

**5<sup>th</sup> Sino-French Joint Workshop  
on Atmospheric Environment**

*Air Quality Improvement and Future Challenges:  
Sciences, Technologies & Solutions*

**Book of Abstracts**

( <https://sfjw2016.sciencesconf/> )



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中国

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Workshop on  
Atmospheric  
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法国  
France

Xi'an - China  
October 11<sup>th</sup> - 14<sup>th</sup>, 2016



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The 5<sup>th</sup> Sino-French Joint Workshop on Atmospheric Environment

**“Air Quality Improvement and Future Challenges:  
Sciences, Technologies & Solutions”**

**Organized by:**

CRAES-MEP	Chinese Research Academy of Environmental Sciences
ICARE-CNRS	Institut de Combustion, Aérodynamique, Réactivité et Environnement
RCEES-CAS	Research Centre for Eco-Environmental Sciences
FD-MOE	Fudan University
SDU-MOE	Shandong University
IRCELYON-CNRS	Institut de Recherche sur la Catalyse et l'Environnement de Lyon
XI'AN-EPB-MEP	Xi'an Municipal Environmental Protection Bureau
JES	Journal of Environment Sciences
SKLECRA-CRAES	State Key Laboratory of Environmental Criteria and Risk Assessment
CICAEET	Collaborative Innovation Center of Atmospheric Environment and Equipment Technology
CITEPA	Centre Interprofessionnel Technique d'Etudes de la Pollution Atmosphérique
CECEP	China Energy Conservation and Environmental Protection Group

**Hosted by:**

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IEE-CAS	Institute of Earth Environment, Chinese Academy of Sciences
SHX-PAES	Shaanxi Provincial Academy of Environmental Science
XI'AN-JTU-MOE	Xi'an Jiaotong University



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# Characterization of the particulate emissions of GDI and Diesel Euro5 vehicles

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Road transport is an important source for particulates emissions around 15% in Europe urban areas. Those emissions are ruled by European standards Euro1 to 6. Particles number started to be regulated with the application of Euro5, especially for those superior to 23 nm. Nevertheless, it has been found out that particles below 23 nm diameter size are often associated to VOCs suspected to be strongly involved into nucleation or condensation processes giving rise to Secondary Organic Aerosols SOA as soon as it exhaust the tailpipe .

We have studied two Euro5 cars on a chassis dynamometer test bench at IFSTTAR in Bron - France. One Diesel car type 1.5 DCI and one gasoline direct injection car GDI type 1.2 TSI. The two vehicles experienced a first urban ARTEMIS cycle at cold start, in the morning, and then a series of nine highway ARTEMIS cycles at hot start. We connected our instruments on a Constant Volume Sampler CVS. During the cycles we measured the particles sizes and numbers SMPS+E, CPC, Mini Particle Sampler using TEM grid, the amount of black carbon MAAAP, the morphology of the particles Mini Particle Sampler using TEM grid, and TEM analyses, and only for the diesel car, the chemical composition of the particles AMS.

On the basis of each day's driving cycle program we could observe a different kind of emission patterns not only due to the different engine types but also due to the depollution system that the diesel car was equipped with.

**Keywords:** vehicle emission, DPF, nucleation, cold start, ultrafine particles.



# Characterization and source apportionment of volatile organic compounds based on 1-year of observational data in Tianjin, China

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From November 2014 to October 2015, the concentrations of volatile organic compounds VOCs, O<sub>3</sub> and NO<sub>x</sub> were simultaneously monitored by using online instruments at the air monitoring station belonged to Tianjin Environmental Protection Bureau TEPB. The results indicated that VOCs concentrations were higher in autumn and lower in spring, while O<sub>3</sub> concentrations were higher in summer, and lower in winter. The diurnal variations of VOCs and NO<sub>x</sub> NO<sub>2</sub> plus NO showed opposite tendency comparing to that of O<sub>3</sub>. The concentrations of alkanes were higher the average of 18.2 ppbv than that of aromatics 5.3 ppbv and alkenes 5.2 ppbv, however, the alkenes and aromatics made larger contributions to ozone because of their high reactivity. Tianjin belonged to the VOC-limited region during most of seasons except summer according to the VOC/NO<sub>x</sub> ratios the 8:1 threshold. The automobile exhaust, industrial emission, liquefied petroleum gas/natural gas LPG/NG, combustion, gasoline evaporation, internal combustion engine emission and solvent usage were identified as major sources of VOCs by Positive Matrix Factorization PMF model in Tianjin, and the contributions to VOCs for the entire year were 23.1 %, 19.9 %, 18.6 %, 10.6 %, 8.7 %, 5.4 % and 4.7 %, respectively. The conditional probability function CPF analysis indicated that the contributing directions of automobile exhaust and industrial emission were mainly affected by source distributions, and that of other sources might be mainly affected by wind direction. The backward trajectory analysis indicated that the trajectory of air mass originated from Mongolia, which reflected the features of large-scale and long-distance air transport, and that of beginning in Jiangsu, Shandong and Tianjin, which showed the features of small-scale and short-distance. Tianjin, Beijing, Hebei and Northwest of Shandong were identified as major potential source-areas of VOCs by using potential source contribution function PSCF and concentration-weighted trajectory CWT models.

Notably, the paper has been accepted by Environmental Pollution.

# Chinese soot on a Vietnamese soup

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Black Carbon BC is an aerosol emitted as soot during biomass burning and fossil fuels combustion together with other carbonaceous aerosols such as organic carbon OC and polyaromatic hydrocarbons PAHs. While the impacts of BC on climate are studied for many years, studies about its deposition and impact on marine ecosystems are scarce. This is rather surprising considering that a large fraction of atmospheric BC deposits on the surface of the ocean via dry or wet deposition. On a global scale, BC deposition estimates on the ocean range between 12 and 45 Tg C yr<sup>-1</sup>, with higher fluxes in the northern hemisphere and in inter-tropical regions, following the occurrence of the hot-spots of concentration. In the present study conducted on shore, in Haiphong and Halong cities, North Vietnam, we measured the seasonal variations of atmospheric BC, OC and PAHs during a complete annual cycle. The presentation will discuss the atmospheric results in terms of seasonal variability and sources. Expected inputs to the marine system are higher during the dry season, concomitantly with the arrival of air masses enriched in BC coming from the North. But the carbon fingerprint can significantly differ at shorter time periods depending on the air mass pathway and speed. Our work leads to the characterization and the determination of the relative contribution of more specific sources like local traffic, which includes tourism and fishing boats, coal dust emitted from the nearby mine, and mediumrange transported aerosols mainly from China. Our results could open the path to a more systematic monitoring of such inputs of carbonaceous aerosols for their possible consequences on the cycling and the repartition of carbon and nutrients in the marine ecosystem of Halong Bay.

# Synergetic formation of secondary inorganic and organic aerosol: Influence of SO<sub>2</sub> and/or NH<sub>3</sub> in the heterogeneous process

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The effects of SO<sub>2</sub> and NH<sub>3</sub> on secondary organic aerosol formation have rarely been investigated together, while the interactive effects between inorganic and organic species under highly complex pollution conditions remain uncertain. Here we studied the effects of SO<sub>2</sub> and NH<sub>3</sub> on secondary aerosol formation in the photooxidation system of toluene/NO<sub>x</sub> in the presence or absence of Al<sub>2</sub>O<sub>3</sub> seed aerosols in a 2 m<sup>3</sup> smog chamber.

The presence of SO<sub>2</sub> increased new particle formation and particle growth significantly, regardless of whether NH<sub>3</sub> was present or not. As shown in Figure 1, Sulfate, organic aerosol, nitrate and ammonium were all found to increase linearly with increasing SO<sub>2</sub> concentrations. The increases in these four species were more obvious under NH<sub>3</sub>-rich conditions, and the generation of nitrate, ammonium and organic aerosol increased more significantly than sulfate with respect to SO<sub>2</sub> concentration, while sulfate was the most sensitive species under NH<sub>3</sub>-poor conditions.

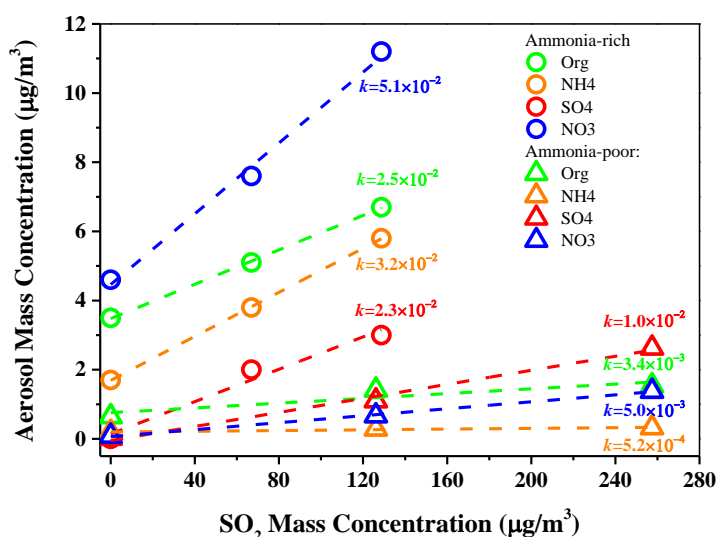


Figure 1. Formation of nitrate blue, organic aerosol green, sulfate red, and ammonium salt orange as functions of SO<sub>2</sub> concentration in the photooxidation of toluene/NO<sub>x</sub> under NH<sub>3</sub>-rich circles or NH<sub>3</sub>-poor triangles conditions. The *k* values are the slopes of the fitted lines for each species.

The synergistic effects between SO<sub>2</sub> and NH<sub>3</sub> in the heterogeneous process contributed greatly to secondary aerosol formation. Specifically, the generation of NH<sub>4</sub>NO<sub>3</sub> was found to be highly dependent on the surface area concentration of suspended particles, and increased most significantly among the four species with respect to SO<sub>2</sub> concentration under ammonia-rich conditions. Meanwhile, the absorbed NH<sub>3</sub> might provide a liquid surface layer for the absorption and subsequent reaction of SO<sub>2</sub> and organic products, and therefore, enhance sulfate and secondary organic aerosol SOA formation. This effect mainly occurred in the heterogeneous process and resulted in a significantly higher growth rate of seed aerosols compared to that without NH<sub>3</sub>.

By applying positive matrix factorization PMF analysis to the AMS data, two factors were identified for the generated SOA. One factor, assigned to less-oxidized organic aerosol and some oligomers, increased with increasing SO<sub>2</sub> under NH<sub>3</sub>-poor conditions, mainly due to the well-known acid catalytic effect of the acid products on SOA formation in the heterogeneous process. The other factor, assigned to the highly oxidized organic component and some nitrogen-containing organics NOC, increased with SO<sub>2</sub> under a NH<sub>3</sub>-rich environment, with NOC organonitrates and NOC with reduced N contributing most of the increase, as shown in Figure 2.

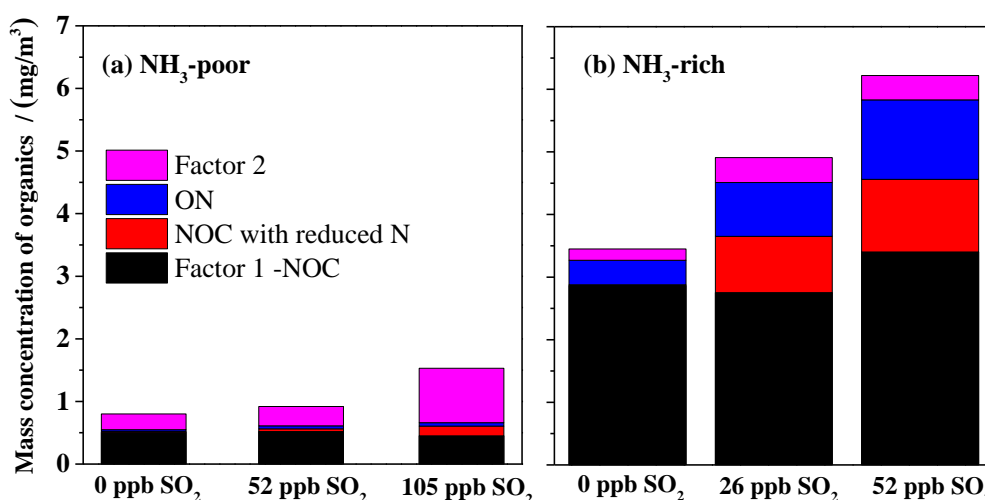


Figure 2. The estimated concentrations of NOCON+NOC with reduced N and the two factors identified by PMF analysis in SOA as a function of SO<sub>2</sub> concentration in photooxidation of toluene/NOx under a NH<sub>3</sub>-poor and b NH<sub>3</sub>-rich conditions.

This study indicated that the synergistic effects between inorganic pollutants could substantially enhance secondary inorganic aerosol formation. Meanwhile, the presence of inorganic gas pollutants, i.e. SO<sub>2</sub> and NH<sub>3</sub>, promoted SOA formation markedly. Synergistic formation of secondary inorganic and organic aerosol might increase the secondary aerosol load in the atmosphere. These synergistic effects were related to the heterogeneous process on the aerosol surface, and need to be quantified and considered in air quality models.

**Acknowledgments**

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# The Impact of SO<sub>2</sub> on HONO measurements by using Wet Chemical Methods

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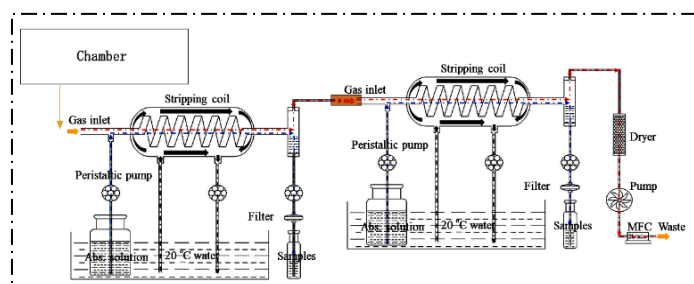


Figure 1. The structure diagram of the sampling method.

The orange and blue alternate long short dash lines represented the gas and liquid flow directions,

Gaseous nitrous acid, generally known as HONO, has drawn great attention by virtue of its remarkable contribution to atmospheric OH radicals which are the key reactive species for initiating atmospheric chemistry. Many studies have revealed that the atmospheric HONO levels

observed during noontime were about one magnitude higher than those simulated by models with input of the known sinks/sources, suggesting strong daytime unknown sources for HONO<sup>1-3</sup>. Because atmospheric HONO measurements are susceptible to various factors, such as wall effect, interference of other pollutants etc., the quality assurance and quality control QA/QC of various methods for measuring HONO are of great importance for estimating the contribution of atmospheric HONO to OH radicals. Although wet chemical methods including the techniques of stripping coils and denuders are currently prevailing for collecting atmospheric HONO, few studies reported the QA/QC of the methods.

As a typical pollutant in polluted areas, SO<sub>2</sub> can affect the acidity of the solution used for collecting atmospheric HONO by wet chemical methods, and thus atmospheric SO<sub>2</sub> is suspected to influence on HONO collection efficiency due to its weak acidity. To explore the possible impact of SO<sub>2</sub> on collecting HONO by using stripping coils which have been adopted by the commercial instruments of LOPAP<sup>4</sup> and GAC<sup>5</sup>, a series of SO<sub>2</sub> concentrations 0-11-23-51-113 ppbv and a fixed NO<sub>2</sub> concentration of 100 ppbv were prepared in a chamber volume is 3.6 m<sup>3</sup> made of Teflon film. As shown in Figure 1, HONO in the chamber was collected by using two stripping coils inside diameter is 6 mm connected in series. Ultrapure water H-method or 25 μ mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> solution N-method were used as the absorption solutions. The pool of the absorption solution in the jar was driven by two peristaltic pumps ShenChen, China into the two stripping coils in parallel at a flow rate of 0.2 mL min<sup>-1</sup>. The air flow from the chamber to the coils was in the same direction as the flow of the absorption solution, and a flow rate of 2.0 L min<sup>-1</sup> was controlled by a mini-pump KNF, Germany and a mass flow controller MFC, China. The stripping coils and absorption solutions were kept at a constant temperature of 20 °C through



thermostatic water bath. To avoid the wall effect of connection tube as possible, a Teflon tube less than 0.5 m was used to connect the gas inlet and the chamber. The chamber was maintained at 25 °C by an air conditioner and kept in dark by a stainless steel cover. The absorption solutions after passing through the two coils and two micro-porous membrane filters the pore size of 0.45 μm and the diameter of 13 mm were collected into the sampling bottles by using two additional peristaltic pumps. Nitrite  $\text{NO}_2^-$  in the sampling bottles was analyzed by the ion chromatography IC-WAYEE IC6200, China for quantifying HONO concentrations. The detection limit  $S/N=3$  of the IC was less than  $0.00025 \text{ mg-N L}^{-1}$ , which was equal to atmospheric HONO of 4 pptv.

The variation of HONO in the chamber under dark condition was firstly tested by preparing a  $\text{NO}_2$  concentration of  $\sim 100$  ppbv, and HONO concentrations in the chamber were collected by using the absorption solution of the ultrapure water and measured by the IC. As shown in Figure 3a, HONO concentration in the chamber without  $\text{SO}_2$  ( $\text{SO}_2=0$  ppbv) was very stable  $2.235 \pm 0.027$  ppbv,  $n=5$  during the experimental period of 2 hours, indicating that the heterogeneous reaction of  $\text{NO}_2$  on the wall of the chamber for HONO formation was negligible.

The HONO concentrations in the samples collected from the fore-and-aft coils and the collection efficiency for the first coil percent of breakthrough by using the two kinds of absorption solutions under different  $\text{SO}_2$  concentrations are illustrated in Figure 3. As shown in Figure 3a and 3b, it is evident that HONO concentrations in the samples collected in the first coils by using both the ultrapure water and  $\text{Na}_2\text{CO}_3$  solution were almost identical without presence of  $\text{SO}_2$ , and percent of breakthrough for the both solutions were less than  $\sim 3\%$  (Figure 3c). However, HONO concentrations in the samples collected in the first coils by using the  $\text{Na}_2\text{CO}_3$  solution were remarkably greater than those by using the ultrapure water with presence of  $\text{SO}_2$  concentrations. With increasing  $\text{SO}_2$  concentration, for the absorption solution of the ultrapure water, HONO concentrations gradually decreased in the samples collected in the first coils while increased in the samples collected in the second coils, implying that the acidification of the ultrapure water due to absorption of  $\text{SO}_2$  in the first coil  $\text{SO}_3^{2-}$  could be detected in the samples collected in the first coil evidently reduce HONO absorption efficiency. In contrast with the samples collected by using the ultrapure water, HONO concentrations sharply increased in the samples collected in the first coils by using the  $\text{Na}_2\text{CO}_3$  solution as  $\text{SO}_2$  concentration increased, and kept almost constant values when  $\text{SO}_2$  concentration less than 51 ppbv. Because the breakthrough of HONO collected by the coils was almost negligible ( $< 3\%$ ) without presence of  $\text{SO}_2$ , about 27% increase of HONO concentration in the samples collected by using  $\text{Na}_2\text{CO}_3$  solution with presence of  $\text{SO}_2 < 51$  ppbv indicated that aqueous chemistry of  $\text{SO}_2$  and  $\text{NO}_2$  under alkaline condition could form HONO, which could be further confirmed by the recovery of HONO concentration as  $\text{SO}_2$  concentration increased to be 115 ppbv when the alkalescency in the absorption solution of  $\text{Na}_2\text{CO}_3$  might be completely neutralized by absorption of  $\text{SO}_2$ .

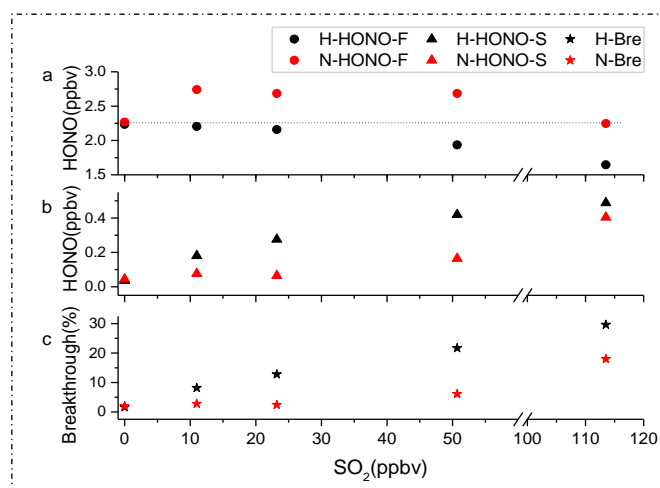


Figure 2. HONO concentrations in the two coils and the percent of breakthrough along with the concentration of SO<sub>2</sub>. a: The black and red solid circles represent HONO in the first coil using H-method and N-method, respectively. The dashed line represents HONO concentration  $2.235 \pm 0.027$  ppbv,  $n=5$  in the

chamber without SO<sub>2</sub> using H-method to detect samples for 5 times in 2 hours. b: The black and red solid triangles represent HONO in the second coil using H-method and N-method, respectively. c: The black and red solid star represent the percent of breakthrough using H-method and N-method, respectively. The percent of breakthrough is calculated from HONO in the second coil divided by that in the first coil.

Because certain concentrations of atmospheric SO<sub>2</sub> present in polluted areas, e.g., few ppbv in summer and tens ppbv in winter for typical polluted areas in China, the application of wet chemical methods for measuring atmospheric HONO should be careful. Based on the results of this study, one stripping coil by using ultrapure water for collecting atmospheric HONO is recommended when SO<sub>2</sub> concentration was less than 23 ppbv, and two stripping coils connected in series were suggested for the collection when SO<sub>2</sub> concentration was above 23 ppbv. As the aqueous chemistry of SO<sub>2</sub> and NO<sub>2</sub> under alkaline condition made evident additional contribution to HONO, the absorption solution of Na<sub>2</sub>CO<sub>3</sub> for the stripping coil method should be discarded.

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# Effects of Simulated Tri-Ethylene Glycol Coating with Soot Aerosol Particle Change on the Morphology Restructuring and Hygroscopicity

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Soot aerosol particle is produced from incomplete combustion of fossil fuels and biomass burning. The major component of soot is graphitic elemental carbon EC, while it can mix with other atmospheric pollutants, which can be coated on the surface of soot aerosol particle in the atmospheric aging transformation and the physical properties of soot aerosol particles will be changed to some extent. In the context of this study, we coat soot aerosol particles, which removed the non-EC material by Thermal Denuder TD, with tri-ethylene glycol TEG and investigate the restructure transformation and hygroscopicity by using self-built Tandem Differential Mobility Analyzer TDMA. We select the particle size 100 nm, 200 nm and 300 nm into the coating measurements through Differential Mobility Analyzer DMA. According to the experiment results, the morphology and hygroscopicity of soot aerosol particle could be changed when TEG coated and TEG may promote the restructure transformation.

**Key words:** soot aerosol particle, elemental carbon, tri-ethylene glycol, hygroscopicity, morphology restructuring, differential mobility analyzer.

# Organosulfate Formation through the Heterogeneous Reaction of Sulfur Dioxide with Unsaturated Compounds

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The atmospheric formation of organosulfur derivatives through reaction with SO<sub>2</sub> is generally mediated by oxidants such as O<sub>3</sub>, OH; recently we have proposed a direct reaction between SO<sub>2</sub> and unsaturated compounds as another possible pathway for organosulfate formation in the troposphere.

For the first time it was shown recently that a heterogeneous reaction between SO<sub>2</sub> and oleic acid OA; an unsaturated fatty acid takes place and leads efficiently to the formation of organosulfur products. Here, we demonstrate that this reaction proceeds on various unsaturated compounds, and may therefore have a general environmental impact.

We used different experimental strategies i.e., a coated flow tube CFT, an aerosol flow tube AFT and a DRIFT diffuse reflectance infrared Fourier transform cell. The reaction products were analyzed by means of liquid chromatography coupled to a high resolution mass spectrometer LC-HR-MS.

We report indeed that SO<sub>2</sub> reacts with large variety of C=C unsaturations and that even in the presence of ozone, SO<sub>2</sub> reacts with OA leading to organosulfur products. A strong enhancement in product formation is observed under actinic illumination, increases the atmospheric significance of this chemical pathway. This is probably due to the chromophoric nature of the SO<sub>2</sub> adduct with C=C bonds, and means that the contribution of this direct addition of SO<sub>2</sub> could be in excess of 5%.

The detection in atmospheric aerosols of organosulfur compounds with the same chemical formulae as the products identified here seems to confirm the importance of this reaction in the atmosphere.

# Atmospheric fine particulate matter: from chemical characterization to the study of toxicological effects on Human bronchial epithelial cells

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## Objectives

Compelling evidence indicates that particulate matter PM is one of the most relevant environment-related health issues all over the world. Indeed, in 2013, the International Agency for Research on Cancer IARC has classified air pollution and PM as a carcinogen for humans Loomis et al., 2013. PM is a complex mixture of liquid and solid particles with different size, from few nanometers up to some micrometers, with a complex chemical composition, comprising polycyclic aromatic hydrocarbons, metals ions and other organic and inorganic compounds. PM physicochemical properties are of pivotal relevance in understanding the particles potential impact on human health. A better understanding of the mechanisms of action of airborne particulates is a priority objective of toxicologists working on biological models. However, the process involved in the toxicity of these particles remains poorly understood, mainly because PM are uniquely complex owing to their physicochemical characteristics. *In vitro* systems are suitable alternatives to study the effects of PM on cells representative of human tissues in the attempt to identify the mechanistic relations between PM exposure and health effects. The airways are the primary target of PM since exposure happens mainly through inhalation. Main biological processes triggered by PM in human lung cells are cytotoxicity, inflammation, DNA damage and oxidative stress Gualtieri et al., 2010; Leclercq et al., 2016; Lepers et al., 2014; Borgie et al., 2015. Recently the role of PM in inducing an epigenetic modification in exposed cells has been evidenced Borgie et al., 2015.

High concentrations of PM are registered in cities from all the continents, and Dunkirk, an industrialized city of the north of France, is not an exception and was chosen as the studied site. The aim of the present study was to characterize PM<sub>2.5</sub> in the Dunkirk city and to evaluate its potential health impact.

## Materials and methods

Fine particles were collected in 2011 in the city center of Dunkirk, northern France Lat: 51.036323; Lon: 2.379408 using several sampling devices. Native PM<sub>2.5</sub> were sampled using a 5 stages high volume cascade impactor Staplex<sup>®</sup> 235, 68 m<sup>3</sup>/h, for toxicological studies. PM<sub>2.5</sub> were also collected on cellulose and quartz fiber filters using Digitel DA80 high volume samplers 30m<sup>3</sup>/h. In parallel, atmospheric



PM<sub>2.5</sub> concentrations were also measured continuously using a MP101 analyzer by the Regional Air quality network, Atmo Nord-Pas-de-Calais. Chemical characterizations were done using ion chromatography for water-soluble species, inductively coupled plasma-atomic emission spectroscopy and inductively coupled plasma-mass spectrometry for major and trace elements, gas chromatography coupled with mass spectrometry for Polycyclic Aromatic Hydrocarbons PAHs and linear alkanes, and elemental analyzer CHNS for total carbon TC.

