Characterization and Source Apportionment of Particulate Matter ≤ 2.5 μm in Sumatra, Indonesia, during a Recent Peat Fire Episode

SIAO WEI SEE,[†]
RAJASEKHAR BALASUBRAMANIAN,*,[‡]
ELISABETH RIANAWATI,[‡]
SATHRUGNAN KARTHIKEYAN,[‡] AND
DAVID G. STREETS[§]

Department of Chemical and Biomolecular Engineering, Block E5, #02-11, 4 Engineering Drive 4, and Division of Environmental Science and Engineering, Block EA, #07-23, 9 Engineering Drive 1, Faculty of Engineering, National University of Singapore, Singapore 117576, and Argonne National Laboratory, DIS/900, 9700 South Cass Avenue, Argonne, Illinois 60439

An intensive field study was conducted in Sumatra, Indonesia, during a peat fire episode to investigate the physical and chemical characteristics of particulate emissions in peat smoke and to provide necessary data for source-receptor analyses. Ambient air sampling was carried out at three different sites located at varying distances from the peat fires to determine changes in mass and number concentrations of $PM_{2.5}$ and its chemical composition (carbonaceous and nitrogenous materials, polycyclic aromatic hydrocarbons, water-soluble inorganic and organic ions, and total and water-soluble metals). The three sites represent a rural site directly affected by the local peat combustion, a semirural site, and an urban site situated downwind of the peat fires. The mass concentration of $PM_{2.5}$ and the number concentration of airborne particles were as high as 1600 μg/m³ and 1.7×10^5 cm⁻³, respectively, in the vicinity of peat fires. The major components of $PM_{2.5}$ in peat smoke haze were carbonaceous particles, particularly organic carbon, NO_3^-, and SO_4^{2-}, while the less abundant constituents included ions such as NH_4^+, NO_2^-, Na^+, K^+, organic acids, and metals such as Al, Fe, and Ti. Source apportionment by chemical mass balance receptor modeling indicates that peat smoke can travel long distances and significantly affect the air quality at locations downwind.

Introduction

Biomass burning is a significant source of particulate matter (PM) (*1*). In Southeast Asia (SEA), forest, bush, and peat fires originating from Kalimantan and Sumatra in Indonesia are a major cause of transboundary haze pollution. For instance, the 1997–98 Indonesian wildfires were particularly severe,

and affected many countries in SEA (*2–4*). With the largest area of tropical peat lands in the world at 27 million hectares (*5*), tropical peat fires are a main source of smoke production in Indonesia during fire disasters (*2*). Peat fires are a problem as exposed dried peat is easily ignited but almost impossible to extinguish. They can smolder deep underground indefinitely, and flare up again during the next dry period, with devastating impacts on the environment and, most importantly, on human health (*6, 7*).

The main component of peat smoke that adversely affects human health is $PM_{2.5}$ (particulate matter ≤ 2.5 μm) (*8*). It is now widely acknowledged that $PM_{2.5}$ is closely associated with morbidity and mortality, due to its efficient deposition in the body and its large surface area, which adsorbs more toxic chemicals per unit mass (*9*). However, studies on $PM_{2.5}$ in peat smoke are notably limited (*10–12*). In addition, earlier reports on PM collected during haze episodes in SEA were limited to selected chemical constituents in total suspended particles (TSP) or to PM_{10} (≤10 μm), which are of less relevance from a health standpoint (*3, 4, 7*).

This study is the first of its kind aimed at characterizing the physical and chemical properties of $PM_{2.5}$ emissions from a peat fire episode in Sumatra. The key objectives were to measure the mass and number concentration of airborne particles and their chemical contents and to estimate the contribution of peat smoke to aerosol composition at downwind locations by receptor modeling. Specific chemical components of interest are carbonaceous and nitrogenous materials, polycyclic aromatic hydrocarbons (PAHs), inorganic and organic ions, and metals, some of which are of concern because of their adverse health effects, especially to individuals being inadvertently exposed, for example, plantation workers and wildland firefighters.

Experimental Procedures

Description of Sampling Sites. Figure 1 shows the location of the three sampling sites in the Riau province of Sumatra, Indonesia, and the prevailing wind direction during the sampling period. The first location is Sungai Sembilan in Dumai, a rural site where peat fires occurred. Air sampling was conducted in the open field within a 100-m circumference from the boundary of the peat fires. The second location is in the nearby village of Belakang Rumah in Dumai (60 km southwest of Sungai Sembilan) and represents a semirural site. The third location (Pekanbaru, 220 km southwest of Sungai Sembilan) is the nearest provincial capital in Riau. The air quality of this urban site is influenced by both local emissions from industries and vehicular traffic and emissions from peat fires during the sampling period, as can be seen from the prevailing wind direction.

Sample Collection: *Mass Concentration.* Particulate sampling was made under ambient conditions at the three locations over 1 week, from 16 to 22 March 2005, during a short peat fire episode in Sungai Sembilan. Two calibrated MiniVol portable air samplers (Airmetrics) were used simultaneously at each sampling site to collect $PM_{2.5}$ on 47-mm filters by drawing air at a flow rate of 0.005 m³ min⁻¹. One of the MiniVol samplers was equipped with a QMA quartz filter (Whatman International Ltd.) and the other was equipped with a Teflon filter of 2.0 μm pore size (Pall Corporation). To obtain sufficient mass for chemical analyses, sampling was conducted for 6 h at Sungai Sembilan and Belakang Rumah and for 24 h at Pekanbaru. Altogether, three Teflon and three quartz filter samples were collected at Pekanbaru, three Teflon and three quartz filters at Belakang

* Corresponding author phone: (65) 6516 5135; fax: (65) 6779 1936; e-mail: eserbala@nus.edu.sg.

† Department of Chemical and Biomolecular Engineering, Faculty of Engineering, National University of Singapore.

