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ESTIMATION OF SECONDARY ORGANIC AEROSOL (SOA) PRODUCTION FROM TRAFFIC EMISSIONS IN THE CITY OF ATHENS

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ABSTRACT

Estimates of the amount of secondary organic aerosol formed in the atmosphere from the degradation of traffic C_6-C_{12} hydrocarbon emissions in the city of Athens are presented. Around 1.26 tn of organic aerosol is estimated to be produced during a six hours air pollution episode from the aromatic hydrocarbons, the other NMHC groups contributing an additional 0.2 tn. The main contributor to the SOA production is m-xylene. It accounts, together with toluene, for around 50% of the produced organic aerosol. The main aerosol products that are expected to form from the Athens NMHC traffic mixture are nitrophenols. Due to predominant wind flow to the S-SE direction in the area, a portion of these aerosols is likely to contribute to the SOA burden of the marine atmosphere over SE Mediterranean. These results are also relevant to ozone abatement strategies involving species-specific NMHC reductions and affecting fine particulate composition and concentrations.

KEY WORDS: Secondary organic aerosol, non-methane hydrocarbons, aromatics.

INTRODUCTION

Urban agglomerations are a major source of non-methane hydrocarbons (NMHC). Some of these NMHCs can contribute substantially to tropospheric secondary organic aerosol (SOA) formation (Grosjean and Friedlander, 1975; Grosjean and Seinfeld, 1989; Grosjean, 1992; Novakov and Penner, 1990). Secondary organic aerosols (SOA) are produced in the atmosphere from the oxidation of NMHC by OH, ozone and NO_3. The oxidized products at concentrations exceeding their saturation vapour pressures may condense on the available aerosol surfaces and form SOA. However, a gas-phase species may be adsorbed on available particles even if its concentration is below its saturation value (Pankow, 1994). In urban air, the organic aerosols produced this way may account for a significant fraction of the total organic carbon. In southern California, for example, this fraction may be up to 70% (Turpin and Huntzicker, 1991).

SOA consists mainly of various acids, dicarbonyls, organic nitrates, nitroaromatics and phenols, some of these substances are of main concern to human health. As fine particles, SOA can contribute to the mortality associated to fine particles (Schwartz et al., 1997).

SOA particles can also influence the radiation budget of the atmosphere either directly or through their role as cloud condensation nuclei (CCN). Recent evidence (e.g. Hobbs et al., 1997) suggests that carbon aerosols may even far outnumber sulphate particles and, hence, the net cooling effect of scattering sulphate aerosols can be more than offset from the net heating effect of absorbing carbon In addition, evidence exists (Novakov and Penner, 1993), that organic CCN, at marine sites influenced by anthropogenic emissions, account for most of the total aerosol number concentration and the CCN fraction, in contrast with the common view that CCN originate primarily from sulphate aerosols. The albedo of marine stratus clouds, and, hence, their radiative properties are determined in a large part by the CCN number density.

In addition, estimates of the organic aerosol produced by traffic emissions could be useful to be taken into consideration on attempts to reduce the photochemical ozone burden in urban or regional scales in Europe. This is because:

1. The efforts to control ozone levels, in the near future, will most probably involve species-selective reductions of NMHC emissions, which will also have effects on the fine particulate composition and burden of urban centres. Since both ozone and PM_{10} particulates are under regulatory consideration, and since species-specific reductions in NMHC emissions are likely to be introduced, it would be useful for cost-effective strategy design if some estimations on SOA production were available. This could help to target these NMHC species, whose reduction would reduce both ozone and fine SOA particulates.

2. In the urban plume, aerosols have a direct effect on the photodissociation rates of both ozone and NO_2 that can lead to very significant enhancements in ozone production (e.g. Dickerson et al., 1997).

Summarising, information on the amount of aerosol produced from NMHCs traffic emissions in urban centres is important in order to assess the effect of various smog abatement strategies pertinent to ozone formation, to fine particulate burden and to CCN availability. The method presented in this paper can also find application in predicting the changes of SOA composition, aerosol toxicity and SOA contribution to PM_{10} as a result of regulatory driven changes in NMHC emissions (Grosjean, 1992).

