UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF HAZE PARTICULATE MATTER

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Master

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DEDICATION

This thesis is especially dedicated to my family and friends who have been giving me lots of support, advice and encouragement in my studies.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

CHARACTERIZATION OF HAZE PARTICULATE MATTER

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LAU TAI MENG

April 2003

Chairman: Dr. Ahmad Makmom Abdullah

Faculty: Science and Environmental Studies

Haze has became a public concern especially after the 1997 haze episode which resulted from large-scale forest fires that caused transboudary spreading of air pollution. Particulate matters are primarily responsible for creating haze in the atmosphere as well as adverse effects on human health. Thus, both of the physical and chemical characteristics of particulate matters are important when attempting to elucidate particle toxicity. Particulate matters, which aerodynamic diameter equal or less than 10 μm (PM_{10}) were measured in the periods from 1997 to 2000 at UPM station. High volume sampler (HVS) was used to collect most of the ambient particle samples and a small portion was collected using particle counter. Sampling of particulate matter was carried out from various emission sources such as peat swamp fire at Sepang, biomass burning at paddy field and several types of vehicle exhaust. Besides that, simulated peat soil and rice straw burning were also conducted in the fumigation chamber to collect particulate matter. Chemical analysis was performed by atomic absorption spectrophotometer (AAS) to identify ten kind of common trace metals, namely potassium (K), zinc (Zn), magnesium (Mg), sodium (Na), calcium (Ca), iron (Fe), manganese (Mn), lead (Pb), chromium (Cr) and copper (Cu). The monitoring of PM_{10} reveals that haze episode was not only due from transboudary air pollution, but also originated from local sources such as peat swamp fire. Meteorological parameters such as temperature, wind speed and rainfall show extremely low correlation with PM_{10} concentrations and also trace metals content in PM_{10}. Particle number concentrations with the aerodynamic diameter of 0.3 μm and 0.5 μm were noticeably higher during the high traffic intensity and haze periods. The fluctuation of particle number concentrations with the aerodynamic diameter of 5.0 μm and 10.0 μm indicate that the variations of coarse particle are more influenced by meteorological factors. Among the measured trace metals in this study, Na, Cr and Fe show significant difference between normal atmospheric condition and hazy condition. The chemical profiles of TSP from peat swamp fire and simulated peat soil burning were nearly similar, which indicate K, Fe and Mn dominate the smoke particle from peat swamp fire. K is the main element that is present in TSP from paddy residue and rice straw burning. On the other hand, Ca and Fe are the main species in PM_{10} released by 2-stroke motorcycles. Compared with petrol powered engine, diesel powered engine emitted less quantity of trace metals except Zn, Ca and Pb. Scanning Electron Microscope (SEM) demonstrated that majority of the haze particles were smaller than 2.5 μm and agglomerate in structure, comprising of a number of individual spheres and liquid droplets. The particle samples collected from peat swamp fire tend to form the compound of clusters up to 10 μm, which are larger than the particles produced from rice straw burning. 2-stroke motorcycle exhaust emission generates particles that appeared as the formation of clusters without clear boundary between the particles. For the diesel exhaust particles, the large agglomerated "spherules" was formed and the entire individual particle was in the range of < 2.5 μm in diameter.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENCIRIAN BAHAN PARTIKULAT JEREBU

Oleh

LAU TAI MENG

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Jerebu telah menjadi isu perhatian awam terutamanya selepas episod jerebu 1997 akibat pembakaran hutan dan telah menyebabkan pencemaran udara melintasi sempadan secara meluas. Partikulat adalah bertanggungjawab pembentukan jerebu dalam atmosfera dan seterusnya mendatangkan kesan buruk kepada kesihatan manusia. Oleh yang demikian, kedua-dua ciri fizikal dan kimia partikulat adalah penting untuk pentafsiran keracunan partikulat. Pengukuran partikulat yang bergarispusat aerodinamik sama dengan atau kurang daripada 10 μm (PM_{10}) telah dijalankan dari tahun 1997 hingga 2000 di stesen UPM. Penyampel berisipadu tinggi (HVS) telah digunakan untuk mengumpul partikulat dalam udara manakala sebahagian kecil partikulat dikumpul dengan menggunakan alat pengira partikulat. Pengumpulan partikulat telah dijalankan dari pelbagai punca seperti pembakaran hutan tanah gambut di Sepang, pembakaran biomes sawah padi dan gas ekzos dari pelbagai jenis kenderaan. Di samping itu, pembakaran simulasi tanah gambut dan batang padi juga dijalankan di dalam kotak uji untuk mengumpul bahan partikulat. Analisis kimia dijalankan dengan menggunakan spektrofotometer penyerapan atom (AAS) untuk menentukan sepuluh jenis logam biasa, iaitu potassium (K), zink (Zn),

