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USING FOURIER TRANSFORM INFRARED (FTIR) TO CHARACTERIZE TSUNAMI DEPOSITS IN NEAR-SHORE AND COASTAL WATERS OF THAILAND

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ABSTRACT

Understanding the tsunami cycle requires a simple method for identification of tsunami backwash deposits. This study investigates Fourier transform infrared (FTIR) spectroscopy followed by careful analysis of variance (ANOVA), Gaussian distribution, hierarchical cluster analysis (HCA) and principal component analysis (PCA) for the discrimination of typical marine sediments and tsunami backwash deposits. In order to test the suitability of FTIR spectra as innovative methods for classifications of tsunami deposits, typical marine sediments and terrestrial soils were classified into three zones, namely zone-1 (i.e. typical marine sediments), zone-2 (i.e. including tsunami backwash deposits) and zone-3 (i.e. coastal terrestrial soils). HCA was performed to group the spectra according to their spectral similarity in a dendrogram and successfully separate FTIR spectra of all three sampling zones into two main clusters with five sub-clusters. The *simplicifolious* (i.e. single-leaved) type of dendrogram was observed with the strong dissimilarity of terrestrial components in subcluster-5. Graphical displays of PC1 vs PC2 highlight the prominent features of zone-1, which is explicitly

different from those of zone-2 and zone-3. The acceptable discrimination of typical marine sediments and tsunami backwash deposits, even six years after the tsunami on Boxing Day 2004, dramatically demonstrates the potential of the method for the identification of paleotsunami.

Keywords: *Tsunami Deposits, Fourier Transform Infrared Spectroscopy (FTIR), Analysis of Variance, Hierarchical Cluster Analysis, Principal Component Analysis, Andaman Sea*

1. INTRODUCTION

The 2004 Indian Ocean earthquake is widely acknowledged by the scientific community as one of the world's greatest natural disasters in modern times. The earthquake-generated tsunami caused more than 225,000 of deaths, and damaged the coastal areas of the Indian Ocean countries. The tsunami studies on modern and ancient onshore sedimentary deposits related to the alteration of geological and sedimentological features received massive attention after the Chile tsunami in 1960. For instance, several tsunami-related studies were conducted in North America (Atwater, 1987; Benson et al., 1997; Clague and Bobrowsky, 1994), Thailand (Choowong et al., 2007, 2008a, 2008b, 2009; Szczuciński et al., 2005, 2006, 2007), Papua New Guinea (Gelfenbaum and Jaffe, 2003), Kamchatka (Pinegina and Bourgeois, 2001), Scotland (Dawson et al., 1988; Dawson et al., 1991) and Norway (Bondevik et al., 1997). In addition, the frequency of hurricane/Indian Ocean monsoon (IOM) contributes to the continental input significantly to the offshore regions (Narayana et al., 2008; Scheffers et al., 2009). Despite of a fairly large number of papers dealing with several impacts of the extreme event onshore, little is known about the geomorphological, sedimentological and geological alterations offshore. Since the offshore physical data is substantially crucial for the study of both the modern and past extreme event, it is therefore important to distinguish the difference between terrestrial deposit and background submarine sediment.

In principle, there are several physical evidences to prove the existence of extreme event--originated terrestrial deposits. For example, it is well known that the enrichment of plant debris in sediment can be considered as signatures of terrestrial records (Cantalamesa and Di Celma, 2005; Narayana et al., 2008; Scheffers et al., 2009). However, there are also several problems associated with the employment of these conventional proxies due to its low preservation potential in the submarine environment. Firstly as the plant fragments settle through the water column, several biogeochemical transformations such as remineralization, chemical decomposition and microbial degradation take place. Secondly, the power of wind-generated waves, hurricane/monsoon waves, daily tides, and even anthropogenic activities such as the clean-up of the contaminated sediments coupled with natural bioturbation can dramatically alter both the topographical and sedimentological features of tsunami deposit. Thirdly, there is no single feature to categorize tsunami, hurricane, monsoon and other types of extreme event deposits except through the careful comprehensive investigation of variability in sediment grain-size, shape, roundness, packing, sorting with the precise assessment of the lateral geometry of the entire sedimentary body (Cantalamesa and Di Celma, 2005; Dawson et al., 1988; Dawson and Shi, 2000). In the light of these difficulties, more alternative well-preserved terrestrial indicators are essentially required to enhance the reliability of data interpretation.

