

Characterization of organic functional groups, water-soluble ionic species and carbonaceous compounds in PM₁₀ from various emission sources in Songkhla Province, Thailand

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Abstract

PM₁₀ samples were collected at nine sampling stations using a high volume (hi-vol) air sampler during the period of June–November 2007. Using the ATR-FTIR technique, the chemical compositions of organic and water-soluble ionic species (WSIS) PM₁₀ aerosols from each emission source were identified. WSIS such as SO₄²⁻, NO₃⁻, CO₃²⁻, NH₄⁺ were mainly found in PM₁₀ aerosols. The highest concentrations of NO₃⁻, NH₄⁺ and CO₃²⁻ were detected in aerosols collected from sampling sites adjacent to traffic roads. This can be explained by the heterogeneous reaction of SO₂/NO₂ mixtures with carbon soot that lead to the highest contribution of WSIS in combustion particles from vehicle exhausts. In addition, the ratios of organic carbon/elemental carbon (OC/EC) collected at heavy traffic road, bus terminal and traffic demonstrated the lowest values of



1.677 ± 0.198 , 2.329 ± 0.570 and 2.770 ± 1.234 respectively. This indicates that the fine aerosols originating from vehicular emission are fresh particles. The relative contribution of organic functional groups like organic nitrate was highly detected in aerosols collected from industrial sampling sites. This could be ascribed to the intensive use of heavy oil and wood materials during the manufacturing process of animal feed and rubber sheet drying, respectively. More important it should be noted that from biomass burning sampling sites the relatively high intensity of carbonyl bands and aliphatic hydrocarbon IR absorption band illustrated the highest values in those PM_{10} associated with high OC/EC ratios. In this study, the oxidation state of sulfate aerosols were detected by using X-ray absorption near edge spectroscopy (XANES). The results show only S_6^+ peak of S-K edge at 2481 eV observed in all samples.

Keywords: PM_{10} , ATR-FTIR, organic carbon, elemental carbon, water-soluble ionic species, organic functional group, secondary organic carbon, XANES.

1 Introduction

It is well known that aerosols affect the Earth's radiation budget [1, 2]. Recent studies have also elucidated the adverse health impact of fine particulate matter associated with respiratory and cardiovascular diseases, affecting the morbidity and mortality in urban areas [3, 4]. The impact of aerosols on both the climate system and public health greatly depends on the chemical characteristics of organic carbon (OC), elemental carbon (EC), water-soluble ionic species (WSIS) and organic functional groups (OFG) such as polycyclic aromatic hydrocarbons (PAHs). Although there has been considerable confusion and debate over the role of carbonaceous aerosol on climate change over the past decades, its negative influences on visibility degradation and adverse ecological impacts are widely recognized [5, 6]. Since EC occurs mainly from imperfect combustion source of carbon based materials and fuels and is solely primary in nature, it appears reasonable to employ EC as an indicator of primary anthropogenic air pollutants. In contrast, the primary OC can react with trace gases and can also be generated as secondary organic carbon (SOC). Furthermore, more recent studies indicated the significant contribution of organic functional groups as precursors of secondary organic aerosols (SOA) [7].

In spite of its great impacts on both the atmospheric system and human health, published papers related to OC, EC, WSIS and OFG in the fine tropical aerosols are extremely limited. At present, it is difficult to accurately predict patterns of climate change and to precisely conduct a risk assessment without knowing the relative contribution of these chemical compounds in fine aerosols, particularly in the tropical atmosphere. Several studies reported significant contributions of WSIS (e.g. SO_4^{2-} , NO_3^{2-} , NH_4^+), and organic species (e.g. nitro aromatic compounds) in PM_{10} using Fourier Transform Infrared Spectroscopy (FTIR). However, these findings showed only the chemical characteristics of fine particles collected as a mixture of aerosols emitted from various sources [8, 9]. In this study, the determination of OC, EC, WSIS and OFG in PM_{10}



aerosols was conducted in order to provide insights into the origin of air pollution problems at the study area.