magnesium (Mg), sodium (Na), kalcium (Ca), ferum (Fe), manganese (Mn), plumbum (Pb), chromium (Cr) dan kuprum (Cu). Pemonitoran PM_{10} mendapati episod jerebu bukan sahaja berpunca dari pencemaran udara melintasi sempadan, tetapi juga dihasilkan dari punca tempatan seperti pembakaran tanah gambut. Parameter meteorologi seperti suhu, laju angin dan hujan menunjukkan korelasi yang terlalu rendah dengan kepekatan PM_{10} dan juga kandungan logam dalam PM_{10}. Kepekatan bilangan partikulat dengan garispusat aerodinamik 0.3 μm dan 0.5 μm didapati tinggi pada waktu kesesakan trafik dan kejadian jerebu. Ketidaksetaraan kepekatan bilangan partikulat dengan garispusat aerodinamik 5.0 μm dan 10.0 μm mencerminkan variasi partikulat kasar adalah lebih dipengaruhi oleh faktor meteorologi. Di antara logam yang diukur dalam pengajian ini, Na, Cr dan Fe menunjukkan perbezaan yang bermakna antara keadaan atmosfera normal dan jerebu. Profail kimia jumlah partikulat terampai (TSP) dari pembakaran tanah gambut dan simulasinya adalah hampir sama, yang mana K, Fe dan Mn merangkum partikulat asap dari pembakaran tanah gambut. K merupakan unsur yang utama dalam TSP dari pembakaran sisa padi dan batang padi. Di samping itu, Ca dan Fe adalah species utama dalam PM_{10} yang dibebaskan oleh motorsikal 2-lejang. Perbandingan dengan enjin petrol, enjin diesel membebaskan kurang kesemua logam kecuali Zn, Ca dan Pb. Mikroskop pengimbasan elektron (SEM) menggambarkan kebanyakan partikulat jerebu adalah lebih halus dari 2.5 μm dan bergabung dengan beberapa sfera individu lain dan titisan cecair. Partikulat dikumpul dari pembakaran tanah gambut berkecenderungan membentuk sebatian "clusters" sehingga 10 μm yang lebih besar daripada partikulat hasil dari pambakaran batang padi. Pembebasan ekzos motorsikal 2-lejang menghasilkan partikulat dalam bentuk "cluster" yang tidak mempunyai sempadan jelas antara partikulat. Untuk partikulat ekzos diesel, gabungan besar "spherules" dibentukkan dan kesemua partikulat individu adalah dalam lingkungan garispusat < 2.5 µm.

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I certify that an Examination Committee met on 23rd April 2003 to conduct the final examination of Lau Tai Meng on his Master of Science thesis entitled "Characterization of Haze Particulate Matter" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirements for the degree of Master of Science. The members of the supervisory committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

LAU TAI MENG

Date: 17 July 2003

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LIST OF ABBREVIATIONS

Aerodynamic Diameter	D_a
Aerosol Scattering Coefficient	Bsp
Air Pollutant Index	API
Atomic Absorption Spectrophotometer	AAS
Computerized Vehicular Inspection Centre	PUSPAKOM
Continuous Air Quality Monitoring	CAQM
Department of Environment	DOE
Department of Environmental Science, Universiti Putra Malaysia	JSAS
Diesel Exhaust Particles	DEP
Environmental Protection Agency	EPA
Glass microfiber filters	GMF
High Volume Sampler	HVS
Inhalable Particles	IP
Intensification of Research in Priority Area	IRPA
Malaysian Agricultural Research and Development Institute	MARDI
Malaysian Air Quality Index	MAQI
mass median diameters	MMD
National Ambient Air Quality Standards	NAAQS
Particulate matter with aerodynamic diameter less than or equal to 10 μm	PM_{10}
Petrol Exhaust Particles	PEP
Pollutant Standard Index	PSI
Recommended Malaysian Air Quality Guideline	RMG