Normal human bronchial epithelial cells BEAS-2B were used as cell model for toxicological analysis. Cytotoxicity, oxidative stress, inflammatory response, PAHs-metabolizing enzymes gene expression, genotoxic and epigenetic alterations were evaluated.

### **Results**

During the sampling period, the mean PM<sub>2.5</sub> concentration was estimated to 33 µg.m<sup>-3</sup>. This value appears higher than the PM<sub>2.5</sub> target value entered into force in 2010 in Europe. The chemical composition revealed, in addition to the major constituents NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup> Total Carbon that represent 95% of the PM<sub>2.5</sub> mass, the presence of metals at trace levels. Some of them appears characteristic of local industrial activities Mn, Zn, Fe, Rb, Pb or more likely related to the road traffic Cu, Zn, ... as well as shipping emissions V, Ni. From PAH ratios analysis, the influence of the road traffic is also evidenced and the contribution of the local coke plant is suggested.

Cytotoxicity of PM<sub>2.5</sub> was evaluated *via* Mitochondrial DeHydrogenase MDH activity in cells and extracellular Lactate DeHydrogenase LDH activity in cell-free culture supernatants. While the underlying mechanisms involved in the air pollution-derived PM-induced lung disorders are still not clear, the development and/or the exacerbation of oxidative conditions have been proposed and recognized as one of the main probable mechanism. The oxidative stress, usually defined as a chronic imbalance of intracellular redox balance in favor of oxidizing conditions was evaluated through malondialdehyde measurement, intracellular reactive oxygen species quantification, oxidized vs reduced glutathione ratio determination, superoxide dismutase activity. High levels of reactive oxygen species exceeding the detoxification capacity of cell antioxidant defenses may trigger a cascade of events closely associated with inflammation and, at higher concentrations, apoptosis and/or genetic and epigenetic alterations. Inflammatory response was measured through interleukins secretion and/or gene expression TNFα, IL1b, IL6, IL8, while apoptosis was pointed out through P21 and P53 quantification. Genotoxicity *via* micronucleus test, pH2A.X determination and PM<sub>2.5</sub> mutagenesis properties, and epigenetic alterations by studying the status of some microRNA of interest mir21A, mir26b, mir27a, let7a... was evidenced. Moreover an induction, after cell exposure to PM<sub>2.5</sub>, of some xenobiotic-metabolizing enzymes gene expression was found.

### **Conclusion**

Toxicological mechanisms under study are potentially involved in the initiation and the promotion of carcinogenesis and were found to be induced by urban PM<sub>2.5</sub>.

Among the encountered compounds bound to PM, metals and PAHs are potentially responsible for the studied mechanisms of toxicity.

**Keywords:** Air pollution, BEAS-2B cells, chemical characterization, fine particles, lung toxicity, oxidative stress and inflammatory responses, genotoxicity, epigenetic alterations.

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# Influence of ships emissions to NO<sub>x</sub>, SO<sub>2</sub> and PM concentrations in a North-Sea harbour in France

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## Objectives :

Harbours are an integral part of social and economic development. In coastal areas, such as Northern France where are located the first European harbours for fishing and for passengers, shipping related activities are an essential link in the development of trade. In the last years, the interest to the scientific community regarding the environmental impact of shipping has grown, resulting in amendments to the regulations in lines with the new knowledge regarding the emissions. Ships are known to emit nitrogen oxides 5-7 Tg.year<sup>-1</sup>, Sulphur oxides 4.7-6.5 Tg.year<sup>-1</sup>, particulate matter PM 1.2-1.6 Tg.year<sup>-1</sup> and 3.3% of the global CO<sub>2</sub> emissions Buhaug et al., 2009; Healy et al., 2009. Even if emissions of in-port ships account for only a few percentage of the global emissions related to shipping Dalsøren et al., 2009, they can have an important impact at a local scale, in port cities, on air quality. The objective of this study is to estimate the influence of ships emissions on air quality in one of the most important European harbour with a focus on the SO<sub>2</sub>, NO<sub>x</sub> and PM<sub>10</sub> concentrations.

## Methods

The main study site was placed in the harbour of Calais, France Lat: 50.9632 ; Long: 1.8538, the first European harbour for passengers number, in front of the boarding platforms and the intra harbour ship channel. Around 80 arrivals and departures of ferries are recorded each day. From January 29<sup>th</sup> 2014 to February 21<sup>st</sup> 2014, PM<sub>10</sub> concentrations were continuously measured using the MP101M analyser Environnement SA, France, as well as those of SO<sub>2</sub> AF21M, Environnement SA, France and NO<sub>x</sub> AC32M, Environnement SA, France. Real-time particle size distribution was monitored in parallel using the DEKATI ELPI, 13 channels from 0.030µm to 10 µm. Meteorological data temperature, wind speed and direction were also recorded on site. The same instrumentation was used at Cape Gris-Nez Lat: 50.9086 ; Long: 1.5972, located 20 km to Calais. This site can be considered as a reference site to deduce the intrinsic contribution of the in-port shipping to the air quality in Calais.

## Results

At Calais, mean PM<sub>10</sub>, NO<sub>2</sub>, NO and SO<sub>2</sub> concentrations were respectively 25.3, 22.0, 8.2, 2.6 µg.m<sup>-3</sup> versus 22.5, 12.5, 2.4 and 1.2 µg.m<sup>-3</sup> for the same species at

Cape Gris-Nez. The comparison of these mean values as well as the pattern of the pollutant roses at the two sites evidences that in-port shipping has an important influence on the  $\text{NO}_x$  and  $\text{SO}_2$  concentrations. During the period several  $\text{PM}_{10}$  concentrations peaks were observed simultaneously at both sites, meaning that  $\text{PM}_{10}$  atmospheric concentrations are rather governed by a regional fluctuating background level. Nevertheless, it is also shown that the  $\text{PM}_{10}$  concentrations can increase drastically in a very short period especially during the in-port vessel operations. In this case, simultaneously, peaks for  $\text{SO}_2$  and  $\text{NO}_x$  concentrations are also recorded. Such evolution appears synchronized with departures and arrivals of ferries in the harbour. For winds blowing from the harbour, when compared to the background level, the number of particles appears 10 times higher, with the highest differences in the 30-60 nm and the 110-170 nm size range.

The punctual impact of in-port ships on  $\text{PM}_{10}$  concentrations has been estimated to + 25  $\mu\text{g}\cdot\text{m}^{-3}$  and concerns mainly the  $\text{PM}_1$  size fraction 40%, the  $\text{PM}_{2.5-10}$  fraction 39%. On a very short time basis,  $\text{PM}_{10}$  can potentially reach a concentration value close to 100  $\mu\text{g}\cdot\text{m}^{-3}$ . An estimation of the shipping impact in the harbour of Calais can be done considering a background concentration Contini et al., 2011. These calculations showed that 70% of total  $\text{SO}_2$  and 51% of total NO in the air of the studied harbour city is related to ships emissions, while 19% of  $\text{NO}_2$  and 3% of  $\text{PM}_{10}$  can be ascribed to these sources.

#### Conclusion

In this study, we showed that in-port ships could have a very important impact on the  $\text{SO}_2$  and  $\text{NO}_x$  concentration in harbour cities, and a moderate impact on  $\text{PM}_{10}$  concentrations. From this study, it is also evidenced that ships emissions have a drastically impact on nanoscale particle number concentrations, which is of particular concern when considering the atmospheric pollution health effects.

# Progress and Prospect of research on the emission characteristics of VOCs emitted by vehicles in China

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Volatile Organic Compounds VOCs are one of air pollutants in atmosphere environment. Vehicles emission is one of the most important VOCs anthropogenic sources. Based on summarizing vehicles VOCs research methods and results, discovering vehicles VOCs emission quantity and emission factors, this passage focuses on researching different VOCs emission results from 4 different testing situations of different types vehicles, and calculating Ozone Formation Protection OFP as well as Secondary Organic Aerosol Formation Protection SOAFP of the major VOCs species. In addition, compared with foreign researches, this passage also points out shortages and disadvantages of vehicles VOCs emission research in China.

In ECE-EUDC situation, toluene, ethene, benzene and i-pentene are the major VOCs species of vehicles emission, and aromatic hydrocarbons is the most in quality rate while alkene is the least. In idling situation, ethene, n-butane, propane and propene are the major VOCs species, and, different from ECE-EUDC situation, aromatic hydrocarbons is the least in quality rate while alkene is the most. Tunnel testing situation is similar to road testing situation that toluene, ethene and ethane are the major VOCs species. The OFP of the major VOCs species in ECE-EUDC, idling, tunnel testing and road testing are 290.43, 640.55, 322.72 and 295.83 ugO<sub>3</sub>/100ugVOC, respectively. The SOAFP of the major VOCs species in ECE-EUDC, idling, tunnel testing and road testing are 1.02, 0.93, 1.18 and 1.18 ugSOA/100ugVOC, respectively.

**Keywords:** VOCs, emission characteristics, vehicles, prospect, China

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# Hydrological restoration of a Sphagnum-dominated peatland invaded by vascular plants: effects on GHG emission and C storage.

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Northern hemisphere peatlands are estimated to contain about 300-400Pg C as peat, corresponding to about 30% of the world's soil C stock in an area accounting for only 3-5% of the land surface. This C-sink function is largely controlled by the low rate of organic matter OM decomposition due to hydrological conditions that favour soil waterlogging, combined with the dominance of vegetation that produces decay-resistant litter i.e. *Sphagnum* mosses that hampers microbial decomposition, resulting in a net accumulation of OM as peat. In Western Europe, many peatlands are close to their critical ecological conditions due to a high anthropogenic pressure: hydrological disturbances i.e. drainage, peat cutting, nutrient amendment. This results in invasion of these environments by vascular plants at the expense of *Sphagnum* mosses. Thus we clearly need to understand how a change in plant species cover due to altered hydrological conditions can affect belowground interactions that greatly control GHG CO<sub>2</sub>, CH<sub>4</sub> emissions and C stocks in peatlands.

Nowadays several ecological engineering actions are undertaken to restore peatland functioning. Our study aims to assess the effect of such actions in a disturbed peatland Le Gnette, France on plant community diversity, dissolved organic matter dynamics and GHG CO<sub>2</sub>, CH<sub>4</sub> fluxes.

The hydrology of investigated site was disturbed for many decades by a road drain at the outlet of the peatland. In February 2014, we installed along the drain eight dams consisting of ditches that were dug perpendicular to the water flow and filled with a mixture of sand and bentonite. Two identical experimental stations were set up: a "downstream" station close to the hydraulic works and a "upstream" station far from the hydraulic works and considered as a control station. In each station 2m x 2m, three treatments n=4 were conducted: i "control" with intact vegetation *Molinia caerulea*, *Erica tetralix*, ii "bared peat" where vegetation and 5cm peat were removed, and iii "*Sphagnum*" corresponding to the bared peat seeded with *Sphagnum* mosses. In each of the two stations 24 plots, GHG CO<sub>2</sub> and CH<sub>4</sub> fluxes and plant cover were measured and dissolved organic C quantity and spectroscopic properties of dissolved OM were determined once a month at the growing season. Environmental parameters air and soil temperature, water table level, soil moisture



were also monitored.

18 months after the restoration works, “bared peat” and “*Sphagnum*” plots were quickly colonised by *Eriophorum angustifolium* up to ca. 90%, *Rynchospora alba* up to ca. 10%, *Trichophorum cespitosum* up to ca. 60%. On the whole, comparing to the downstream station, ecosystem respiration tended to be higher in the upstream station where water table level was lower. However, in both experimental stations, control plots functioned as C sink with lower CH<sub>4</sub> emissions comparing to the other treatments which functioned as C source.

Although vegetation colonisation is proceeding fast, two years seem not enough to trigger a C sink function in restored peatlands.

# Mechanism for the Growth of Polycyclic Aromatic Hydrocarbons from the Reactions of Naphthalene with Cyclopentadienyl and Indenyl

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Polycyclic aromatic hydrocarbons PAHs are globally concerned atmospheric particle-bound pollutants due to their toxicities. A mechanistic understanding of their formation from other environmental sources is of crucial importance for successful prevention of PAH. In the present work, the formation and growth mechanism of PAHs from the reactions of naphthalene with the cyclopentadienyl and indenyl radicals was investigated by using the hybrid density functional theory DFT. The rate constants for the crucial elementary steps were deduced using the canonical variational transition-state CVT theory with the small curvature tunneling SCT contribution. The formation of PAHs was involved in six elementary processes including: the addition reaction, ring closure, intramolecular H-shift, C-C cleavage, intramolecular H-shift and unimolecular elimination of CH<sub>3</sub> or H. The C-C cleavage steps were revealed as the rate determining steps. At high temperature conditions like the combustion and pyrolysis of many hydrocarbons, the main products are phenanthrene, 4-methyl-phenanthrene and 1-methyl-phenanthrene from the reactions of naphthalene and cyclopentadienyl, and benzoanthracene, 12-methyl-phenanthrene and 7-methyl-phenanthrene from the reactions of naphthalene

and indenyl radicals. The reaction of naphthalene with indenyl radical is slightly more difficult than the reaction of naphthalene with cyclopentadienyl radical because of the bigger HOMO-LUMO orbital energy difference of naphthalene with indenyl relative to that of naphthalene with cyclopentadienyl.

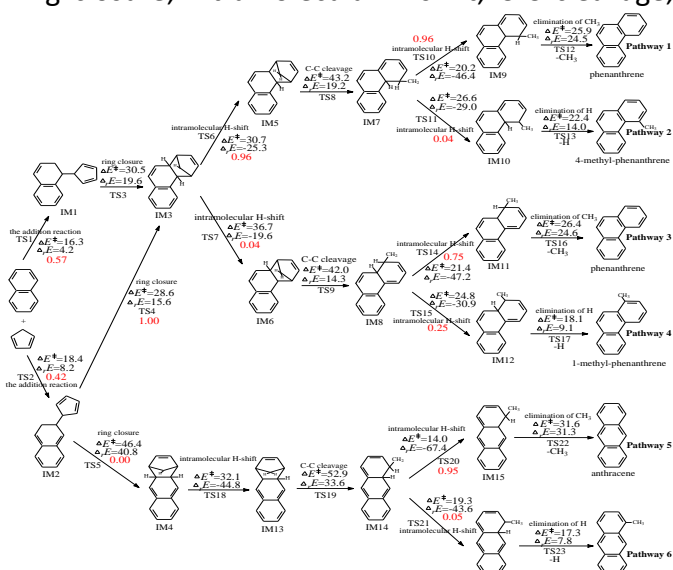


Figure 1. The formation schemes embedded with the potential barriers and reaction heats in the reaction of naphthalene with cyclopentadienyl.  $\Delta_r E$  is calculated at 0 K

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# Ozonolysis of $\alpha$ -phellandrene: Gas- and particle-phase characterization

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## Objective

Monoterpenes play an important role in the chemistry of the atmosphere due to their large emission rates 30 – 127 Tg C year<sup>-1</sup> and high reactivities<sup>2</sup>, influencing its oxidative capacity, the tropospheric ozone budget and by producing secondary organic aerosol SOA with impacts to both health and climate. One of the most reactive monoterpenes is  $\alpha$ -phellandrene Fig. 1, which to date has received little attention in the literature. Identified as a major constituent of extracts from various Eucalypt species<sup>3,4</sup>, the world's most widely planted hardwood tree,  $\alpha$ -phellandrene is expected to be an important contributor to the blue haze commonly associated with Eucalypt forests.  $\alpha$ -phellandrene is also found in the indoor environment, as an additive to household cleaning products, detergents and air fresheners.<sup>5</sup> In this study, the reaction of  $\alpha$ -phellandrene with ozone is experimentally characterized in detail for the first time, with both gas- and particle-phases are explored.

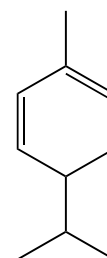


Figure 1.  
 $\alpha$ -phellandrene

## Method

Nineteen dark, dry,  $\alpha$ -phellandrene ozonolysis experiments were conducted using the indoor smog chamber facility at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences GIG-CAS. A complete description of the facility and chamber setup is given in Wang *et al.*<sup>6</sup>. Briefly, the smog chamber allows reactants to be introduced into a clean, highly controlled reactor simulating atmospheric conditions, with the subsequent reaction followed by a suite of analytical instruments. Trace gas-species O<sub>3</sub> and NO<sub>x</sub> were measured online using dedicated monitors, while gas-phase organics were measured online using a commercial proton-transfer-reaction time-of-flight mass spectrometer PTR-TOF. Particle number size distributions were measured online with a scanning mobility particle sizer SMPS, with a high-resolution time-of-flight aerosol mass spectrometer AMS used to measure particle chemical composition in real time. Initial mixing ratios of reactants varied from 10 – 175 ppb for  $\alpha$ -phellandrene and 40 – 470 ppb for O<sub>3</sub>. Experiment run times ranged from 172 – 305 minutes.

## Results and Conclusions

### 3.1 Gas-phase analysis

Upon ozonolysis of  $\alpha$ -phellandrene a large number of product ions are detected in the PTR-TOF. However none of the product ions detected were observed to decrease over the course of the chamber experiments, suggesting that all ions are likely second-generation. Of these the largest yields were found for formaldehyde 5 – 11%, acetaldehyde 1 – 10%, glyoxal 8 – 21%, methyl glyoxal 3 – 9%, formic acid 15 – 25% and acetic acid 12 – 16%. A number of larger second-generation products have also been identified. Using cyclohexane as a radical scavenger, OH yields from both  $\alpha$ -phellandrene and its first generation products were quantified as  $21 \pm 7\%$  and  $25 \pm 6\%$  respectively. These yields can be taken as an indication of the prevalence of the hydroperoxide channel in  $\alpha$ -phellandrene's ozonolysis mechanism.

### 3.2 Particle-phase analysis

Rapid aerosol formation is observed in all experiments, characterized by a nucleation burst of fresh aerosol followed by a steady growth in aerosol mass through enhanced gas-aerosol partitioning. The addition of a CI scavenger formic acid was found to impair aerosol growth through reducing the number of SOA nucleating agents, with stabilized CIs therefore important precursors to forming species of low volatility. The average SOA density was determined to be  $1.41 \pm 0.05 \text{ g cm}^{-3}$ , indicating that the aerosol likely exists in a solid or waxy state, whilst elemental analysis determined the average composition to be  $\text{CH}_{1.54}\text{O}_{0.36}$ .

SOA mass loadings were corrected for first-order wall losses and quantified in terms of fractional aerosol yields  $Y$ , defined as the amount of particulate matter produced  $\Delta M_0$ ,  $\mu\text{g m}^{-3}$  for a given amount of precursor VOC reacted  $\Delta \text{HC}$ ,  $\mu\text{g m}^{-3}$ . Yields are shown plotted against aerosol mass in Fig. 2, and are fitted by the two-parameter fit model of Odum *et al.*<sup>7</sup>:

$$Y = \frac{\Delta M_0}{\Delta \text{HC}} = \Delta M_0 \sum_{i=1}^2 \frac{\alpha_i K_{om,i}}{1 + K_{om,i} \Delta M_0}$$

where the stoichiometric factor  $\alpha_1 = \alpha_2 = 0.58 \pm 0.08$  and equilibrium partitioning constant  $K_{om,1} = K_{om,2} = 0.025 \pm 0.01 \text{ m}^3 \mu\text{g}^{-1}$ . These values offer little physical insight, but can be used in regional and global transport modeling. Figure 2 shows that compared to other monoterpenes<sup>6,8,9</sup>

$\alpha$ -phellandrene produces a large amount of SOA, an artifact of two highly reactive endocyclic double bonds. The implication is that if emitted in polluted environments  $\alpha$ -phellandrene will make a considerable contribution to the particle phase.

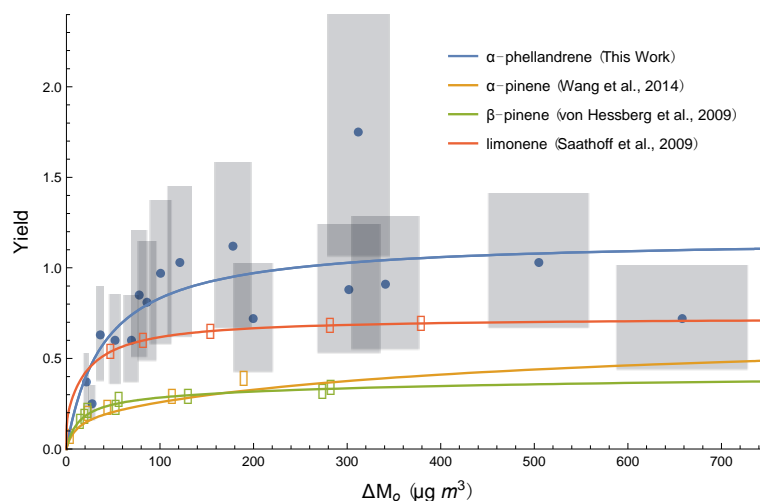


Figure 2. SOA yield data for  $\alpha$ -phellandrene compared to other monoterpenes.

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# Monitoring of Volatile and Semi-Volatile Organic Compounds In Urban and Rural Tropical Environments

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Rapid urbanization and economic development in South-East Asia in past decades has led to air pollution problems such as excess of nitrogen oxides NO<sub>x</sub>, carbon monoxide CO, Polycyclic Aromatic Hydrocarbons PAHs, Semi-Volatile Organic Compounds SVOCs and volatile organic compounds VOCs. Motor vehicle exhaust, industrial emissions, chemical solvents as well as biogenic emissions are the major anthropogenic sources of SVOCs, VOCs and PAHs.

The goal of this study is to identify and quantify the types of VOCs and SVOCs in tropical environment and compare the results with data obtained in temperate climate in France, near Bordeaux.

Two automated Thermal-Desorber Gas Chromatographs equipped with Flame Ionization Detectors auto TDGC-FID were used to monitor continuously the concentrations of VOCs and SVOCs in Thailand in June 2014 in a mobile unit on three different sites: near Bangkok, near an industrial area in the Rayong province site and near seaside in the Phetchaburi province.

First a laboratory study has been carried out to optimize the system before installation in tropical area. One analyzer is dedicated to the monitoring of C2 to C6 airmoVOC C2-C6, Chromatotec, France and another for C6 to C12 airmoVOC C6-C12, Chromatotec, France. It was possible to adjust the time, gas flow and temperature for the pre-concentration of the sample independently for both analyzers. Columns, pressure and temperature gradient have been optimized to obtain a good separation for more than 100 VOCs. The separation and identification of all compounds were carried out using an Electron Ionization Mass Spectrometer equipped with an Electron Multiplier DET QMS, Chromatotec, France. Finally, humid samples were produced to check the efficiency of the drying systems and evaluate the impact of humidity on VOCs adsorption and modification of retention times.

Then the field deployable system has been installed in Bordeaux and on three different sites in Thailand. Ethylbenzene, m-xylene, p-xylene and o-xylene EX were found to be the most abundant molecules in the ambient air near Bangkok. Benzene concentration was much lower than EX. Naphthalene, which is a PAH and a SVOCs, has been used as a marker of the PAHs pollution. We observe that the naphthalene concentration is higher in Bangkok 0.4 µg.m<sup>-3</sup> than in the other places 0.13 µg.m<sup>-3</sup> for seaside. Hydrocarbons emitted by trees such as isoprene or monoterpenes were found to be insignificant at this time of the year in Thailand less than 1% of the total emission while they represent the major part of VOCs emitted in the Bordeaux region. Sum of dichlorobenzene and styrene come from anthropogenic emissions and can be used as marker for industrial activity. They were logically measured at



high concentrations in Bangkok and in the industrial area.

**Keywords:** Gas Chromatography, Mass spectroscopy, Volatile Organic Compounds, On-line Monitoring, Polycyclic Aromatic Hydrocarbons, Semi-Volatile Organic Compounds.

# PolEASIA Project: Pollution in Eastern Asia - towards better Air Quality Prevision and Impacts' Evaluation

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The rapid economic development and urbanization of China during the last decades resulted in rising pollutant emissions leading to amongst the largest pollutant concentrations in the world, largely exceeding the recommended outdoor air pollutant thresholds from the World Health Organization for the major pollutants ozone, PM<sub>2.5</sub>, and PM<sub>10</sub>. Robust monitoring and forecasting systems associated with downstream services providing comprehensive risk indicators are highly needed to establish efficient pollution mitigation strategies. In addition, a precise evaluation of the present and future impacts of Chinese pollutant emissions is of importance to quantify: first, the consequences of pollutants export on atmospheric composition and air quality all over the globe; second, the additional radiative forcing induced by the emitted and produced short-lived climate forcers ozone and aerosols; third, the long-term health consequences of pollution exposure. To achieve this, a detailed understanding of East Asian pollution is necessary. Building on a ambitious synergistic approach combining observations and modeling to bridge the scales from local to global, the French PolEASIA project aims at addressing these different issues by providing a better documentation and quantification of the sources and the distribution of the major pollutants such as ozone and aerosols, and of their past, present and future evolution. The main objectives, methodologies and tools of this starting 4-year project will be presented.

A multi-scale approach coupling innovative satellite observations, in situ measurements and chemical transport model simulations is developed to characterize the spatial distribution, the interannual to daily variability and the trends of the major pollutants ozone and aerosols and their sources over East Asia, and to quantify the role of the different processes emissions, transport, chemical

transformation explaining the observed pollutant distributions. A particular attention is paid to assess the natural and anthropogenic contributions to East Asian pollution. Progress made with the understanding of pollutant sources, especially in terms of modeling of pollution over East Asia and advanced numerical approaches such as inverse modeling will serve the development of an efficient and marketable forecasting system for regional outdoor air pollution. Additional modules will be coupled with the forecasting system including end-user friendly applications to provide comprehensive indices for health and visibility risks to public authorities and populations. The performances of this upgraded forecasting system will be evaluated and promoted to ensure a good visibility of the French technology. In addition, the contribution of Chinese pollution to the regional and global atmospheric composition, as well as the resulting radiative forcing of short-lived species will be determined using both satellite observations and model simulations. Health Impact Assessment HIA methods coupled with model simulations will be used to estimate the long-term impacts of exposure to pollutants PM<sub>2.5</sub> and ozone on cardiovascular and respiratory mortality.

First results obtained in this framework will be presented. In particular, the unexpected negative short-term trends~ -0.50%/yr of lower tropospheric ozone columns surface-6 km inferred from IASI satellite observations over the North China Plain for the 2008-2015 period will be discussed.