2 Methodologies

2.1 Sampling sites and descriptions

Songkhla Province is located 950 km south of Bangkok with a population over 1.32 million people. This province is situated on the eastern side of the Malayan Peninsula facing to the Gulf of Thailand. Hat-Yai, an economic center of Songkhla, has a complex urban environment with a mixture of commercial, residential and industrial establishments. All samples were collected during the period of June-November 2007. The sites descriptions and abbreviations were listed in Table 1.

Table 1: Sampling positions and periods.

Site	Sampling Period	Latitude				Longitude			
Group 1: Background									
SL1	27/07/07-29/07/07	7°	10'	02.92"	N	100°	35'	11.36"	E
SL2	20/10/07-22/10/07	7°	10'	02.92"	N	100°	35'	11.36"	E
KHH	03/11/07-05/11/07	7°	00'	57.92"	N	100°	31'	12.76"	E
Group 2: Traffic									
BT	05/08/07-07/08/07	6°	59'	42.78"	N	100°	28'	58.02"	E
PR	27/08/07-29/08/07	7°	00'	52.99"	N	100°	28'	20.50"	E
Tesco	05/07/07-07/07/07	7°	00'	30.81"	N	100°	29'	39.21"	E
Group 3: Industry									
CPF	24/07/07-26/07/07	6°	54'	16.38"	N	100°	28'	05.15"	E
RMF1	30/07/07-01/08/07	7°	03'	19.97"	N	100°	37'	58.90"	E
RMF2	02/08/07-04/08/07	7°	03'	06.28"	N	100°	24'	07.77"	E
Group 4: Biomass									
RSB	16/11/07	7°	27'	00.52"	N	100°	25'	19.02"	E
PTB	18/11/07	6°	57'	40.45"	N	100°	33'	06.68"	E

SL: Songkhla Lake, KHH: Kor Hong Hill, BT: Bus Terminal, PR: Petkrasam Road, Tesco: Traffic Intersection in front of Tesco-Lotus, CPF: Charoen Pokphand Factory (Fish Can Factory), RMF: Rubber Manufacturing Factory, RSB: Rice Straw Burning, PTB: Para Tree Burning.

Four groups were categorized based on the different nature of emission sources. The site descriptions and abbreviations are clearly displayed in Table 1 and given as follows:



Group 1: This group was carefully selected as a representative of background sampling sites namely:

Songkhla Lake sampling stations (SL): It was situated about 13 km far away from the northern side of Prince of Songkla University (PSU) at the south of Songkhla Lake and approximately 14 km away from the western side of the Gulf of Thailand. This sampling station is far away from many industrial and traffic emission sources, including metallurgy factories and power plants, and the residential areas. Therefore it seems reasonable to consider SL as a representative of rural background sampling station. SL1 and SL2 represent the sampling period of July (27th to 29th July, 2007) and October (20th to 22nd October, 2007) in Songkhla Lake sampling station respectively.

Kor Hong Hill sampling stations (KHH): It was located on the top of Kor-Hong hill with the elevation of 356 m. This site represents as a mixture of all emission sources in urban area. Therefore, the samples collected at KHH can be considered as a representative of urban background air mass. The sampling was conducted during the period of 3rd-5th November, 2007.

Group 2: This group is categorized as a mixture of diesel and gasoline engine exhausts. Three sampling stations were classified into this category namely:

Bus terminal (BT): This site was located at the southwestern side of PSU and approximately 1.4 km far away from the campus. Since the majority of vehicles are diesel engine buses, it appears reasonable to consider BT as a source of diesel emissions. The air samples were collected during the period of 5th-7th August 2007.

Petkrasam road (PR): This site was situated at the heart of Hat-Yai city. This site suffers from air pollutions caused by heavy traffic congestions with a mixture of diesel and gasoline exhaust emissions. The sampling was conducted on 27th – 29th August, 2007.