In the present study, recent estimates of speciated NMHC traffic emissions from the city of Athens (one of the biggest urban conglomerations with a 4 million population at the North coast of Eastern Mediterranean) have been used in order to calculate the organic aerosol amount produced during a photochemical urban air pollution episode. The NMHC emissions have been obtained from a compilation of an extensive dataset of ambient concentration data (Kourtidis et al., 1999). The organic aerosol production estimates were made according to the approach followed by Grosjean (1992). This approach is applicable to urban areas for which reliable emission and/or ambient concentration data are available for aerosol-forming NMHCs (Grosjean, 1992). Up to now, no estimations have been made of SOA production in Athens, due to a lack of speciated NMHC emission estimates. The mains aims of the present study are to provide of a first estimation of the magnitude of SOA production, to target the species that contribute mostly to SOA, and identify the expected products using an approach that requires minimum recourses. For an accurate prediction of SOA concentration produced in the atmosphere, detailed modeling is required (e.g. Pandis et al., 1992).

RESULTS AND DISCUSSION

The speciated NMHC traffic emission inventory for Athens, used here, contains 35 species in the C_5-C_{12} range and refers to 1994 (Kourtidis et al., 1999). Thirty out of these species have the potential to form aerosols (Table 1). NMHCs that do not form aerosols include benzene as well as all alkanes and alkenes with six or less C atoms (Grosjean and Seinfeld, 1989). Thus, most of the NMHCs that are important aerosol precursors, are included in the inventory.

For an estimation of the organic aerosol, that could be produced by the emitted NMHCs in the Greater Athens Area, data regarding the aerosol forming potential of various NMHCs which have been compiled by Grosjean (1992) are used. The approach followed by Grosjean (1992) is also adopted.

The aerosol is calculated as:

Amount of aerosol produced = Amount of NMHC x Fraction of NMHC reacted x Fractional Aerosol Coefficient where,

$$\text{Fractional Aerosol Coefficient (FAC)} = \frac{\text{Aerosol from NMHC}}{\text{Initial NMHC}}.$$

Table 1. Non-methane hydrocarbon emission rates and amount of aerosol produced by each NMHC.

Species	Emission rate (kg day^{-1})	Fractional Aerosol Coefficient %*	Fraction of NMHC reacted+	Amount of aerosol produced (kg (6-hours-episode)$^{-1}$)
AROMATICS	(sum of aromatics = 1,264.6 kg day^{-1})			
toluene	42,959	5.4	0.12	278.0
m-xylene	17,989	4.7	0.4	338.0
o-xylene	12,967	5	0.26	168.6
ethylbenzene	9,296	5.4	0.15	75.3
p-xylene	8,493	1.6	0.28	38.0
m-ethyltoluene	3,929	6.3	0.31	76.7
p-ethyltoluene	1,277	2.5	0.21	6.7
1,3,5-trimethylbenzene	2,611	2.9	0.74	56.0
isopropyl benzene	548	4	0.13	2.8
substituted C10 benzenes	7,576	6.3	0.47	224.3
CYCLOALKANES	(sum of cycloalkanes = 15.2 kg day^{-1})			
methylcyclopentane	5,110	0.17	0.1	0.9
methylcyclohexane	2,118	2.7	0.2	11.4
ethyl cyclohexane	849	2.7	0.12	2.7
cyclohexane	803	0.17	0.14	0.2
ALKANES	(sum of alkanes = 50.9 kg day^{-1})			
nonane	3,825	1.5	0.2	11.5
n-heptane	3,353	0.06	0.14	0.3
2-methyl heptane	2,444	0.5	0.1	1.2
3-methyl heptane	2,258	0.5	0.1	1.1
2,4,4-trimethylpentane	3,263	0.73	0.16	3.8
n-octane	2,430	0.06	0.17	0.2
n-decane	3,005	2	0.22	13.2

