SAMPLING AND ANALYSIS OF ORGANIC COMPOUNDS IN DIESEL PARTICULATE MATTER

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Abstract. The fraction of atmospheric semi-volatile organic compounds (SVOC) is partitioned between the gaseous and particulate phases. Certain of these compounds eg. polynuclear aromatic hydrocarbons (PAH) and their derivatives have been shown to exhibit mutagenic or carcinogenic properties. Emissions from diesel engines are an important source of these contaminants. In a dilution chamber, we studied a diesel engine emissions. It is shown firstly, that the gaseous fraction is predominant (by up to 20 times) with respect to the particulate phase. Secondly, the polar compounds, neglected in the majority of previous studies, are the predominant species. A test campaign was carried out in Paris-Porte d’Auteuil which yielded similar results to the laboratory experiments.

Key words: diesel emissions, dilution chamber, atmospheric organic matter, gas/particle partitioning, PAH, oxygenated PAH

1. Introduction

In urban air 50 to 80 % of fine particles come from traffic sources. In France, diesel engines account for 30 % of total traffic. In 1995 the French motor industry estimated that diesel vehicles were the source of 87 % of these particles. The contribution of gasoline vehicles without catalysed engines was 12 % and 1 % for the vehicles with catalysed engines (Société française de santé publique, 1996).

Diesel particles are very small, the average diameter is near 0.2 µm. These particles consist of solid carbonaceous soot particles (black carbon), that are associated with a complex mixture of organic compounds.

This paper presents the results of a laboratory study on diesel particles organic composition (gas and particulate phases) and a comparison with the results obtained in a yield campaign in Paris.

2. Diesel particles

The particle phase of diesel emissions consist of aggregates of spherical carbonaceous particles (about 0.2 µm in mass median aerodynamic diameter), onto which significant amounts of high-molecular-weight organic compounds are adsorbed when the hot engine exhaust cools down to ambient temperature.
The particles in diesel emissions are unique, because they have large surface areas allowing adsorption of organic compounds.

Organic compounds account, typically, for 10 to 40% of the diesel particulate mass. These include high-molecular-weight hydrocarbons and semi-volatile hydrocarbons distributed between the gas and particle (adsorbed) phases (Kado et al., 1996; Simoneit, 1986; Westerholm et al., 1991) depending on physico-chemical properties; e.g. ambient temperature and humidity. This distribution between the two phases can occur during sampling, which leads to modification of the sample composition. Such modifications are called artefacts. The phase partitioning is important since it dictates the pollutants lifetime, hence their transport range and accumulation in the atmosphere. These facts are directly linked to health risk.

We can classify the organic compounds present in diesel particles into three groups:

- aliphatic hydrocarbons: alkanes, alkenes ...
- aromatic hydrocarbons: polycyclic aromatic hydrocarbons (PAH)
- polar hydrocarbons: oxygenated and nitrated PAH, dicarboxylic acids, alcanoic acids... (Allen et al., 1997)

Diesel particles have been classified by the “Centre International de Recherche sur le Cancer (CIRC)” and the US EPA (Environmental Protection Agency) as being “probably carcinogenic” in humans (Classe 2a of CIRC), and several hydrocarbons present in these particles are or are suspected to be carcinogenic and/or mutagenic (e.g. Benzo(a)pyrene (BaP), Benzo(a)anthracene (BaA), Dibenzo(a,h)anthracene (DBahA), nitro-pyrene, fluorenone).

After inhalation these compounds can be absorbed by the organism and have the potential to induce mutations in humans. Therefore, they could conceivably play a role in both genotoxic and non-genotoxic carcinogenesis (H.E.I., 1995; Nielsen et al., 1996):

3. Objectives of this works

Our work was focused on three axes:

- the study of the effects of temperature in the vaporisation losses of organic compounds from filters during sampling (with a High Volume Sampler, HVS)
- characterisation of organic compounds in the diesel particles in a dilution tunnel, both in the particle and the gas phases and in different size fractions, with special emphasis on oxygenated PAH.
- the collection of atmospheric particles during a test campaign at Paris-Porte d’Auteuil in order to compare their composition with that of particles collected in the dilution tunnel experiments.