Tesco: This station was located at the ion in front of the main gate of PSU adjacent to Tesco-Lotus supermarket. Tesco locates on the eastern side and approximately 2.5 km far away from the Hat-Yai city center encompassed with urban residential zones. It seems plausible to regard Tesco as a traffic emission source influenced by complex emissions from trucks, buses, cars and motorcycles. The air samples were collected from 5th to 7th July, 2007.

Group 3: This group was selected as a representative of industrial emission sources. Three sampling stations were classified into this group namely:

Charoen Phokphand Factory (CPF): This site was located at the animal feed factory of CP. This factory is the largest business conglomerate in Thailand. CPF can be considered as an emission source of diesel oil burning. The sampling was conducted from 24th to 26th July 2007.

Rubber Sheet Manufacturing Factory (RMF): RMF was situated at Tumbol Tungwan, Hat-Yai district. Wood materials were used as fuel for the rubber sheet drying process. The rubber sheet was treated with steam of high temperature and high pressures and then purified with sulfuric acid solution. RMF1 and RMF2 represent the sampling period of 30th July-1st August 2007 and 2nd-4th August 2007 respectively.



Group 4: This group can be classified as a biomass burning site and further categorized into two groups namely:

Para Rubber Tree Burning (PTB): This station was located at Namom district, Songkhla Province and can be recognized as an emission source of Para rubber tree burning. The air samples were collected on 18th November, 2007.

Rice Straw Burning (RSB): This station was situated at the rice field in Satingpra district, Songkhla Province. Agricultural burning is the practice of using fire to reduce or dispose of vegetative debris from an agricultural activity. Although this practice is considered as the most effective measure to prevent plant disease, it produces a large amount of smoke that causes air pollution problems in Thailand every year. This station was regarded as a source of biomass burning. The sampling was conducted on 16th November, 2007.

2.2 Sample collection and analysis

A total of 33 samples were collected by Graseby-Anderson high volume air sampler with PM₁₀ sampling inlet (TE-6001). The high volume air sampler was operated at the ground level at the flow rate of 1.4 m³ min⁻¹. PM₁₀ samples were continuously collected from group 1, group 2 and group 3. Samples from each location were collected for 24 h for three consecutive days. In addition, the group 4-PM₁₀ was monitored for 3 h and collected for three times per day in order to avoid any overloading of air particulate matters due to heavy smoke from biomass burning. PM₁₀ aerosols were collected on 47 mm Whatman quartz microfibre filters (QM/A). All the quartz fiber filters were preheated at 800°C for 12 h prior to sampling.

2.2.1 (ATR)-FTIR Spectroscopy analysis

The experiments were performed at 4 cm⁻¹ resolution and 32 scan from 450 to 4000 cm⁻¹. The Infrared spectra were collected using the Attenuated Total Reflectance (ATR)-FTIR Spectroscopy with single reflection ATR sampling module containing a deuterated triglycine sulfate (DTGS) detector. Each spectrum was subtracted from the blank filter spectrum to remove the background infrared spectrum off the target sample. Spectra were collected by averaging 160 co-added of each samples. The normalized spectra of PM₁₀ collected from each emission source will subsequently be averaged and employed as the representative normalized spectra of aerosol samples. To resolve overlapping bands in the mid IR regions, band fitting analysis was performed using OPUS 5.5 software (Bruker optic, German).

2.2.2 OC/EC analysis

The samples were analyzed for OC and EC using DRI Model 2001 (Thermal/Optical Carbon Analyzer) with the IMPROVE A thermal/optical reflectance (TOR) protocol. The protocol heats a 0.526 cm² punch aliquot of a sample quartz filter stepwise at temperatures of 140°C (OC1), 280°C (OC2), 480°C (OC3), and 580°C (OC4) in a non-oxidizing helium atmosphere, and 580°C (EC1), 740°C (EC2), and 840°C (EC3) in an oxidizing atmosphere of 2% oxygen in a balance of helium.



2.2.3 XANES analysis

XANES measurements were carried out using synchrotron radiation source at the Siam Photon Laboratory. The experiment was performed with transmission mode of S-K edge measured between 2460 and 2580 eV. Each sample was mounted on the holder and employed to measure the current signals, I_0 and I , before and after passing through the samples, respectively. The results were expressed as the sample absorption which is the ratio of $\ln(I_0/I)$.