# Molecular distributions and stable carbon isotope compositions of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in Beijing during the 2014 Beijing APEC Event

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To ensure the good air quality for the 2014 APEC, stringent emission controls were implemented in Beijing and its surrounding regions, leading to a significant reduction in PM<sub>2.5</sub> loadings. To investigate the impacts of the emission controls on aerosol composition and formation, high-volume PM<sub>2.5</sub> samples were collected in Beijing from October 8 to November 11, 2014 and determined for secondary inorganic ions SIA, i.e., SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, dicarboxylic acids, keto-carboxylic acid and  $\alpha$ -dicarbonyls, as well as stable carbon isotope composition of oxalic acid C<sub>2</sub>. Our results showed that SIA in PM<sub>2.5</sub> are 52 ± 47, 18 ± 13 and 33 ± 29  $\mu\text{g m}^{-3}$  before-, during- and after-APEC, accounting for 29%, 18% and 20% of PM<sub>2.5</sub>, respectively. Compared to that before-APEC, SIA during the APEC period decreased by 65%. As the leading dicarboxylic acid, C<sub>2</sub> in PM<sub>2.5</sub> during the three phases are 502 ± 564, 101 ± 69 and 166 ± 157 ng m<sup>-3</sup>, accounting for 46%, 31% and 34% of total detected organic compounds TDOC, i.e., the sum of dicarboxylic acids, keto-carboxylic acids and  $\alpha$ -dicarbonyls. Similarly, C<sub>2</sub> during the event decreased by around 80% in comparison with that before APEC. The higher values of concentrations and relative abundances of SIA and C<sub>2</sub> before-APEC suggest that PM<sub>2.5</sub> aerosols during this stagnant period are more enriched with secondary products, mainly due to an enhanced photochemical oxidation under the higher temperature and humid conditions. SIA, C<sub>2</sub> and related SOA in PM<sub>2.5</sub> during-APEC were 2–4 times lower than those before-APEC, demonstrating the effectiveness of the pollutant emission controls.

Based on the 72-hr backward trajectory analysis, air masses during the field observation period can roughly be categorized as three types. 1 Regional type, of which the 72-hr air masses originated from Shandong and Henan provinces and

moved slowly into Beijing, 2 Long-range transported type, of which the 72-hr air masses originated from Siberia and moved quickly into Beijing from the north, and 3 Local type, of which the 72-hr air mass originated also from Siberia but moved into Hebei province first and then returned into Beijing from the south area. As shown in Figure 1,  $C_2$  in the regional air masses, which mostly occurred before-APEC, are abundant and enriched in  $^{13}C$ . On the contrary,  $C_2$  in the long-range transport air masses, which mostly occurred during-APEC, is much less abundant but still enriched in  $^{13}C$ . In the local air masses, which mostly occurred after-APEC,  $C_2$  concentration is lower than that before-APEC but higher than that during-APEC and enriched in lighter  $^{12}C$ . A comparison of chemical composition of  $PM_{2.5}$  and  $\delta^{13}C$  values of oxalic acid in two events that are characterized by the highest  $PM_{2.5}$  levels before- and after-APEC, respectively, further showed that after-APEC SIA and TDOC are much less abundant and fine aerosols are enriched with primary organic markers such as PAHs and levoglucosan, and thus is relatively fresh. See Figure 2, compared with those before-APEC. Such reduction in secondary aerosols after-APEC, along with a similar reduction during-APEC, is largely due to the decreasing temperatures that were  $13\pm 2.6^\circ C$  before-APEC and gradually decreased to  $4.3\pm 1.3^\circ C$  after-APEC. Our results indicate that the significant reduction in  $PM_{2.5}$  during-APEC is mainly due to the efficient emission controls, but the effect of the decreasing temperatures, which suppressed secondary aerosol production, may also take an important role.

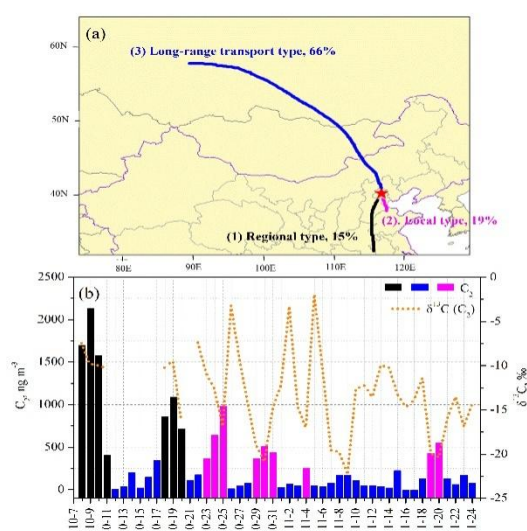


Figure 1 a 72-h backward trajectories determined by the National Oceanic and Atmospheric Administration Hybrid Single Particle Lagrangian Integrated Trajectory HYSPLIT model arriving at the sampling site to reveal the major air mass flow types during the study period. whole study period Colors in Fig. 6a are corresponding

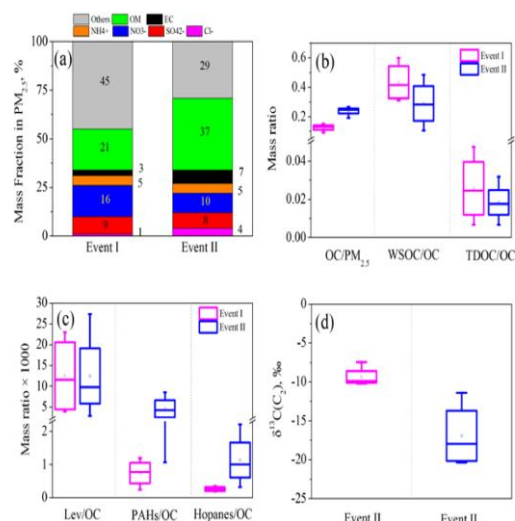


Figure 2. Comparison of chemical composition of  $PM_{2.5}$  during two air pollution events. a Percentages of major species in  $PM_{2.5}$ ; b, c mass ratios of major species and organic tracers in  $PM_{2.5}$ ; d stable carbon isotope composition of oxalic acid  $C_2$

Note: Main part of this work is published in Atmos. Chem. Phys. Discuss. doi: 10.5194/acp-2016-662, 2016, and under review for ACP

# Temporal and Spatial Variation Characteristics of Atmospheric Emissions of Hazardous Heavy Metals from Anthropogenic Sources under Multi-scale Regions

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With rapid progress of the industrialization and urbanization of the world, pollution control of hazardous heavy metals have attracted world wide attention. Based on economic development and technology diffusion theory, anthropogenic atmospheric emission inventory of 12 typical heavy metals Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn characterized by multi-scale regions, long-term spans and high spatiotemporal resolutions were elaborately established by synthetically using the best available representation of time-varying emission factor methods and ArcGIS tools. The main conclusions are summarized as follows: The historical emissions of 12 hazardous heavy metals in China, during the period of 1949-2012, increased by about 20-128 times, totally reaching about 79807.7 tons in 2012, which contributed about 36.8% of global emissions 216893.1 tons. Therein, coal combustion sources, liquid fuel combustion, nonferrous metal smelting and brake wear were regarded as the primary contribution sources for the corresponding heavy metals. Generally, Shandong for As, Se, Cd, Cr, Ni, Sb and Cu, Hebei for Pb and Zn, Guizhou for Hg, Inner Mongolia for Mn and Shanxi for Co ranked as the largest provinces with corresponding heavy metal emissions in China, respectively. One notable feature of the spatial distribution of China's heavy metal emissions was that the heavy metal emission intensities were much higher in central and eastern China than those in western China, and the coastal regions were classed as the most polluted areas of varied heavy metals. Worldwidely speaking, China, Chile, India, Russia, the United States and South Africa were the countries with high heavy metal emissions from anthropogenic sources. Therein, China ranked as the top one largest country with heavy metal except for Sb emissions. Asia represented the highest heavy metals emitting continent, which accounting for approximately 58.6% of the global emission in 2012. The top emission intensities of heavy metals were found in Eastern and Southern Asia and Eastern Europe.

**Key Words:** multi-scale regions, heavy metals, emission inventory, temporal and spatial distribution.

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# A 10-year monitoring of PM<sub>2.5</sub>-bound nickel in Xi'an, Northwestern China

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## Objective

This research has been conducted as part of a 10-year monitoring of daily PM<sub>2.5</sub> in Xi'an, one of the most polluted cities in the world, aimed to expand our knowledge base regarding to the temporal distribution, source characteristics, and health risks of Ni in PM<sub>2.5</sub>. Owing to these purposes, the concentrations of airborne Ni were measured in an urban environment of Xi'an during the period 2004-2013. We aimed at i) investigating the contributions of industrial sources including fuel oil and coal combustions and motor vehicle emissions to the Ni pollution in this typical urban area, and ii) assessing the effects of the control of such emissions on Ni concentrations and related health risks.

## Sample collection

The sampling site was located in the southeastern part of downtown Xi'an, China, where stands the Xi'an hi-tech industries development zone. 24-hour integrated daily PM<sub>2.5</sub> samples were collected from 10:00am to 10:00am on the next day, local time from 1<sup>st</sup> January 2004 to 31<sup>th</sup> December 2013. A total of 3,534 valid samples were collected during the study period. The PM<sub>2.5</sub> samples were collected on pre-fired 780°C, 3hours 47 mm Whatman quartz microfibre filters QM/A<sup>®</sup>, Whatman Inc., U.K. with the mini-volume air samplers Airmetrics, Eugene, OR, USA that operated at a flow rate of 5 L min<sup>-1</sup>. The samplers were deployed ~10 m above ground level, on the roof of a two-story building.

## Mass analysis

The PM<sub>2.5</sub> mass concentrations were obtained by weighing the filters with a Sartorius ME 5-F electronic microbalance that had a sensitivity of ±1 µg Sartorius, Gottingen, Germany after equilibration at a temperature of 20°C-23°C and a relative humidity RH of 35%-45% for at least 24 hours.

## Ni analysis and QA/QC

Energy Dispersive X-Ray Fluorescence ED-XRF spectrometry Epsilon 5 ED-XRF analyzer, PANalytical, Netherlands was used to determine the Ni concentrations on the quartz fiber PM<sub>2.5</sub> filters. ED-XRF spectrometer was calibrated with thin-film standards obtained from MicroMatter Co. Vancouver, Canada. National Institute of Standards and Technology NIST Standard Reference Material SRM 2783 was employed to validate the accuracy of Ni measurement. The reference value for Ni in



SRM 2783 is  $68 \pm 12 \text{ ng filter}^{-1}$ , which was similar to the results analyzed by our ED-XRF system: the average concentration of Ni was  $63 \pm 14 \text{ ng filter}^{-1}$  with seven replicate analyses. The relative error was 7.3% between certificated value of SRM 2783 and our data, which is well within the acceptance range. The details of experimental description for the ED-XRF measurements are shown in Xu et al.

### Result and conclusion

A large data set of  $\text{PM}_{2.5}$ -bound nickel Ni concentration has been produced from filter samples collected in urban environment of Xi'an, Northwestern China, over 10-year period 2004-2013, in order to determine the trend of Ni pollution status, its potential sources and health risks. The average concentration of Ni measured during the whole study period was  $5.9 \pm 5.5 \text{ ng m}^{-3}$ , ranging from  $<0.08 \text{ MDL}$  to  $88.1 \text{ ng m}^{-3}$ . Annual average Ni concentration increased firstly and then decreased obviously. The turning point was 2008. Table 1, owing to changes in strengthening management and improvement techniques in industrial sources and motor vehicles Tian et al., 2012.

Table 1. A statistical summary of Ni concentrations over ten years 2004-2013.

Year	Ni $\text{ng m}^{-3}$		
	Average	Stdev <sup>a</sup>	Range
2004	6.5	5.0	0.44- 53.8
2005	6.6	5.3	MDL <sup>c</sup> -32.8
2006	7.3	6.6	MDL-88.1
2007	7.7	8.3	0.76-76.6
2008	6.2	5.2	0.90-56.6
2009	7.0	7.1	MDL-59.4
2010	5.8	5.1	1.20-41.9
2011	4.8	4.2	0.43-59.5
2012	4.2	5.4	0.13-70.9
2013	3.0	2.6	0.44-19.6

To assess the effect of major sources of Ni on the long term distribution, comparisons of Ni concentration, enrichment factor, and potent sources between workday and non-workday periods were examined over these ten years. It can be seen that weekend-affected-sources, i.e., industrial and motor vehicle emissions Cempel and Nikel, 2006, of Ni was reduced obviously. Figure 2.

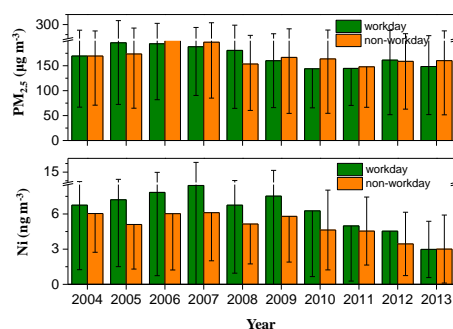


Figure 1.  $\text{PM}_{2.5}$  and Ni concentrations comparisons between workday and non-workday from 2004 to 2013.

Moreover, the health risk assessment showed that non-cancer risk of Ni can be

ignored in Xi'an, but not for cancer risk Figure 2. Although Ni incremental lifetime cancer risk was relative significance on workday period in Xi'an, Ni showed a distinct decline for both workday and non-workday periods from 2006, due to more and more strict air pollution control policies Cao et al., 2012.

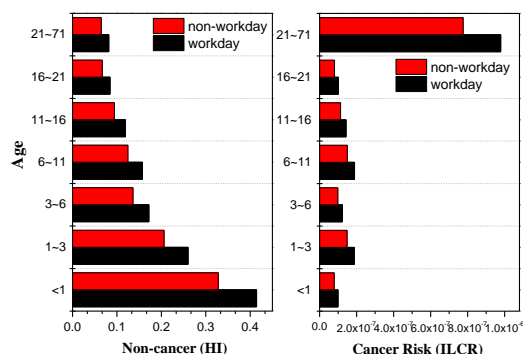


Figure 2. Comparison of non-cancer HI and cancer ILCR risks of Ni for different age groups and for workday and non-workday periods in Xi'an.

Implementations of motor vehicle and industrial emissions control policies and advanced technologies have led to a great healthy benefit, and it can be served as a positive sign for China air pollution source control strategies over these years.

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**Keywords:** Nickel Ni, long-term monitoring, PM<sub>2.5</sub>, health risk assessment.

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# The OH-initiated Oxidation of Peroxyacetic Acid: a study of experiment and model

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Peroxyacetic acid PAA plays an important role in the atmospheric chemistry, serving as oxidant and affecting radical recycling. The addition of PAA-related chemistry in models has obvious impact on the predictions of HO<sub>2</sub> radical and sulfate formation. However, previous studies revealed the gap between modeled and observed concentrations of atmospheric PAA, which may be partly ascribed to the uncertainty in the mechanism and kinetic i.e. rate constant of OH-oxidation. In this study, we measured the rate constant of OH radical reaction with PAA and investigated the mechanism in order to develop a more robust atmospheric PAA chemistry in models. Using relative rates technique and employing toluene and meta-xylene as references, the data was calculated to be  $9.53 \pm 0.50 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K and 1 atm, which is 2.5 times larger than the value used in previous models  $3.70 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Incorporation of a box model and revised PAA chemistry with the raised parameter resulted to a better simulation of atmospheric PAA during the field measurements in summer Wangdu 2014. It is found from the modeled results that OH-oxidation was the important sink for atmospheric PAA in Wangdu, accounting for ~30% of the total loss. Additionally, the major terminal products of OH-oxidation of PAA are identified as formaldehyde HCHO, acetaldehyde CH<sub>3</sub>CHO and formic acid [HCOOH]. We speculate that the formed HCOOH and CH<sub>3</sub>CHO may be produced from the process of H-abstraction from methyl hydrogen or OH-addition to the carboxylic carbon, indicating that there exist other pathways of OH-oxidation, except for the widely acknowledged channel of H-abstraction from acidic hydrogen.

# Investigation of O<sub>3</sub> mixing ratios and formation mechanism in a coastal city of China

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The U.S. EPA Models-3 Community Multiscale Air Quality CMAQ modeling system with the process analysis tool is applied to study the O<sub>3</sub> pollution characteristics and formation mechanisms in May and November, 2013 over Qingdao, a coastal city of China. O<sub>3</sub> mixing ratios from 6 national monitoring sites of Qingdao were used for model evaluation and spatial distribution analysis. The averaged O<sub>3</sub> mixing ratio was 37 ppb in May late spring, which was twice of the values in November late autumn, 18 ppb. The rural site showed relatively higher O<sub>3</sub> mixing ratios than urban sites during both two periods. Model simulation analysis showed that higher O<sub>3</sub> mixing ratios at the rural area would be due to the high altitude transportation from surrounding area. As a crucial index to reflect the impact of longer exposure of O<sub>3</sub>, the 8-h O<sub>3</sub> mixing ratios were always be found to exceed the Ambient Air Quality Standard over all sites. 80% of the late spring period exceed the standard at the rural site, while nearly 50% at the urban area. O<sub>3</sub> mixing ratios in Qingdao showed typical diurnal variation and obviously “weekend effect”. The O<sub>3</sub> always reaches peak values after the noon while decreasing to the minimum during rush hours in the morning due to the reaction of  $\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$ . The O<sub>3</sub> “weekend effect” generally happens over the urban area instead of the rural site due to the NO titration. The process analysis showed that dominate processes that contribute to the accumulation and loss of O<sub>3</sub> in Qingdao were horizontal and vertical transport. Production of O<sub>3</sub> through gas-phase chemistry was found at the higher latitude over whole Qingdao. Three photochemical indicators were used to indicate the sensitivity of O<sub>3</sub> to changes in its precursors’ emissions to assess the effectiveness of VOCs or NO<sub>x</sub> emission controls in reducing O<sub>3</sub>. In late spring, all three indicators showed NO<sub>x</sub>-limited O<sub>3</sub> chemistry in Qingdao, suggesting that reduction of NO<sub>x</sub> emissions will be helpful to O<sub>3</sub> decrease. In late autumn, the VOCs-limited O<sub>3</sub> chemistry was found, which may be due to relatively less emissions of biogenic VOCs in cold days.

**Keywords:** CMAQ; O<sub>3</sub> chemistry; process analysis; VOC- and NO<sub>x</sub>-limited

# Multi-pollutants emissions and health exposure assessment from the burning of major agricultural straws in China

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The burning of 5 major agricultural straws including wheat, rice, corn, cotton, and soybean straws was conducted to investigate emission factors of organic carbon OC, elemental carbon EC, water soluble inorganic ions WSI, water soluble organic acids WSOA and ammonium WSA, trace heavy metals THM, PAHs, and phenols in PM<sub>1.0</sub> and PM<sub>2.5</sub> using an aerosol chamber. The distribution and difference of multi-pollutants were compared within straw types in PM<sub>2.5</sub> and PM<sub>1.0</sub>. The emission factors of PM<sub>2.5</sub> and PM<sub>1.0</sub> and in them of OC, EC, WSI, WSOA, WSA, THM, PAHs and Phenols are 3.25-15.16 and 1.34-6.04, 1.54-7.42 and 0.58-2.08, 0.61-2.18 and 0.51-3.52, 0.52-3.81 and 0.13-0.64, 0.14-0.77 and 4.39-85.72, 4.51-104.79 and 11.8-51.1, 14.0-131.6 and THM,  $1.8-8.3 \times 10^{-3}$  and  $1.1-4.0 \times 10^{-3}$ ,  $9.7-41.5 \times 10^{-3}$  and  $7.7-23.5 \times 10^{-3}$  mg/kg, respectively. Average ratios of OC/EC and char-EC/soot-EC inside of PM<sub>2.5</sub> to PM<sub>1.0</sub> are 3.82 and 7.82, respectively, indicating EC or soot-EC mainly consisting in PM<sub>1.0</sub>. Single particle analysis by TEM showed that soot particles are mostly within hundred nanometers. Moreover, fly ash particles bearing more heavy metals that are over micrometer also verify more THM emitted in the form of smoke PM<sub>2.5</sub>.

To assess health effect and help source-specific air quality control, permissible exposure limits PEL of smoke PM<sub>2.5</sub> are assessed for carcinogenic risk concern using selected hazard pollutants including PAHs and THM. Daily exposure concentration changes a lot among straws and should be constrained within 0.2, 0.3, 0.4, 1.4, and 0.8  $\mu\text{g m}^{-3}$  for wheat, corn, rice, cotton, and soybean straw, respectively. Flux concentrations of annual PM<sub>2.5</sub> that are calculated using box-model method from 5 version emission inventories all exceed the PEL.

# Characterization and source apportionment of aerosol light extinction with a coupled model of CMB-IMPROVE in Hangzhou, Yangtze River Delta of China

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To investigate the characteristics and sources of aerosol light extinction in the Yangtze River Delta of China, a campaign was carried out in Hangzhou from December 2013 to November 2014. Hourly data for air pollutants including PM<sub>2.5</sub>, SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> and CO, and aerosol optical properties including aerosol scattering coefficient and aerosol absorbing coefficient was obtained in the environmental air quality automatic monitoring station. Meteorological parameters were measured synchronously in the automated meteorology monitoring station. Additionally, around seven sets of ambient PM<sub>2.5</sub> samples per month were collected and analyzed during the campaign. The annual mean aerosol scattering coefficient, aerosol absorbing coefficient and aerosol single scattering albedo measured in this study was  $514 \pm 284 \text{ Mm}^{-1}$ ,  $35 \pm 20 \text{ Mm}^{-1}$  and 94% respectively. The aerosol extinction coefficient reconstructed using the modified IMPROVE (Interagency Monitoring of Protected Visual Environment) formula was compared to the measured extinction coefficient. Better correlations could be found between the measured and reconstructed extinction coefficient when RH was under 90%. A coupled model of CMB chemical mass balance and modified IMPROVE was used to apportion the sources of aerosol light extinction in Hangzhou. Vehicle exhaust, secondary nitrate and secondary sulfate were identified as the most significant sources for aerosol light extinction, accounted for 30.2%, 24.1% and 15.8% respectively.

# Aged status changes of soot particles upon smog chamber ageing

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Soot particles exerts profound impacts on air quality and climate because of its high absorption cross-section over a broad range of electromagnetic spectra, but the current results on physical properties changes of soot particles during atmospheric aging remain conflicting. Here, we quantified the aging and variation in the physical properties of soot particles under ambient conditions in Beijing, China, using a novel environmental chamber approach. Particles collected from different stages of aging time were characterized by their shape, size and elemental composition using electron microscopes. Soot particles aging were classified three distinct stages, i.e., fresh stage, initial transformation stage, and compact particles stage. In the fresh stage, most of the soot particles exhibited open spherule's chain or agglomerate shape. More than 60% of the particles had circularity factor in the range of 0.15-0.40. In the initial transformation stage, some of the soot particles have changed aged shape shrunk clusters. In the compact particles stage, most of the soot particles exhibited shrunk clusters shape. 75% particles' circularity factor in this stage appeared in the range of 0.45-0.65. The timescales to achieve 75% morphology modification for soot particles are estimated to be 3 h on a sunny day in this study. Morphologies of the particles on sunny days and cloud days were compared. The results indicate that the aged status of soot particles in two different kinds of weather were not very different, suggesting that fresh soot particles in chain or aggregate shape could be modified into clusters shape rapidly.

**Key words:** soot; ageing; smog chamber; circularity factor; electron microscopes

# Size distributions and sources of elements in particulate matter on Weizhou Island of the Cross-border area between Northern South China Sea and Southeast Asia country

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To investigate the composition and possible sources of fine particles especially during March of 2015 in the Cross-border area lines between Northern South China Sea and Southeast Asia country, a single particle aerosol mass spectrometer SPAMS was deployed to measure the changes of single particle species and sizes, in the Weizhou Island. During the observation, a total of 3100597 particles were sized and 769525 particles with both positive and negative mass spectrum were collected and characterized in combination with the ART-2a neural network algorithm. The number distribution of sized particles were mainly in from 520nm to 600nm, the average hit rate of 25.8% was obtain and hit rate of diameters ranging from 340 to 1000nm was above 90%, and 10 types of particles were classified, as well as the relative ratio and size distribution of each type: Cobalt containing particles Co, 0.40%, 540 nm, Elemental Carbon EC, 48.1%, 620nm, Organic Carbon OC, 12.7%, 440nm, EC and OC combined particles ECOC, 8.31%, 680nm, K-Na containing particles NaK, 3.4%, 760nm, K-containing particles K, 23.5%, 600nm, mineral particles KWZ, 0.6%, 680nm, Fe containing particles Fe, 2.4%, 640nm, Heavy Metal-containing particles HM, 0.4%, 660nm, Vanadium containing particles V, 0.2%, 620nm. considering the mass concentration of PM<sub>2.5</sub> and the back trajectory results from the Hysplit-4 model. Results showed that EC, OC and K were the major components of single particles during haze pollution periods, which showed a bit increasing ratios compared with those in clean periods. EC were mainly from local vehicle emissions during pollution episodes, OC were mainly from local contribution and secondary formation, combined with those from the regional transportation of fossil fuel combustion, biomass burning mainly from Guangdong province Thailand and Vietnam.



# Development of Ultrasensitive VOCs Mass Spectrometer

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Based on a laboratory-assembled vacuum ultraviolet VUV light source, an ultrasensitive VUV photoionization mass spectrometer was built in Research Center for Eco-Environmental Sciences, CAS. A novel photoionizer consisting of a photoionization cavity and a VUV light baffle was invented to improve the limit of detection. A detection limit  $2\sigma$  of 3 pptv is achieved for benzene after an acquisition time of 10 s. The sensitivity for benzene reaches more than 5000 counts/ppbv, which is the highest ever reported in the literature. The instrument has been used in online monitoring urban air, real-time observation of VOCs released from incubated cells and the study of secondary aerosol formation. The detailed design of the instrument and initial experimental results will be presented in the talk.

# Effect of environment risk factors on birth weight of neonates in Taiyuan, China

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To explore the effect of environment risk factors on the birth weight of neonates, we collected the medical information for neonates from 2006 to 2012 through the public health monitoring system of Taiyuan. The SGA and LBW were as the end points of outcome. Correlation analysis, single and multiple logistic regression analysis were used to explore the relationship between environment risk factors and birth weight of neonates.

The incidence of SGA infants was 7.91% based on the distribution of birth weight for neonates in Taiyuan. The incidence rate for boy was 8.26%, which was higher than that for girl 7.52%. The incidence of LBW was 2.88%. On the contrary with the SGA, the incidence rate of LBM for boy was 2.64%, which was lower than that for girl 3.14%.

For the SGA, the correlation analysis showed that the incidence were strongly negative associated with maternal height, maternal weight, the percentage of kitchen with ventilation equipment significantly  $P < 0.05$  and positive associated with annual average concentration of ambient air pollutants including PM<sub>10</sub>, SO<sub>2</sub> and CO, the percentage of maternal smoking and drinking, using coal as fuel, coal furnace heater significantly  $P < 0.05$ . Single logistic regression analysis showed that the relative risk of SGA were 1.2995%CI:1.08-1.56 for maternal smoking, 1.1095%CI:1.01-1.20 for maternal passive smoking, 1.2295%CI:1.01-1.46 for maternal drinking and 1.2595%CI:1.00-1.56 for maternal harmful exposure including pesticides, heavy metals or X-ray. The Coal and electricity as fuel, coal furnace and electric heater were also associated with SGA. The relative risk were 1.3295%CI:1.27-1.37, 1.3395%CI:1.26-1.39, 1.7195%CI:1.65-1.78 and 1.5395%CI:1.35-1.73, respectively. Multiple logistic regression showed that electricity as fuel 1.32, 95%CI:1.27~1.37 and electric heater 1.33, 95%CI:1.26~1.39 were independent risk factors for SGA and the kitchen with ventilation equipment 0.91, 95%CI:0.87~0.95 would decline the incidence of SGA after controlling the confounding.

