and industrial contribution, but it clearly showed its limitations when the contribution from other sources became non negligible.

3.3. Characterization of pollution-source emissions- Nitrogen isotopes

Nitrogen concentrations from pollution sources showed large fluctuations (Widory *et al.*, 2007): Particles by Waste incinerators yielded $\delta^{15}\text{N}$ values from 5.5 ‰ to 8.0 ‰, while particles emitted by the combustion of diesel ($\delta^{15}\text{N}$ from 3.9 ‰ to 5.4 ‰), fuel oil ($\delta^{15}\text{N}$ from -19.4 ‰ to 2.9 ‰) and natural gas ($\delta^{15}\text{N}$ from 2.9 ‰ to 15.4 ‰) indicated very large fluctuations ranged from -19.4 ‰ to 15.4 ‰.

Nitrogen concentrations in PM₁₀ varied from -4.8‰ to 5.6‰ (Fig. 1). Sampling period started on November 29, 2010 and ended on December 4, 2010. So these nitrogen isotopic contents represent the highly enriched values of nitrate formed in winter due to additional positive fractionation resulting from N₂O/NO₃/N₂O₅ equilibrium (Freyer *et al.*, 1993).

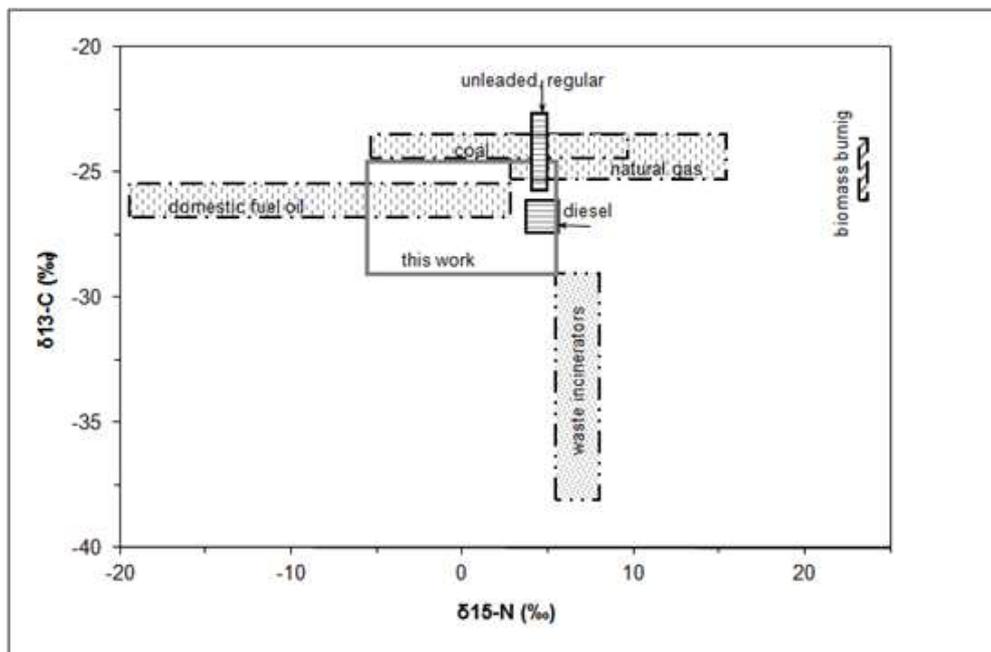


Figure 1: $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ characterization of pollution source emissions and air samples.

These values are comparable to those measured in various urban sites. According to Heaton results (1990), road traffic and point sources are the main pollution sources. In fact, using $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ contents it is possible to discriminate among the different pollution sources; The positive isotopic signal of $\delta^{15}\text{N}$, with rather negative $\delta^{13}\text{C} (< -27)$, is related to the industrial combustion, whereas the negative signal of $\delta^{15}\text{N}$, with rather negative $\delta^{13}\text{C} (-26.5 < \delta^{13}\text{C} < -25.5)$, indicates the contribution of traffic emissions.

4. Conclusions

Both stable carbon and nitrogen isotopes as tracers of aerosols sources in Piombino area give the following results:

- carbon isotope discriminate between vehicles (vehicles) and heating sources (fuel oil, coal, natural gas) from other sources (industrial contribution)

- nitrogen isotopes are an important tool for discriminate between fuel oil and vehicles but indicates its limitations when the contribution from other sources becomes non negligible (natural gas, waste incinerators)
- use of both carbon and nitrogen isotopes is a reliable tool for understand air pollution origin.

REFERENCES

1. Freyer, H.D., Kley, D., Volz-Thomas, A., Kobel, K. (1993), On the interaction of isotopic exchange processes with photochemical reactions in atmospheric oxides of nitrogen. *Journal of Geophysical Research* 98, 14791–14796.
2. Heaton, T. H. E. (1990), $^{15}\text{N}/^{14}\text{N}$ ratios of NO_x from vehicle engines and coal-fired power stations, *Tellus, Ser. B*, 42, 304–307.
3. Jacobson, M.C., Hansson, H.C., Noone, K.J. and Charlson, R.J. (2000), Organic Atmospheric Aerosols: Review and State of the Science. *Rev. Geophys.* 38: 267–294.
4. Wedepohl, K.H. (1995), The composition of the continental crust. *Geochimica et Cosmochimica Acta* 59, 1217–1232.
5. Widory, D. and Javoy, J. (2003), The carbon isotope composition of atmospheric CO_2 in Paris. *Earth and Planetary Science Letters*, 215, 289–298.
6. Widory, D., Roy, S., Le Moullec, Y., Goupil, G., Cocherie, A., Guerrot, C. (2004), The origin of atmospheric particles in Paris: a view through carbon and lead isotopes. *Atmospheric Environment* 38, 953–961.
7. Widory D. (2006), Combustibles, fuels and their combustion products: A view through carbon isotopes, *Combustion Theory and Modelling*, 10:5, 831-841
8. Widory, D. (2007), Nitrogen Isotopes: Tracers of Origin and Processes Affecting PM10 in the Atmosphere of Paris. *Atmos. Environ.* 41, 2382–2390.