3 Results and discussions

All the assigned bands are indicated in Table 2. Samples collected from transportation and industry sampling sites mainly consist of WSIS and OFG such as SO_4^{2-} , NO_3^- , CO_3^{2-} , NH_4^+ , organonitrates and aromatic nitro compounds. According to the measurement results from transportation sampling sites, the integral areas of IR spectra of NO_3^- , CO_3^{2-} , NH_4^+ were approximately 7.0%, 11.8%, 6.4% respectively. Interestingly, those observed at the background sites were similar order at approximately 4.7%, 8.7 %, 6.3 % in that order (Fig. 1). There is a general tendency that the sum of relative integral areas of these three WSIS in traffic aerosols (26%) was higher than those of background sampling sites (19%). (Table3) The heterogeneous reaction of NO_2 on soot particles occurring inside the internal combustion engine may be responsible for the relatively high contribution of NO_3^- and NH_4^+ detected in the emitted particles from vehicle exhaust. Since the traffic sites are spaciouly enclosed with the

Table 2: Infrared absorption bands and vibrational modes of observed species on PM_{10} aerosols collected from each emission sources.

Absorbance bands (cm^{-1})	Vibration mode	Species
1660-1620	NO_2 asymmetric stretching (R- ONO_2)	Organonitrates
1550-1500	NO_2 asymmetric stretching (Arom- NO_2)	Aromatic nitro compound
1485-1390	NH_4^+	Ammonium ions
1345-1315	vasym (NO_3^-)	Nitrate ions
1390	vasym (CO_3^{2-})	Carbonate
879	vasym (CaCO_3^{2-})	Calcium carbonate
1180-900	S=O stretching - SO_4^- - HSO_4^-	Sulfate species - Sulfate ions - Bisulfate ions
3000-2800	R-H	Aliphatic carbons
3750-3500	R-OH	Alcohols
1750-1700	C=O	Carbonyl species - Hemicellulose - Pectin - Lectin