There were negative correlation between maternal weight and LBW incidence  $P > 0.05$  and strong positive correlation between maternal age, percentage of maternal smoking, percentage of maternal drinking, percentage of coal furnace heater, annual average concentration of PM<sub>10</sub> and CO and LBW incidence  $P > 0.05$ .

Maternal smoking, daily passive smoking less than 2 hours, harmful exposure pesticides, heavy metals or X-ray, electricity as fuel, coal furnace heater and electric heater might increase the risk of LBW. However, only the RR of maternal smoking, electricity as fuel, coal furnace heater and electric heater increased significantly. The RR were 1.4095%CI:1.05,1.86, 1.1295%CI:1.03,1.21, 1.3295%CI:1.25,1.41 and 1.3495%CI:1.11,1.64, respectively.

All results suggested that maternal smoking, drinking, passive smoking, harmful exposure pesticides, heavy metals or X-ray and electricity as fuel and electric heater during pregnancy were the risk factors for SGA. Maternal smoking, electricity as fuel, coal furnace heater and electric heater are the risk factors for LBW. The incidence of SGA and LBW can be reduced through improving the living conditions and developing healthy living habits.

**Key words:** Environment risk factors; Small-for-gestational-ageSGA infants; Low birth weightLBW; Incidence

# Vertical structure of foggy haze over the Beijing Tianjin-Hebei area in January 2013

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In January 2013, frequent episodes of intense air pollution occurred in the Beijing–Tianjin–Hebei area BTH, China. Besides the occurrence of region-wide dry haze pollution, foggy haze conditions also developed across the region on numerous days, lasting into the afternoon. Synergistic analysis, using multisatellite datasets, air sounding and surface meteorological observations, indicated that there was a vertical overlap of fog and aerosol layers during the foggy haze episodes in the region. Fog appeared at a low level of the atmosphere. The altitude of the upper boundary of the fog differed across the region, but it was always below 1 km. The aerosol layer that closely contacted with the top of the underlying fog was rather dense, having a high concentration comparable to that during severe pollution on the ground. Above the dense aerosol layer, aerosol with a concentration equivalent to that of moderate pollution stretched up to an altitude of 2 km. Beyond that, a tenuous aerosol layer extended 5 km into the atmosphere. This overlapping of fog and haze layers frequently occurred across the region in January 2013. The occurrence of a foggy haze over BTH could worsen the regional air quality, and its appearance across this region would have notable effects on the radiation balance.

# Distribution and control of PM<sub>2.5</sub> pollution in China

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Awareness of pollution by atmospheric particulate matter in China began to grow in the 1970s and 80s, and those concerns over air pollution led to both national and international studies that initially focused on TSP and PM<sub>10</sub>. Beginning in 2011, large-scale haze pollution events in China shifted the focus of interest to PM<sub>2.5</sub>, and in the last four years PM<sub>2.5</sub> has gotten unprecedented attention from both politicians and the general public. Indeed, China suffers from some of the most severe PM<sub>2.5</sub> pollution in the world, and ~80% of the cities have been unable to reach the newly-established ambient air quality standards. According to our studies of 14 Chinese cities conducted in 2003 and repeated in 2013, it will take ~20 years until 2034 to meet the new national PM<sub>2.5</sub> air quality standards in those cities. During heavy haze events in Beijing, Shanghai, Guangzhou and Xi'an, secondary sulfates, nitrates and organic matter typically are the main components of PM<sub>2.5</sub>. The five main air pollution sources in China are 1 coal combustion; 2 industrial emissions, especially those from steelmaking, heavy chemicals, building materials and metallurgy, etc.; 3 motor vehicle exhaust; 4 biomass burning; and 5 fugitive dust. The main factors that have led to China's high PM<sub>2.5</sub> pollution levels are the country's coal-dominated energy infrastructure; frequent haze events related to the rapid and extensive economic development; and regional pollution brought by the cross-border transportation of pollutants. The complexity and long-term trends in PM<sub>2.5</sub> pollution result from varying levels of prevention and management among regions, with most significant complicating factors being regional differences in a emission sources, b energy structure and economic development, and c terrain and weather. Future efforts in PM<sub>2.5</sub> pollution control will center on the basic policy of "government leadership, treatment with science and technology, and promotion by the public" as this is likely the best strategy for establishing a new system for prevention and treatment. Science and technology will continue to provide the core information on the spatial and temporal patterns of PM<sub>2.5</sub> needed to develop effective management plans. For example, advanced nuclear energy was put forth to address air pollution as well as climate change challenges in China. In addition, new technological applications in pollution prevention and treatment should be encouraged and strengthened—for example, development of a new nano air purification technology, the Solar-Assisted Large-Scale Cleaning System SALSCS, etc.

**Key words:** haze pollution, PM<sub>2.5</sub>, pollution sources, control strategy, SALSCS

# Characteristics of heavy metals in atmospheric particles in summer in Chang-Zhu-Tan city clusters, China

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To understand the pollution characteristics of heavy metals in atmospheric particles in summer in Chang-Zhu-Tan City clusters, China, total suspended particulate TSP and PM<sub>10</sub> samples were collected in cities of Changsha, Zhuzhou and Xiangtan from March to May 2012. The concentration of heavy metals of cadmium Cd, lead Pb, chromium Cr, and arsenic As in both TSP and PM<sub>10</sub> samples were measured. Results showed that the average TSP concentration in Changsha, Zhuzhou and Xiangtan were  $59 \pm 7$ ,  $90 \pm 15$  and  $77 \pm 6 \mu\text{g}/\text{m}^3$  respectively, and the average PM<sub>10</sub> were  $53 \pm 7$ ,  $80 \pm 16$  and  $73 \pm 8 \mu\text{g}/\text{m}^3$  respectively. The lowest concentrations of TSP and PM<sub>10</sub> occurred at the background Shaping site of Changsha. The average ratio of  $\rho\text{PM}_{10}/\rho\text{TSP}$  was 89.5%, ranging from 83.0% to 98.0%. Concerning heavy metals, in TSP samples, the concentration of Cr, As, Cd and Pb were 30.5-57.5, 16.8-72.8, 2.8-21.8 and 81.2-458.4  $\text{ng}/\text{m}^3$ , respectively, while in PM<sub>10</sub> samples, were 17.1-21.5, 15.3-69.8, 2.5-20.3 and 77.3-403.7  $\text{ng}/\text{m}^3$ , respectively, in Chang-Zhu-Tan City clusters. The enrichment factor of Cd was the highest 255-5332, 462-6367 in TSP and PM<sub>10</sub>, followed by Pb and As, while that of Cr was the lowest 7-24, 5-15 in TSP and PM<sub>10</sub>.

**Key words:** heavy metals; atmospheric particles; pollution characteristics; enrichment factors; Chang-Zhu-Tan city clusters

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# Study of Chinese pollution with the 3D regional chemistry transport CHIMERE model and remote sensing observations

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Since the end of the 20th century, China has observed important growth in numerous sectors. China's Gross Domestic Product GDP has been multiply by 4 during the 2000-2010 decade National Bureau of Statistics of China, mostly because of the industry's growth. Also, important rise of China's Energy consumption and vehicle numbers have been noticed during the same decade, and it is still growing now Wang Y. et al, Energy Policy, 2011. These evolutions have been accompanied by important increases of atmospheric pollutants emissions Yinmin X. et al, Atmo Env, 2016.

As a consequence and for about 10 years now, Chinese authorities have been working to reduce pollutant levels, because atmospheric pollution is a major health issue for Chinese population especially within cities, for which World Health Organisation's standards for major pollutants Ozone, PM2.5, PM10 are often exceeded.

Particles have multiple issues, as they impact on health and global warming. Their impacts will depend on their sources primary or secondary pollutants and natures Particle size distribution, chemical composition.... Controlling particles loading is a complex task as their sources are various and dispersed on the Chinese territories: mineral dust can be emitted from Chinese deserts in large amount Laurent et al., Change, 2006, ammonia can be emitted from agriculture and livestock and lots of urban primary pollutants can be emitted from urbanized areas. It is then necessary to work from a continental to local scales to understand more precisely pollution of urbanized areas. It is then mandatory to discriminate and quantify pollution sources and to estimate the impact of natural pollution and the major contributing sources.

We propose here an approach based on a model and satellite observation synergy to estimate what controls Chinese pollution. We use a regional chemistry transport model CHIMERE to simulate atmospheric pollutants concentrations and to reproduce the atmospheric environment and estimate the air quality. A large domain 72°E-145°E; 17.5°N-55°N, with a  $\frac{1}{4}^{\circ} \times \frac{1}{4}^{\circ}$  resolution is used to make multi-annual simulations. CHIMERE model include most of the pollutants sources, and using a soil properties database is able to model Dust emission Laurent et al., JGR, 2005. Several satellite products are available IASI: NH<sub>3</sub>, O<sub>3</sub>, CO, PM; MODIS: AOD and will be used to evaluate model simulation NH<sub>3</sub> column, O<sub>3</sub> profiles. When available, ground based measurements will also be used, as the AOD from the AERONET network, to improve model evaluation. Using remote sensing observations we are able to estimate modelling simulation quality, verify that processes that control pollutant concentrations are correctly represented, it is after possible to

study annual variability of pollutants and determine which pollutant will be contributing the most to atmospheric pollution at a time, and which are the most present at an annual scale.

In this work, we will present results of one year aerosol simulation. More specifically, we will show the impact of dust. April 2011 has been investigated as it is an interesting study case from a dust point of view. Important winds will generate a heavy Dust storm, from the Taklimakan desert, which will transports mineral particles all over China and will impact and sometimes be the main atmospheric pollutant for many Chinese cities and for several days. This dust storm event will also represent about 30% of total mineral dust emission for 2011. Also, particles precursor's emissions and concentrations are investigated: Urbanized areas NO<sub>x</sub> annual variation shows extremum during winter season, due to a less effective atmospheric diffusion; simulated ammonia concentrations often associated to agricultural practice are compared to IASI observations.



# Unrevealing the internal mixing of BC-containing particles in East Asia

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Soot particles is a research focus due to its strong capacity of absorbing solar radiation and acute health effects. With the help of sandstorm outbreak, soot particles emitted from heavy polluted North China Plain can transport to leeward areas, such as Korea and Japan.

During a sandstorm outbreak episode, aerosol particulate matter samples were collected in four East Asian sites: a coastal urban site T1 China, an inland urban site T2 China, a coastal rural site T3 Japan, and an ocean site T4 East China Sea. Transmission electron microscopy coupled with an energy dispersive X-ray spectrometer TEM-EDX was employed to obtain morphology, size, mixing state and composition of aerosol particles.

Our results shows that soot particles are highly internal mixed with secondary materials sulfate and nitrate after a remote transportation. The proportion of internal mixed soot particles in leeward areas 53% for T3 and 56% for T4 is much higher than T1 13% and T2 5%.

# Seasonal variations and chemical characteristics of PM<sub>2.5</sub> in Verneuil, central France

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To expand our knowledge of regional fine particles in Central France, a field observation study of PM<sub>2.5</sub> was carried out at Verneuil from 2011 to 2014. The mass concentrations of water-soluble inorganic ions WSIs, organic carbon OC, elemental carbon EC and biomass burning tracer Levoglucosan in PM<sub>2.5</sub> were measured. The annual average PM<sub>2.5</sub> mass concentrations from 2011 to 2014 were 11.8, 9.5, 12.6 and 10.2  $\mu\text{g m}^{-3}$ , respectively, reached the WHO guideline of 10  $\mu\text{g m}^{-3}$ . SIA and OM appeared to be the major components in PM<sub>2.5</sub> in Verneuil, contributing 30.1% to 41.8% and 36.9% to 46.3%, respectively. Main chemical species were observed in the following order: winter  $\geq$  spring > autumn > summer. Backward atmospheric trajectories were performed using Hysplit and suggested that the PM<sub>2.5</sub> pollutants caused by atmospheric transport were mainly came from European inland, mainly east to north-east areas. During the 4 years, five pollution events were reported. Not only the polluted air masses from central Europe but also the biomass burning from East Europe will influence the air quality in Verneuil.

# Characteristics of ambient volatile organic compounds and their sources at an urban site in Nanjing

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Nonmethane volatile organic compounds NMVOCs were measured continuously from 01 January 2015 to 31 December 2015 at an urban site in the Nanjing residential area. Characteristic of NMVOCs including mixing ratio, temporal variation, reactivity and source apportionment were analyzed in this region. During this period, the NMVOCs concentration was 21.6 ppbv, which displays a seasonal variation with a maximum in spring and a minimum in summer. Alkanes contributed the most nearly 47% of the total NMVOCs, then followed by alkynes and aromatics which contributed about 24% and 19%. Although Alkenes only accounted about 10% of the total mixture, the results showed that alkenes and aromatics were the dominant contributor to total NMVOCs reactivity and ozone-formation potential. Propene, ethene, m,p-xylene, toluene and acetylene were the top 5 species contributed nearly 60% of the ozone-formation potential. The PMF model was used to identify the source of NMVOCs. Solvent usage 34%, gasoline vehicular exhaust 31%, diesel vehicular exhaust 22%, gasoline evaporation 9% and biogenic emission 4% were identified as the dominant sources.

**Key words:** volatile organic compounds, ozone-formation potential, PMF, Solvent usage

# Physicochemical characteristics of aerosol particles in the Tibetan Plateau: new insights from TEM-EDX analysis

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The Tibetan Plateau TP is a vast and elevated Asian plateau that extends over 27–45°N, 70–105°E, with a mean elevation of more than 4 km above sea level, and it is an ideal site for studies of atmospheric background, and human impact on the natural environment by long-distance pollutant transport. To improve our knowledge regarding particles in the TP, atmospheric aerosol particles were collected in July–August 2011 from the remote Nam Co station 30°46.44'N, 90°59.31'E, 4730 m located beside the Nam Co salt lake on the Tibetan Plateau. The morphology and elemental composition of the individual particles were investigated using Transmission Electron Microscopy with an Energy Dispersive X-ray detector TEM-EDX.

The aerosol particles in the Tibetan Plateau showed complex compositions. The EDX detected more than 15 elements in addition to C, including Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Fe, P, Zn, and Mn. For ultra-light elements, such as B, C, N, and O, which have low fluorescent yields and serious absorption, it was difficult to obtain accurate results. Fig. 2 shows the frequency of element presence in the 281 analyzed particles. Silica was detected in more than 90% of the particles, followed by Mg and S >70%, K >60% and Ca ~60%, and Na, Al, Fe and Cl in descending order. P, Ti, Zn, Mn, and heavy metals e.g., Ni, Sr, La, Ce, Pb, Te, Cr and Sc were present less than 10% of the analyzed particles.

Based on their possible sources, we classified the aerosol particles into eight types, which were further classified in three groups: natural, combustion, and secondary particles. The natural particle group included NaCl, biogenic and crustal mineral particles, while the combustion particle group included tar balls, soot, and metal particles. The secondary particle group mainly included secondary mineral particles and sulfates.

Crustal mineral particles and secondary particles were the main particle types, and they were dominated by Si- rich, Na- rich, Ca- rich, S- rich and Fe-rich particles, followed by Mg- rich, K- rich, Cl- rich, Ti- rich and Al-rich particles. About 85% of the individual particles showed an internal mixing state. Soot, organic matter, and fine mineral particles were often internally mixed with S-rich particles. The Cl-Na-S and Ca-Si-S triangular phase diagram showed the particles in TP were in serious aging state. High concentrations of acid gases from anthropogenic sources and a high relative humidity facilitate heterogeneous reactions on the surface of mineral particles, generating shells. In the particles analyzed, the mixing states were more

complicated in non-sunny than in sunny days, since the relative humidity in cloudy 66.5 and 64.3% and light drizzle days 89.4 and 99.9% is higher, thereby enhancing the chemical reactions of particles.

The Na-containing particles are one of the common particles which account for 54% of the total particles and include “Na+S”, “Na+Mg”, “Na+Si”, “Na+K”, “Na+Cl”, “Na+Ca” subtypes. The Na of the aerosol particles is sourced from the salt particles carried in from lake Nam Co by lake-land breeze. Detection frequencies of four kinds of particles including “Na + Cl”, “Na without Cl”, “Cl without Na” and “none of Na and Cl” are compared, and it is noticed that in the light drizzle days the frequency of the “Na without Cl” particles is the highest, and the frequency of “none of Na and Cl” particles is zero. The Cl-Na-S phase diagram further illustrated that the NaSO<sub>4</sub> and NaCl were abundant in the light drizzle days, indicating that the high relative humidity may facilitate heterogeneous reactions of the salt particles with acid gases, which can transfer more NaCl into NaSO<sub>4</sub>.

The aging process of individual particles in the atmosphere influence particle evaporation and the chemical reactions with gases and solutions, and the heterogeneous reactions between salt particles and gas in the atmosphere can reduce the SO<sub>2</sub> pollution which has the effect of cleaning air. The 24 h isentropic backward trajectories indicated that high-altitude contaminated particles, mostly of anthropogenic origin, were transported from southwestern Tibet and the Indian subcontinent.

# New Particle Formation and Aerosol Growth due to Surfactant Photochemistry at the Air/Water Interface

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## Introduction and Objective

Films of organic compounds exposed to the atmosphere are ubiquitously found on surfaces of cloud droplets, aerosol particles, buildings, plants, soils and the ocean. The sea-surface microlayer is one example of organic films that are host to countless biogenic amphiphilic compounds concentrated there with respect to bulk water. Yet, organic materials present in the bulk, such as humic acids and other photosensitizing compounds, can still have a tremendous impact on the surfactants George, 2015.

In laboratory studies we investigated formation and growth of secondary organic aerosol SOA from the reaction of ozone with volatile organic compounds VOCs, originating from photo-induced processes in surfactant-containing water. The results underscore the environmental importance of photochemical reactions at the air–water interface to produce SOA precursors in significant amounts, leading to significant particle formation and growth.

## Methods

Laboratory experiments were either conducted in a 30 cm<sup>3</sup> quartz-cell or in a custom-built 2 m<sup>3</sup> Teflon reaction chamber with a water reservoir. Nonanoic acid was used as a proxy for surfactants, such as fatty acids, residing in environmental surface microlayers. In other experiments nonanol was used as a surfactant for comparison. For more realistic conditions, additional experiments were conducted using riverine biofilms that were grown under natural but controlled conditions. VOC concentrations were measured over time using a proton transfer reaction–time of flight–mass spectrometer PTR–ToF–MS as a function of irradiation UV and visible light in a humidified low NO<sub>x</sub> and low ozone environment. Characterization of organic compounds in water was performed with liquid chromatography–high resolution mass spectrometry LC–HRMS utilizing a quadrupole-orbitrap detector. Aerosol size distribution and numbers were continuously monitored during all experiments.

## Results and Conclusion

Production of VOCs occurred while the chamber air and water were irradiated with UV light for the nonanoic acid–water system as well as for biofilm-containing water. Gas-phase products included alkenes, aldehydes and dienes, as observed by PTR–ToF–MS in different ionization modes H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> and O<sub>2</sub><sup>+</sup>. Upon ozone

injection under dark conditions, aerosol nucleation and particle growth was observed, further indicating the presence of unsaturated VOCs. Concentrations of aerosol particles were typically on the order of  $10^2$ – $10^3$   $\text{cm}^{-3}$ . The addition of humic acids typically enhanced photochemical VOC production and aerosol formation, where SOA numbers exceeded  $10^4$   $\text{cm}^{-3}$  after ozone injection and particle nucleation. We note that when nonanol was used as a surfactant, VOC and aerosol formation was never observed. This result highlights the potential importance of the carbonyl functionality of the acid group in the photochemical mechanism. LC–HRMS measurements indicate that the photochemically produced compounds were not only emitted to the gas phase, but also into the bulk water. In addition, high molecular weight compounds such as highly oxidized organic molecules and molecular recombination products were identified in experiments with the nonanoic acid surfactant.

We suggest that light absorption precedes radical chemistry at the organic surfactant interface. Recent experimental findings in our group, supported by quantum chemical calculations, reveal the possibility of exciting nonanoic acid molecules to their triplet state even under irradiation of 300–320 nm wavelengths. Subsequent inter- and intra-molecular reactions have been proposed generating OH and other radicals, leading to a broad range of products. At an organic interface neighboring organic molecules are likely to react, especially in molecular layers such as those existing in organic or biogenic films. This proximity of organic molecules is unique to an interface, in contrast to the bulk or gas phase and, thus, may also result in unique chemical reaction pathways leading to VOC formation. Fatty acid and organic compound-coated surfaces are ubiquitous and photo-induced chemistry at organic interfaces may have important implications for VOC fluxes and the formation of SOA at the Earth's surface and aloft.

**Keywords:** multiphase chemistry, air/water interface, surface microlayer, SOA, VOCs.

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# Silica-Titania Composites for the Air De-Pollution

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## Objective

Environmental photocatalysis is a promising “green” technology for the urban air de-pollution, however showing some limitations in full-scale applications [1], but possessing open perspectives for China and other Countries.

The aim of this study was to prepare a silica/titania SiO<sub>2</sub>/TiO<sub>2</sub> photocatalyst and to test its performance toward Methyl Ethyl Ketone MEK and Nitrogen Oxide NO degradation. Two different methods were used to prepare silica-titania composites. For each method, three samples having different compositions were synthesized.

## Methods

Silica gel Carlo Erba Reagents Silica gel 60A 6 - 35µm and pure titanium dioxide Evonik AEROXIDE TiO<sub>2</sub> P25 were used as purchased. Titanium powder 325 mesh, 99.9% purity was provided by Metalpolveri Srl. Two different methods were used to prepare the silica-titania composites.

In the first method a determined amount of TiO<sub>2</sub> was dispersed and sonicated for one hour in ultrapure water. A given amount of silica were added to the solution and sonicated for another hour. Subsequently, the solution was mechanically stirred for 2 hours, vacuum filtered and dried in oven at 105°C for 24h.

In the second method, several samples of photoactive materials were obtained by high temperature hydrolysis of titanium precursors with the formation of titanium dioxide and its deposition on the matrix. For the preparation of the precursor, titanium have been used [2].

For both the methods, different solutions were prepared 3%, 7%, 12% w/w to vary the titanium dioxide content in the samples.

The experimental apparatus for the NO<sub>x</sub> removal consisted in a tubular reactor with the sample inside. An UVA lamp is located over the sample, outside the reactor. The NO<sub>x</sub> flux inside the reactor is kept constant with a permeation and dilution system which is alimented with a NO<sub>x</sub> tank 499ppb NO. Dilution is obtained by mixing with atmospheric air and NO<sub>x</sub> concentrations are determined using a chemiluminescent analyzer. Concentrations were monitored during dark and UV-light conditions. The NO removal efficiency was evaluated as ratio between the NO removed and the NO concentration in dark-condition.

Methyl-ethyl-ketone MEK oxidation experiments have been carried out in a batch reactor. The photocatalytic reactor consists of a 1.05L thermostatically controlled glass chamber. A magnetic stirring guarantee continuously air recirculation.



Inside the reactor the sample can be irradiated by an UV LED with peak at 365 nm. Air samples inside the box are collected and analysed by a photoacoustic transducer system both in dark and UV-light condition for every sample. The initial amount of MEK injected into the test box is 5  $\mu$ L. Data was treated as an apparent second order kinetics.

## Results and discussion

It is possible to observe very clearly in Figure 1 whiter TiO<sub>2</sub> spots on the silica surface having dimensions of the order of about ten to hundred micrometers for the SiO<sub>2</sub>/TiO<sub>2</sub> composite obtained by simple wet impregnation c, while TiO<sub>2</sub> seems to be evenly distributed on the silica surface for the composite obtained by hydrothermal method b.

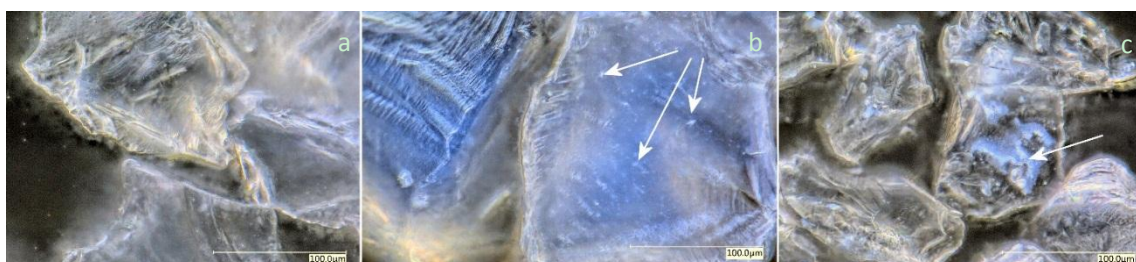


Figure 1 – Magnification of raw silica a, SiO<sub>2</sub>/TiO<sub>2</sub> composite obtained by hydrothermal method b and SiO<sub>2</sub>/TiO<sub>2</sub> composite obtained by simple wet impregnation c.

Result of MEK and NO degradation efficiencies, as previously defined, are reported in Figure 2. Despite the different production method, results are following the same trend and the hydrothermal one exhibits slightly higher efficiency in the MEK removal.

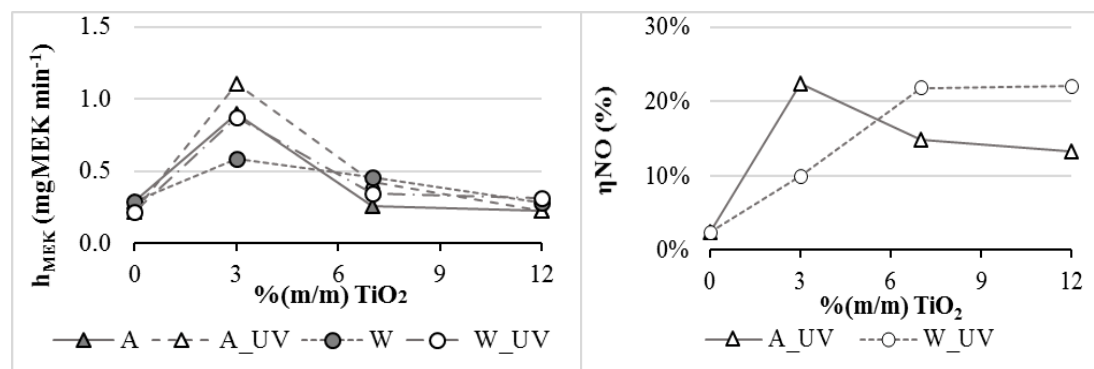


Figure 2 – Methyl Ethyl Ketone MEK and Nitrogen Oxide NO degradation efficiencies for different samples obtained through hydrothermal method A and simple wet impregnation W.