In this study, the authors hypothesize that the employment of Fourier Transform Infrared Spectroscopy (FTIR) coupled with various analogies of statistical analysis assist in a better understanding of offshore terrestrial deposit distribution pattern, which can be subject to erosion by tsunami/monsoon waves and surface runoff by heavy rain in the tsunami-affected coastal areas of Andaman Sea, Thailand. Note that it is the purpose of this paper to illustrate the general principle of using organic functional group analyzed by FTIR for the first time as an innovative proxy to separate the terrestrial deposit from the background sediment in tsunami-affected coastal areas. Neither the source apportionment, nor the analysis of spatial variation of organic functional group in sediments is the main focus of this study. In addition, the risks and possibilities of applying FTIR spectral feature as an alternative extreme event proxy will be reviewed and discussed.

2. MATERIALS AND METHODS

2.1 Study area and sampling methods

The Phang Nga coastal zone was chosen as the study area, where is located in the Andaman Sea, eastern part of the Indian Ocean (see Fig. 1). The study area is approximately 1000 km² (east-west extension: 25 km, north-south extension: 40 km) where some part was heavily destroyed by the Tsunami 2004. Soil samples were also collected along the coastline from Thub Lamu to Ban Nam Khem in Phang Nga province. The surface sediment samples were collected along the Phang Nga coastal area during December 2007 and March 2010. The criteria for selecting the sampling station was based on the evidence of sedimentary deposit in the study area which Feldens and co-worker (2009) surveyed by using the combination of Multi-beam, Side Scan Sonar and Boomer system. One hundred and seven surface sediment samples were collected by using Van-veen Grab Sampler. Sediment samples were kept in clean aluminum foil, placed in a glass bottle, and stored at - 20°C. After removing stones and shell residuals, they were freeze-dried and sieved to <0.076 mm (200 mesh), and then kept at -20°C until analysis. Soil sampling stations (27 stations) were collected during 18-22 July 2009. The areas, which were affected by the 2004 tsunami (Szcucinski, et al., 2005), were taken into consideration for choosing the sampling station. About a half kilogram of composite sample from 2-m² area of each station was collected by using the shovel and then pre-treated as follows as surface sediment samples. All samples were investigated using FTIR to discriminate between the terrestrial sediment and background marine sediment.

2.2 FTIR and statistical analysis

Infrared spectroscopy technique has been widely used for determinations of chemical compositions in sediments (Kovač et al., 2006; Moros et al., 2009; Ramasamy et al., 2009). Recently, in the past few years, FTIR has received much attention as an alternative analytical instrument for determination of organic functional groups in both terrestrial soils and marine sediments because of its relatively fast processing speed, simple operating system and reasonable costs (Moros et al., 2010; Parikh et al., 2008). In this study, the sediment samples were mixed with KBr at various ratios. The optimum

condition for KBr mixing was chosen at 1:15 ratio (sample: KBr) as it gives the highest signal to noise ratio. The mixture was then pressed into a transparent disc in an evacuable pellet die at sufficiently high pressure. The infrared spectra were collected using FTIR Spectroscopy with transmission sampling module and coupled with the highly sensitive mercury cadmium telluride (MCT) detector cooled with liquid nitrogen over the measurement range from 4000 to 600 cm^{-1} . The measurements were performed with a spectral resolution of 4 cm^{-1} with 64 scans co-added. (Bruker Optics Ltd, Ettlingen, Germany). The relative integral areas of each peak were then performed using OPUS 6.5 software (Bruker optic, German). In addition, statistical analysis of T-Test, ANOVA, Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) were performed by using SPSS Version 13.0.