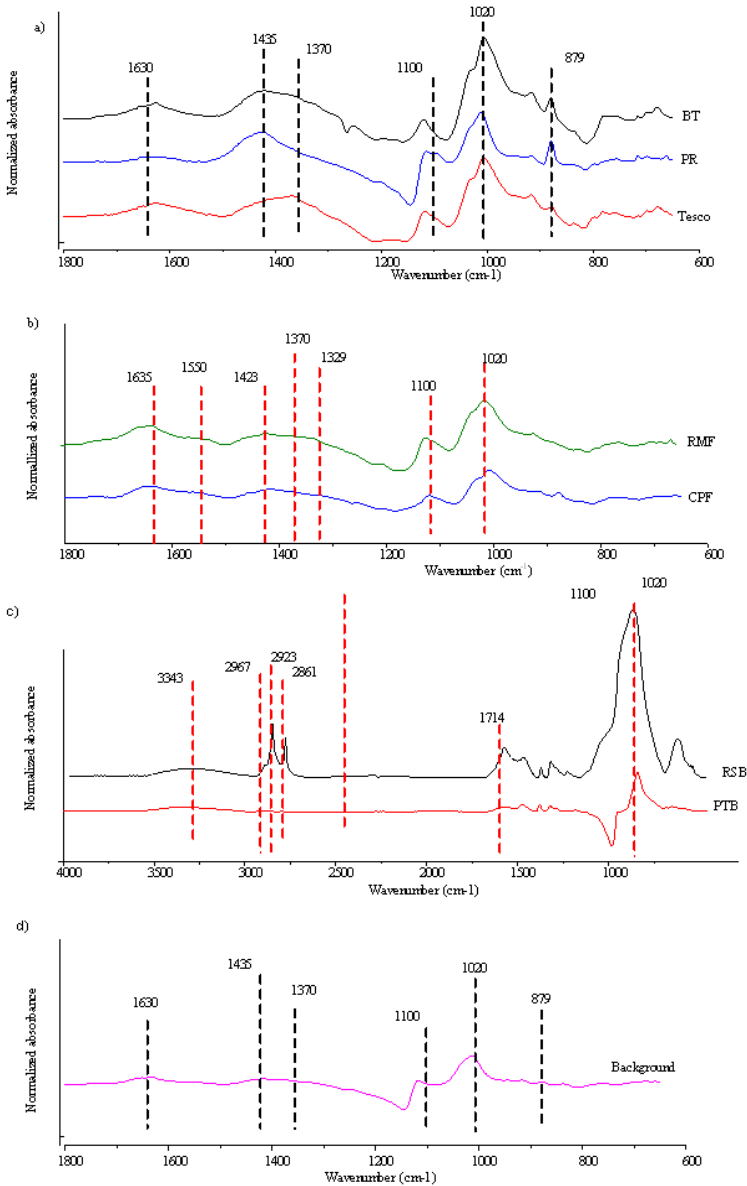


Figure 1: a) FTIR spectra of PM₁₀ samples from each transportation sampling site, b) FTIR spectra of PM₁₀ samples from each industrial sampling site, c) FTIR spectra of PM₁₀ samples from each biomass burning sampling site d) average FTIR spectra of PM₁₀ samples from each background sampling site. Subtract spectra were manipulated by spectra of PM₁₀ aerosols minus spectra of quartz fiber filter (blank filter).

under-construction buildings, it is plausible to ascribe the relatively high level of CO_3^{2-} in traffic aerosols to the building materials (i.e. CaCO_3 in cement).

Also, it is important to note that the industrial aerosols clearly demonstrate the highest level of IR absorption band of aromatic nitro compound and organo nitrate in comparison with those of other emission sources (Fig. 1).

Table 3: Relative integral area (%) of Infrared absorption bands of averaged representative spectra of PM_{10} samples collected from each emission source.

Species	Relative Integral area (%)			
	Transportation	Industry	Biomass burning	Background
CaCO_3	9.5	2.4	-	6.3
SO_4^{2-}	57.0	54.6	62.1	63.6
Nitrate ions	7.0	4.5	-	4.8
Carbonate	11.9	8.1	3.3	8.7
Ammonium ions	6.7	4.3	5.8	6.4
Aromatic nitro compound	3.4	5.7	8.3	4.5
Organonitrates	4.4	18.2	11.8	5.7
Carbonyl	-	2.2	3.9	-

This can be explained by the imperfect combustion of diesel oils and wood materials employed during the heating and drying processes in the CPF and RMF respectively. In addition, it is well known that the polycyclic aromatic hydrocarbons could occur from industrial processes such as petroleum refining, coal coking and thermal power generation. On the other hand, the IR spectrum of biomass burning aerosols showed the highest intensity in the wavenumber ranged from 2,800 to 3,000 cm^{-1} indicating the aliphatic C-H bond absorption bands. There was also some evidence for the presence of CH_2 aliphatic carbon stretching (2,924 and 2,958 cm^{-1}), CH_3 aliphatic carbon stretching (2,850 cm^{-1}), alcohol (3,750-3,500 cm^{-1}), hemicellulose, pectin and lignin (1750-1700 cm^{-1}) measured in the biomass burning samples. It is also interesting to note that the band fitting results of background aerosols showed the highest integral area of sulfate species with 64% of relative contribution, plausibly influenced by dimethyl sulfide in maritime aerosols.