Species	Emission rate (kg day^{-1})	Fractional Aerosol Coefficient (%)*	Fraction of NMHC reacted+	Amount of aerosol produced (kg (6-hours-episode)$^{-1}$)
undecane	2,189	2.5	0.25	13.7
2,3,4-trimethyl heptane	1,337	2	0.22	5.9
ALKENES	(sum of alkenes = 71.7 kg day^{-1})			
1-nonene	1,551	6	0.57**	53
1-heptene (R2=0.6)	1,364	2	0.52**	14.2
1-octene (R2=0.6)	819	1	0.55**	4.5
TOTAL	1,402.4 kg day^{-1}			

* From Grosjean and Seinfeld (1989)

\+ Calculated from reaction rate constant, $[OH]=1*10^6$ molecules/cm^3, $[O_3]=100$ ppb, $[NO_3]=0$ ppb and a reaction time of 6 hrs.

** The amount shown is for reaction with ozone only, which is assumed to lead to aerosol formation, while reaction with OH does not.

For more details, the reader is referred to Grosjean (1992). FACs values are obtained by Grosjean's compilation (Grosjean, 1992) as well as data from Grosjean and Seinfeld (1989), Izumi and Fukuyama (1990) and Wang (1992). NMHCs react with OH (all NMHCs), ozone (all except alkanes and aromatics) and NO_3 (all except alkanes and aromatics). Aerosol production from alkenes is realised only through reaction with O_3 (Grosjean, 1992). The estimations are performed for a hypothetical 6 hours air pollution episode scenario, with $[O_3]=100$ ppb, $[OH]=1x10^6$ molecules cm^{-3} and $[NO_3]=0$.

As shown in Table 1 and Fig. 1, the aromatics alone produce around 1.26 tn over 6-hours-episode

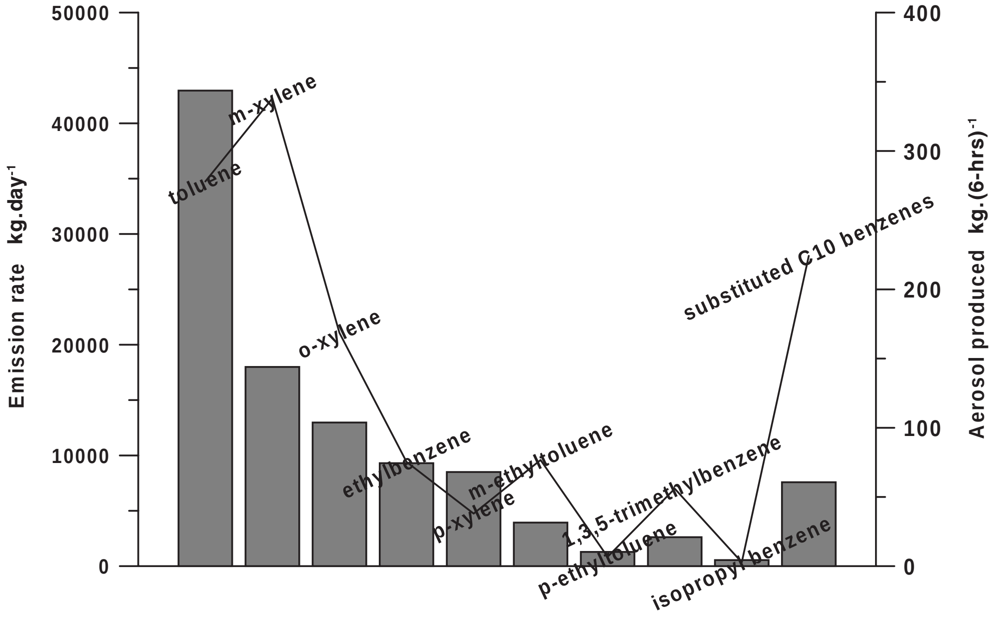

Figure 1. Emission rates (bars) and aerosol produced (line) from aromatic hydrocarbons in the Athens area.

of organic aerosol, another 0.16 tn over 6-hours-episode being produced from alkanes, cycloalkanes and alkenes. Hence, from the species of the NMHC inventory, aromatics produce 90% of the calculated SOA. This is in agreement with recent experimental results showing that the aromatic content controls a fuel's SOA formation potential (Odum et al., 1997). Odum et al. (1997), during smog chamber studies found that the ratio value, SOA concentrations predicted to form from a fuel's aromatic constituents over observed SOA concentration (averaged over 12 different fuels) was 1+/- 0.16 (1 σ). Greek unleaded fuels contain around 50% aromatics (Lappas et al., 1996). Results from the Auto/Oil Air Quality Improvement Research Program show that reformulated gasolines contain 20-48% aromatics (European Union, 1994). Hence, there is a considerable potential to reduce SOA by the introduction of certain types of reformulated gasoline.

