Role of the binary H$_2$SO$_4$–H$_2$O homogeneous nucleation in the formation of volatile nanoparticles in the vehicular exhaust

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Abstract

High concentration of volatile nanoparticles (NPs) formed in vehicular exhaust may lead to adverse health effects, and a clear understanding of the nucleation mechanisms of these particles remains to be achieved. We investigate the role of H$_2$SO$_4$–H$_2$O binary homogeneous nucleation (BHN) in the formation of NPs in the diluting vehicular exhaust, using a recently developed kinetic H$_2$SO$_4$–H$_2$O BHN model suitable for studying the nucleation process in rapidly diluting exhaust. For the vehicles running on the fuel with fuel sulfur content (FSC) of $\sim$330 ppm we found that BHN may significantly contribute to the NP formation, especially when the ambient temperature is low and the relative humidity is high. Our simulations show that BHN rate is very sensitive to FSC and sulfur to sulfuric acid conversion efficiency ($e_s$). For $e_s$ value of 1%, BHN is negligible under typical conditions when FSC is $<\sim$100 ppm. However, NP formation via BHN may still be significant if $e_s >\sim$4% even after FSC is reduced to below $\sim$50 ppm. The sensitivities of NP formation via BHN to key factors (including ambient temperature and relative humidity, FSC, $e_s$ and the soot number concentration) are presented.

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1. Introduction

Motor vehicles are known to be a significant source of NPs that may cause adverse health effects due to their high number concentration and lung-deposition efficiency (Donaldson et al., 1998). It is important to have a clear understanding of the mechanisms controlling the formation of these NPs. Such an understanding is not only critical to help establish criteria for engine design, operation, after-treatment, fuel and lubricating oil compositional modifications that would effectively reduce NP emissions, but also is important to develop NP emission inventories.

Only sulfuric acid is likely to become super-saturated enough for homogeneous nucleation during diluting vehicular exhaust (Tobias et al., 2001); and various versions of the classical H$_2$SO$_4$–H$_2$O BHN theory have been applied to study the new particle formation in diluting engine exhaust (Baumgard and Johnson, 1996; Shi and Harrison, 1999; Kim et al., 2002; Zhang and Wexler, 2004). However, there exists a limitation
in using classical BHN theory to calculate the particle formation rates in vehicular exhaust. The classical BHN theory assumes that steady-state equilibrium distribution of critical clusters is achieved instantaneously at given H$_2$SO$_4$ concentration ([H$_2$SO$_4$]), temperature (T) and relative humidity (RH). The classical BHN model cannot keep track of the clusters of all sizes in the RH and [H$_2$SO$_4$], and thus is a more robust method made in the past (Doyle, 1961; Jaecker-Voirol et al., 1999), focusing mainly on the effect of the cluster distributions in the rapidly diluting engine exhaust due to the dramatic changes in T, RH and [H$_2$SO$_4$] (and resulting size of critical clusters) when fresh engine exhaust mixes with ambient air, the cluster distributions in the rapidly diluting engine exhaust are likely to change quickly and the classical BHN model cannot keep track of these changes properly. Recently Yu (2005, 2006) showed that the BHN of H$_2$SO$_4$–H$_2$O can be treated as quasi-unary nucleation of H$_2$SO$_4$ in equilibrium with H$_2$O vapor and developed a kinetic H$_2$SO$_4$–H$_2$O nucleation model. This kinetic model can keep track of the clusters of all sizes in the diluting exhaust experiencing rapid changes in T, RH and [H$_2$SO$_4$], and thus is a more robust method to study engine-generated NPs.

The main objective of this study is to investigate, with the recently developed kinetic H$_2$SO$_4$–H$_2$O nucleation model, the conditions in which the BHN is significant in engine exhaust. We first re-analyze the laboratory measurements of Shi and Harrison (1999), focusing mainly on the effect of the T and RH of the dilution air on the homogeneous nucleation rates. Then, we investigate the key parameters controlling the H$_2$SO$_4$–H$_2$O homogeneous nucleation rates in the vehicular exhaust experiencing continuous dilution in the atmosphere.

2. Kinetic H$_2$SO$_4$–H$_2$O quasi-unary nucleation (QUN) model

The H$_2$SO$_4$–H$_2$O BHN theory has been intensively studied in the last few decades and a number of updates to the classical BHN theory have been made in the past (Doyle, 1961; Jaecker-Voirol et al., 1987; Noppel et al., 2002). In this study we use a kinetic method to investigate the NP formation because of rapid changes in the T, RH of engine exhaust and [H$_2$SO$_4$] during the exhaust continuous dilution.