In order to categorize the PM_{10} particles emitted from different sources, the cluster analysis was applied to discriminate the samples into class on the basis of a distance mean based on peak shape, intensity, and peak position by using IR spectrum. As expected, Fig 2 shows the results of hierarchical tree (dendrogram) categorizing PM_{10} aerosol into four clusters namely traffic (BT and Tesco),

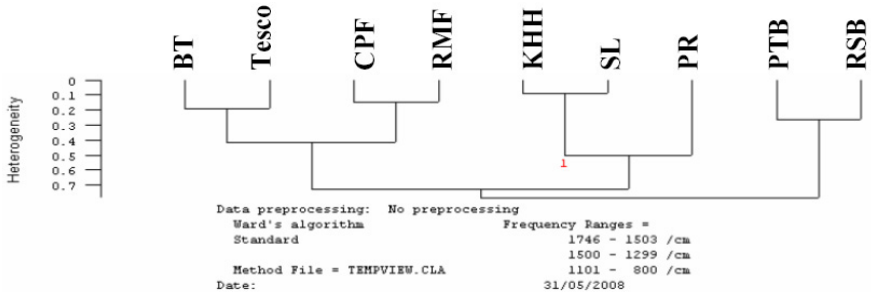


Figure 2: Hierarchical Cluster Analysis (HCA) dendrogram calculated from normalized mean spectra in the range of 1747-1298 cm^{-1} and 1101-800 cm^{-1} of PM_{10} aerosols from each emission sources Cluster Analysis was performed using the Ward's Algorithm.

Table 4: Concentration of TC, OC, EC, OC/EC ratio at different sampling sites.

Sampling sites		PM_{10} ($\mu\text{g m}^{-3}$)	TC* ($\mu\text{g m}^{-3}$)	OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	OC/EC ($\mu\text{g m}^{-3}$)
Background	1. SL1	13.8 ± 2.88	4.30 ± 2.00	3.06 ± 1.43	1.23 ± 0.115	2.48 ± 1.15
	2. SL2	11.6 ± 3.68	0.977 ± 1.85	0.757 ± 0.397	0.221 ± 0.401	3.43 ± 6.48
	3.KHH	9.57 ± 3.97	1.85 ± 1.22	1.35 ± 0.894	0.499 ± 0.256	2.71 ± 1.79
Transportation	4. Tesco	46.9 ± 30.6	14.8 ± 37.4	8.57 ± 10.6	6.25 ± 13.8	1.37 ± 3.45
	5.BT	42.8 ± 24.9	14.1 ± 29.4	8.06 ± 8.15	6.05 ± 11.0	1.33 ± 2.77
	6. PR	25.1 ± 9.19	9.65 ± 22.9	5.43 ± 8.69	4.21 ± 7.38	1.29 ± 3.06
Industry	7. CP	24.5 ± 5.37	7.38 ± 15.4	5.16 ± 4.44	2.21 ± 4.22	2.33 ± 4.86
	8. RMF1	34.4 ± 8.58	15.8 ± 31.7	10.9 ± 17.2	4.97 ± 6.09	2.18 ± 4.36
	9. RMF2	36.7 ± 15.7	11.0 ± 24.8	6.92 ± 10.4	4.10 ± 6.83	1.68 ± 3.79
Biomass burning	10. RSB	218 ± 96.1	80.4 ± 91.9	65.0 ± 52.0	15.4 ± 12.6	4.22 ± 4.83
	11. PTB	83.7 ± 23.2	48.4 ± 66.5	38.6 ± 35.2	9.81 ± 10.1	3.93 ± 5.40

*Total carbonaceous (TC) aerosol was calculated by the sum of organic matter and elemental carbon.

industry (CPF and RMF), background (SL and KHH) and biomass burning (RSB and PTB). It is worth noting that PR shows distinctively a separation group of the cluster. This result can be explained by the relative highest integral area of

CaCO₃ band (shown at 879 cm⁻¹). These findings encourage policy makers to consider IR spectrum as an alternative parameter to conduct the source ratios of aerosols are displayed in Table 4. In general, the OC/EC ratios were observed in the range of 1-4, which is in good agreement with those of other cities around the world. In this study, the highest OC/EC ratios were found with the value of 3.9-4.2 in biomass burning aerosols. It is also interesting to note that the OC/EC ratios of PM₁₀ collected at Tesco, PR and BT were lower than two, indicating the overwhelming influence of traffic exhaust over the three sampling stations. On the contrary, the relatively high OC/EC ratios (3.9-4.2) were analyzed from biomass burning samples. This can be due to the relatively high loadings of aliphatic hydrocarbon, ester carbonyl components such as hemicelluloses, pectin, and lignin as previously mentioned.