‡ Division of Environmental Science and Engineering, Faculty of Engineering, National University of Singapore.
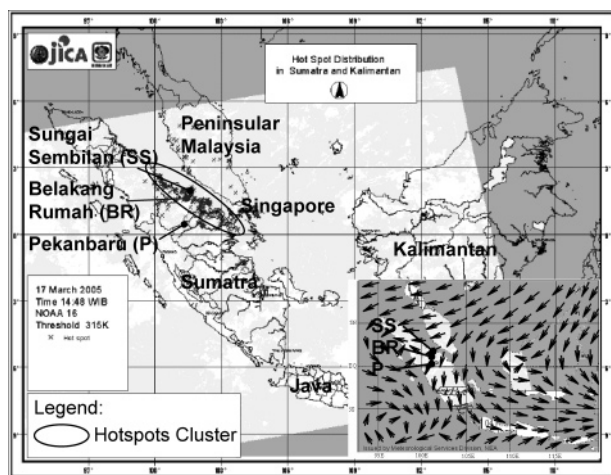
§ Argonne National Laboratory.

FIGURE 1. Location of hot spots and sampling sites on the island of Sumatra, Indonesia. The prevailing wind direction is shown as an inset for one of the sampling days (March 17, 2005).

Rumah, and four Teflon and three quartz filters at Sungai Sembilan.

Number Concentration. Snapshot measurements of the particle number concentration were also made during the filter sampling period with the calibrated condensation particle counter (CPC) (Model 3007, TSI Inc.), which detects particles in the range from 10 nm to >1 μm at a flow rate of 100 cm^3 min^{-1}. As particles with >2.5 μm diameter make negligible contributions to the number concentration, the particle concentration obtained here can be taken to be that of PM$_{2.5}$. Zero check was performed daily with the supplied high-efficiency particulate air (HEPA) zero filter before and after measurements.

Extraction and Chemical Analysis: *Measurement of Carbonaceous and Nitrogenous Materials.* Quartz filters were cut into four equal parts. One quarter was used to determine total carbon (TC) and total nitrogen (TN), and another quarter, to determine elemental carbon (EC) analysis. Since the total carbon (TC) is made up of elemental carbon (EC) and organic carbon (OC), the filter used for the EC analysis was first combusted in a furnace (Carbolite) at 350 °C for 24 h to remove OC. Carbonaceous and nitrogenous contents were then determined by use of the 2400 series II CHNS/O analyzer (Perkin-Elmer Life and Analytical Sciences Inc.), which was operated in CHN mode with acetanilide (71.09% C, 6.71% H, 10.36% N) as a calibration standard.

Polycyclic Aromatic Hydrocarbons. The remaining two parts of the quartz filters were extracted and analyzed for PAHs. Sixteen priority PAHs were analyzed, namely, naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1,2,3-cd*]pyrene (Ind), dibenz[*a,h*]anthracene (DBA), and benzo[*g,h,i*]perylene (BPe).

The filters were treated with 20 mL of 1:1 (v/v) reagent-grade acetone/hexane in the microwave digestion system (MDS) (MLS1200 MEGA model, Milestone srl) for 20 min at 150 W (*13*). The extracts were then concentrated to dryness under a gentle stream of pure nitrogen gas and redissolved in 1 mL of extraction solvent for PAHs analysis by use of a gas chromatograph–mass spectrometer (GC-MS, HP6890, Agilent Technologies) fitted with a DB-5MS 5%-phenyl-methylpolysiloxane 30 m × 0.2 mm internal diameter × 0.25 μm film thickness capillary column (J&W Scientific).

Water-Soluble Ions. Teflon filters were similarly cut into four equal parts. One of the four parts was extracted for water-

soluble ions and metals. Ten milliliters of 18.2 MΩ ultrapure water was added to the filter samples, which were then ultrasonicated at 60 °C for 1 h. The extract was subsequently filtered through a 0.45-μm poly(tetrafluoroethylene) (PTFE) membrane filter (Whatman plc). A 5 mL aliquot of the extract was set aside for water-soluble metals analysis (see below). The remaining extract was used for analysis of inorganic anions [fluoride (F$^-$), chloride (Cl$^-$), nitrite (NO$_2^-$), nitrate (NO$_3^-$), sulfate (SO$_4^{2-}$), and phosphate (PO$_4^{3-}$)], organic anions [acetate, formate, methanesulfonate, pyruvate, succinate, malonate, and oxalate], and cations [lithium (Li$^+$), sodium (Na$^+$), ammonium (NH$_4^+$), potassium (K$^+$), calcium (Ca^{2+}), and magnesium (Mg^{2+})] by use of the ICS-2000 integrated reagent-free ion chromatography (IC) system (Dionex Corporation) (*14*).

Water-Soluble Metals. An aliquot (5 mL) of the water-soluble extract was acidified with 2% nitric acid and analyzed for 13 water-soluble metals, namely, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V, and Zn, on an ELAN 6100 inductively coupled plasma mass spectrometer (ICPMS) (Perkin-Elmer Inc.) in triplicate.

Total Metals. Another part of the Teflon filter was extracted and analyzed for total metals. The extraction solvents, made up of reagent-grade mixtures, 4 mL of nitric acid, 2 mL of hydrogen peroxide, and 0.2 mL of hydrofluoric acid, were added to the filter samples and processed in MDS for 5 min at 250 W, 5 min at 400 W, and 2 min at 600 W (*15*). Again, the extracts were analyzed by use of the ICPMS.