The kinetic QUN model (Yu, 2005, 2006) simulates the evolution of cluster size spectra explicitly, which are necessary when the ambient conditions change rapidly. It has been demonstrated that the nucleation rates predicted by the kinetic QUN model (Yu, 2005, 2006) are in good agreement with recent experimental BHN data. The detailed description of the kinetic QUN model is given in Yu (Yu, 2005, 2006). Here, the physical basis and the key assumptions of the QUN model are summarized briefly:

1. At given T and RH, the sulfuric acid clusters of various sizes are in equilibrium with water and their average compositions (i.e. the number of H$_2$O molecules $i_p$ in a cluster containing $i_a$ H$_2$SO$_4$ molecules) can be approximated using the most stable compositions (Yu, 2005).
2. The binary H$_2$SO$_4$–H$_2$O nucleation is controlled by the growth/shrink of (H$_2$SO$_4$)$_{i_a}$(H$_2$O)$_{i_p}$ clusters (named $i_a$-mers therefore) through the uptake/evaporation of H$_2$SO$_4$ molecules. The cluster forward/growth rate ($\beta_{i_a}$) is the kinetic collision rate of the hydrated monomers with $i_a$-mers, and the reverse/evaporation rate ($\gamma_{i_a}$) is the escape frequency of H$_2$SO$_4$ molecules from $i_a$-mers calculated using the Kelvin equation. The intersection points of $\beta_{i_a}$ and $\gamma_{i_a}$ curves are those where the critical clusters are located and the properties of the critical clusters (number of the sulfuric acid molecules $i_a^*$, radius $r^*$, the acid mole fraction $x^*$, etc.) are simulated explicitly.
3. When the compositions, $\beta_{i_a}$ and $\gamma_{i_a}$ for $i_a$-mers are known, the time-dependent cluster number concentration size distributions ($n_{i_a}(t)$) can be obtained by solving the following set of the differential equations:

$$\frac{dn_{i_a}}{dt} = \delta_{i_a-1,1}\beta_{i_a-1}n_{i_a-1} - \gamma_{i_a}n_{i_a} - \beta_{i_a}n_{i_a} + \gamma_{i_a+1}n_{i_a+1} + \frac{1}{2} \sum_{k=2}^{i_a-2} k_{i_a-k}n_{i_a-k}n_k - \sum_{j=2}^{\infty} k_{i_a-j}n_{i_a-j}n_j - \frac{kT}{2\pi na}A_p n_{i_a}, \quad i_a \geq 2,$$

$$\frac{dn}{dr} = P - \sum_{i_a=1}^{\infty} \beta_{i_a}n_{i_a} + 2\gamma_{i_a}n_{i_a} + \sum_{i_a=3}^{\infty} \gamma_{i_a}n_{i_a} - \frac{kT}{2\pi n_1}A_p n_1, \quad (2)$$
where $P$ is the production rate of sulfuric acid molecules ($P = 0 \text{ cm}^{-3} \text{s}^{-1}$ in this study). $k_{i,j}$ is the coagulation kernel. $\delta_{i-1,j} = 1$ when $i_s > 2$ and $= 0.5$ when $i_s = 2$. $A_p$ is the total surface area associated with soot particles (assumed to be $50 \text{ nm}$ in diameter) in the exhaust and entrained background aerosols, $k$ is Boltzmann’s constant, and $m_{i_o}$ is the mass of $i_o$-mers.

3. Modeling results

3.1. NPs formation in the two-stage laboratory dilution tunnel

Shi and Harrison (1999) investigated the NP formation in the diesel exhaust experiencing two-stage dilution in the laboratory. Their experiments have shown a considerable sensitivity of the NP production to the dilution conditions. Here we apply the kinetic QUN model to study in detail the BHN in laboratory conditions. The study is divided into case (a) and case (b). The parameters ($T$, RH, dilution ratio DR, residence time for both stages, initial sulfuric acid vapor concentration ($[\text{H}_2\text{SO}_4]_{\text{initial}}$) and soot concentration) for case (a) are taken from the laboratory study (Shi and Harrison, 1999). The only change in parameters for case (b) is that the $T_e$ of first-stage dilution air is decreased by $12 \text{ K}$. Here we treat all volatile particles with diameter $> 3 \text{ nm}$ as nucleated particles. The condensation of organic species on the nucleated particles was not considered in the current study as the main focus of this paper is on the number of particles formed via BHN under different conditions. Organic compounds are known to contribute to the growth of the nucleated particles (and thus their sizes) but their effect on the number of particles nucleated appears to be limited though further research is needed. In order to compare simulated size distributions with those measured, the condensation of organics has to be included in the model which will require information about the types of organic compounds involved in the condensation and their properties (vapor pressure, surface tension, etc.).