Respirable Particulate	RSP
standard deviation	S.D.
Suspended Particulate Matter	SPM
Total Suspended Particulate	TSP

CHAPTER I

INTRODUCTION

Atmospheric Aerosols

In recent years, there has been a growing concern about atmospheric problems, such as ozone layer depletion, acid rain and the fates of toxic chemicals in the atmosphere. These problems are affected by a wide variety of complex chemical and physical processes. Atmospheric aerosols are currently eliciting strong research interest because of their important in affecting climate, restricting visibility and causing adverse effects on human health. Monitoring of atmospheric particulate matter concentration is the fundamental to interpret the characterization of particulate matter. Current techniques used to measure the mass concentration of particles in air make use of size-specific sampling devices and thus the PM_{10} (particles with aerodynamic diameter equal or less than 10 μm) may be determined as an index of the mass concentration of particles that can penetrate into the human thorax (WHO, 1999).

Atmospheric aerosols are recognized as important contributors to global climate change (Piketh et al., 1999; Finlayson-Pitts and Pitts, 2000). Once in the atmosphere, those compounds may influence the properties of the atmosphere since the particles can absorb, scatter and reflect solar radiation (Andreae et al., 1996; Yamasoe et al., 2000; Xu et al., 2002) and some of the emitted gases such as CO_2 and CH_4 can contribute to the greenhouse effect. The radiative effects of anthropogenic aerosols are relatively large compared to their mass contribution because they are in the size range, which is radiatively most active (Simoneit and Elias, 2000). Light extinction by aerosols also reduces the quantity and quality of solar radiation reaching the surface, which may influence crop production (Xu et al., 2002).

The most obvious characteristic of air pollution is the loss of visibility. This is primarily due to suspended airborne particles, which are caused by the combination of ammonia with the oxidation products of atmospheric pollutants forming reflective particles of NH_4HSO_4, $(NH_4)_2SO_4$ and NH_4NO_3 (Wellburn, 1993). Such particulate scatters light efficiently, absorb and reflect incoming solar radiation, giving the atmosphere a hazy appearance. Particles with diameters in the range 0.38-0.76 μm have comparable dimensions to the wavelength of visible radiation and will therefore affect its transmission producing haze (Fergusson, 1991). Although haze occurrences have been noted as early as the sixties, the haze episodes of September 1982, April 1983, August 1990 and September-October 1991 in Malaysia have attracted a great deal of public attention and concern (Abas and Simoneit, 1996).

Aerosol size is the major factor to determine the atmospheric behavior of aerosol particles and thereby controls the residence time and removal mechanisms of atmospheric pollutants (Bidleman, 1988). In the case of grits and most coarse dusts, only particles greater than 50 μm in diameter are visible and those less than 10 μm across remain suspended for some time and, if very small (0.1-2 μm), act as nuclei for the condensation of water during cloud formation. They are only removed as rain or when hit by falling rain (wash-out) (Wellburn, 1993).

Biomass Burning

Biomass combustion giving rise to the release of large quantities of gaseous emissions and particulate matter (Cofer III et al., 1990; Yamasoe et al., 2000; Jayaratne et al., 2001) with instantaneous and long-term effects on quality, global climate and biogeochemical distribution of nutrients. Emissions from domestic biomass burning activity, combined with adverse geographical and meteorological conditions, contribute to poor air quality in both large and small urban area around the world (Koe et al., 2001). Generally, there are several major sources of biomass burning around the world. For instance, in India, biomass burning is originated by shifting cultivation, accidental fires, controlled burning, fire wood burning, burning from agricultural residues and burning due to fire lines (Prasad et al., 2001). Combustion processes produce a wide range of particulate whose composition and morphology depend on a number of factors, such as fuel type, oxygen flow, temperature, etc. (Lim and Renberg, 1997). According to Garstang et al. (1997), the mechanisms by which the particulate smokes from biomass fires are removed from the atmosphere can be stated in order of decreasing importance:

- wet scavenging by cloud and precipitation;
- gravitational removal by sedimentation assisted by coagulation;
- dry removal by wind-driven impaction near the earth's surface.