Source Apportionment. The chemical mass balance air quality receptor, model EPA-CMB8.2 (*16*), was used to estimate the relative contributions of peat smoke and other sources to ambient PM$_{2.5}$ concentrations measured at downwind locations. This CMB model has been successfully used by a number of researchers to quantify the relative contribution of various particulate sources in both urban and rural areas (*17, 18*). The framework proposed by Watson et al. (*19*) was closely followed in this work. The source profiles of inorganic ions and trace elements used in the model were obtained from SPECIATE 3.2 (*20*). Since there is currently no information available for tropical peat fires, the profile obtained at Sungai Sembilan is assumed to represent the source profile of peat fires and was used in the modeling work to estimate the contribution of peat fires to the ambient air quality at Belakang Rumah and Pekanbaru.

Results and Discussion

Mass Concentrations. The mass concentrations of PM$_{2.5}$ at the three sampling sites were found to vary in accordance with their respective distances from the peat fires. Sungai Sembilan (the site most affected by local peat combustion) showed the highest average PM$_{2.5}$ concentration at 1600 μg m^{-3}, followed by Belakang Rumah (moderately affected semirural site) at 600 μg m^{-3}, and finally Pekanbaru (the urban site influenced by the advection of peat fire emissions) at 140 μg m^{-3}. As there were no major sources of air pollution at the first two sites, their high concentration were possibly due to peat fire emissions. Pekanbaru was also partially affected, probably as a result of the transport of peat fire emissions by the prevailing wind.

Number Concentrations. The average number concentrations of particles were 1.7×10^5 cm^{-3} at Sungai Sembilan, 4.3×10^4 cm^{-3} at Belakang Rumah, and 2.1×10^4 cm^{-3} at Pekanbaru. The number concentration measured at Sungai Sembilan was higher than that at Belakang Rumah by a factor of 4, although the mass concentration was higher only by a factor of 2.5. This observation is consistent with the fact that particles released from combustion processes, that is, peat fires in this case, are predominantly submicrometer particles and thus do not make a substantial contribution to the particle mass at Sungai Sembilan. On the other hand, the particles

TABLE 1. Mass Concentrations of PM$_{2.5}$ and Its Chemical Components

	Sungai Sembilan	Belakang Rumah	Pekanbaru
PM$_{2.5}$, μg m^{-3}			
PM$_{2.5}$	1600 $\pm$ 400	640 $\pm$ 420	140 $\pm$ 40
Carbonaceous and Nitrogenous Particles, μg m^{-3}			
EC	310 $\pm$ 200	110 $\pm$ 40	21 $\pm$ 12
OC	750 $\pm$ 500	230 $\pm$ 170	30 $\pm$ 20
TN	40 $\pm$ 13	14 $\pm$ 20	6.4 $\pm$ 3.1
Polycyclic Aromatic Hydrocarbons (PAHs), ng m^{-3}			
Nap	6.4 $\pm$ 3.4	4.4 $\pm$ 3.2	2.7 $\pm$ 0.5
Ace	10 $\pm$ 12	4.9 $\pm$ 2.8	2.9 $\pm$ 0.9
Acy	20 $\pm$ 28	8.4 $\pm$ 5.9	4.7 $\pm$ 1.6
Flu	31 $\pm$ 36	12 $\pm$ 7	11 $\pm$ 7
Phe	131 $\pm$ 119	55 $\pm$ 31	7.0 $\pm$ 3.1
Ant	25 $\pm$ 23	11 $\pm$ 6	27 $\pm$ 18
Flt	39 $\pm$ 18	10 $\pm$ 8	3.9 $\pm$ 1.9
Pyr	64 $\pm$ 30	19 $\pm$ 13	4.0 $\pm$ 2.4
BaA	59 $\pm$ 27	19 $\pm$ 12	16 $\pm$ 10
Chr	22 $\pm$ 17	4.2 $\pm$ 1.4	1.8 $\pm$ 0.1
BbF	46 $\pm$ 22	16 $\pm$ 6	2.4 $\pm$ 1.3
BkF	9.1 $\pm$ 4.8	20 $\pm$ 25	9.6 $\pm$ 0.9
BaP	25 $\pm$ 12	4.2 $\pm$ 1.6	0.8 $\pm$ 0.1
Ind	33 $\pm$ 23	29 $\pm$ 34	18 $\pm$ 1
DBA	21 $\pm$ 17	6.7 $\pm$ 0.8	15 $\pm$ 10
BPe	20 $\pm$ 10	9.4 $\pm$ 5.9	8.4 $\pm$ 0.1
Water-Soluble Ions, μg m^{-3}			
F$^-$	1.2 $\pm$ 0.6	0.62 $\pm$ 0.21	1.0 $\pm$ 1.1
Cl$^-$	11 $\pm$ 7	6.8 $\pm$ 0.1	1.0 $\pm$ 0.3
NO$_2^-$	12 $\pm$ 4	7.9 $\pm$ 0.2	5.6 $\pm$ 2.6
NO$_3^-$	31 $\pm$ 37	29 $\pm$ 6	2.6 $\pm$ 0.2
SO$_4^{2-}$	30 $\pm$ 9	21 $\pm$ 1	15 $\pm$ 1
Na$^+$	45 $\pm$ 15	32 $\pm$ 11	18 $\pm$ 9
NH$_4^+$	13 $\pm$ 6	4.3 $\pm$ 3.0	1.1 $\pm$ 1.5
K$^+$	12 $\pm$ 5	1.6 $\pm$ 2.8	1.9 $\pm$ 1.9
Ca^{2+}	9.4 $\pm$ 6.0	6.7 $\pm$ 1.8	2.1 $\pm$ 2.1
Mg^{2+}	0.66 $\pm$ 0.49	0.37 $\pm$ 0.43	0.10 $\pm$ 0.12
acetate	9.5 $\pm$ 3.8	5.4 $\pm$ 1.1	1.6 $\pm$ 1.4
formate	6.7 $\pm$ 1.4	4.2 $\pm$ 0.5	1.8 $\pm$ 1.3
methanesulfonate	1.7 $\pm$ 0.8	1.9 $\pm$ 1.7	0.43 $\pm$ 0.10
pyruvate	below detection limit	0.14 $\pm$ 0.12	0.15 $\pm$ 0.15
succinate	1.5 $\pm$ 1.1	1.0 $\pm$ 0.2	0.54 $\pm$ 0.56
malonate	0.32 $\pm$ 0.12	0.32 $\pm$ 0.13	0.22 $\pm$ 0.09
oxalate	2.9 $\pm$ 1.7	2.0 $\pm$ 0.2	1.3 $\pm$ 0.5
Total Metals (Water-Soluble Metals), ng m^{-3}			
Al	26 200 $\pm$ 16 400 (90 $\pm$ 19)	8690 $\pm$ 2550 (28 $\pm$ 2)	3780 $\pm$ 1710 (70 $\pm$ 86)
As	135 $\pm$ 16 (6.3 $\pm$ 1.4)	93.3 $\pm$ 23.8 (7.1 $\pm$ 3.1)	46.9 $\pm$ 21.4 (1.7 $\pm$ 0.3)
Cd	16.1 $\pm$ 3.9 (0.90 $\pm$ 0.35)	10.8 $\pm$ 4.0 (0.30 $\pm$ 0.08)	4.95 $\pm$ 1.49 (0.30 $\pm$ 0.21)
Co	18.1 $\pm$ 4.1 (0.25 $\pm$ 0.13)	11.7 $\pm$ 4.2 (0.10 $\pm$ 0.01)	4.71 $\pm$ 2.02 (0.11 $\pm$ 0.08)
Cr	949 $\pm$ 343 (540 $\pm$ 140)	827 $\pm$ 336 (500 $\pm$ 200)	483 $\pm$ 204 (330 $\pm$ 170)
Cu	111 $\pm$ 26 (35 $\pm$ 9)	100 $\pm$ 37 (30 $\pm$ 6)	54.3 $\pm$ 9.0 (3.8 $\pm$ 0.3)
Fe	7930 $\pm$ 2970 (120 $\pm$ 40)	4810 $\pm$ 1510 (85 $\pm$ 33)	2610 $\pm$ 1280 (41 $\pm$ 17)
Mn	146 $\pm$ 79 (13 $\pm$ 6)	56.8 $\pm$ 17.1 (5.7 $\pm$ 3.6)	29.0 $\pm$ 11.6 (1.2 $\pm$ 0.5)
Ni	277 $\pm$ 40 (12 $\pm$ 14)	221 $\pm$ 73 (2.2 $\pm$ 1.5)	102 $\pm$ 51 (0.91 $\pm$ 0.03)
Pb	181 $\pm$ 43 (4.5 $\pm$ 1.1)	122 $\pm$ 49 (2.3 $\pm$ 0.5)	105 $\pm$ 6 (3.8 $\pm$ 1.8)
Ti	11 500 $\pm$ 3600 (58 $\pm$ 17)	8040 $\pm$ 2760 (440 $\pm$ 23)	4630 $\pm$ 1990 (25 $\pm$ 11)
V	360 $\pm$ 105 (1.9 $\pm$ 0.5)	295 $\pm$ 113 (2.9 $\pm$ 0.9)	173 $\pm$ 80 (1.8 $\pm$ 0.2)
Zn	6280 $\pm$ 2790 (2660 $\pm$ 870)	3830 $\pm$ 1000 (1010 $\pm$ 530)	2500 $\pm$ 840 (470 $\pm$ 140)