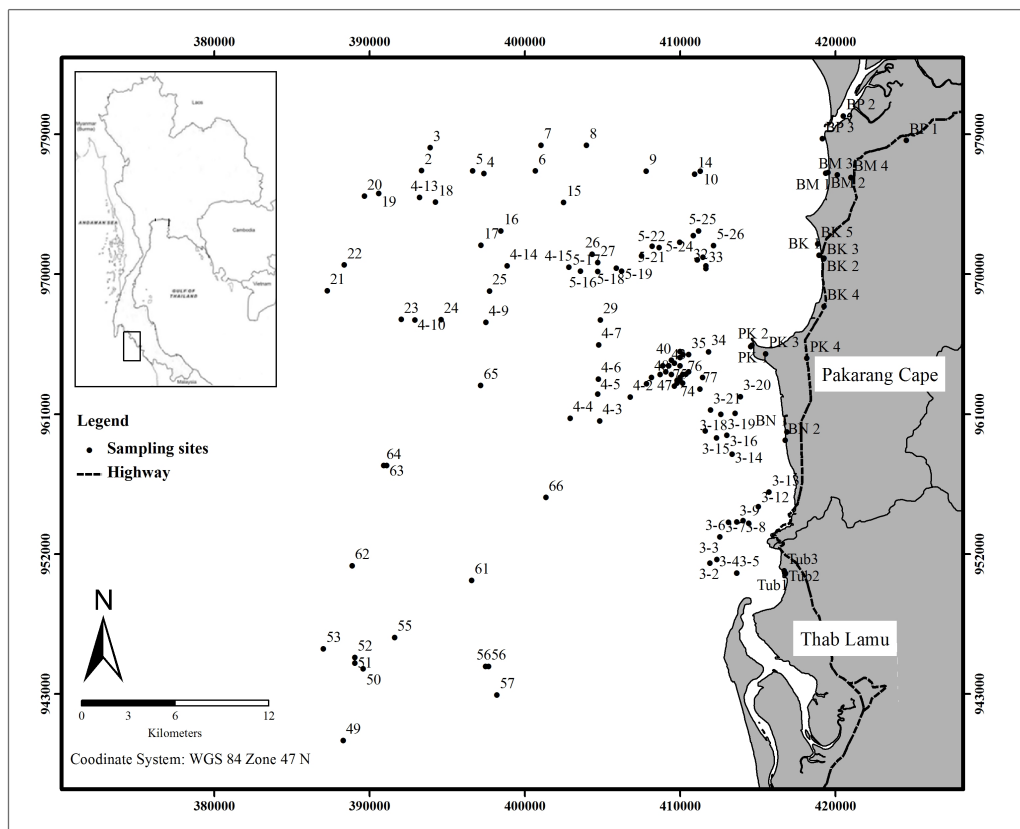


Fig. 1. Sampling site locations at Khao Lak coastal areas, Phang Nga Province, Thailand. (The study area is indicated by the black box; numbers indicate sampling stations).

3. RESULTS AND DISCUSSION

3.1. Characteristics of FTIR spectra

In order to test the availability of FTIR spectra as fingerprints for characterization of tsunami deposits, all marine sediments and terrestrial soils were classified into three zones, namely zone-1 (typical marine sediments), zone-2 (tsunami backwash deposits) and zone-3 (coastal terrestrial soils).

All sampling codes and zone descriptions are clearly illustrated in Table 2.

Table 1. Sampling code, date and description of marine sediments and terrestrial soil samples.

Sampling code	Sampling date	Sampling description
		Terrestrial Soil
Tub1	July-18-2009	Canal bank
Tub2	July-18-2009	Tsunami deposit layer
Tub3	July-18-2009	Rubber Plantation
PK 1	July-19-2009	Beach
PK 2	July-19-2009	Tsunami deposit layer
PK 3	July-19-2009	Shrimp pond
PK 4	July-19-2009	Road side
BK 1	July-19-2009	Tsunami deposit layer
BK 2	July-19-2009	Rubber Plantation
BK 3	July-19-2009	Rubber Plantation
BK 4	July-19-2009	Rubber Plantation
BK 5	July-19-2009	Tsunami deposit layer
BN 1	July-20-2009	Canal bank
BN 2	July-20-2009	Canal bank
BM 1	July-20-2009	Tsunami deposit layer
BM 2	July-20-2009	Pond
BM 3	July-20-2009	Rubber Plantation
BM 4	July-20-2009	Palm Plantation
BP 1	July-20-2009	Pond
BP 2	July-20-2009	Mangrove
BP 3	July-20-2009	Nam Khen port
		Sediment
2,3,4,5,6,7,8,9,10	December-1-2007	Pakarang cape sediment
11,12,13,14,15,16,17,18,19,20	December-2-2007	Pakarang cape sediment
21,22,23,24,25,26,27,29	December-3-2007	Tsunami affected sediment
31,32,33,34,35,36,37,39,40,41,42,43,44,45,46,47,48	December-5-2007	Tsunami affected sediment
49,50,51,52,53,55,56,57,58,61,62,63,64,65,66	December-7-2007	Thup Lamu Sediment
68,69,70,71,72,73,74,75,76,77,78	December-8-2007	Tsunami affected sediment
3-1,3-2,3-3,3-4,3-5,3-6,3-7,3-8,3-9,3-10,3-11,3-12,3-13-3-14,3-15,3-16,3-17,3-18,3-19,3-20,3-21,3-23	March-3-2010	Khao lak near shore sediment
4-1,4-2,4-3,4-4,4-5,4-6,4-7,4-9,4-10,4-13,4-14,4-15	March-4-2010	Pakarang cape sediment
5-16,5-17,5-18,5-19,5-20,5-21,5-22,5-23,5-24,5-25,5-26	March-5-2010	Pakarang cape sediment