We start the simulation from the beginning of first-stage dilution where the raw exhaust was just diluted by a factor of $9.9$. $[\text{H}_2\text{SO}_4]_{\text{initial}}$ in the first-stage dilution tunnel is $1.14 \times 10^{12} \text{ cm}^{-3}$. Fig. 1 shows $\beta_{i_o}$ and $\gamma_{i_o}$ of $i_o$-mers at different time points in the first-stage dilution tunnel for cases (a) and (b). In case (a), the diluted exhaust temperature ($T_e$) is $321 \text{ K}$ and relative humidity (RH) is $16.2\%$ (3). In case (b), $T_e = 310 \text{ K}$, RH = $17.3\%$. $[\text{H}_2\text{SO}_4]_{\text{initial}}$ in both cases.

According to Figs. 1(a) and (b), $\gamma_{i_o}$ decreases rapidly as $i_o$ increases, especially when $i_o$ is small, and is very sensitive to $T_e$ and RH but independent of $[\text{H}_2\text{SO}_4]$. $\beta_{i_o}$ is proportional to $[\text{H}_2\text{SO}_4]$ and the effect of $T_e$ and RH on $\beta_{i_o}$ is small. $\beta_{i_o}$ decreases as time elapses as a result of decrease in $[\text{H}_2\text{SO}_4]$ due to
nucleation process and soot scavenging. The intersection points of \( \beta_{\text{ia}} \) and \( \gamma_{\text{ia}} \) curves correspond to the sizes of critical clusters. Clusters smaller than critical clusters tend to evaporate while clusters larger than critical clusters tend to grow.

We solved Eqs. (1) and (2) using values of \( \beta_{\text{ia}} \) and \( \gamma_{\text{ia}} \) shown in Fig. 1 to obtain the evolution of cluster size spectra. Fig. 2(a) shows the cluster size distributions at \( t = 0.01, 0.1, 0.25, 0.5 \) and \( 1.0 \) s for case (a). Few clusters grow beyond \( 1.0 \) nm before \( 0.01 \) s, while cluster size distributions begin to shift backwards as a result of evaporation since then. Evaporation of small clusters occurs mainly due to the decrease in \( [\text{H}_2\text{SO}_4] \) associated with soot scavenging.

Obviously, no NPs can form via BHN under Shi and Harrison’s (1999) experimental conditions based on our simulation. The maximum nucleation rate estimated based on an earlier version of the classical BHN theory (Kulmala et al., 1998; Shi and Harrison, 1999) was much higher than our simulations but was still \( \sim 60 \) times smaller than the observed value. The difference in the predicted nucleation rates is not surprising because the kinetic model used in this study is quite different from the classical BHN theory used in Shi and Harrison’s estimation. A detailed comparison of QUN and BHN has been given in Yu (2005, 2006). It should also be noted that the estimation given by Shi and Harrison (1999) was the maximum value because the scavenging of precursor molecules and small clusters by soot particles was not considered.

Yu (2001) has shown that ion-mediated nucleation mechanism may explain the observed NPs if the concentration of chemiions in the raw exhaust can reach \( 1.5 \times 10^8 \) cm\(^{-3}\). While nucleation on ions is thermodynamically more favorable than binary nucleation of \( \text{H}_2\text{SO}_4–\text{H}_2\text{O} \), the number of NPs formed via ion nucleation is limited by the availability of ions. Nevertheless, the ion nucleation does not exclude the possibility of homogeneous nucleation and the contribution of BHN in certain circumstances still maybe significant, as indicated in Fig. 2(b), which shows that a lower first dilution stage exhaust temperature significantly reduces the cluster evaporation rates (see Fig. 1(b)) and thus enhances the nucleation. A clear nucleation mode with the mean size of \( \sim 3.5 \) nm emerges at \( t = 0.1 \) s and grows rapidly to a larger size. The minimum in the size distributions around \( 1.5 \) nm is where the critical size locates.