received at Belakang Rumah were probably aged as a result of their growth during transport by a combination of coagulation and surface reaction (21), which might explain the difference in trends of mass and number concentrations between the two sampling sites.

A similar growth in the size of particles of peat fire origin could have occurred during their long-range transport to Pekanbaru. However, due to the presence of various local combustion sources such as industries and vehicles, additional smaller particles could be found at the urban site compared to those at Belakang Rumah. The difference in the origin of particles may explain why the number concentration at Belakang Rumah was higher by only a factor of 2.1 compared to Pekanbaru, while the increase in mass con-

centration was by a factor of 4.5. In any case, the elevated mass and number concentrations of airborne particles observed at Sungai Sembilan, combined with their small sizes, are of health concern since such particles tend to have high surface areas and thus promote active surface chemistry. The chemical characteristics of these particles are discussed below.

Chemical Speciation: *Mass Balance.* Table 1 presents the average concentrations of EC, OC, TN, PAHs, ions, and metals, and their corresponding standard deviations, as observed at the three sampling sites. The levels of the speciated chemical components of PM$_{2.5}$ were highest at Sungai Sembilan and lowest at Pekanbaru. This trend is consistent with that seen for the mass concentration of PM$_{2.5}$. PO$_4^{3-}$ and Li$^+$ are not
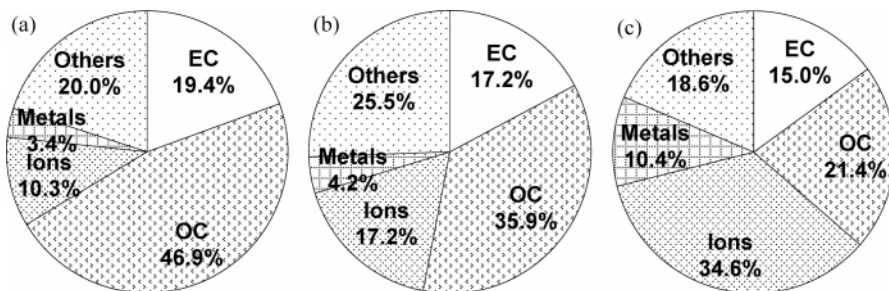
FIGURE 2. Overall mass balance of PM$_{2.5}$ sampled at (a) Sungai Sembilan, (b) Belakang Rumah, and (c) Pekanbaru.