## Conclusion

It was found that the higher density of active surface sites achieved by using a porous catalyst support, enhance the process performance. Of the two methods used to prepare SiO<sub>2</sub>/TiO<sub>2</sub> composite, the hydrothermal method gives a slightly higher efficiency in the NO<sub>x</sub> and MEK removal. Both catalyst types exhibit activity maxima at TiO<sub>2</sub> concentration of 3%. Lower and higher TiO<sub>2</sub> concentrations can

negatively affect the process.

Silica-titania composites are found to be low-cost and easy-implementable control techniques of air pollutants.

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[2] V. Bondarenko et al. 2016 Ageing of photocatalytic materials: Investigation, assessment and possible solving, *Chemical Engineering Transactions* 47

# Characterization and Source Apportionment of Size-Segregated Atmospheric Particulate Matter Collected on the Ground Level and the Urban Canopy in Tianjin

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To investigate the size distributions of chemical compositions and sources of particulate matter PM on the ground level and the urban canopy, a campaign was carried out on a 255m meteorological tower in Tianjin from December 2013 to January 2014. 13 sets samples of 8 size-segregated particles were collected with cascade impactor at 10m and 220m. Twelve components of particles including water-soluble inorganic ions and carbonaceous species were analyzed and were used to apportion the sources of PM with PMF. Our results indicated that the concentrations, size distributions of chemical compositions and sources of PM at urban canopy were affected by regional transport due to a stable layer around 200m and higher WS at 220m. The concentrations of PM and  $\text{Cl}^-$  and EC in fine particle at 10m were higher than that at 220m, while the reverse was true for  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ . The concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and EC in coarse particle at 10m were higher than that at 220m. The size distributions of major primary species such as  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and EC were similar at two different heights, indicating that there were common and dominant sources. The peaks of  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and OC which were partly secondary generated species shifted slightly to the smaller particles at 220m, indicating that there was different formation mechanism. Industrial pollution and coal combustion, resuspended dust and marine salt, traffic emission and transportation, and secondary inorganic aerosol were the major sources for PM at 10m and 220m. With the increase of vertical height, the influence of traffic emission, resuspended dust, biomass burning on PM is weakening, but the characteristics of regional transport gradually become obvious. However, the contributions of industrial pollution and coal combustion to PM changed little.

# Atmospheric photochemistry of fatty acid and biofilms at the air-water interface and effect on atmospheric nitric oxide

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Interfaces coated by organic material exposed to the atmosphere are ubiquitous and can include aerosol particles, cloud droplets, built surfaces and oceans. We hypothesize that photochemical interactions occur at these interfaces impacting sources and sinks of various compounds, and thus atmospheric composition.

The oceans cover the majority of the Earth, and the interactions potentially taking place at their surface may play an important role on the air-water exchange of trace gasses. The sea surface microlayer SML is concentrated in reactive light absorbing organic material, such as dissolved organic matter DOM with a high proportion of functional groups such as carbonyls and carboxylic acids. Photochemical reactions taking place there may lead to unique chemical pathways and products not previously considered or observed in the overlying gas phase or underlying bulk.

Here, we present an investigation of photochemistry at the air-water interface using nonanoic acid as a model carboxylic acid surfactant. Irradiation by UV light results in products released both to the gas and aqueous phases, with and without a photosensitizer in solution. This photochemistry also leads to the formation of saturated and unsaturated aldehydes along with other oxygenated photo-induced products Rossignol et al., 2016; Tinel et al., 2016. Two different aspects of that chemistry will be discussed i.e., peroxy radicals production at the air-water interface and their impact on NO deposition, and VOC production from natural biofilms.

In fact, the reaction mechanism producing aldehydes and oxygenated products passes through the formation of peroxy radicals Rossignol et al., 2016. In turn, peroxy radicals may react with nitric oxide NO to form nitrogen dioxide NO<sub>2</sub> and organonitrate compounds Finlayson-Pitts and Pitts, 1999. Thus, we pose the question: could the photochemistry at the ocean surface, or at any other air-water interfaces, be a new path of NO loss in the atmosphere? Here we show that NO loss is induced when an air-water interface coated with nonanoic acid is irradiated.

Marine biological processes are known to be important contributors to water and SML composition. Thus, we use a suspension of biofilm material as a natural surrogate in some experiments. Irradiation of biofilms with a Xenon lamp results in volatile saturated and unsaturated oxygenated gas phase compounds. The organic

compounds formed were monitored using a PTR-ToF-MS Proton Transfer Reaction-Time of Flight-Mass Spectrometer. Those compounds in water were analysed by UPLC-HESI-HRMS. The results showed a production of saturated and unsaturated fatty acids, oxo-fatty acids as well as saturated and unsaturated dicarboxylic acids. The nature of the photochemical reactions occurring and their impacts on atmospheric nitric oxide will be discussed.

Overall, we highlight some specificities of the chemistry taking place at the air-water interface.

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# Linking in-canopy volatile organic compound reactivity to nocturnal new particle formation

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Atmospheric aerosols play a central role in both air quality and climate change. However, the evaluation of aerosol radiative forcing is still one of the greatest uncertainties in predicting future climate IPCC, 2013. It is therefore crucial to better assess aerosol sources and related processes. At a global scale, New Particle Formation NPF is one of the most important aerosol sources, which could represent half of the Cloud Condensation Nuclei CCN rate Merikanto *et al.*, 2009. Several studies have observed NPF, over rural as well as urban areas, mostly during daytime, related to photochemical processes Kulmala *et al.*, 2004. But, only a few studies have reported nocturnal NPF Lee *et al.*, 2008. The origin of these nocturnal events remains sparse, mostly due to the lack of investigations. In addition, the role of biogenic volatile organic compounds BVOCs in NPF is still not clearly understood, even if recent advances Riccobono *et al.*, 2014 were proposed. Hence, new studies about NPF and their link with BVOCs are of great interest, especially in locations still poorly investigated.

The Landes forest, located in southwestern France, is one of the largest monospecific forest in Europe ~1 million ha and composed of 95% of maritime pines *pinus pinaster*, a large monoterpene emitter, mainly  $\alpha$ - and  $\beta$ -pinene, two well-known SOA precursors. Flat, with few anthropogenic inputs, under the direct influence of the Atlantic Ocean with strong photochemical periods, this forest may be considered as an “open-air laboratory”. Hence, the Landes forest appears to be one of the best suitable ecosystem to investigate NPF related to BVOCs emissions.

This work is a part of the LANDEX coordinated project, aiming to assess the formation and fate of Secondary Organic Aerosols SOA generated from the French Landes forest. To achieve this goal, two preliminary field campaigns have been conducted in summer 2014 and 2015, in order to explore SOA related photochemistry and NPF in this forest. During both campaigns, BVOCs and their corresponding oxidation products were measured in the gas phase using online GC-FID and PTR-TOF-MS. Ozone, nitrogen oxides NO<sub>x</sub> and sulfur dioxide were also monitored. Aerosol size distribution and concentration were measured with a SMPS, whereas quartz fiber filter daily collected particles for off-line chemical analysis. Local meteorology T, P, RH, solar radiations, wind speed and direction were characterized, and completed by air mass backward trajectory calculations. The physiologic state of the ecosystem has been evaluated through latent and sensible heat fluxes and CO<sub>2</sub> flux measurements. Ozone deposition was also measured, including its potential

reactivity with very reactive BVOCs.

During both preliminary campaigns, night-time NPF have been observed at high frequency rates. Through this presentation, we will focus on the 2015 field campaign, which took place during a strong hydric stress period. This period presented the highest NPF frequency rate 56% with extremely high monoterpene concentrations. Gas phase oxidation products such as nopinone and pinonaldehyde have been successfully identified thanks to the PTR-TOF-MS. In-canopy monoterpene reactivity with ozone will be discussed in light to nocturnal NPF observation, to assess its potential contribution. Finally, the effect of hydric stress on nocturnal NPF, in the context of global warming, will be evaluated.

**Keywords:** New Particle Formation, Monoterpenes, Volatile Organic Compounds

**Funding:**

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# Tropospheric NO<sub>2</sub>, SO<sub>2</sub>, HCHO and aerosol observations by the MAX-DOAS network in China

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Optical remote sensing techniques have been extensively used to investigate the formation process of regional air pollution by its many advantages, e.g. various species, large area and complex information of temporal and spatial variability of pollutants. Multi-Axis Differential Optical Absorption Spectroscopy MAX-DOAS measurements allow for the retrieval of trace gases and aerosol extinction profiles in the planetary boundary layer. In this paper, the home-made MAX-DOAS systems and the MAX-DOAS network in the eastern China were introduced. The long-term MAX-DOAS observations of NO<sub>2</sub>, SO<sub>2</sub>, HCHO and aerosol are analyzed to characterize the annual, seasonal, diurnal and weekly variations in boundary layer. In addition the MAX-DOAS data are applied to the validation of models and satellite data.



# Multiscale air quality impact from power plants in cities

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China's urbanization continues at a high rate of speed. It is estimated that ~100 million new urban residents are expected in the next years. This growth will imply environmental challenges including air quality. Air quality is and will be a major concern for long term in China. The global air quality level is improving though recent national air quality control system and action plan for emission reduction. The use of sustainable energy is considered as one of the action for emission control.

Within this project, the focus is on the use of a natural gas fired "combined cooling, heat and power" CCHP or trigeneration power plant which generates simultaneously electricity and useful heating and cooling, thus increasing the overall system efficiency. Measurement campaigns on CCHP emissions and ambient air pollutant concentrations such as NO<sub>x</sub>, VOC, O<sub>3</sub>, PM<sub>10</sub> and PM<sub>2.5</sub> are planned. The impact and the benefits of the use of CCHP with respect to conventional coal-fired power plant on ambient air quality are studied at both regional and local scales on an assumed new district in Shanghai. The Eulerian photochemical transport model CHIMERE is used for the regional study, while a micro-scale Lagrangian particle dispersion model PMSS is used to for the local scale study. The public global emission inventory HTAP V.2 with a resolution of 0.1° is used and downscales to the smallest nested domain with a resolution of 3 km, centered in Shanghai.

First results are presented here for the regional scale model evaluation against the hourly averaged measurement data from 7 stations during 6 episodes for all seasons, mainly including heavy pollution days and typical pollution events such as dust episode and photochemical pollution in summer. The model reasonably well reproduces the episode and the intensity of the PM, NO<sub>2</sub> and O<sub>3</sub> concentrations over the domain. The correlation coefficient is up to 0.8 for primary and secondary pollutants for some episodes while it is much lower for others. Some large difference ~a factor of two between the predicted and measured concentrations exists sometimes in some urban stations, probably related to the bias of meteorology input from WRF simulation under stagnant air condition and the projection of HTAP emission inventory to a finer resolution of 3 km. Better results with local emission data information and with a more refined meteorology condition are expected for the regional scenario study and from the local-scale simulation with a resolution of 3 meters.

# Heterogeneous Reaction Mechanism of Gaseous HNO<sub>3</sub> with Solid NaCl: a Density Functional Theory Study

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Sea salt particles containing NaCl are among the most abundant particulate masses in coastal atmosphere. Reactions involving sea salt particles potentially generate Cl radicals, which are released into coastal atmosphere. This paper aimed at the heterogeneous reaction between gaseous HNO<sub>3</sub> and solid NaCl. The mechanism was investigated by density functional theory DFT. The results simply that water molecules induce the surface reconstruction, which is essential for the heterogeneous reaction. The surface reconstruction on the defective 710 surface has a barrier of 10.24 kcal/mol and is endothermic by 9.69 kcal/mol, whereas the reconstruction on the clean 100 surface has a barrier of 18.46 kcal/mol and is endothermic by 12.96 kcal/mol. The surface reconstruction involved in water-adsorbed 710 surface is more energetically favorable. In comparison, water molecules adsorbed on NaCl 100 surface likely undergo water diffusion or desorption. Further, it reveals that the coordination number of the Cl<sup>-</sup><sub>out</sub> is reduced after the surface reconstruction, which assists Cl<sup>-</sup><sub>out</sub> to accept the proton from HNO<sub>3</sub>. The theoretical calculation of the reaction of gaseous HNO<sub>3</sub> with the reconstructed 710 surface suggest two possible reaction pathways.

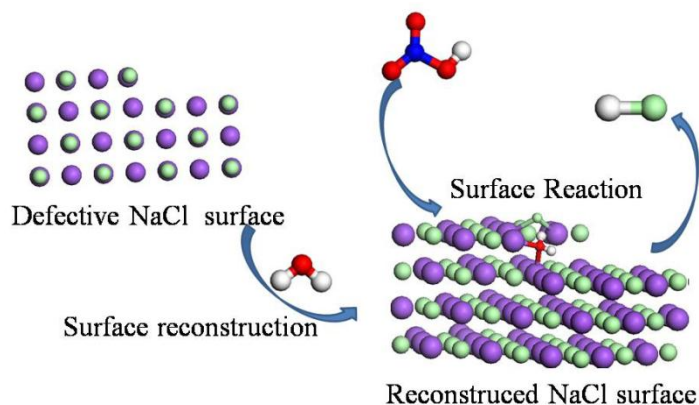


Figure 1. Proposed Reaction Mechanism of Gaseous HNO<sub>3</sub> with Solid NaCl **Keywords:**

Seasalt particles, NaCl, HNO<sub>3</sub>, Heterogeneous Reaction mechanism, Density functional theory

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# Emissions of nitrated phenols in fine particles from biomass burning

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Nitrated phenols have nonnegligible impacts on the living things and the earth's environment. They are toxic and do harm to human health and productivity of ecosystem. Due to its ability to absorb sunlight around the wavelength of UV and visible light, they act as a major part of brown carbon BrC and cause influences on the Earth's radiative forcing and the climate.

Nitrated phenols in the atmosphere originate from not only the primary emissions of various anthropogenic activities combustions of biomass and fossil fuels, production and use of pesticides, etc., but also the secondary formation of VOCs in the presence of reactive nitrogen oxides and oxide. Among the diverse emission sources of nitrated phenols, biomass burning is recognized as one of the most important origins in regional and global scope. However, little is known about the emission characteristics of nitrated phenols arising from burning of commonly used biomass fuels in China.

In this study, combustion experiments were conducted with five kinds of biomass fuels fallen yellow leaves, branches, corncob, corn stalk and wheat straw under three different burning conditions flaming, weekly flaming and smoldering. PM<sub>2.5</sub> samples of the biomass burning smokes were collected with subsequent chemical analyses of nitrated phenols by HPLC/MS.

Emission ratios of nitrated phenols to PM<sub>2.5</sub> increased with completion of combustion, varying from several to dozens  $\mu\text{g}/\text{mg}$  and 240 to 1080  $\mu\text{g}/\text{mg}$  for smoldering and flaming conditions, respectively. The most abundant nitrated phenols in the biomass burning smokes were nitrocatechols, i.e., 4-nitrocatechol, 4-methyl-5-nitrocatechol, 3-methyl-5-nitrocatechol and 3-methyl-6-nitrocatechol, which accounted for 88-95% of the total nitrated phenols in flaming condition. The emission factors of nitrated phenols were approximate 1.99-15.11 mg/kg for five kinds of biomass fuels in flaming condition. We estimated that the total fresh emission of nitrated phenols in fine particles from biomass burning of corncob, cornstalk and wheat straw in mainland China may reach 1230 kt in 2013.

**Keywords:** biomass burning, nitrated phenols, fine particle, emission factor, emission characteristics.

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# The impacts of mixed aerosols on the properties of atmospheric particles

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Haze with high level of fine particulate matter with diameters less than 2.5  $\mu\text{m}$  PM<sub>2.5</sub> occurs frequently in China in recent years. Emissions of gases pollutants, e.g., SO<sub>2</sub>, NO<sub>x</sub>, NH<sub>3</sub>, and volatile organic compounds VOCs, result in a series of atmospheric chemical reactions, which are responsible for the formation of secondary particles and the occurrence of haze. Chemical analyses show that sulfate, nitrate, ammonium, and secondary organic aerosol SOA are the major aerosol constituents of PM<sub>2.5</sub>. However, the effect of mixed aerosols on the properties of atmospheric particles has little investigated. The impacts on chemical reactions and hygroscopic properties have been studied by our group.

Since most researches are focused on the pristine surfaces of atmospheric particles, we try to find some impacts of mixed aerosols on heterogeneous reactions by comparing the processes of the formation of nitrate on mixed particles. We found that the presence of sulfate appears to promote the heterogeneous uptake of NO<sub>2</sub> on particle. And relative humidity has a correlation with the uptake. It is a result of different morphology on particles and different interaction of coexist when RH changed. The reactivity of mixed aerosol is markedly depend on the chemical composition.

The hygroscopic properties of single component and multicomponent water-soluble organic compounds with ammonium sulfate are investigated with the HTDMA. These findings suggest that the presence of coexisting hygroscopic species has a great impact on the phase behaviors and hygroscopic growth of oxalic acid. Organic mixture has more complex effect on the hygroscopicity of ammonium sulfate than single species. Considering the abundance of oxalic acid in the atmospheric aerosols, its mixtures with hygroscopic species may promote water uptake under high RH conditions and thus affect the cloud condensation nuclei CCN activity, optical properties and chemical reactivity of atmospheric particles.

Our results indicated that to better understand the role of particles in the atmospheric chemistry, the effects of mixed aerosol on the properties of atmospheric particles should be considered.

# Insight into diamine-involved aerosol nucleation reaction mechanism enhanced by the lower energy barrier and its atmospheric implication

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## Objective

Acid-base mechanism has been thought to be very important in atmospheric aerosol nucleation. However, so many studies have been focused on monoamines like dimethylamine DMA instead of diamines. Here we report the direct evidence that one of the diamines, ethylenediamine EDA, which shows strongest nucleating ability in the very recent experiment, could participate in the aerosol nucleation cluster formation. The actual Gibbs free energy analysis indicates that much lower energy barrier in EDA-involved systems compared with that for DMA-involved ones enhances the formation of nucleating clusters. After analyzing the cluster growth flux and subsequent growth route, we propose the diamine-involved aerosol nucleation reaction mechanism that one SA binding with one EDA is critical for further growing into particles. Comparing the dependence of formation rate on the base concentration for EDA and DMA indicates that for regions around diamines sources, EDA-involved aerosol nucleation needs to be underlined.

## Method

Here we conducted the density function theory calculations in Gaussian 09 software package, RIMP2 as well as DLPNO-CCSDT calculations in ORCA 3.0 package and CCSDT-F12 calculations in Molpro 2012. Dynamics simulation is based on our home-built dynamics python codes solving the ordinary differential equations ODEs to obtain the time evolution of molecular cluster concentration and formation rate.

## Results

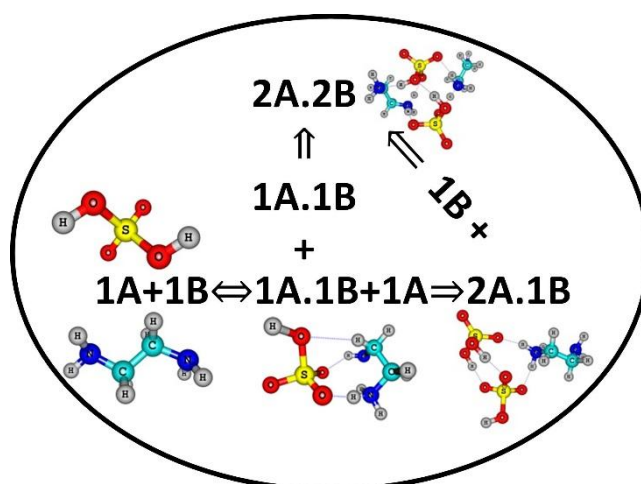


Figure 1. The reaction mechanism of SA binding with EDA derived from cluster thermodynamics and dynamics A: SA; B: EDA.

Various reaction could occur to become the same product, for instance, four reactions could be found in product cluster 2A.2B. However, the growth flux ratio limit the reaction channels into some certain ones. For this case, such a reaction mechanism could be obtained after taking the evaporation rates and growth flux ratio into account shown in Figure 1. In that way, 1A.1B, 2A.1B and 2A.2B would be the main products as shown in Figure 1. 1A.1B is formed through reversible reaction characterized by the relatively larger evaporation rate. And once 1A.1B is formed, it continues to form 2A.1B and 2A.2B with kinetically controlled processes. So here formation of 1A.1B is very important for further cluster growth.

### Conclusion

Based on reliable thermodynamic data proved by delicate method benchmark and the actually Gibbs free energy calculation derived from dynamics simulation, we found that EDA could nucleate with SA with lower energy barrier comparing with DMA. The growth route obtained by evaporation rates and cluster growth flux calculations show us the EDA-involved reaction mechanism that 1A.1B is critical for further growth into particles. In the region where the base concentration is low acid-rich, the enhancement ratio of EDA to DMA is large indicating the stronger nucleation ability of EDA while in the base-rich region while in the base-rich region like amines sources e.g., sewage, live-stock, industrial operations, and tobacco smoke, higher formation rate of EDA-involve clusters comparing with DMA-involved clusters and the positive correlation of formation rate with the base concentration underline the important role of EDA-involved aerosol nucleation.

# Study on Air Pollution Prevention in Xi'an

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With the rapid development of social economy, the situation of air pollution in Xi'an has changed to compound pollution from single coal-smoke pollution in the past. Therefore, Xi'an Academy of Environmental Protection Sciences carried out the analysis of the causes of ozone pollution and the research of motor vehicle pollution.

Causes of ozone pollution are studied by collecting hourly values of O<sub>3</sub>, VOCs, NO<sub>x</sub> and other pollutant concentrations and meteorological parameters from July to September of 2015, thus, the spatial and temporal distribution of ozone pollution and the analysis of sensitivity of ozone generation are completed. Study shows that the high concentration ozone pollution in Xi'an occurred mostly in summer, especially in July. The ozone concentration in urban fringe is slightly higher than that in urban central area. The maximum hourly ozone concentration appears at about 15:00. The study proves that the ozone formation in the fringe area of Xi'an is in VOCs-control; while, in urban central area, it is controlled by VOCs and NO<sub>x</sub> synergistically. The analysis of Ozone Formation Potential (OFP) indicates that VOCs with high OFP contribution rate are mainly composed of butene, isoprene, vinyl acetate, toluene and 1-pentene, sum of that rate is as high as 76.4%.

The results of PMF analysis suggest that the emission of mobile sources is not only the primary source of VOCs in the atmosphere of Xi'an, but also one of the main sources of NO<sub>x</sub> emission. In addition, the results of source apportionment of atmospheric particulate matter indicate that the primary emission and secondary blowing dust of the vehicle reaches 20% in the particulate matter.

Researches on vehicle pollution included collecting local vehicle quantity, vehicle type, age distribution, fuel information, road network layout and driving characteristics, carrying out bench test and tunnel test to obtain the local vehicle emission factors, establishing models to calculate the vehicle pollutant emission list at high spatiotemporal resolution, analyzing the effect of various measures to reduce pollutant emissions. Up to July 2016, the number of motor vehicles in Xi'an has reached 2.5 million, with an average annual growth rate of about 14.3%. The vehicle exhaust pollutants have a great impact on the air quality, especially on both sides of roads. Monitoring shows that NO<sub>2</sub> concentration in traffic environment is 2.4 times that of the atmospheric environment. Among them, the operating mileage and some emission factors of commercial vehicles buses and taxis are relatively high, whose impact on the atmospheric environment can't be ignored. For example, the VOCs emission coefficient of taxis is 15 times that of cars. Various measures can be taken to reduce the emission of vehicle pollutants effectively, like higher average speed on urban roads, the replacement with clean energy vehicles, the elimination and renewal of old vehicles, and the improvement of new vehicle emission standards, etc. At the same time, due to the structural feature of the Ming dynasty city wall and regional planning requirements and traffic jam within the walls, the urban center area has the inherent advantages and necessity of planning the establishment of "low emission area". Study analyzes the effect of the "low-emission area" measures

of the Ming dynasty city wall via the scenario model, and find that whenever there is a 10% restriction on the vehicles because of the corresponding measures, the motor vehicle emissions will be lowered by about 8% within the city walls.

The above studies can lay a solid foundation for researching the mechanism of compound air pollution. Meanwhile, it can also provide technical support for the environmental management department to work out measures for pollution prevention, enhance air quality and reduce pollution occurrence.



# Response of Fatty Acid Coated Air-Water Interface to the Atmospheric Inorganic Ions Solution

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## Objective

Atmospheric aerosols are usually composed of a mixture of organic and inorganic compounds. Adsorption of VOCs onto liquid or solid surfaces results in aerosols coated by organic films.<sup>1</sup> Such organic films may affect the chemical and physical properties of aerosol particles, which in turn might have effects on different atmospheric processes.<sup>2</sup> Direct photolysis of a fatty acid at an air-water interface leads to the formation of different oxidized products in the gas phase and aqueous phase.<sup>3</sup> The cloud droplet formation of organic aerosol is affected by surface activity via both the influence of surface to bulk partitioning on the Raoult effect and surface tension.<sup>4</sup> Stearic acid and arachidic acid are typical surface active organic fatty acids, representatives of many surfactant compounds present on the aerosol surface. We discuss the surface to bulk partitioning and the stability properties related to the surfaces of aqueous solution comprising surface active organics mixed with inorganic ions in atmospheric aerosols.

## Methods

Langmuir monolayers are used as proxies of organic coated aerosols. The activities of common atmospheric inorganic ions  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  and fatty acid molecules at air-aqueous interface were investigated by Langmuir trough methods and Infrared reflection-absorption spectroscopy IRRAS. Surface pressure-area  $\pi$ -A isotherms were acquired to elucidate the effects of inorganic ions on the stability of the monolayers. IRRAS was used to examine the intermolecular interactions of the monolayers at molecular level.

## Results

The presence of  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  ions in the subphase gives rise to condensation of the stearic acid monolayer, while  $\text{Al}^{3+}$  ions in the subphase induces an extending effect. It is worthy to note that on the  $\text{Ag}^+$ -containing subphase, the  $\pi$ -A isotherms show extremely compressed characteristics. However, the  $\pi$ -A isotherms of arachidic acid monolayer on ion-containing subphase except  $\text{Ag}^+$  exhibits extended characteristics in comparison with the isotherm on pure water. IRRAS spectra confirm that the existence of inorganic ions in the fatty acid monolayer changes the surface properties of aqueous-phase aerosols. The  $\nu_{\text{a}}\text{CH}_2$  and  $\nu_{\text{s}}\text{CH}_2$  bands are formed with highly ordered hydrocarbon chains. For the stearic acid monolayer, the new bands of the stretching vibrations of carboxylate groups  $\nu_{\text{o}}\text{COO}$  and  $\nu_{\text{s}}\text{COO}$  appear in the presence of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ . All the bands are enhanced in the case of  $\text{Zn}^{2+}$  and  $\text{Ag}^+$ . For the arachidic acid monolayer, the intensities of  $\nu_{\text{o}}\text{COO}$ ,  $\nu_{\text{s}}\text{COO}$ , and  $\delta\text{CH}_2$  bands decrease in the presence of subphase containing  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  ions.

## Conclusion

Carboxylate is much more soluble and less surface active than carboxylic acid. The new carboxylate group bands show the formation of more carboxylate for the stearic acid monolayer on the ion-containing subphase. The decrease of the carboxylate group bands indicates that the existence of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  ions in the subphase lead to more arachidic acid molecules at the surface. The experimental results support the reported model and theoretical results which take the surface to bulk partitioning into account in the Raoult effect. The stability of surface film and the change of surface to bulk partitioning may have significant impacts on nucleating cloud droplets.