Since \( T \) and RH of dilution air (\( T_D \) and RH\(_D\)) have significant effects on NP formation in laboratory conditions as shown in the above simulations, we further investigate the sensitivities of NP formation to \( T_D \) and RH\(_D\), aiming at understanding the laboratory conditions in which BHN could make a significant contribution to NPs production. For simplicity, we assume the same \( T_D \) and RH\(_D\) for both dilution stages with other parameters the same as case (a).

Fig. 3 illustrates the number concentration of particles larger than \( 3 \) nm in diameter (\( N_{d>3\text{ nm}} \)) at \( t = 1.8 \) s as a function of \( T_D \) at three different RH\(_D\).
3.0 coagulation-related NP number limitation.

[H₂SO₄]initial and soot number concentration are 1.14 times of 

It shows that NPs production via BHN can be significant under a wide range of T_D and RH_D in laboratory conditions. The sensitivities of N_d>3 nm to T_D and RH_D become negligible when T_D < ~273 K because N_d>3 nm is coagulation limited. Larger than 90% of RH_D is needed in order to have obvious NP production via BHN (N_d>3 nm > ~1000 cm⁻³) if T_D is > ~288 K.

Our simulations indicate that BHN can lead to significant NP particle formation under favorable laboratory conditions, especially when T_D is low. In addition to T_D and RH_D, other factors affecting the nucleation include the [H₂SO₄] in the exhaust (a function of FSC and ε_s), dilution ratio, residence time and soot particle concentrations. Some of these factors are addressed in the next section.

3.2. NPs formation in the vehicular exhaust diluting in the atmosphere

Unlike two-stage dilution process, vehicular exhaust experiences continuous dilution in the real atmosphere that leads to rapidly continuous changes of T_e, RH_e and [H₂SO₄] in the exhaust. Such rapid changes would thermodynamically affect the physical properties, growth and evaporation rates of each cluster, and thus impact NP formation in vehicular exhaust.

Appropriate characterization of the dilution profile of vehicular exhaust is critical because it delineates the continuous evolution of T_e and RH_e, which affects cluster evaporation rates, and [H₂SO₄], which impacts cluster growth rates. Laboratory and field studies (Kittelson et al., 1988; Kim et al., 2001; Shi et al., 2002) indicate a rapid dilution near the tailpipe within a few seconds. Dilution ratio as a function of plume age (i.e. time elapsed since the exhaust left the tailpipe) used in this study was obtained using the nonlinear regression of experimental data of Kittelson et al. (1988). The equation for the dilution ratio has been obtained in the form of DR = 1.0 + 700 × t¹.413 (t ≤ 1 s) (see Fig. S1 in Supporting information).

The initial [H₂SO₄] in exhaust before continuous dilution is a function of FSC and ε_s (see Appendix 1 in Supporting information) and is proportional to ε_s when FSC is fixed. As far as we know, neither direct measurements nor chemical modeling of ε_s for motor engines is available in the literature. It is expected that ε_s depends on engine types, operation conditions and exhaust treatment systems. Evidence indicates that the change of T in catalytic converters appears to affect ε_s. In contrast to the lack of study of ε_s in motor engine exhaust, there exist extensive investigations of ε_s in jet engine exhaust (Lukachko et al., 1998). Direct measurements and chemical simulations indicate that ε_s for jet engine can range from 0.1% to 10% (Lukachko et al., 1998; Kawa et al., 1999). ε_s is assumed to be 1.0% in our baseline study and sensitivity of results to ε_s will be presented.

Due to the wide possible ranges of key parameters (T, RH, FSC, ε_s and soot concentration), we first present the time-dependent evolution of cluster size distribution for a baseline scenario. Then, the sensitivity study of NP formation to various key parameters will be given. The values of the key input parameters used in the simulations for both the baseline scenario and sensitivity study are given in Table 1. The temperature and relative humidity of raw exhaust at the tailpipe exit are assumed to be 373 K and 0.033%, respectively. For the time scale we studied here (plume age ≤ 1 s), the effect of background aerosols on condensation of H₂SO₄ and scavenging of newly formed particles is not important. However, such effect may become important in far wake when the plumes are transported further away from roads.

3.2.1. Baseline scenario

The exhaust T and RH rapidly approach ambient levels as exhaust mixes with ambient air (Fig. S2(a)
number concentration of clusters with diameter \( \sim 0.8 \text{ nm} \) at \( t > 0.1 \text{ s} \) is largely due to evaporation. The decrease in the monomer concentration and the increase in \( N_{d > 3 \text{ nm}} \) are the result of the condensation of \( \text{H}_2\text{SO}_4 \) vapors onto larger NPs and dilution.