reported here as they were not in detectable concentrations. The relative contributions of various chemical species to the total mass concentration of PM$_{2.5}$ are illustrated in Figure 2. In this figure, "others" refers to the fraction of PM$_{2.5}$ not identified by any of the chemical analyses used in this study, where

others =
  PM$_{2.5}$ − (EC + OC + inorganic ions + total metals) (1)

Overall, the total mass of the various components of PM$_{2.5}$ as measured by chemical analyses agreed reasonably well with the gravimetric mass. The deficiency in the mass as determined through chemical measurements (ranging from 18.6% to 25.5%) can be attributed to the various functional groups in organic aerosols (i.e., the conversion of OC to organic matter), water content, and measurement errors. The chemical composition of PM$_{2.5}$ collected at Sungai Sembilan and Belakang Rumah is quite similar and is possibly a result of the dominant influence of peat fires on the particulate air pollution at the two rural sites, in the absence of strong interference from other pollution sources. On the other hand, the air quality in Pekanbaru is also influenced by local industries and vehicular traffic, and thus the chemical makeup of PM is different from that in the other two sites. The major components of PM$_{2.5}$ and their possible sources are discussed below in detail.

Carbonaceous Particles. The overall mass balance indicates that the major component of PM$_{2.5}$ is carbonaceous particles. EC and OC together accounted for 66.3%, 53.1%, and 36.4% of PM$_{2.5}$ at Sungai Sembilan, Belakang Rumah, and Pekanbaru, respectively. The high percentage of carbonaceous particulates, especially OC, at those locations closer to the peat fires was consistent with the fact that peat lands are carbon sinks and rich in organic matter. During peat fires, carbon is released to the air (*6*) and more than half of the carbon is in organic form. As compared to Sungai Sembilan and Belakang Rumah, which showed a much higher proportion of OC relative to EC, the percentage of OC is not significantly higher than that of EC at Pekanbaru. This suggests that there existed more dominant sources of EC at Pekanbaru in contrast to the two other sites. One such source could be motor vehicles, which are more prevalent in the urban city of Pekanbaru than in the rural areas of Sungai Sembilan and Belakang Rumah.

Polycyclic Aromatic Hydrocarbons. The average mass concentrations of the 16 PAHs were 562 ng m^{-3} (0.04% of PM$_{2.5}$, 0.07% of OC), 233 ng m^{-3} (0.04%, 0.10%) and 135 ng m^{-3} (0.10%, 0.45%) at Sungai Sembilan, Belakang Rumah, and Pekanbaru, respectively. The diagnostic ratios of PAHs are often used to evaluate the impact of various sources to a specific region. It has been suggested that Ind/Ind + BPe ratios lower than 0.20 imply direct emissions from petrogenic sources, ratios between 0.20 and 0.50 imply liquid fossil fuel (vehicle and industrial sources) combustion, and ratios larger than 0.50 imply grass, wood, and coal combustion (*22*). The average Ind/Ind + BPe ratios at the above-mentioned sites

were 0.62, 0.76, and 0.68, respectively, demonstrating that combustion processes, rather than unburned fossil fuels, were the origin of PAHs measured at the sampling sites.

Ions. SO$_4^{2-}$, NO$_3^-$, and NO$_2^-$ are the most abundant of all inorganic anions. These ions probably came from sulfurous and nitrogenous materials stored in peat that were converted to SO$_4^{2-}$ and to NO$_3^-$ and NO$_2^-$, respectively, through gas-to-particle conversion processes upon combustion. Alternatively, both NO$_3^-$ and NO$_2^-$ could also be formed during (flaming) combustion. The inorganic nitrogen, that is, NH$_4^+$, NO$_2^-$, and NO$_3^-$, together accounted for a substantial fraction (52%) of TN (as determined by the CHN analysis), which means that the remainder of the total nitrogen could exist in the form of organic nitrogen compounds such as aliphatic and aromatic amines, amino acids, alkyl amides, and nitriles (*23*). The speciation study of organic nitrogenous compounds is currently underway in our laboratory, and the results will be communicated elsewhere. In addition, Cl$^-$ was found to constitute a bigger fraction of anions at Sungai Sembilan and Belakang Rumah than at Pekanbaru. Apart from the peat combustion source, the chloride could also come from the sea spray due to the proximity of Sungai Sembilan and Belakang Rumah to the sea, whereas Pekanbaru is situated further inland.

In the case of organic anions, monocarboxylic acids [acetate (A) and formate (F)] were much more abundant than dicarboxylic acids [succinate (C4), malonate (C3), and oxalate (C2)]; oxalate was the most dominant dicarboxylic acid. The mass concentration of organic acids found in this study is much higher than that found at other urban areas (*24−26*), suggesting that the peat smoke is a dominant source of organic acids present at these sites. These organic ions could have been directly emitted from the peat fires and/or formed in the atmosphere as a result of chemical conversions in the peat smoke. Previous studies in SEA and elsewhere had also reported a substantial increase in water-soluble organics in smoke aerosols including organic acids (*27, 28*).

The concentration ratio of the organic anions, in particular F/A ratio and C3/C4 ratio, could be used to identify possible sources of PM$_{2.5}$. A low ratio of less than unity is indicative of direct emissions, whereas a high ratio (>1) suggests that these organic acids could be formed in the atmosphere by photochemical reactions (*26*). The F/A ratio was found to be 0.71 at Sungai Sembilan, 0.78 at Belakang Rumah, and 1.13 at Pekanbaru, implying that the first two sites were very strongly influenced by direct emissions from peat fires that took place in the vicinity of the sites, whereas the last site appeared to be affected by both primary and secondary particulate sources. The similar ratios of F/A at Sungai Sembilan and Belakang Rumah suggests that an F/A ratio of 0.7−0.8 could be indicative of peat fires. In the case of dicarboxylic acids, the C3/C4 ratio was the lowest at Sungai Sembilan (0.21), followed by Belakang Rumah (0.32), and Pekanbaru (0.41), which again indicate that the three sites were influenced by the peat smoke.