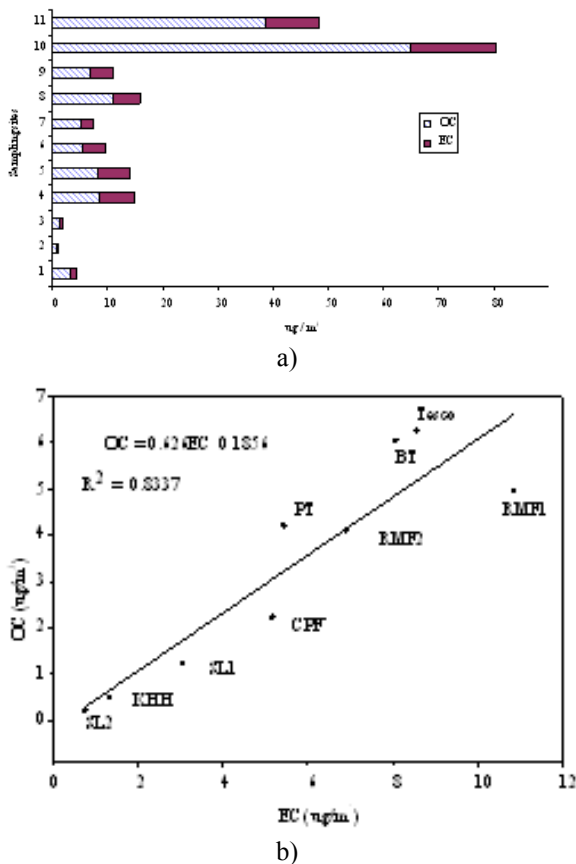


Figure 3: a) Concentrations of OC and EC at different emission sources. b) Relationship between OC and EC in PM₁₀ aerosols collected at Hat-Yai, Songkhla Province.

In this work, XANES technique was used to study the oxidation state of sulfur on the surface of PM₁₀. Since the sulfuric aerosol can be formed through a series of complex multi-phase interactions, involving the balance between acidic and basic ionic components in cloud and rain water, it is therefore important to recognize the oxidation state of particulate sulfuric compounds. Assuming that the aerosols collected from various emission sources are different in nature, it seems plausible to presume the distinctive differences of sulfuric oxidation state among air samples. Surprisingly, the S K-edge with the range of 2460-2520 eV was clearly identified in all samples. More importantly, the aerosols collected at the transportation and industrial sampling sites demonstrate predominantly only S₆⁺ peak at 2481 eV in comparison with other oxidation states of sulfuric compounds (Fig. 4). Thus, in the future, we plan to use the XANES technique for determining the specification of sulfate species by comparing the results of standard reference material such as (NH₄)₂SO₄, CaSO₄ and MnSO₄ to ensure the correct data interpretation of sulfuric oxidation state associated with aerosol samples.

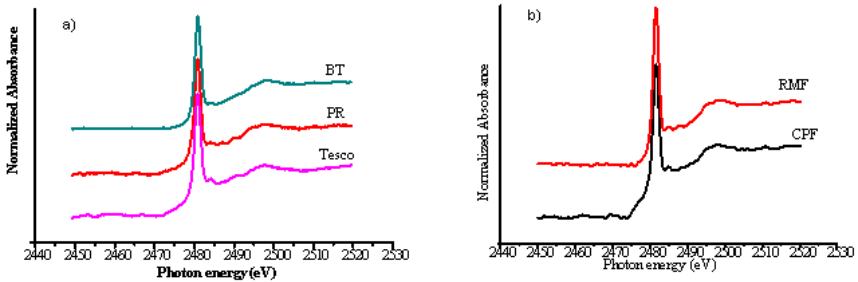


Figure 4: Sulfur K- edge XANES in aerosols collected from a) transportation and b) industry sampling sites.

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