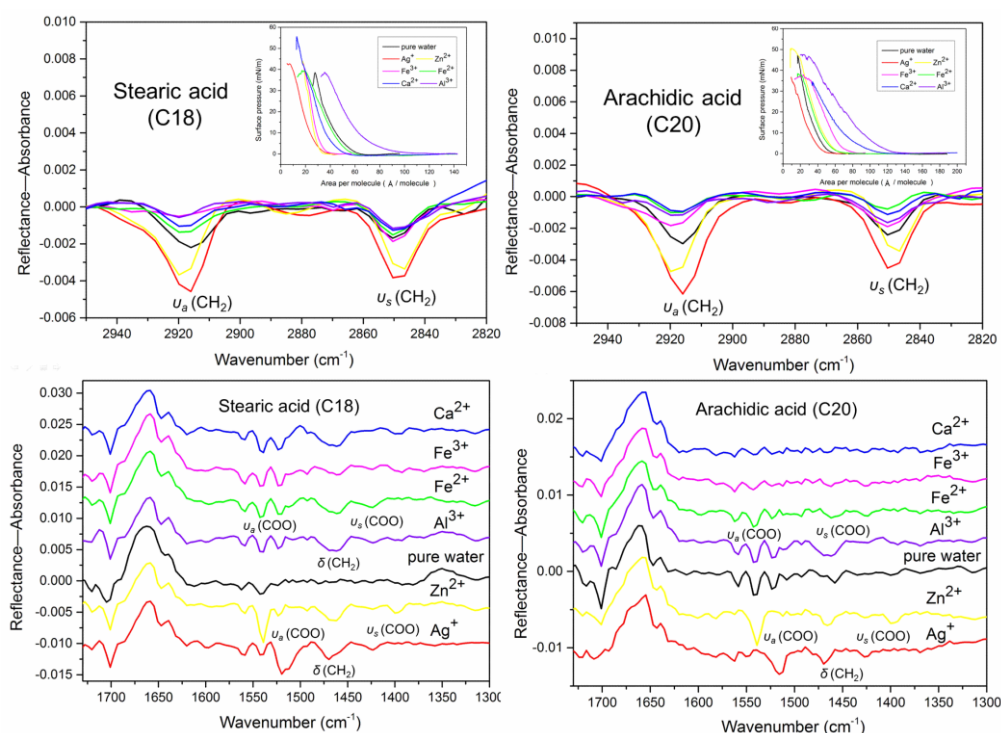


Fig 1. IRRAS spectra and  $\pi$ -A isotherms of stearic and arachidic acid monolayers

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# On the Role of Nitryl Chloride in the Production of Secondary pollutants

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Nitryl chloride  $\text{ClNO}_2$  is produced from heterogeneous reactions of dinitrogen pentoxide  $\text{N}_2\text{O}_5$  on aerosols containing chlorine. Recent studies have shown that it can affect radical budget and concentrations of ozone and other secondary pollutants. However, the abundance and impact of  $\text{ClNO}_2$  are not fully understood in China. This presentation gives an overview of recent field campaigns of  $\text{ClNO}_2$  and related chemical constituents in China, including one at a mountain top 957 m a.s.l in Hong Kong of South China in winter 2013 and three in North China urban Ji'nan, semi-rural Wangdu, and Mt Tai 1534 m a.s.l in summer 2014.  $\text{ClNO}_2$  and  $\text{N}_2\text{O}_5$  were measured with a chemical ionization mass spectrometry CIMS system with iodide as the primary ions. Ambient concentrations of several hundreds ppt and up to 4.7 ppbv of  $\text{ClNO}_2$  were observed in these locations, suggesting existence of elevated  $\text{ClNO}_2$  in both coastal and inland atmospheres of China. Measurements in North China exhibited generally low concentrations of  $\text{N}_2\text{O}_5$ , indicative of its fast uptake of on aerosols under humid conditions. Indications of anthropogenic sources of chlorine were observed at all these sites. The impact of photolysis of  $\text{ClNO}_2$  on radical budget and ozone enhancement was assessed with a MCM model which was updated with detailed chlorine chemistry and constrained by measurement data for the southern and a northern site. A chemistry-transport model WRF-Chem was used to evaluate the spatial distribution and impact of  $\text{ClNO}_2$  on ozone, nitrate and  $\text{PM}_{2.5}$  in southern China. The results suggest important impact of  $\text{ClNO}_2$  on ozone and haze.

# Characterization of Atmospheric Particulate Number Concentration of Tianjin City In Spring Festival Period

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From February 1<sup>st</sup> to March 10<sup>th</sup>, by combining with meteorological conditions, the characteristics of particulate number concentration PNC of Tianjin were investigated during the typical spring festival period and atypical period. On-line measurements of particle mass concentration PMC and PNC were conducted on a building which 15m high above the ground and have a wide Surroundings in the courtyard of the Tianjin environmental monitoring station by using TEOM and APS. The results showed that the average value of PNC during the typical spring festival period SFP was up to  $342 \pm 210$  1/cm<sup>3</sup>, which was 20% higher than that of atypical period. The accumulation mode PNC with the size range from 0.5 $\mu$ m to 1 $\mu$ m accounted for 93.88% of the total PNC, which was slightly lower than that of in atypical period. For the whole period, PNC and the particle mass concentration PMC showed the significant correlation  $r=0.774 \sim 0.829$ ,  $P < 0.01$ , while that of illustrated significant difference on size distribution. PNC and PMC performed the “surge and plunge” tendency in the process of fireworks burning. PNC<sub>0.5~10</sub> showed rapid increase because of the firework burning on Spring Festival’s Eve, which was 6 times than prior to the Spring Festival’s Eve. Significant liner relationships existed between PNC and relative humidity RH, as well as between PNC and wind speed WS. Furthermore, step regression analysis revealed that WS was major affecting factor for PNC, which accounted for 47% of the variance in PNC<sub>0.5~10</sub>.

**Keywords:** Atmospheric particle; Number concentration; Spring festival; Meteorological parameters

# Chemical characteristics of PM<sub>1</sub>/PM<sub>2.5</sub> and influence on visual range at the summit of Mount Tai, North China

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Daytime and night-time PM<sub>1</sub> and PM<sub>2.5</sub> samples were simultaneously collected at the summit of Mount Tai during summer and autumn 2014. The mass concentrations and chemical compositions were analysed to determine the temporal variations of PM<sub>1</sub> and PM<sub>2.5</sub> and their contributions to visibility impairment. In summer, the average mass concentrations of PM<sub>1</sub> and PM<sub>2.5</sub> were 38.16 µg/m<sup>3</sup> and 53.33 µg/m<sup>3</sup>, respectively. In autumn, the values were 42.75 µg/m<sup>3</sup> and 59.61 µg/m<sup>3</sup>. The concentration of PM<sub>1</sub> relative to that of PM<sub>2.5</sub> was greater in autumn than in summer. Water-soluble inorganic ions were the most abundant species in both PM<sub>1</sub> and PM<sub>2.5</sub>, followed by organic mass OM. Among the major water-soluble ions, SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> had higher concentrations in summer than in autumn, whereas the concentration of NO<sub>3</sub><sup>-</sup> showed the opposite seasonal trend. Lower concentrations of organic carbon OC, elemental carbon EC and water-soluble organic carbon WSOC were obtained in summer than in autumn. The water-soluble components SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and WSOC showed a clear diurnal variation due to the specific meteorological conditions of Mount Tai. The water content in PM<sub>1</sub> and PM<sub>2.5</sub> was enhanced by the water-soluble components, especially NH<sub>4</sub>NO<sub>3</sub>. The decreased visibility results from the combined influence of particulate matter and relative humidity RH. The threshold PM<sub>2.5</sub> concentration corresponding to a visibility of <10 km was 56.60 µg/m<sup>3</sup>, which decreased with an increase in RH. A revised IMPROVE equation was applied to estimate the light-extinction coefficient  $b_{ext}$ , which was found to be lower for these chemicals in autumn 364 Mm<sup>-1</sup> than in summer 482 Mm<sup>-1</sup>. NH<sub>4</sub>SO<sub>4</sub> made the largest contribution to  $b_{ext}$  in both summer and autumn, with an average rate of 56.97%. OM 17.32% and NH<sub>4</sub>NO<sub>3</sub> 15.13% were also important contributors, with similar contribution rates. The contribution of NH<sub>4</sub>NO<sub>3</sub> to  $b_{ext}$  was higher during summer, and OM contributions were higher during autumn.

# The Atmospheric Reactivity Studies Platform of Orléans - France

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The Atmospheric Reactivity studies Platform of Orléans PRAT is dedicated to the characterization of atmospheric air pollution and chemical and dynamic processes associated with air quality and global change issues. PRAT is composed of:

- The atmospheric simulation chamber with natural irradiation of Orleans HELIOS which is dedicated to studies of photochemical processes in the atmosphere under controlled and realistic conditions. HELIOS is a large hemispherical chamber volume of 90 m<sup>3</sup>, made of FEP film and positioned on the top of ICARE-CNRS building. It is equipped with advanced analytical instruments that allow the characterization and monitoring of the evolution of pollutants under the influence of sunlight or in the dark.

- The Super-Site VOLTAIRE HELIOS, located on the CNRS campus of Orleans, dedicated to the measurement and monitoring of air pollutants gas and particles. The measurements are conducted continuously for certain law-regulated pollutants such as ozone O<sub>3</sub>, nitrogen oxides NO and NO<sub>2</sub> and particulate matter PM10.

- The other two instrumental sets are being developed in our laboratories: *in situ* spectrometry with four infrared lasers SPECIES; compounds which can be simultaneously measured with sub-ppb detection limits, among others: CO, CH<sub>4</sub>, NO, N<sub>2</sub>O, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HCl, HOCl, COF<sub>2</sub>, HCHO, HCOOH, O<sub>3</sub>, NH<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>O, OCS and Atmospheric Mass Spectrometry AMS with Orbitrap dedicated to the detailed study of the chemical composition of organic aerosols and SAMU a chemical ionization mass spectrometer: CIMS for HO<sub>2</sub>, OH, RO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> detection.

This "PRAT" is part of a large regional project PIVOTS which is a coordinated set of experimental and analytical platforms dedicated to the development of "engineering and environmental metrology for high consumption of natural resources activities" and federating public bodies and private players. Its objective is to achieve the integration of academic players and companies at all levels of the value chain of the quality of the environment monitoring and the sustainable management of natural resources soil, subsoil, surface water, groundwater, sediment, air.

The characteristics of this platform will be presented.

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation

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Emissions from human activities have led to important changes in the composition of the atmosphere. Computational models are used to understand the impacts of emissions on air quality on local, regional, and global scales and the global climate system. An accurate representation of atmospheric chemistry is of critical importance in these models. The mission of the International Union of Pure & Applied Chemistry IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation is to provide evaluated kinetic data for gas-phase, heterogeneous, and aqueous-phase reactions.

More than 1000 datasheets are maintained on the website here <http://iupac.pole-ether.fr>. From the website, it is possible to join the mailing list, access datasheets, search the database by species names, formula, InChI, or SMILES and download summary tables. The Summary Tables provide kinetic data on:

- Gas-phase reactions of Ox, NOx, HOx, SOx, organic compounds, inorganic and organic halogens
- Heterogeneous reactions on solid surfaces
- Heterogeneous reactions on liquid surfaces.

The datasheets provide summaries of experimental data and procedures organized in four broad groups:

- Gas-phase reactions.
- Photolysis reactions.
- Heterogeneous reactions on solid substrates.
- Heterogeneous reactions on liquid substrates

Datasheets are being added for aqueous-phase reactions. Recommended data are published periodically in a special issue of Atmospheric Chemistry and Physics here [http://www.atmos-chem-phys.net/special\\_issue8.html](http://www.atmos-chem-phys.net/special_issue8.html)



# Tackling air pollution episodes: comparison between Paris region and Beijing

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Beijing and its surrounding area is becoming well-known with frequent heavy pollution events in heating seasons since 2013. Paris, in the meantime, although has much better overall air quality, also suffers particulate pollution episodes in spring. The two capital cities both issued their highest alert and triggered emergency “anti-smog” measures including driving restriction.

Thanks to the international collaboration between the air quality agencies of the two capital, for offering the opportunity to compare how the two sides tackle air pollution episodes. The experience from different background will sure inspire each other and help improving the future response of pollution episodes.

The comparative study is performed from the aspects of regulation, forecasting, measures, post-analysis and public information. Discussion is followed at the end.

Beijing municipal environmental monitoring center BJMEMC and Airparif are the air quality agencies of Beijing and Paris who are responsible for monitoring, forecasting and public information. Paris complies with the national-wide air quality standard which is mostly inherited from EU. The standard contains both the compliance values of each ambient pollutant and the two level thresholds of pollution episode. The latest version of standard includes the factors of exceeded land proportion and population exposure into account. China sets national air quality compliance values, but delegate the regulation of heavy pollution to local authorities. Beijing further divides pollution episodes into 4 levels in accordance of predicted severity and duration of air quality. The threshold values are quite high in Beijing than Paris region, but actually pretty aggressive if considered average pollution level and the exceedance.

Both city established air quality forecasting team with the aid from variety of computing models and information exchanged from other channels. Airparif uses a self-developed CHIMERE-MM5 based model chains, called Esmeralda, with the full collection of emissions, to generate hourly simulations of next 2 days, covering Paris and surrounding 5 regions. Beijing implements both statistical model and series of chemical models. Since the lack of updated emission data and correction approach, model results often need to be adjusted by daily internal consultation before Beijing published. During the pollution episode, both Airparif and BJMEMC assign more manpower into the team on duty, and an experienced expert will be responsible to answer the media.

The temporary emission cut-down measures are predefined at both cities, but

are implemented in different way. French side prepares a repository of comprehensive temporary measures which to be selected into action when pollution episode comes. While in Beijing, certain measures are defined for each polluted level as a fixed plan with strong force to execute. This guarantees the efficiency in operation, but is in some cases not flexible enough.

The immediate report was published online 1 week after the 2014 episodes by a Paris based laboratory of LSCE. The systematic monitoring of the chemical composition of fine particles during pollution episode indicates that the secondary particles was the majority which supports the implemented measures towards the control of precursor gases. Airparif published model simulation results 2 months later, showing that the traffic restriction contributed 2%-15% decrease of PM10 depending the location. BJMEMC maintains the air quality monitoring network in Beijing and has the capability itself of particulate characterizing. The results directly support local authorities to make decision. Because of the complexity and frequent occurrence, the post analysis of heavy pollution in Beijing are often studied and discussed within academic community.

Both cities have established well air quality information publishing channels including TV, website, mobile app and social media. During the pollution episode, French side provides more specific health advices based on WHO and HCSP's study. French Environment & Energy Management Agency ADEME conducted a survey to collect valuable feedback about the traffic alternate day.

The two cities respectively tackled air pollution episodes under own circumstance. Few practice could be simply duplicated elsewhere, but all of them offer important lessons and reference for the future, especially to Beijing and those who will confront more air pollution challenges.

Some perspectives for better tackling air pollution episode are: 1 Regulate region-wise, cities in the region share same forecast result and act together. 2 Improve model tools, for more accurate prediction and scenario assessment. 3 Maintain a dynamic list of measures for different scenarios 4 Push the health information directly to the target population, in cooperation with local public department.

# On-road measurements of VOCs and NO<sub>x</sub>: determination of light-duty vehicles emission factors from tunnel studies in Brussel city center

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In urban areas, vehicular emissions are a major source of Volatile Organic Compounds VOCs. In the early 1990's, road transport was the most important source of VOCs in the European Union: about 6 000 kt of VOCs ≈33% of the total VOCs were emitted by vehicular exhaust [1]. Twenty-five years later, the VOCs emissions have been reduced by 87% [1]. Despite this drastic decrease, emissions of VOCs by the road transport sector still have to be closely controlled: recent studies, based on in-situ measurements, have stated that road transport remains the main VOCs emission source in urban agglomeration [2]–[4]. Traffic is also a substantial emission source of nitrogen oxides NO<sub>x</sub>=NO+NO<sub>2</sub>: in 2014, road transport contributed 40% of the NO<sub>x</sub> emissions in Europe, while this contribution has already dropped by 59% since 1990 [1].

Both VOCs and NO<sub>x</sub> are known to have hazardous effects. Respiratory symptoms have been observed at high NO<sub>2</sub> exposure, leading to the implementation of an annual threshold value for NO<sub>2</sub> concentrations of 40 µg m<sup>-3</sup> in Europe. VOCs can be as dangerous on people's health: benzene and formaldehyde, e.g., are carcinogenic [5], [6]. Besides, both VOCs and NO<sub>x</sub> are involved in photochemical processes, which lead to the formation of a various secondary pollutants, including ozone and secondary organic aerosols. For all these reasons, emissions of NMVOCs and NO<sub>x</sub> by traffic must be closely controlled. Controlling the VOCs emissions from traffic requires a good and accurate knowledge of their emission factors EFs. In this context, we determined the emission factors of 25 VOCs and of the nitrogen oxides, in the frame of the PhotoPAQ project.

Two tunnel experiments September 2011 and January 2013 have been conducted in a 100 m section of the Leopold II tunnel Brussels, Belgium crossed only by light-duty vehicles. During each campaign, in-situ measurements of 25 hydrocarbons have been performed by deploying online GC-FIDs. NO<sub>x</sub> were measured using chemiluminescence-based instruments coupled to molybdenum converters.

NO<sub>x</sub> and VOCs EFs have been derived from their correlation with CO<sub>2</sub> using a single point analysis method. VOCs emission factors are comprised between  $0.26 \pm 0.09$  mg vehicle<sup>-1</sup> km<sup>-1</sup> for cis-but-2-ene and  $8.11 \pm 2.71$  mg vehicle<sup>-1</sup> km<sup>-1</sup> for toluene. NO<sub>x</sub> EF is  $544 \pm 199$  mg vehicle<sup>-1</sup> km<sup>-1</sup>. Good agreement is observed between VOCs EFs determined in the Leopold II tunnel and the most recent EFs determined in another European roadway tunnel in 2004, with only a slight decrease of the EFs during the last decade. The temporal evolution of the VOCs EFs between late 1980's and today reflects the changes in the car fleet composition, in the fuels and/or the engine technology that have occurred in Europe.

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# Progress of Atmospheric Pollution Monitoring by Optical Technology in China

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The formation, transport and evolution process of air pollution have obvious temporal and spatial correlation. Various on-line monitoring technologies based on optical detection and spectral retrieval play an irreplaceable role in air pollution monitoring with high sensitivity, high resolution, high selectivity, multi-component and real-time etc. advantages. The new development of monitoring technologies for air quality, emission sources, traffic emission and regional air pollution in China are introduced. By studying the interaction of light and environmental material, the database of the spectral characteristic and the spectrum quantitative analysis algorithm have been developed. Combined with the engineering technology, air pollution monitoring systems have been developed on DOAS, TDLAS, FTIR, LIF and LIDAR techniques. Application demonstrations have been carried out in many Chinese Cities, e.g. Beijing, Shanghai, Guangzhou, Nanjing etc. And the requirements and suggestions about further research of atmospheric monitoring technologies are proposed.

# The High Emission of Sulfate from Coal-fired Power Plants Equipped with WFGD

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In the past ten years, a large number of wet flue gas desulfurization (WFGD) have been extensively equipped in the coal-fired power plant, which accounted for more than 90%. In this study, particle and gaseous emissions of three different coal-fired power plant units in the size range 125-300 MW and equipped FGD were studied.

The Plant A wasn't equipped the WFGD system. The Plant B and C were equipped the calcium base WFGD. The particulate and droplet emitted along with the high humidity fuel gas. It includes  $\text{CaSO}_4$ ,  $\text{CaSO}_3$ ,  $\text{CaHSO}_4$  which form fine particulate after discharge to the atmosphere. Power plants have high effective for the retention of  $\text{SO}_2$ , but high growth percentage of sulfate, which about 300%. The reason of sulfate emitted included that the desulfuration reaction mechanism and shortage of technology in defogger and gas-gas heater (GGH). It's indicated that the emission of  $\text{SO}_2$  have been decreased, but a great number of particulate emitted to the atmosphere as the sulfide which was one of the important reasons that the sulfate increased in the ambient.

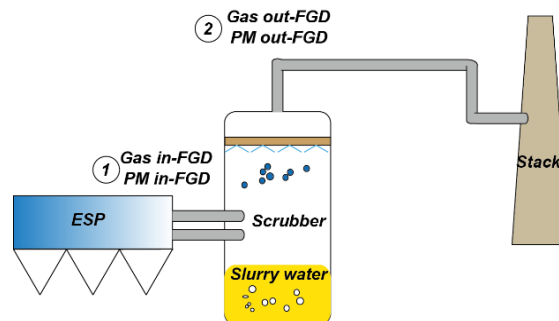


Fig. 1. Diagram and sampling positions of the WFGD system

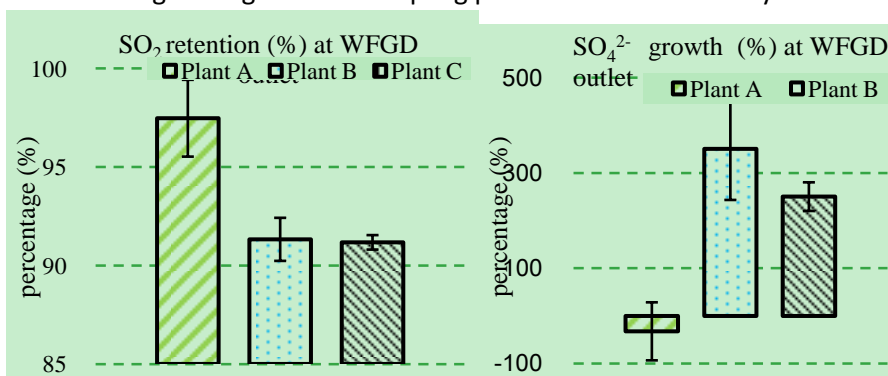


Fig. 2. SO<sub>2</sub> retention % at WFGD outlet

Fig. 3. SO<sub>4</sub><sup>2-</sup> growth % at WFGD outlet

# Heterogeneous Nucleation of Trichloroethylene Ozonation Products in the Formation of New Fine Particles

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Free radicals in the atmosphere have played an important role in the atmospheric chemistry. The intermediates produced in trichloroethylene ozonation on the heterogeneous nucleation of the fine particles is investigated using molecular dynamics simulation.

The detailed nucleation process are reported. The chloro-Criegee free radicals are produced easily in the decomposition of primary ozonide POZ of the TCE, and can react with O<sub>2</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub> and H<sub>2</sub>O subsequently. Then the inorganic salts, polar organic nitrogen and organic sulfur compounds, oxygen-containing heterocyclic intermediates and polyhydroxy compounds can be obtained. According to molecular dynamics simulation, the nucleation with a diameter of 2 nm is formed in the Organic Compounds-NH<sub>4</sub>SO<sub>4</sub>-H<sub>2</sub>O system. The spontaneous nucleation is an important process in the formation of fine particles in atmosphere.

# Air mass-dependent aerosol forming potential observed using PAM reactor at Gosan Climate Observatory

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A PAM potential aerosol mass reactor was deployed with a SMPS scanning mobility particle sizer to investigate secondary aerosol forming potential of air masses at Gosan Climate Observatory GCO, South Korea, in the fall of 2010 and spring of 2011. PAM reactor was designed to simulate the atmospheric oxidation process by high level of OH and O<sub>3</sub> produced by two UV lamps.

The amount of aerosol formed in PAM chamber was mainly dependent on the concentration of SO<sub>2</sub>. The SO<sub>2</sub> concentration was higher in relatively less aged Chinese outflows, where aerosol mass was increased in PAM chamber. When SO<sub>2</sub> was low, the aerosol mass increased under high NO<sub>2</sub> condition in air mass coming from the Korea Peninsula. In addition, mass gain in PAM reactor was mainly found in nucleation mode, but mass loss occurred in condensation mode.



# Hydroxyl Radical Production from Size-segregated Particles in a Surrogate Lung Fluid and Its Deposition in Human Airway in Beijing

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Adverse health effects by ambient fine particulate matter PM have been suggested to be associated with production of reactive oxygen species ROS, such as hydroxyl radical  $\cdot\text{OH}$ , the strongest biological ROS, hydrogen peroxide  $\text{HOOH}$ , and superoxide  $\cdot\text{O}_2^-$ . Besides chemical composition of PM, particle size also plays an important role in the adverse health effects of particles. The goals of this study include: 1 to quantify the amount of  $\cdot\text{OH}$  produced by different size particles collected by a Micro-Orifice Uniform Deposition Impactors MOUDI and extracted in a surrogate lung fluid SLF solution, 2 using the Multiple-Path Particle Dosimetry MPPD model to simulate particle deposition in human airway, and to calculate the oxidative potential of particles inside human body.

Size-segregated particles are collected on 47 mm Teflon filter by a MOUDI model 110-NR on the campus of Peking University, Beijing. The production of  $\cdot\text{OH}$  induced by PM was measured in a SLF solution with spiked anti-oxidants including ascorbate, uric acid, glutathione, and citrate, which are important antioxidants in human lung fluid. Of available probes, Terephthalate TA is the most sensitive. It reacts with  $\cdot\text{OH}$  to produce 2-hydroxyterephthalic acid TAOH, which is fluorescent and can be detected by a sensitive fluorometer. The oxidative potential of particles deposited in human airway is then calculated with the MPPD model.

During the sampling period, size distributions of PM mass concentration mostly peak at 0.56-1.0  $\mu\text{m}$  and 3.2-5.6  $\mu\text{m}$ . However, the production of  $\cdot\text{OH}$  by unit mass of fine particle peaks at a much smaller size range, less than 0.18  $\mu\text{m}$ , and most are ultrafine particles. In heavily polluted days, it could be 17 times higher. Our results indicate that particles in small size, especially for ultrafine particles, exhibit higher oxidative potential. More details about the oxidative potential of particles deposited in human airway in Beijing will be discussed during presentation.

# Size-resolved chemical composition, effective density, and optical properties of biomass burning particles

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Effective density, chemical composition, and optical properties of biomass burning particles in the size range of 50-400 nm were measured by a series of comprehensive methods in this study. The Differential Mobility Analyzer DMA-Aerosol Particle Mass analyzer APM- Condensation Particle Counter CPC system offered detailed information on the effective density as well as mixing state of particles. The DMA in-line with a single particle aerosol mass spectrometer SPAMS provided individual particle effective density and chemical composition simultaneously. The size-resolved single scattering albedo SSA and Ångström absorption exponent AAE were calculated based on the extinction and scattering coefficients measurements by the Cavity Attenuated Phase Shift spectroscopy CAPS at 450 and 530 nm wavelengths, respectively. The size-resolved effective density measured by two methods had well consistent results. The multiple modes observed in the effective density distribution indicated size-dependent external mixing states including black carbon BC, organic carbon OC and potassium salts. Particles of 50 nm had the smallest effective density  $1.16 \text{ g/cm}^3$  on account of a relative large proportion of BC. Averaged effective densities of 100-400 nm particles ranged from  $1.35\text{-}1.51 \text{ g/cm}^3$  with dominant OC components. Both density distribution and single-particle mass spectrometry showed more complex mixing states in larger particles. Upon heating, the separation of the effective density distribution modes testified the existence of less volatile BC or soot and potassium salts. The SSA in the size range of 50-400 nm particles showed close values at each wavelength. The AAE values for all particles were above 1.6, the acceptable standard of brown carbon. Size-resolved chemical information was used to interpret the optical properties of biomass burning particles.