Metals. The mass concentrations of the 13 metals also followed a trend similar to that of PAHs. High concentrations
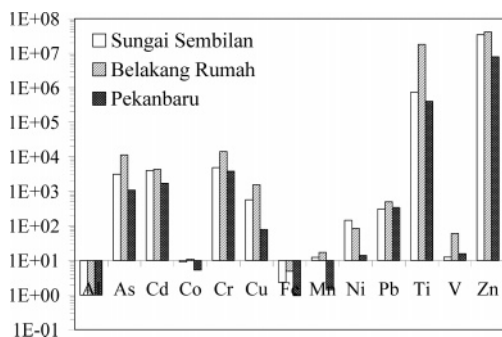
FIGURE 3. Enrichment factor analysis of trace metals with the use of Al as an indicator of crustal source.

were observed nearer the peat fires, but their proportions in $PM_{2.5}$ were lower. The 13 metals together accounted for 54.1 $\mu g\, m^{-3}$ (3.4% of $PM_{2.5}$) at Sungai Sembilan, 27.1 $\mu g\, m^{-3}$ (4.2%) at Belakang Rumah, and 14.5 $\mu g\, m^{-3}$ (10.4%) at Pekanbaru. Al, Fe, and Ti were the most abundant trace metals at all the sampling sites, making up more than 75% of the total metals. Since the same three metals are also the top three most abundant metals in the Earth's crust (29), it is postulated that these metals were released into the air from the local soil upon high-temperature combustion of the peat. Furthermore, due to biogeochemical processes, peat soils tend to accumulate all kinds of metals supplied by atmospheric deposition (30), which can be subsequently discharged into the ambient air, made airborne, and transported by the prevailing winds upon high-temperature combustion of peat soil. Therefore, it is not surprising to see an unusually high concentration of metals at the affected sites.

To gain further insights into possible sources of trace metals, enrichment factors (EFs) were calculated according to the following formula:

$$\text{EF} = \frac{(\text{X/Al})_{\text{air}}}{(\text{X/Al})_{\text{crust}}} \qquad (2)$$

where $(\text{X/Al})_{\text{air}}$ and $(\text{X/Al})_{\text{crust}}$ refer to ratios of the concentration of metal X to that of reference metal, Al, in the air and crust, respectively. EF ≈ 1 suggests low-temperature crustal weathering and soil remobilization, while EF > 1 suggests high-temperature man-made processes. However, as the types of crustal materials are unique in different areas and not much is known about uncertainties concerning fractionation during weathering, EFs are not resolvable within an order of magnitude (EF < 10) for crustal materials (31). This means that EF < 10 implies that the metal is most likely derived from crustal sources, whereas EF > 10 implies that the metal primarily originates from anthropogenic sources.

EFs, based on the average values of total metals, are shown in Figure 3 for all sampling sites. The x-axis is intentionally

set to cross at 10, so those metals with EFs < 10 are crustal materials and those with EFs > 10 are anthropogenic or combustion-derived materials. Since the trace-metal composition of local peat soils in Indonesia is not available, the continental crustal averages (32) were used in this study. Most metals exhibited EF > 10, suggesting that the combustion of peat contributed significantly to the metal loadings in the airborne particulate matter.

Unlike the total metals, the relative proportions of water-soluble metals in total metals were in fact quite similar among the three sites, ranging from 6.5% (Sungai Sembilan and Pekanbaru) to 7.8% (Belakang Rumah). Although these proportions are quite comparable at the three sites, the high concentrations of water-soluble metals at Sungai Sembilan, Belakang Rumah, and to a lesser extent at Pekanbaru, are of concern. This is because it has been reported that the bioavailable, or water-soluble, metals play an important role in inducing adverse health effects through the formation of reactive oxygen species such as hydroxyl radicals and thus inducing oxidative stress and causing tissue injury (33).

In comparison to other studies conducted in urban areas (34–36), the solubility of trace metals at these three sampling sites tends to be lower, with the exception of Cr. In fact, Cr was reported to be one of the least soluble in the previous studies but appeared to be the most soluble here as evident from the large fraction of water-soluble Cr in total Cr. This could be due to the attachment of organic matter to Cr. The presence of organics ligands can lead to the formation of soluble Cr(III) complexes (37). The lower solubility of other metals could be due to the chemical forms in which they are found. For example, most metal oxides, which are often produced during high-temperature combustion, tend to be more insoluble as compared to metal nitrates.

Source Apportionment. Source apportionment was attempted to gain further insights into the effect of the peat smoke on the ambient air quality at Belakang Rumah (Figure 4a) and Pekanbaru (Figure 4b). The contribution of peat fires to $PM_{2.5}$ at Sungai Sembilan is assumed to be 100% and thus is not presented. The CMB performance indices are all within the target ranges recommended by the U.S. EPA: $r^2 > 0.8$, $\chi^2 < 4$, and % mass = 80–120% (normalized to 100% in the figures). The major sources of $PM_{2.5}$ at the two sites include peat fires, motor vehicles, refineries, crustal matter, and secondary aerosols. As deduced from the results of chemical speciation, $PM_{2.5}$ source contribution estimates demonstrated that the influence of the peak smoke tended to decrease in significance as the distance from the fires increased, falling to 51.0% at Belakang Rumah and just 18.1% at Pekanbaru.