### 3.2.2. Sensitivity study of different parameters

In baseline scenario, we showed NP production in vehicular exhaust in terms of the cluster size evolution mainly to visualize the evolution of volatile NP and understand the physical processes associated with NP formation and evolution in a given ambient condition. In the following sections, we will show how different parameters impact NP production and the significance of such influences. We also provide information on vehicle emission index of the NP (EI, in \( \# \text{ kg}^{-1} \text{ fuel} \)) (see Appendix (2) in Supporting information). For the simulations presented below with regard to the sensitivity of NP formation to a certain parameter, we use baseline values for other parameters unless otherwise indicated.

#### 3.2.2.1. Effects of \( T_a \) and \( RHa \)

Fig. 5 illustrates \( N_{d > 3 \text{ nm}} \) as a function of \( T_a \) at four \( RHa \) at plume age of 1 s. The corresponding EIs are indicated as well. It shows that NPs formation in vehicular exhaust via BHN is significant under wide ranges of ambient temperature and relative humidity. More particles are formed at lower \( T_a \) and higher \( RH \). The effect of \( RHa \) on \( N_{d > 3 \text{ nm}} \) is more significant under high \( T_a \) conditions. Under favorable conditions, \( N_{d > 3 \text{ nm}} \) at plume age of 1 s can reach \( 10^6 \text{ cm}^{-3} \) which corresponds to an EI of \( \sim 10^{16} \# \text{ kg}^{-1} \text{ fuel} \).

Kittelson et al. (2004) showed that on-road particle NP EIs on two freeways of Minnesota are in the range of \( \sim 2.2–11 \times 10^{15} \# \text{ kg}^{-1} \text{ fuel} \) for a gasoline-dominated vehicle fleet in wintertime conditions with \( T_a \) of 274–286 K, \( RH_a \) of 40–60% and FSC of 330 ppm. On-road particle NP EI of around \( 8.3 \times 10^{15} \# \text{ kg}^{-1} \text{ fuel} \) has been reported for Helsinki metropolitan area, Finland (Yli-Tuomi et al., 2005). Our simulations indicate that BHN may explain these observed high vehicular NP EIs.

#### 3.2.2.2. Effects of FSC

Fig. 6 shows \( N_{d > 3 \text{ nm}} \) at plume age of 1 s as a function of FSC at six ambient conditions. We assume \( e_s \) (1.0% in this case) does not change with FSC. Our kinetic model predicts strong sensitivity of \( \text{H}_2\text{SO}_4–\text{H}_2\text{O} \) nucleation rate to FSC. For example at \( T_a = 298 \text{ K} \) and \( RH_a = 80\% \), the nucleation rate decreases by a factor of \( \sim 10^4 \)
when FSC decreases from 400 to 200 ppm. When FSC < 100 ppm, H$_2$SO$_4$–H$_2$O nucleation is very small in all typical ambient conditions. This indicates that in the states like California in which FSC$_o$/C$_{24}$ < 30 ppm or in the future when fuel with ultra-low sulfur content (FSC$_o$ < 15 ppm) is used, the contribution of binary H$_2$SO$_4$–H$_2$O homogenous nucleation to new NP formation is negligible if $e_s$ does not change with FSC. In such cases, the observations of new NP formation in the exhaust of engines running on ultra-low sulfur fuel (FSC < ~15 ppm) may indicate the involvement of other species such as ions (Yu, 2001), organics, metal or ammonia.

3.2.2.3. Effects of $e_s$. Fig. 7 illustrates $N_{d>3\,nm}$ at 1 s of plume age as a function of $e_s$ in five atmospheric conditions. With a given FSC, the initial [H$_2$SO$_4$] in exhaust is proportional to $e_s$. From Fig. 7 we could see that $N_{d>3\,nm}$ is very sensitive to $e_s$, especially when $e_s$ is small. $N_{d>3\,nm}$ increases by ~10$^6$ when $e_s$ increases from 1.5% to 4.0% for the case of 100 ppm of FSC. Thus, it is clear that $e_s$ is a critical parameter controlling NPs production in exhaust.
However, as we mentioned earlier, no direct studies of \( e_s \) for motor vehicles are available. Since different vehicles have different catalytic converters, engine designs and operation conditions, it is reasonable to expect a range of \( e_s \) for vehicles running on roadways. Obviously, more studies on \( e_s \) for vehicles and the parameters affecting \( e_s \) should be carried out. Since catalytic converters may play an important role in oxidizing sulfur into sulfuric acid, future development of catalytic converter should assess its oxidizing capacity as increase in \( e_s \) may offset the effect of FSC reduction on new NP formation.