# Observations of nitrated phenols in four sites in North China: concentrations, sources, and secondary formation

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Nitrated phenols, among the major components of BrC brown carbon, have drawn extensive attention in recent years due to their toxicity and light absorbing ability. However, little is known about the levels and sources of nitrated phenols in polluted atmospheric environment in North China. In this study, we collected filter samples of PM<sub>2.5</sub> at an urban site of Ji'nan, rural sites of Yucheng and Baoding, and a mountain site of Mt. Tai in North Chinas. Nine nitrated phenols in fine particles were detected using HPLC-MS, including nitrophenols NPs, nitrocatechols NCs, and nitrosalicylic acids. The concentrations of nitrated phenols exhibited apparent seasonal, diurnal, and spatial variations, with the highest values appearing in urban site in winter. To understand the main sources of nitrated phenols, source apportionment was conducted using PMF model. Five major contributors were identified including coal combustion, urban plume and the transport, biomass burning, secondary formation, and aged coal combustion plume. Among them, coal combustion was the most important source in the wintertime, with a contribution of ~55%. In the summertime, however, biomass burning and secondary formation contributed more than other sources. The secondary formation processes of nitrated phenols were primarily controlled by the levels of atmospheric oxidants and NO<sub>x</sub> at the rural and mountain sites. The secondarily formed nitrated phenols increased with decreasing temperature both in the day and at night, suggesting significant influence of gas-particle partition on the fine nitrated phenols.

**Key words:** nitrated phenols, PM<sub>2.5</sub>, sources, coal burning, secondary formation

# Chemical Characteristics of Organic Aerosols in Shanghai: A Study by Ultra-High-Performance Liquid Chromatography Coupled with Orbitrap Mass Spectrometry

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Organic compounds are major constituents of atmospheric aerosol particles. In the present study, we collected 12-hr daytime or nighttime ambient aerosol samples on quartz filters for several days during July and October 2014, January and April 2015, at an urban site in Shanghai. The collected filters were analyzed using Ultra-High-Performance Liquid Chromatography UHPLC coupled with a Heated ElectroSpray Ionization HESI and an Orbitrap mass spectrometry MS.

The chromatogram-mass spectra obtained from the negative ionization mode were analyzed by the MZmine software, and more than 1000 formulas of organic compounds with various numbers of isomers for each formula were tentatively determined for each sample. The assigned formulas can be subdivided into five groups: compounds containing only carbon, hydrogen, and oxygen CHO, sulfur-containing organics CHOS, nitrogen-containing organics CHON, compounds containing both nitrogen- and sulfur CHONS, and organics without oxygen CHNS including CHN and CHS. Only organic compounds found in all daytime or all nighttime samples for a particular season were considered as representative species, and then selected to reconstruct the mass spectra of urban atmospheric organic aerosols Figure 1.

In all samples, CHO compounds accounted for 28%~38% of the assigned formulas, and more than 60% of the formulas contain nitrogen and sulfur functional groups; in addition to oxidized compounds, organic compounds without an O atom were also detected, but only accounted for 2%~4% of the assigned formulas. More CHO compounds were found in the daytime samples suggesting a photochemical source, whereas organics with nitrogen-containing groups CHON and CHONS had greater numbers in the nighttime samples, consistent with nitrate radical chemistry as a likely source for those compounds.

Inter-season comparison indicates that only about 23.7% of total assigned formulas existed in all samples, suggesting that the organic aerosol composition at this urban site varied sharply between seasons. Winter samples were generally richer in organics, in terms of both number and abundance. The fraction of CHON compounds in summer was lowest probably due to the lowest average NO<sub>x</sub>

concentration compared to those in three other seasons. On the other hand, the fraction of compounds with oxidized sulfur groups CHOS in summer daytime samples was larger than those in three other seasons indicating a photochemical formation route of these compounds.

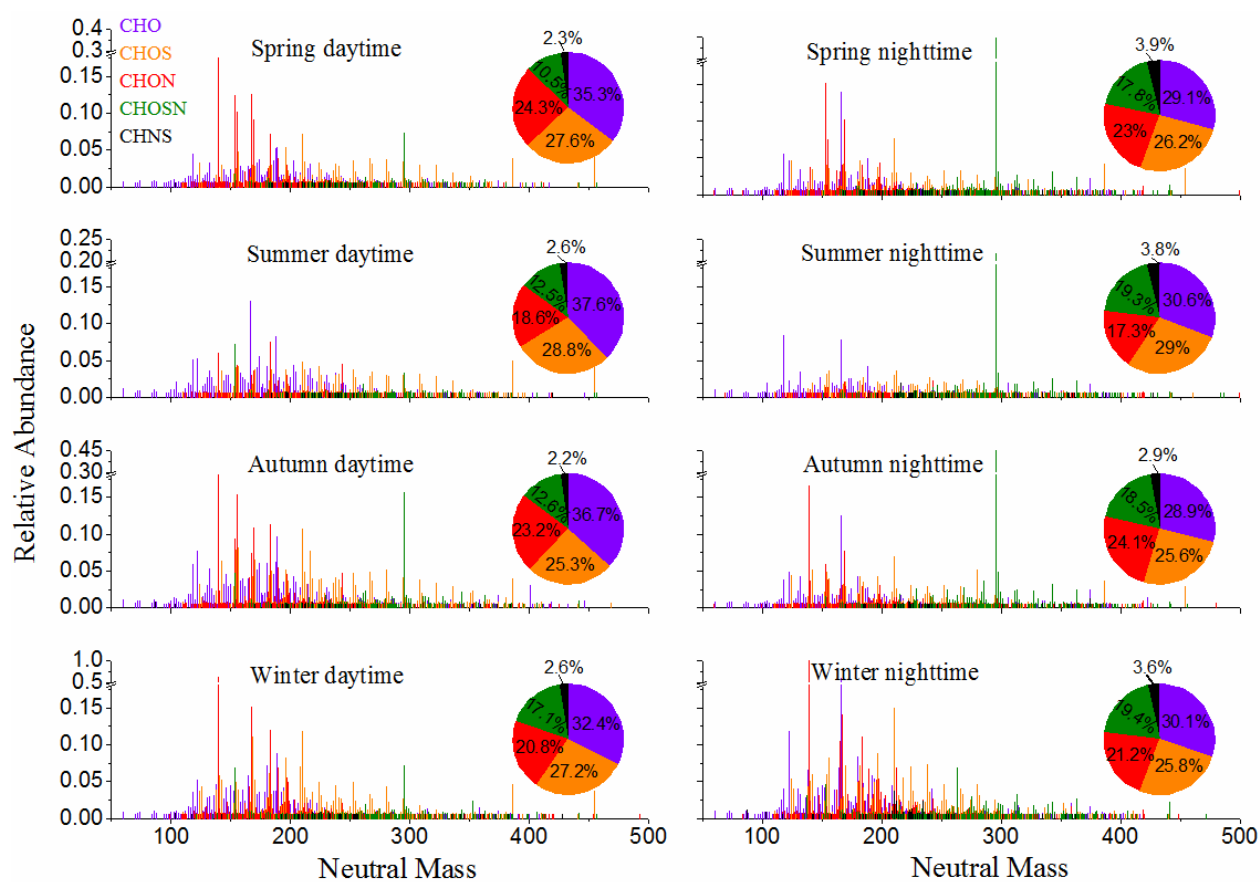


Figure 1. Mass spectra of tentatively detected CHO, CHOS, CHON, CHONS, and CHNS including CHS and CHN reconstructed from extracted ion chromatograms UHPLC-Orbitrap MS analysis, negative ionization mode. Pie charts show the percentage of compounds for each season averaged over 5 days. Note that the average abundance of  $C_6H_5NO_3$  in the winter nighttime samples the highest one from all samples was set arbitrarily to 100%.

# Carbonyl compounds at Mount Tai in North China Plain: Characteristics, sources, and effects on ozone formation

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Carbonyl compounds are important intermediate products of atmospheric photochemical reactions and play important roles in ozone formation and atmospheric oxidizing capacity. To better understand the characteristics, sources of carbonyl compound and their effects on ozone formation, C1-C8 carbonyl compounds were measured at Mount Tai, the highest mountain in the North China Plain NCP, in summer 2014. Acetone  $3.57\pm 0.55$  ppbv, formaldehyde  $3.48\pm 0.98$  ppbv and acetaldehyde  $1.27\pm 0.78$  ppbv are the three most abundant carbonyl species, comprising as high as 90% of the total observed carbonyls. Isovaleraldehyde  $0.37\pm 0.17$  ppbv presents another important carbonyl compound despite its high reactivity. Comparison with the observations available in the world highlights the serious situation of the carbonyl pollution in the NCP region. Examination of diurnal variation patterns reveals that the sources of carbonyls were dominated by photo-oxidation of VOCs in the daytime and by regional transport at night. The relative contributions of primary and secondary sources to atmospheric carbonyls were derived from the multi-linear regression analysis, with secondary processes contributing about 44% to the ambient HCHO levels. Formaldehyde and acetaldehyde played the most important roles in OH removal as well as in the ozone formation potentials OFPs. This study shows that the carbonyl compounds make a significant contribution to the OH reactivity and ozone formation in North China Plain, and hence understanding their sources is essential for developing science-based ozone pollution control measures.

# Reaction of OH radical with ethyl and propyl nitrates: Kinetics and products

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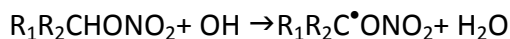
Organic nitrates are the intermediates of the atmospheric oxidation of volatile organic compounds in the presence of nitrogen oxides. They are formed in the minor channel 1b of the reaction of peroxy radicals with NO:



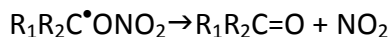
and also in the NO<sub>3</sub>-initiated oxidation of unsaturated organic compounds. Organic nitrates are temporary reservoirs of NO<sub>x</sub> with a tropospheric lifetime from a few days to a few weeks, depending on the reactivity of nitrates toward OH radicals and their photolysis rate. Photolysis of organic nitrates is known to produce NO<sub>2</sub> and alkoxy radicals. The products of OH radical initiated degradation of nitrates are not so well characterized, in particular, with regard to the release of NO<sub>2</sub>. In the present work, we report the results of the kinetic and mechanistic experimental study of the reactions of ethyl ETN and propyl nitrates PN with OH radicals.

The title reactions were studied at 1 Torr total pressure of helium over the temperature range 238–500 K. Highest temperature of the study was limited by thermal decomposition of the nitrates. Experiments were carried out in a discharge flow tube combined with modulated molecular beam mass spectrometer used for monitoring the reactants and reaction products. The measurements of the rate constants were carried out under pseudo-first order conditions in high excess of nitrates over OH radicals. For both reactions, the rate constants were found to increase with temperature showing non-Arrhenius behavior:  $k_{\text{ETN}} = 1.55 \times 10^{-21} \times T^{-3.035} \exp(436/T)$  and  $k_{\text{PN}} = 4.87 \times 10^{-19} \times T^{-2.363} \exp(165/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

Abstraction of an  $\alpha$ -hydrogen atom in organic nitrates by OH radicals leads to the formation of an  $\alpha$ -substituted alkyl radical:



These radicals are known to be unstable, dissociating spontaneously without an energetic barrier to form a carbonyl compound and NO<sub>2</sub>:



In this respect, the measurements of the yield of corresponding carbonyl compound provide the information on the extent of H-atom abstraction from  $\alpha$  carbon. We have determined the yield of the carbonyl compounds formed in reactions of OH with ETN acetaldehyde, CH<sub>3</sub>CHO and PN propanal, CH<sub>3</sub>CH<sub>2</sub>CHO at T = 298K:  $0.77 \pm 0.12$  and  $0.22 \pm 0.03$ , respectively.

The kinetic and mechanistic data from the present study are in good agreement with previous experimental results and those calculated within structure-activity relationship.

# Experimental study of multichannel O<sup>3</sup>P + C<sub>2</sub>H<sub>4</sub> Reaction: Primary products as a function of temperature

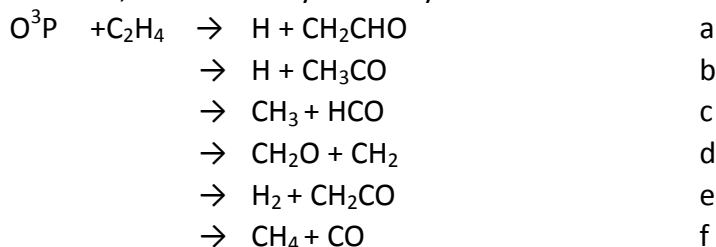
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Reactions of small alkenes, which are known to be intermediates in the combustion of many hydrocarbons, with ground-state oxygen atoms <sup>3</sup>P are important oxidative steps in the combustion mechanisms. The understanding and description of the mechanism of transformation of an organic compound in the combustion process requires first of all the information on kinetics and primary products of its reactions with active species, atoms and radicals, present in the reactive system. Reaction of oxygen atoms with ethylene has been extensively studied, experimentally and theoretically, during the last decades. The total rate constant of the reaction seems to be well established; however the information on the distribution of the reaction products still remains somewhat uncertain, particularly with regard to the temperature dependence. Indeed, almost all previous work, except for a few crossed molecular beam studies, was conducted at room temperature. The objective of the present study was to carry out a systematic experimental investigation of the products of the title reaction as a function of temperature. The total rate constant of the reaction was also determined in an extended temperature range.

Experiments were carried out in a discharge flow reactor using modulated molecular beam mass spectrometer for detection of the reactants and reaction products. The total rate constant of the reaction was determined from the consumption kinetics of oxygen atoms monitored under pseudo-first order conditions in high excess of C<sub>2</sub>H<sub>4</sub> over O. The following expression,  $k = 3.96 \times 10^{-17} \times T^{1.8} \times \exp(-132/T)$ , obtained for the rate constant at T = 230 – 902 K and 1 Torr total pressure of helium, is in excellent agreement with current recommendation.

The products of the title reaction have been investigated at temperatures between 298 and 900 K and pressures from 1 to 8 Torr of helium. Under experimental conditions used, the thermodynamically feasible channels of the title reaction are:



Experiments were carried out in presence of molecular bromine in the reactor, which allowed to rapidly transform H atoms channels a, b and CH<sub>3</sub> radicals channel c to stable species, HBr and CH<sub>3</sub>Br, respectively, which were detected with mass spectrometry. Formaldehyde channel d and H<sub>2</sub> channel e were detected directly at



their parent peaks. Preliminary results show that the absolute yields of H, CH<sub>3</sub> and CH<sub>2</sub>O are in the ranges 0.25-0.35, 0.45-0.55 and 0.15-0.20 virtually independent of temperature and total pressure under experimental conditions of the study. The yield of H<sub>2</sub> channel e was measured to be less than 0.02. These results will be discussed in comparison with existing room temperature and crossed molecular beam data and those from theoretical studies.

# Kinetic and Product studies of OH radical Reactions with a series of Ketones

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In order to understand the atmospheric fate of 2-methyl-3-pentanone 2M3P, 3-methyl-2-pentanone 3M2P and 4-methyl-2-pentanone 4M2P, three widely used chemicals in the industry, the kinetic and products of reactions of OH radical with these ketones were investigated using two complementary techniques: Pulsed laser photolysis-laser-induced fluorescence PLP-LIF and simulation chamber. Kinetic studies were conducted using both absolute and relative methods. The obtained rate constants values were used to estimate the atmospheric lifetimes of the studied ketones.

In addition to the kinetic studies, a number of experiments were performed to investigate the OH-initiated mechanism of the three ketones. The experiments were conducted in a 7300 L simulation chamber coupled to FTIR, PTR-ToF-MS, UHPLC and GCMS as analysis tools. The possible reaction mechanisms are discussed based on the identified reactions products and their yields.

**Keywords:** kinetic, OH radical, 2-methyl-3-pentanone, 3-methyl-2-pentanone, 4-methyl-2-pentanone, mechanism

# Third-Party Investment and Operational Solutions to Air Pollution for Industrial Park

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At present, most domestic industrial parks are facing severe air pollution problems. The atmospheric pollutants with complex components refer to varied monitoring and controlling technology. It is difficult to achieve effective reduction of pollutants because of the high cost and lacking of control technology. Meanwhile, government regulators have great regulatory pressure. Therefore, we put forward the mode of Third Party Investment and Operational Solutions to Air Pollution for Industrial Park to carry out air pollution control work.

To realize the effective reduction of atmospheric pollutants in Industrial Park, a systematic work process and management method need to be established. Pollution source emission inventory should be established by investigating the pollution source . Real-time monitoring of pollutant emission can be realized through online monitoring system. The cost of governance can be reduced through overall planning and unified operation.

According to the practice in Shandong, Jiangsu and other places, Third Party Investment and Operational Solutions to Air Pollution for Industrial Park has improved the enterprise enthusiasm and the ability of government management, sped up the air pollution control work of the industrial park, and effectively achieved the reduction of air pollutants.

The mode of Third Party Investment and Operational Solutions to Air Pollution for Industrial Park could acheive good environmental benefits, economic benefits and social benefits. It would has good practice effect and market prospects in the futher.

# Variation Characteristics of Atmospheric Carbonyl Compounds in Zhangjiajie Forest

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The atmospheric carbonyls in Zhangjiajie Forest were measured by using EPA TO-11A from August 2014 to January 2015. Formaldehyde, acetaldehyde, acetone, propionaldehyde and methacrolein MACR were found to be the most abundant carbonyls, with average concentrations of 4.32, 0.95, 3.01, 0.48 and 0.51  $\mu\text{g}/\text{m}^3$ , respectively.  $\rho$  formaldehyde,  $\rho$  acetaldehyde and  $\rho$  MACR seasonally changed; the concentrations of carbonyls were high in summer and autumn and low in winter. The daily concentrations of carbonyls changed significantly too. Except in October and December when human factors were greater, maximum carbonyl concentrations usually occurred between 13:00-15:00. Zhangjiajie Forest atmospheric C1/C2 was 5.72, which was higher than in urban areas where C1/C2 is about 1, but lower than remote forest areas where C1/C2 is about 10.  $\rho$  formaldehyde,  $\rho$  acetaldehyde and  $\rho$  MACR were positively correlated, and reached a significant level, while  $\rho$  acetone and  $\rho$  formaldehyde,  $\rho$  acetaldehyde and  $\rho$  MACR had poor correlation. Compared with the literature Canada Ontario, Mexico Langmuir and other regions, the atmospheric concentrations of carbonyls in Zhangjiajie Forest were higher, but lower than Beijing, Shanghai and other urban areas. The study showed the Zhangjiajie Forest atmospheric formaldehyde, acetaldehyde and MACR were mostly from photochemical reactions of plant VOC emissions in forest areas, but sources of acetone were not only from photochemical reactions of plant VOC emissions but also other human-made sources. The study further showed that the change of carbonyl concentrations in Zhangjiajie Forest atmosphere were mainly influenced by photochemical reactions in natural forest, but human factors couldn't be ignored.

**Keywords:** carbonyls; photochemical reaction; Zhangjiajie Forest atmosphere

# Impact of Weather Conditions on PM<sub>2.5</sub> Pollution in Eastern Coastal Provinces of China during winter

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China has been suffering from severe particulate matter PM pollution in recent years. Both pollution area and pollution levels are increasing gradually. The PM pollution episodes not only occur in the traditional developed areas like Yangtze River Delta YRD and Beijing-Tianjin-Hebei BTH region, but also frequently happen in the whole eastern coastal provinces ECPs of China. Based on hourly PM<sub>2.5</sub> concentrations during Dec 2013 ~ Feb 2014 of 55 cities located in the ECPs, we investigated the spatial and temporal variabilities of PM<sub>2.5</sub> concentrations and the corresponding meteorological conditions during winter. The results shown that basically the seasonal mean concentrations over the whole ECPs exceeded the China's national standard of 75  $\mu\text{g}/\text{m}^3$ , and the most polluted area with mean concentrations greater than 150  $\mu\text{g}/\text{m}^3$  were located in the southwest of Hebei and the west of Shandong provinces. From December to February, there was a decrease trend for the PM<sub>2.5</sub> pollution in most areas, especially in the YRD region, while the PM<sub>2.5</sub> concentrations over north of Hebei province increased. The spatial distributions and monthly variations are strongly related to the weather conditions. Overall, severe PM pollution was corresponding to a stable weather condition, i.e., small sea level pressure gradient, lower PBL height and weaker wind fields. Statistics shown that the variations of PBL height and wind speeds could explain about 71% of the variations of PM<sub>2.5</sub> concentrations over the ECPs. This study gives a full insight into the PM<sub>2.5</sub> pollution in the area of eastern coastal provinces of China during winter, which would be helpful to predict and control the PM<sub>2.5</sub> pollution for this area in the future.

**Keywords:** PM<sub>2.5</sub>; Weather condition; Eastern coastal provinces; Impact

# **The strategical ambition of integration in France including some mathematical correlations between contaminants and GHG**

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France is one of the most integrated countries in the world insofar as the emission inventories as well as policies and measures. What is at stake? Why does France implement such a system at national and regional levels? Are there any reasons regarding the emissions of contaminants and GHG themselves, such as possible correlations, explaining variables, and multi variate analysis, which justify this choice?

# Temporal and Spatial Variation Characteristics of Atmospheric Emissions of Hazardous Heavy Metals from Anthropogenic Sources under Multi-scale Regions

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With rapid progress of the industrialization and urbanization of the world, pollution control of hazardous heavy metals have attracted world wide attention. Based on economic development and technology diffusion theory, anthropogenic atmospheric emission inventory of 12 typical heavy metals Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn characterized by multi-scale regions, long-term spans and high spatiotemporal resolutions were elaborately established by synthetically using the best available representation of time-varying emission factor methods and ArcGIS tools. The main conclusions are summarized as follows: The historical emissions of 12 hazardous heavy metals in China, during the period of 1949-2012, increased by about 20-128 times, totally reaching about 79807.7 tons in 2012, which contributed about 36.8% of global emissions 216893.1 tons. Therein, coal combustion sources, liquid fuel combustion, nonferrous metal smelting and brake wear were regarded as the primary contribution sources for the corresponding heavy metals. Generally, Shandong for As, Se, Cd, Cr, Ni, Sb and Cu, Hebei for Pb and Zn, Guizhou for Hg, Inner Mongolia for Mn and Shanxi for Co ranked as the largest provinces with corresponding heavy metal emissions in China, respectively. One notable feature of the spatial distribution of China's heavy metal emissions was that the heavy metal emission intensities were much higher in central and eastern China than those in western China, and the coastal regions were classed as the most polluted areas of varied heavy metals. Worldwidely speaking, China, Chile, India, Russia, the United States and South Africa were the countries with high heavy metal emissions from anthropogenic sources. Therein, China ranked as the top one largest country with heavy metal except for Sb emissions. Asia represented the highest heavy metals emitting continent, which accounting for approximately 58.6% of the global emission in 2012. The top emission intensities of heavy metals were found in Eastern and Southern Asia and Eastern Europe.

**Key Words:** multi-scale regions, heavy metals, emission inventory, temporal and spatial distribution.

## **Acknowledgment**

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# **Air emission and GHG control policies and measures**

Julien VINCENT

Centre Interprofessionnel Technique d'Etudes de la Pollution Atmosphérique

Regulation at International, European and national levels on air pollution and GHG emission reduction will be presented. The aim will be to discuss the policies and measures applied and under preparation, the sectors and pollutants covered as well as the impact of these measures in the past and in projections.



# Trends of air pollutants and GHG in France since 1990.

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Based upon the publications of the French national inventories for UNFCCC, European Union and National Emission Ceiling Directive, we will show how French emission levels of NO<sub>x</sub>, PM<sub>2.5</sub> and CO<sub>2</sub>, fluctuated over time since 1990 until 2014. Which are the main reasons that can explain those evolutions? Which limits and problems are yet to be resolved in France? Also, we will plot that gainst GDP and per capita. We will show those trends for all sectors as well as we will make a particular focus on road transport.

# Current Situation and Trend of Air Pollutants Emission Inventories Technology in China

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Through analyzing current situation and progress of air pollutants emission inventory in China, the main achievements of governmental departments, research institutions and universities on air pollutants emission inventories has been summarized. Generally speaking, emission inventory research has made great progress in recent years, but it is still in a disorderly development situation. Then the problems and challenges faced by the air pollutants emission inventories of China has been listed, such as shortage of uniform air Pollutant emission sources Classification and Coding method in the whole country, the emission factor database has not been updated based on huge amount of research results of emission measurement, and the emission inventory data of different cities and regions cannot be compared with each other because of the different method. In order to guide healthy development of air pollutant emission inventory and provide technical support for establishment of national and local air pollutant inventories, the CRAES and other 7 research institutions and universities focused in the general technical guideline for Air Pollutants Emission Inventory from 2014, which include the classification method of emission sources, emission factors and calculation method of different kind of emission sources, activity level data acquirement ,technical route and QA/QC of air pollutants emission inventory. The quality of air pollutants emission inventories will be improved quickly based on the the general technical guideline.

**Key Words:** Current situation , trend, air pollutant, emission inventory.

# **A sector-based emission factor uncertainty database and its application to quantify uncertainties in PRD regional air pollution emission inventories**

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Uncertainties are inherent in compiling emission inventories. Quantifying uncertainties in Emission Inventories (EIs) can help prioritize source categories for future improvement and assess the quality of EIs, analyze the impact of uncertainty in EIs on air quality modeling results, and quantify exposure risks of humans to air pollution. However, subject to data availability, quantification of uncertainties in EIs is challenging due to lack of quantitative uncertainty information in key parameters, especially in emission factors. In order to address this challenge, this study attempted to utilize various data sources including field measurements and such as EPA AP-42, IIASA, EEA emission factor databases, to develop a sector-based emission factor uncertainty database, with the use of bootstrap simulation, statistical analysis and expert judgment approach. The emission factor uncertainty database was demonstrated to quantify uncertainty in regional air pollution emission inventories in the Pearl River Delta region, China, and applied to assess the impact of uncertainty in EIs on PM<sub>2.5</sub> simulation in this region. The developed emission factor uncertainty database can be also used to quantify uncertainty of EIs in other regions or countries, and to identify key sectors or sources with high uncertainty, and thereby guide the development of local emission factors or emission testing.

# **INTEGRATION - FRENCH experience on national emission inventories**

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The national French emission inventory system, in the frame of the Ministerial Order, has the general goal to cover all sectors and all pollutants, including GHGs, to follow the French obligations in terms of emission reduction at international, European and national levels. The organization, role of the different stakeholders and main characteristics of this system will be presented.