Table 2. Secondary organic aerosol produced from traffic NMHC emissions in Athens during a 6 hrs air pollution episode according to functional groups.

	Aerosol produced kg.(6-hours episode)$^{-1}$			
Precursor NMHC	Carbonyl	Aliphatic acid	Nitrophenols	Aliphatic--nitrate
Aromatics	-	-	1264.6	-
Alkenes	-	71.7	-	-
Alkanes	33.6	-	-	17.3
Cycloalkanes	10.6	-	-	4.6
Total	44.2	71.7	1264.6	21.9

The main contributors to SOA are m-xylene and toluene accounting for around 50% of the estimated SOA production of the species presented in Table 1. Most of the SOA is produced by m-xylene. The present results suggest that m-xylene emission reductions lead to sizeable reductions in total SOA in Athens, since m-xylene is responsible for 24% of the SOA production from the 30 hydrocarbon species of the inventory used here and has a relatively high FAC value of 4.7% w/w. In California, m-xylene is predicted to constitute a much lesser fraction of the SOA production (Grosjean, 1992; Pandis et al., 1992). This is due to the much lower contribution of m-xylene to the NMHC burden in California, compared to that of Athens.

Following the functional group assignments of Grosjean (1992), the aerosol composition of Table 2 was derived. The main products belonging to the functional group of nitrophenols, are being formed by the oxidation of aromatics, nitrophenols, dinitrophenols and dixydroxynitroaromatics. Other products formed, but in much lesser amounts, from the degradation of the other compound classes of Table 2, are aliphatic acids, carbonyls, hydroxycarbonyls and organic nitrates. To our knowledge, there are no experimental data available for Athens to compare the estimates of Table 2 with. This study suggests that the relatively high contribution of aromatics to the total NMHC burden of the Athens atmosphere (Moschonas and Glavas, 1996; Rappenglueck et al., 1998) makes it possible that nitrophenols, which contain toxic substances, will make up the major fraction of urban SOA in Athens.

Besides its high FAC value, m-xylene has also a high ozone creation potential (Derwent et al., 1996 and references therein). Projections on fuel HC speciation for Europe assume a decrease in the aromatic content of the fuel and increase in the paraffin content of the fuel (European Union, 1994). The paraffin class is the most unreactive ones, the paraffins considered to yield one order of magnitude less ozone than other VOC classes (Russell et al., 1995), and also have low FAC values. These changes in fuel speciation, if introduced, will also affect the SOA produced in the Athens plume.

The main flow pattern in the NE Mediterranean is from north to south (e.g. Kallos et al., 1998). Based on its reaction rate constant for the reaction with OH (5.96×10^{-12} cm^3 molecule^{-1} s^{-1}; Atkinson, 1990), toluene is calculated to have a sufficiently long lifetime (i.e. time required for the initial concentrations to decrease to 1/e) of around 8 days in winter and 1 day in summer (Singh and Zimmerman, 1992) and hence a fraction of toluene emissions could survive even a 4 day travel and contribute to in-situ SOA formation over the marine SE Mediterranean atmosphere. This fraction, for a toluene lifetime of 1 day, would be 2% of the initial emissions after 4 days during summer, but might be an order of magnitude greater under cloudy conditions. It should be noted, that once formed, secondary organic aerosol will not remain necessarily in the liquid phase but it might evaporate again, depending on temperature and particle surface availability. Hence, in-situ physicochemical characterisation of aerosols combined with detailed chemistry-transport modelling is required to assess the mesoscale atmospheric effects of these particles.

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