In summary, the peat fire episode investigated in this study led to an elevation in both the mass and number concentration of fine particulate matter as well as that of the toxic components in them (e.g., PAHs and bioavailable metals) at downwind locations, as evident from the observational data and the source-apportionment calculations.
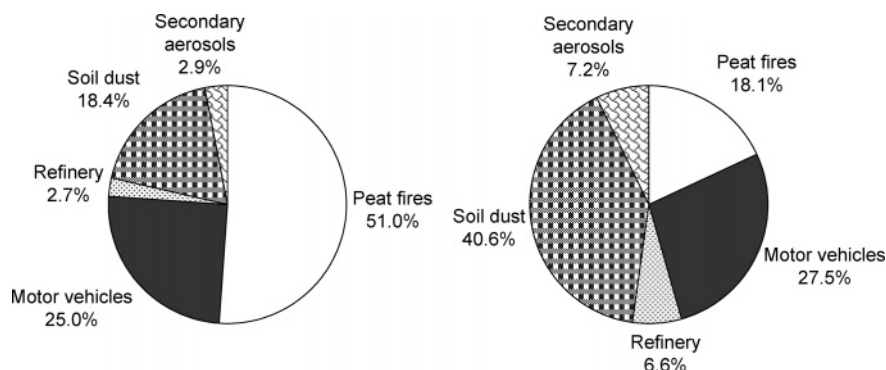

FIGURE 4. Source contributions to $PM_{2.5}$ at (a) Belakang Rumah and (b) Pekanbaru.

On the basis of the concurrent measurements of the particle mass and number concentration, it can be deduced that airborne particles at Sungai Sembilan and Pekabaru were smaller in size due to their fresh emissions from combustion sources, while those measured at Belakang Rumah were larger as a result of aging and possibly hygroscopic growth of freshly emitted particles. In terms of aerosol mass balance, the gravimetric mass of $PM_{2.5}$ collected at the three sites agreed reasonably well with that constructed from the measured individual chemical components such as ions, metals, EC, and OC. However, chemical makeup of $PM_{2.5}$ collected at the urban site, Pekanbaru, was different from that obtained at Sungai Sembilan and Belakang Rumah due to the influence of urban pollution sources such as industrial and traffic emissions apart from the peak smoke. In conclusion, the results obtained from this preliminary work call for more comprehensive speciation studies of aerosols of both pyrogenic and anthropogenic origins at a larger network of sites within SEA, given that the recurring forest and land fires in this region have health and climatic implications on regional and global scales, respectively.

Acknowledgments

Literature Cited

(1) Crutzen, P. J.; Andreae, M. O. Biomass burning in the tropics—impact on atmospheric chemistry and biogeochemical cycles. *Science* **1990**, *250*, 1669−1678.

(2) Langmann, B.; Heil, A. Release and dispersion of vegetation and peat fire emissions in the atmosphere over Indonesia 1997/1998. *Atmos. Chem. Phys.* **2004**, *4*, 2145−2160.

(3) Siegert, F.; Ruecker, G.; Hinrichs, A.; Hoffmann, A. A. Increased damage from fires in logged forests during droughts caused by El Nino. *Nature* **2001**, *414*, 437−440.

(4) Levine, J. S. The 1997 fires in Kalimantan and Sumatra, Indonesia, Gaseous and particulate emissions. *Geophys. Res. Lett.* **1999**, *26*, 815−818.

(5) Wulandari, F. Reckless farming in peatland forests major cause of fires. *The Jakarta Post*, Aug 25, 2002; http://www.thejakartapost.com/detailweekly.asp?fileid=20020825.@02 (accessed Nov 2005).

(6) Page, S. E.; Siegert, F.; Rieley, J. O.; Boehm, H. D. V.; Jaya, A.; Limin, S. The amount of carbon released from peat and forest fires in Indonesia during 1997. *Nature* **2002**, *420*, 61−65.

(7) Kunii, O.; Kanagawa, S.; Yajima, I.; Hisamatsu, Y.; Yamamura, S.; Amagai, T.; Ismail, I. T. S. The 1997 haze disaster in Indonesia, Its air quality and health effects. *Arch. Environ. Health* **2002**, *57*, 16−22.

(8) Dawud, Y. Smoke episodes and assessment of health impacts related to haze from forest fires: Indonesian experience. Health Guidelines for Vegetation Fire Events, Lima, Peru, Oct 6−9, 1998; WHO, 1999. http://www.who.int/docstore/peh/Vegetation_fires/Backgroundpapers/BackgrPap12.pdf (accessed Nov 2005).

(9) Brunekreef, B.; Holgate, S. T. Air pollution and health. *Lancet* **2002**, *360*, 1233−1242.

(10) Chand, D.; Schmid, O.; Gwaze, P.; Parmar, R. S.; Helas, G.; Zeromskiene, K.; Wiedensohler, A.; Massling, A.; Andreae, M. O. Laboratory measurements of smoke optical properties from the burning of Indonesian peat and other types of biomass. *Geophys. Res. Lett.* **2005**, *32*, Art. No. L12819.

(11) Christian, T. J.; Kleiss, B.; Yokelson, R. J.; Holzinger, R.; Crutzen, P. J.; Hao, W. M.; Saharjo, B. H.; Ward, D. E. Comprehensive laboratory measurements of biomass-burning emissions, 1. Emissions from Indonesian, African, and other fuels. *J. Geophys. Res.* **2003**, *108*, Art. No. 4719.

(12) Muraleedharan, T. R.; Radojevic, M.; Waugh, A. Caruana, A. Emissions from the combustion of peat, an experimental study. *Atmos. Environ.* **2000**, *34* (18), 3033−3035.

(13) Karthikeyan, S.; Balasubramanian, R.; See, S. W. Optimization and validation of a low temperature microwave-assisted extrac-

(14) Karthikeyan, S.; See, S. W.; Balasubramanian, R. Simultaneous determination of inorganic anions and selected organic acids in airborne particulate matter by ion chromatography. *Anal. Lett.* **2007**, doi 10.1080/00032710601017920.