# Status of China's inventories of Greenhouse gases and short-lived climate pollutants

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China has so far released two official emission inventories for its greenhouse gases GHGs as responses to the requirement of UNFCCC. The Initial National Communication on Climate Change provides a 1994 national greenhouse gas inventory, where the national total amount of carbon dioxide emission in 1994 was 3,073 million tons. China began to prepare its Second National Communication in 2008, with 2005 as the base year. Compared with previous inventory 1994, the estimated GHGs were extended from three to six types. In order to better perform the international obligations on information communication, the State Leading Group for Statistical work of Climate Change was founded in Feb. 27, 2014 and the preparation of the third Communication was launched at the same year, with 2010 and 2012 as the base years. Meanwhile, the GHG emission inventories for local individuals were also initiated. China will update its inventory every 2 years in accordance to the Decision 1/CP.16 and 2/CP.17. There are so far no officially published national inventories of black carbon emissions, although they have frequently been developed by lots of researchers and institutions in China and around the world. During 2013-2015, through the collaboration of United Nations Environment Programme UNEP and Policy Research Center for Environment and Economy of the Ministry of Environmental Protection of the People's Republic of China PRCEE, an assessment report, the Climate and Environmental Benefits of Controlling SLCPs in P.R. China, was developed to provide information on China's SLCPs emissions and the climate-health co-benefits through emission control efforts.

# Development of Emission Inventory of Air Pollutants for Shanghai

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## 1 Purpose of research

In order to create an accurate and complete emission inventory of criteria air pollutants, and to develop a continuously updating mechanism for emission inventory to facilitate the air pollution control effectively for Shanghai, the first emission inventory was accomplished for criteria air pollutants PM, PM<sub>10</sub>, PM<sub>2.5</sub>, SO<sub>2</sub>, NO<sub>x</sub>, CO, VOCs and NH<sub>3</sub> in large urban scale with high precision of gridding in 1km×1km basis. Thereafter, the emission inventory data had been updated irregularly in 2006, 2007, 2010, 2012 and 2014, respectively. Establishment of the emission inventory for Shanghai has contributed significant technical support to both the source appointment of airborne fine particulate matter, and to the formulation and implementation of the Clean Air Action Plan and Air Pollution Control Project.

## 2 Inventory methodologies

**2.1 Stationary sources originate from fossil fuel combustion.** CEMS data were adopted to estimate the discharge amount of pollutants of the main emitting enterprises and the efficiency of environmental facilities was analyzed.

**2.2 Source of technological process of production.** VOCs emissions of sub technological procedures were determined by actual measuring, material balancing and emission coefficient method.

**2.3 Mobile sources.** The emission inventory of vehicle was calculated using IVE model. The emission inventory of vessel was calculated based on the dynamic technique, optimizing of emission factors, and application of interpreted AIS database. Besides, the emission inventory of non-road mobile machineries was calculated using the NON-ROAD model and revised emission coefficients.

**2.4 Solvent sources.** Point sources were printing, dyeing, surface coating industry, while non- point sources were architectural coating, municipal engineering, pesticides, dry cleaning and e.g.

**2.5 Agricultural sources.** By applying of NARSES model for ammonia emission due to nitrogen fertilizer consumption for farming, combined with the emission coefficient measured by micrometeorological flux level method, the emissions from agricultural sources were estimated.

**2.6 Other sources.** The emission inventory of cooking was calculated using local emission coefficients; the emission inventory of vegetation were estimated on the basis of forest and arable area, and major species; moreover, VOCs emissions of liquid bulk terminals were determined in variant stages, such as in leakage and loading-unloading processes of fixed tanks, floating roof tanks and pipeline sealing points and e.g.

## 3 Results and discussion

### 3.1 Total Emissions

All the districts, counties and vessel boundary water areas under the jurisdiction of Shanghai were taken into account in the emission inventory for Shanghai. Major air contaminants are composed of SO<sub>2</sub>, NO<sub>x</sub>, CO, VOCs, NH<sub>3</sub>, TSP, PM<sub>10</sub>, PM<sub>2.5</sub>, BC and OC, whereas emission sources include stationary combustion, technological process of production, mobile sources, dust source, solvent using, wastes disposal, biomass burning, as well as storage and transport of oil and gas and other sources Fig. 1.

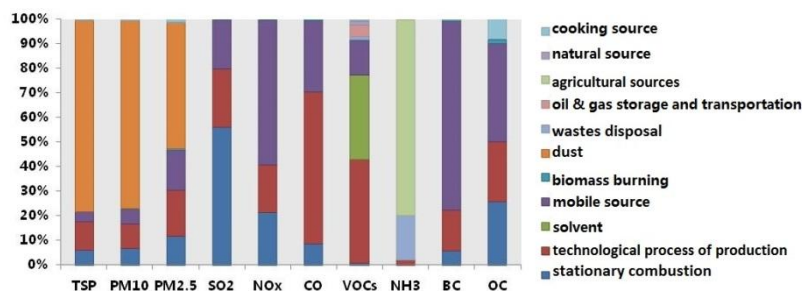


Fig. 1: Contribution of major air pollutants of Shanghai in 2014

### 3.2 Contribution of major pollutants

Construction sites, storage piles and road dust accounted for the main primary sources for PM<sub>2.5</sub>, which contributed 52% of total PM<sub>2.5</sub> emission in Shanghai, while industrial boilers, heat and power generation industries constituted the greatest emission of SO<sub>2</sub>, accounting for 31% and 18%, respectively. Automobiles, vessels, non-road moving machineries represented the major emission sources for NO<sub>x</sub>, contributing 32%, 17%, 12%, respectively. Among mobile vehicles, the large lorries, long-distance buses, trucks and public buses made up 34%, 23%, 13% and 9% respectively of total NO<sub>x</sub> emission, whereas the heavy vehicles large lorries and trucks released 47% of the total NO<sub>x</sub>. Apart from that, the contribution of motor vehicle for VOCs emission should be significantly taken into consideration, as the minibuses constituted 80% of total VOCs emission by motor vehicle in Shanghai. Besides, international marine machineries, contributed the greatest air pollutants in vessel category, which released 79% of primary PM<sub>2.5</sub>, 54% of NO<sub>x</sub>, 84% of SO<sub>2</sub> and 51% of the total VOCs emission from vessels, while the petrochemical and chemical industry and solvent use constituted the most emission of VOCs, accounting for 32% and 19%, respectively. In addition, livestock and poultry breeding emitted the most NH<sub>3</sub> among all agricultural affairs, which represented 59% and 17%, respectively. Similarly, wastewater contributed 9% of the total NH<sub>3</sub> emission.

### 4 Conclusion and recommendations

According to the emission inventory established for Shanghai, Stationary combustion, technological process of production, dust sources and mobile vehicle contributed the most air pollutants. Therefore, air pollution prevention and control strategies must be feasible and specifically applicable to Shanghai in terms of the air contamination circumstance. Recommended measures are as follows: First of all, adjusting industrial structure intensively and substantially increasing the proportion of clean energy supply, thus to eliminate high energy consumption and high pollution emission production processes in iron and steel, petrochemical industries

and e.g. comprehensively. Secondly, ensuring the pollution emission per unit of product to reach a world leading level by strict enforcement and supervision. Besides, enhancing the refinement of urban management and reducing overall primary particle matter emissions contributed by road dust. In addition, introducing more stringent vehicle license policies, to limit the vehicle population growth rate within 2%, and meanwhile, to enhance the capacity of rail transportation up to 40%-60%. Moreover, adjusting the structural development of harbors in Shanghai, and specifically focusing on elimination of dry bulk cargo transportation, in the meanwhile, boosting "clean fuel" vessel control zone, to reduce emissions from vessels by more than 40%. Lastly, complying with the Yangtze River Delta Region Joint Prevention and Control Policy, to reduce PM<sub>2.5</sub> emissions of Shanghai and its surrounding area simultaneously.



# The Research Progress of Tianjin Air Pollutant Emission Inventory

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The research of air pollution emission inventory in Tianjin began from 2010, relying on the study of Tianjin Air Pollution Joint Prevention and Control Plan in 12th Five-Year Plan, we make the 2010 emission inventory, and it includes industrial source, the domestic source, and motor vehicle. Began in 2014, relying on the project of Ambient Air Monitoring and Early Warning System Construction, we start the work of emission inventory establishment by the cooperation of several technical units, and Tianjin participated in the Pilot Projects of Emissions Inventory Preparation in 2015, and then we make a more comprehensive inventory of 2013 with a coverage of primary pollutant sources and several kinds of pollutants. As a petroleum and chemical industry intensive city, VOCs emissions has important effects on ambient air quality of Tianjin, in recent years, we make a more perfect VOCs emissions data collection and management system, and using this system, Tianjin has made great progress in the establishment of VOCs emission inventory. Since 2015, combined with the emission inventory and air quality models, Tianjin embarked on implementation effect evaluation of The Fresh Air Action Plan,

# The Establishment of Air Pollutant Emissions Inventory in Chengdu

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Based on the investigation of the air pollutant emissions inventory in 2014 in Chengdu, the total discharge as well as temporal and spatial distribution of the  $\text{SO}_2$ 、 $\text{NO}_x$ 、 $\text{CO}$ 、 $\text{VOCs}$ 、 $\text{NH}_3$ 、 $\text{PM}_{2.5}$ 、 $\text{PM}_{10}$ 、 $\text{BC}$ 、 $\text{OC}$  is inferred that contributed by ten types of anthropogenic emissions, like fossil fuel and stationary combustion source. The amount of air pollutant emissions of  $\text{SO}_2$  are  $5.7 \times 10^4$  t,  $\text{NO}_x$  are  $9.7 \times 10^4$  t,  $\text{CO}$  are  $4.6 \times 10^5$  t,  $\text{VOCs}$  are  $1.9 \times 10^5$  t,  $\text{NH}_3$  are  $6 \times 10^4$  t,  $\text{PM}_{10}$  are  $1.1 \times 10^5$  t,  $\text{PM}_{2.5}$  are  $4.8 \times 10^4$  t. Analysing the pollutant emission, we can find that  $\text{SO}_2$  mainly come from fossil fuels, stationary combustion and process source.  $\text{NO}_2$  mainly come from fossil fuels, stationary combustion sources and vehicle gas.  $\text{CO}$  mainly come from vehicle gas and process source.  $\text{VOC}$  mainly come from process and solvent source.  $\text{NH}_3$  mainly come from agricultural source emission. Fugitive dust is the primary contribution of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ .  $\text{BC}$  mainly come from process source.  $\text{OC}$  come from process and catering oil fume source.

# Atmospheric emissions of typical toxic heavy metals from open burning of municipal solid waste in China

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Open burning is the disposal behavior of solid waste by uncontrolled combustion in open areas or in barrels. Due to its simpleness and convenience, open burning is a common disposal way of municipal refuse, construction waste, agricultural residues, etc. in urban and rural areas, besides landfill, composting treatment, and incineration. Compared with rural waste burning, the small-scale, widely-distributed open burning of municipal solid waste MSW in urban areas deserves highlighted attention since metropolitan areas are heavily populated. MSW contains considerable hazardous components and the widely-distributed open MSW burning in heavily-populated urban areas can cause direct exposure of hazardous materials to citizens.

By determining the best available representation of composition-varying and time-varying emission factors with fuzzy mathematics method and S-shape curves, a comprehensive atmospheric emission inventories of 9 typical toxic heavy metals THMs, e.g. mercury Hg, arsenic As, lead Pb, cadmium Cd, chromium Cr, selenium Se, copper Cu, zinc Zn, and nickel Ni from open MSW burning activities in China is established during the period of 2000-2013 for the first time. Further, the emissions in 2013 are allocated at a high spatial resolution of 0.5°×0.5° grid by surrogate indexes. The results show that 9 typical THMs emissions from open MSW burning in 2013 are estimated at 21.25 t for Hg, 131.52 t for As, 97.12 t for Pb, 10.12 t for Cd, 50.58 t for Cr, 81.95 t for Se, 382.42 t for Cu, 1790.70 t for Zn, and 43.50 t for Ni, respectively. In terms of spatial variation, the majority of emissions are concentrated in relatively developed and densely-populated regions, especially for the eastern, central and southern regions. The results will be supplementary to all anthropogenic emissions and useful for relevant policy-making and the improvement of urban air quality as well as human health.

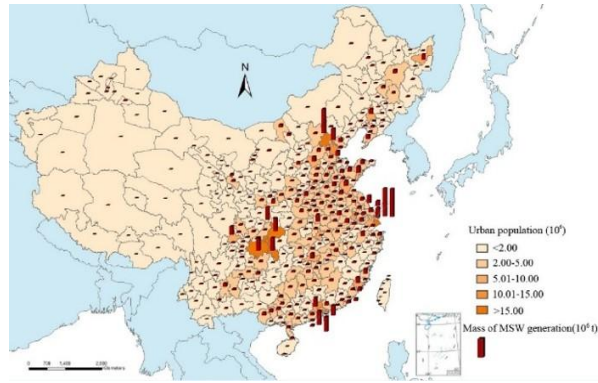


Fig.1 The annual amount of MSW generated by different cities in China, 2013.

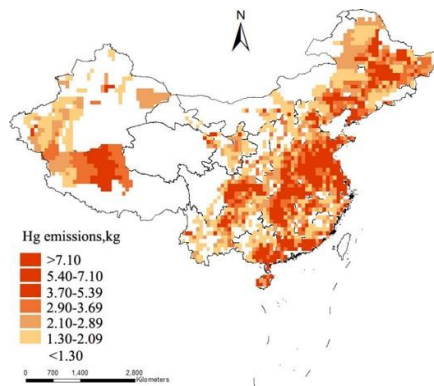


Fig.2 Spatial distribution of atmospheric Hg emission from open MSW burning in China in 2013,  $0.5^{\circ} \times 0.5^{\circ}$ .

# Comprehensive Prevention and Control of Air Pollution in China

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**Abstract:** Due to the rapid economic and industrial development, China has been suffering from degraded air quality and visibility. This paper mainly analyzes the pollution levels, sources, and spatial distribution of PM<sub>2.5</sub>, PM<sub>10</sub>, O<sub>3</sub>, SO<sub>2</sub> and NO<sub>x</sub> in the ambient air. At the end, the countermeasures implemented by Chinese Central Government to improve ambient air quality are introduced. “State Council Air Pollution Prevention and Control Action Plan”, “Air Control Law”, “Ambient air quality standard GB3095-2012” and “Clean Air Research Program CARP” are the key parts.

**Key words:** PM<sub>2.5</sub>, PM<sub>10</sub>, O<sub>3</sub>, SO<sub>2</sub>, NO<sub>x</sub>

# Research and Practice of Guohua Power's High Quality Green Power Generation Technology

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Guohua Electric Power is committed to improve the clean coal fired power generation technology. The flue gas pollutants control technologies were studied and firstly proposed the "ultra-low emission" conception. The best flue gas pollution reduction technologies all over the world in coal fired units were integrated and applied in coal fired units, three typical "ultra-low emission" of pollutants control technical routes were summed up. The depth of purification and removal of dust, sulfur dioxide, nitrogen oxides were also achieved and better than the gas unit emission standards. All the four units were updated in the Sanhe power plant, compared to the former coal discharge standards, the annual emissions were reduced of soot 508 tons, SO<sub>2</sub> 1169 tons, NO<sub>x</sub> 2185 tons, respectively. Till June 2016, Shenhua Group has already completed 65 units of environmental protection upgraded, including all the units in the Beijing-Tianjin-Hebei region. To the end of next year, all the thermal power units about 75 million kilowatts in Shenhua Group will be accomplished. In the mean time, the whole process of flue gas pilot test platform is in the course of constructing. The on-site mercury emission control testing was applied in Sanhe power station, and mercury concentration can be reduced of 30%, the overall removal efficiency is of 75 to 90%. The Oxy-fuel combustion technology and post-combustion carbon capture and storage are under researched and developed, the oxy-fuel combustion foundation research, 35MW<sub>th</sub> oxy-combustion tests and the system integration and design of 200MW oxy-fuel combustion demonstration have been fulfilled, and the whole process of 100,000 tons post-combustion carbon capture and storage demonstration project is in the process of construction.

**Key words:** ultra-low emission; environmental protection upgraded practice ; Pollutants control technical routes; mercury emission control; oxy-fuel combustion; post-combustion carbon capture

# **Veolia Experience in waste incineration: an example Hong Kong Sludge incinerator**

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Veolia is a global environmental company which designs and deploys water, energy and waste management solutions to improve efficiency for cities, industries and citizens, ensuring Sustainable management of natural resources by supporting circular economy, contributing to combat climate change, and conservation and restoration of biodiversity. For waste management the preferred solution of Veolia is “waste to energy” solutions, with Dry process treatment of air emission, to ensure a minimum atmospheric pollution, and reduce the green house gases emissions. An overview of the non hazardous waste energy recovery facilities ERF and detail presentation of the sludge incineration plant project are discussed

# The Strategic Value of Natural Gas in Air Pollution Control

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Natural gas is the cleanest energy among hydrocarbon, thus with high environmental value. In the other hand, natural gas is also abundant in reserve. In a broad sense, natural gas refers to an ensemble of conventional gas, shale gas, gas-hydrate and bio-gas etc. It is very likely to play a role of pilot-energy or one of the ultimate energy in the future energy mix. The main environmental benefit of using natural gas in end-user side comparing with other fossil fuel includes flexibility of employing combustion equipment in area of intense population, High efficiency and low emission in combine heat and electricity production and that its storage and distribution system allows to complement with intermittent renewable generation.

To better implement natural gas, several measures are discussed.

1. The government should play a major role in air pollution control than market. According to the environment law, coal-to-gas replacement should be strictly executed in prefecture level city above. Mining of low-quality coal should be prohibited and heating in remote villages should be replaced by high-grade coal.

2. Natural gas fired combined heat and electricity power plant should be constructed in mego-city central area to replace coal-fired power plants, further leads to more integration of renewable power. Local government should guarantee the basic income profitability of these power plants and the environmental cost is supposed to force the industrial structure to adjust.

3. To increase gas purchasing in low oil price period. China is expecting to have 100 billion natural gas contracted and another 100 billion domestic production capability in 2020.

4. Encourage underground storage and pipeline construction. Underground storage offers advantage in cost competitiveness, stability, safety and sustainability, along with hydro-pump it's the primary choice in China's energy storage system as well as an inevitable infrastructure serving as strategic gas reserve.

5. Implement regulation and TPA in mid-stream infrastructure, including high-pressure pipeline, LNG terminal and underground storage to prevent high cost from natural monopoly blocks added into the gas value chain. An independent regulating institute is supposed to be found led by the government.

Therefore, we as CNOOC, suggest to open mid-stream facilities of China's NOC rather than establish a national gas company. CNOOC's LNG terminal and gas network along the south-east coast of China can interconnect with CNPC's W-E line 2 and line 3, thus fulfilling its tight gas supply in the north of China in winter season by 'gas exchange', CNOOC is expecting to add 20 billion natural gas supply to China's market. We also suggest a coal-to-gas replacing plan in 50 big prefecture level city in the grand Huabei area to help solving the pollution issue.



# Numerical Simulation in Henan Province based on Localized Emission Inventory and Source Apportionment in the Central Plain Urban Agglomeration of China

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Henan is the most populous province and one of the most serious air polluted areas in China at present. In this study, on accounting of the detailed activity level data of 11 categories of primary anthropogenic emission sources, and by determining the best available representation of emission factors with “bottom-up” and “top-down” method, we established the integrated atmospheric emission inventories of primary air pollutants in Henan province for the target year of 2012. Further, we allocated the annual emissions of these air pollutants into the high spatial resolution of 3km × 3km grids with ArcGIS methodology and surrogate indexes, such as regional population distribution and gross domestic product GDP. In addition, the uncertainties of the total emissions in our inventories were quantified by the Monte Carlo simulation. The results show that the emission of BC, OC, CO, NH<sub>3</sub>, NO<sub>x</sub>, PM<sub>2.5</sub>, PM<sub>10</sub>, SO<sub>2</sub> and VOCs is about 0.23, 0.24, 8.34, 1.29, 2.40, 1.23, 2.62, 2.33 and 1.38 million tons, respectively. The uncertainties of emission inventory of SO<sub>2</sub>, VOC, PM<sub>2.5</sub>, PM<sub>10</sub>, CO, NH<sub>3</sub>, NO<sub>x</sub>, BC and OC ranged with -19.11%~20.39%, 29.41%~32.23%, -36.74%~40.23%, -32.24%~40.9%, -24.3%~25.53%, -24.37%~49.05, -22.4%~22.49%, -35.48%~49.53% and -43.85%~70.55%, respectively. In terms of spatial variation, the majority of emissions are concentrated in the relatively developed regions such as Zhengzhou, Luoyang, Xinxiang, Pingdingshan, Jiaozuo, Anyang and Nanyang, and most of these cities are located in the central plain urban agglomeration of China CPUA. Furthermore, this study built a numerical simulation platform for CPUA’s air pollution based on WRF-SMOKE-CMAQ system. To evaluate the performance of the modeling system, ground-level observed data, OMI Satellite remote sensing NO<sub>2</sub> column concentration data and MODIS satellite remote sensing AOD data were used to compare with the simulated results. Compared with air quality monitoring data and satellite remote sensing data, the WRF model shows the good simulation consistency for wind speed and temperature and the CMAQ model shows the good simulation consistency for time series and spatial distribution of SO<sub>2</sub>, NO<sub>x</sub> and PM<sub>10</sub>. The results demonstrate that Jiaozuo, Jiyuan and Xinxiang represent the heavily polluted areas of SO<sub>2</sub>, NO<sub>2</sub> and PM<sub>2.5</sub>. And the seasonal variation feature of SO<sub>2</sub>, NO<sub>2</sub> and PM<sub>2.5</sub> is shown as: Winter>Fall>Spring>Summer. Further, sensitivity analysis, like CMAQ-DDM, have been used to explore the region contribution in CPUA region. The results reveal that SO<sub>2</sub> and NO<sub>2</sub> are mainly affected by local emissions, whereas PM<sub>2.5</sub> is more

easily affected by long distance transport. The pollution interactions among CPUA cities have been simulated and the results indicate that Zhengzhou, Luoyang, Jiaozuo and Xinxiang were more influenced by local contribution and Kaifeng was more affected by the surrounding cities. Therefore, we believe that Zhengzhou, Luoyang, Jiaozuo and Xinxiang should be highlighted and treated as prior air pollution control areas in Henan province, and based on local air pollutant emission reductions, joint prevention should be strengthened both in CPUA's inside and outside region.

**Keywords:** emission inventory, PM<sub>2.5</sub>, bottom-up method, spatial and temporal variation

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# Continuous on-line monitoring of hazardous air pollutants by TD-GC-FID

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## Summary

This Application Note shows how the TT24-7™ Series 2 thermal desorber Markes International can be used for the continuous on-line detection of hazardous air pollutants, and how the time profiles and concentration data obtained can be of value for source apportionment.

## Background to TT24-7 Series 2

The TT24-7 Series 2 is an advanced thermal desorption TD system for continuous near-real-time NRT monitoring of volatile and semi-volatile organic compounds in air or gas. Its two reciprocating focusing traps and cryogen-free operation make it ideal for continuous unattended monitoring, either in static or mobile laboratories.

The TT24-7 Series 2 is an ideal choice for a wide range of challenging applications, including advanced environmental research, routine monitoring of air pollution and odour, controlling the purity of piped air/gas supplies, flavour or fragrance profiling, and monitoring of chemical agent stockpiles.

## TD :

Instrument: TT24-7 Series 2 Markes International

Sample flow path: 120°C

Sample flow rate: 50 mL/min

Sample time: 30 min average

Cold traps: Two 'Ozone precursors' traps

Markes International part number T-110P

Trap low: -30°C

Trap high: 25°C

Trap hold: 5 min

Split flow: 5 mL/min

## GC-FID:

Column: GasPro 30 m × 0.32 mm

Oven program: 40°C hold 6 min then 20°C/min to 200°C hold 10 min

Column flow: 3 mL/min

## Results : Continuous monitoring of airborne pollutants

1.5 L of air was sampled every 30 minutes at 50 mL/min, providing a higher data frequency than is typical for this method ca. 60 minutes but without compromising sensitivity. Air was pumped first through trap A. Sampling then automatically switched to trap B while trap A was desorbed and analyzed. This process can be repeated continuously and indefinitely, ensuring complete sample coverage with no 'blindspots'.

## Conclusions

In this Application Note, we have shown that continuous on-line monitoring using the TT24-7 Series 2 allows highly time-resolved ambient air concentration data to be collected, even at trace levels and for the most volatile target compounds.

A key advantage of using the twin-trap TT24-7 Series 2 to generate rapid, near-real-time air monitoring data is that there are no sampling blind spots, thus ensuring that even transient pollution events will be captured.

If the system was applied to more polluted environments, for example urban, indoor or industrial air, it would be possible to speed up sampling and reduce cycle times still further, provided the TT24-7 Series 2 was used in conjunction with an appropriately fast GC method.

Data from the system described has also been shown to be useful for source apportionment, by comparing the abundances of different compounds. This approach is particularly relevant given the emergence of large-scale hydraulic fracturing 'fracking'. In this case, the relative concentrations of hydrocarbons specifically associated with the fracking process may provide useful markers for pollution events, even though the compounds themselves are present in the wider atmospheric environment.

## **Vidéo presentation:the air pollution and GHG emission reduction efforts made by GEODIS**

Part 1: the context of Geodis

GEODIS is a worldwide Lead Logistics Provider who manage our customers' supply chain by providing end-to-end solutions enabled by our infrastructure, our people, processes and systems.

As such, we at GEODIS are aware of our impact on the environment and we strive to further lower the latter by enabling our 5 lines of business and our corporate global accounts department to meet their environmental challenges and those of their customers, with a special focus on a the reduction of energy consumption and b the reduction of emissions CO2 and pollutant emissions .

Part 2: our innovative management system on CSR to really reduce our impact and that of our customers on the environment.

To ensure that all the green initiatives we launch do reach both the above objectives in a consistent and sustainable way, we have put in place a worldwide management system called STS for "Stakeholders' Total Satisfaction" which is articulated around 7 common business principles called Golden Rules, one of which "Be a good citizen" is dedicated to CSR.

Our "Be a Good Citizen" Golden Rule is indeed key as it provides the indispensable framework for our green initiatives to be successful and generate their expected benefits in terms of respect for the environment and business soundness.

Part 3: our Urban Logistics Offer: a concrete example of how we apply STS by combining our concerns and those of our customers for business soundness and the protection of the environment

GEODIS selected Shanghai as the ideal location for the launch of its Green Logistics Offer in Asia in 2015 due to the city's high demand for logistics and its severe pollution levels:

The air quality is severely polluted there and reached almost 15 times the level considered safe by WHO.

GEODIS consequently started its Urban Logistics offer in Shanghai in 2015 with Sephora, with the management of deliveries to 28 Stores in Shanghai with 2 to 3 dedicated electric trucks

Since then, GEODIS has been expanding its operations in China both in Shanghai and in other Chinese megacities.

GEODIS is now the pioneer of last-mile delivery by 100% electric trucks in China. The electrical trucks are used on short urban delivery rounds from local logistics centers to customers' doors stores.

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