### 3.2.2.4 Effects of soot scavenging

Fig. 8 illustrates \( N_{d>3\, \text{nm}} \) as a function of soot concentration at five conditions. Soot scavenging effect is small when soot concentration is \(<1.0 \times 10^7\, \text{cm}^{-3}\) but is significant when soot concentration is \(>1.0 \times 10^7\, \text{cm}^{-3}\). For the conditions investigated here, a reduction of soot particle concentration from \(10^8\) to \(10^7\, \text{cm}^{-3}\) increases the NP formation via homogeneous nucleation by up to 5five orders of magnitude. This is consistent with some measurements which indicate that a reduction in soot concentration as a result of cleaner modern engines
or of using a particulate filter actually leads to an increase in volatile NP emissions (Bagley et al., 1996; Graves, 1999). Nevertheless, our simulations suggest that the effect of soot emission reduction on volatile NP formation is limited after the soot concentration in the raw exhaust is reduced below $\sim 10^7 \text{ cm}^{-3}$.

4. Summary and discussion

The main objective of this study is to investigate the conditions, both in laboratory and real atmosphere, in which significant NP production via BHN in vehicular exhaust can be observed, using a recently developed kinetic QUN model which agrees well with experimental binary nucleation results. Firstly, we carried out the simulations on two-stage laboratory dilutions and found out that NP formation via BHN may become significant under favorable laboratory conditions, especially when $T$ of first-stage dilution air is low.

Secondly, we conducted simulations on vehicular exhaust diluting continuously in real atmosphere, and found out that BHN can lead to significant NP productions under wide ranges of ambient conditions. BHN is generally favored under low $T$, high RH, high FSC and $e_s$, and low soot concentration. For the conditions investigated in this study, the effect of soot scavenging on NP formation via BHN is significant only when soot particle concentration in the raw exhaust is $> \sim 10^7 \text{ cm}^{-3}$. In addition, our model predicts strong sensitivity of H$_2$SO$_4$–H$_2$O nucleation rate to FSC and $e_s$. We found that NP formation via BHN may be still possible even if FSC is reduced to ultra-low levels if $e_s$ is high enough ($\sim 10\%$). However, if $e_s$ is around a few percentage, BHN is likely to be negligible in the exhaust of engines running on ultra-low sulfur fuel. The observations of volatile NP formation in such cases (ultra-low FSC) may indicate the involvement of other species such as ions, organics, metal, solid cores or ammonia.

Since NP production via BHN strongly depends on $e_s$, measurements of $e_s$ for motor engines are needed in order to properly assess the contribution of BHN to NP formation in the vehicular exhaust. Simultaneous measurements of nucleated NPs, dilution conditions, FSC and $e_s$, and soot emission are needed to better constrain the nucleation model and verify the nucleation mechanisms. Since BHN is very sensitive to FSC (at fixed $e_s$), measurements of formed NPs as a function of FSC will also be useful to test the BHN mechanism.

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Appendix A. Calculation of initial H$_2$SO$_4$ number concentration and emission index

(1) Calculation of initial H$_2$SO$_4$ number concentration in vehicular exhaust before dilution. The initial [H$_2$SO$_4$] in exhaust is calculated based on FSC and $e_s$ and can be expressed as

$$[\text{H}_2\text{SO}_4] = \frac{\text{FSC} \times N_A \times e_s \times \rho_{\text{exhaust}}}{(1 + \text{AFR}) \times M_s},$$

(A.1)

where $N_A$ is Avogadro constant, AFR is the air fuel ratio which is assumed to be 15 in this study, $M_s$ is the molecular weight of sulfur and $\rho_{\text{exhaust}}$ is the density of exhaust.

(2) Calculation of emission index from number concentration of particles larger than 3 nm. Vehicle NP number emission index (EI, in # kg$^{-1}$ fuel), which could be calculated from $N_{d>3\text{ nm}}$ at the plume age of 1 s, is expressed as

$$\text{EI} = N_{d>3\text{ nm}} \times \frac{\text{volume of exhaust}}{\text{mass of fuel}}.$$  

(A.2)

Assuming the AFR to be 15, we obtain the volume of exhaust at 1 s (diluted $\sim 700$ times in 1 s) as a result of burning 1 kg of fuel, which gives the second term on the right-hand side of the equation.

Appendix B. Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2006.07.012.

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