(15) Karthikeyan, S.; Joshi, U. M.; Balasubramanian, R. Microwave assisted sample preparation for determining water-soluble fraction of trace elements in urban airborne particulate matter: Evaluation of bioavailability. *Anal. Chim. Acta* **2006**, *576*, 23−30.

(16) U.S. EPA. *EPA-CMB8.2 Users Manual*. EPA-452/R-04-011. Office of Air Quality Planning & Standards, Research Triangle Park, NC, 2004.

(17) Chow, J. C.; Watson, J. G.; Lowenthal, D. H.; Countess, R. J. Sources and chemistry of PM(10) aerosol in Santa Barbara County, CA. *Atmos. Environ.* **1996**, *30*, 1489−1499.

(18) Chan, Y. C.; Simpson, R. W.; Mctainsh, G. H.; Vowles, P. D.; Cohen, D. D.; Bailey, G. M. Source apportionment of $PM_{2.5}$ and PM_{10} aerosols in Brisbane (Australia) by receptor modelling. *Atmos. Environ.* **1999**, *33*, 3251−3268.

(19) Watson, J. G.; Zhu, T.; Chow, J. C.; Engelbrecht, J.; Fujita, E. M.; Wilson, W. E. Receptor modeling application framework for particle source apportionment. *Chemosphere* **2002**, *49*, 1093−1136.

(20) *SPECIATE: VOC/PM Speciation Database Management System, Version 3.2*; U.S. Environmental Protection Agency: Research Triangle Park, NC, 2002.

(21) Lighty, J. S.; Veranth, J. M. Sarofim, A. F. Combustion aerosols: factors governing their size and composition and implications to human health. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1565−1618.

(22) Yunker, B. M.; Macdonald, R. W.; Brewer, R.; Mitchell, R. H.; Goyette, D.; Sylvester, S. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* **2002**, *33*, 489−499.

(23) Simoneit, B. R. T.; Rushdi, A. I.; Abas, M. R.; Didyk, B. M. Alkyl amides and nitriles as novel tracers for biomass burning. *Environ. Sci. Technol.* **2003**, *37*, 16−21.

(24) Kawamura, K.; Yasui, O. Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere. *Atmos. Environ.* **2005**, *39*, 1945−1960.

(25) Li, Y. C.; Yu, J. Z. Simultaneous determination of mono- and dicarboxylic acids, ω-oxo-carboxylic acids, midchain ketocarboxylic acids, and aldehydes in atmospheric aerosol samples. *Environ. Sci. Technol.* **2005**, *39*, 7616−7624.

(26) Ho, K. F.; Lee, S. C.; Cao, J. J.; Kawamura, K.; Watanabe, T.; Cheng, Y.; Chow, J. C. Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong. *Atmos. Environ.* **2006**, *40*, 3030−3040.

(27) Graham, B.; Mayol-Bracero, O. L.; Guyon, P.; Roberts, G. C.; Decesari, S.; Facchini, M. C.; Artaxo, P.; Maenhaut, W.; Koil, P.; Andreae, M. O. Water-soluble organic compounds in biomass burning aerosols over Amazonia. 1. Characterization by NMR and GC-MS. *J. Geophys. Res.* **2002**, *107*, 8047.

(28) Gao, S.; Hegg, D. A.; Hobbs, P. V.; Kirchstetter, T. W.; Magi, B. I.; Sadilek, M. Water-soluble organic components in aerosols associated with savanna fires in southern Africa: identification, evolution, and distribution. *J. Geophys. Res.* **2003**, *108*, Art. No. 8491.

(29) Geophysics, Astronomy, and Acoustics, Abundance of Elements in the Earth's Crust and in the Sea. In *CRC Handbook of Chemistry and Physics*, Internet Version (http://www.hbcpnetbase. com); Lide, D. R. Ed.; CRC Press: Boca Raton, FL, 2005; pp 14−14.

(30) Gorham, E.; Janssens, J. A. The distribution and accumulation of chemical elements in five peat cores from the mid-continent to the eastern coast of North America. *Wetlands* **2005**, *25*, 259−278.

(31) Kaya, G.; Tuncel, G. Trace element and major ion composition of wet and dry deposition in Ankara, Turkey *Atmos. Environ.* **1997**, *31*, 3985−3998.

(32) Mason, B. The Structure and Composition of the Earth. *Principles of Geochemistry*, 3rd ed.; Wiley & Sons, New York, 1966; pp 45−46.

(33) Costa, D. L.; Dreher, K. L. Bioavailable transition metals in particulate matter mediate cardiopulmonary injury in healthy and compromised animal models. *Environ. Health Perspect.* **1997**, *105*, 1053−1060.

(34) Heal, M. R.; Hibbs, L. R.; Agius, R. M.; Beverland, L. J. Total and water-soluble trace metal content of urban background PM10,

PM2.5 and black smoke in Edinburgh, U.K. *Atmos. Environ.* **2005**, *39*, 1417−1430.

(35) Fujiwara, F.; Dos Santos, M.; Marrero, J.; Polla, G.; Gomez, D.; Dawidowskia, L.; Smichowski, P. Fractionation of eleven elements by chemical bonding from airborne particulate matter collected in an industrial city in Argentina. *J. Environ. Monit.* **2006**, *8*, 913−922.

(36) Qureshi, S.; Dutkiewicz, V. A.; Khan, A. R.; Swami, K.; Yang, K. X.; Husain, L.; Schwab, J. J.; Demerjian, K. L. Elemental composition of $PM_{2.5}$ aerosols in Queens, New York: Solubility and temporal trends. *Atmos. Environ.* **2006**, *40*, S238−251.

(37) Gaberell, M.; Chin, Y. P.; Hug, S. J.; Sulzberger, B. Role of dissolved organic matter composition on the photoreduction of Cr(VI) to Cr(III) in the presence of iron. *Environ. Sci. Technol.* **2003**, *37*, 4403−4409.