Table 2. Sample members of each zone

Zone	Sample members	Zone description
Zone-1	25, 04-09, 04-10, 6, 7, 4-13, 16, 17, 18, 19, 20, 22, 50, 52, 53, 55, 56, 49, 57, 61, 62, 63, 64, 66, 23	Zone-1 sediment samples seem not to be affected by tsunami backwash and can be considered as typical marine sediments. All sampling positions were located within the range of 12 to 24 km offshore.
Zone-2	2, 3, 4, 5, 8, 9, 10, 11, 12, 14, 15, 26, 27, 29, 30, 31, 32, 34, 35, 36, 37, 39, 40, 42, 43, 44, 45, 46, 47, 48, 54, 69, 70, 71, 72, 73, 76, 77, 3-02, 3-03, 3-04, 3-05, 3-06, 3-07, 3-08, 3-10, 3-13, 3-14, 3-15, 3-16, 3-17, 3-18, 3-19, 3-20, 3-21, 4-01, 4-02, 4-03, 4-04, 4-05, 4-06, 4-07, 4-08, 4-14, 4-15, 5-12, 5-16, 5-17, 5-18, 5-19, 5-20, 5-21, 5-22, 5-23, 5-24, 5-25, 5-26	According to the acoustic profile data, Zone-2 is most likely to be influenced by the tsunami backwash deposits. All sampling positions were situated within 12 km from the shoreline.
Zone-3	Tub1, Tub2, Tub3, PK1, PK2, PK3, PK4, BK1, BK2, BK3, BK4, BK5, BN1, BN2, BM1, BM2, BM3, BM4, BP1, BP2, BP3	Zone-3 is characterized as natural samples of onshore terrestrial soils.

The FTIR spectra for all sampling zones are compared in Fig. 2. Overall, the spectra of all samples are generally quite similar to each other, which can be characterized by *i*) broad and strong absorption band in the 3750-3000 cm^{-1} intervals (OH vibration of hydroxyl groups in alumino-silicates and OH vibration of water and OH groups organic fraction of sediments) followed by moderate C-H stretching bands in the interval from 2960 to 2800 cm^{-1} ; *ii*) moderately strong CO_3^{2-} absorption peaks in the frequency range of 2660-2450 cm^{-1} ; *iii*) the overlap of several possible absorption peaks, namely free water, C-C stretching of aromatics and alkene double bonds, C=O stretch of secondary amides corresponding NH, COO asymmetric stretching of metal carboxylates and carbonate minerals (calcite) in the interval from 1756 to 1268 cm^{-1} and *iv*) strong Si-O (silicate mineral) absorption peaks in the frequency range of 1270-895 cm^{-1} .

Although FTIR spectra of all sampling zones display relatively similar distribution pattern in the frequency range from 3750 to 750 cm^{-1} , some subtle differences were observed in the vibrational modes of organic components indicating the dissimilarities of chemical compositions in each sampling zones. For instance, the prominent feature of three small sharp peaks on the first broad main peak was detected in the interval of 3750-3500 cm^{-1} of zone-3, highlighting the differences in contribution of hydrogen bond lengths and orientations that mostly corresponding to the OH and NH groups (Wolkers et al., 2004). This can possibly be explained by the relatively high contribution of kaolinite in terrestrial soils, which had previously been mentioned in several studies (Martinez et al., 2010; Rong et al., 2008; Yusiharni and Gilkes, 2012). Interestingly, the characteristic peaks of humic acids (HA) and fulvic acids (FA), which can be explained by two intense bands at 1700 cm^{-1} and 1640 cm^{-1} were always observed for all sampling zones. The first absorption band is characterized as C=O stretching vibration of carboxylic acid groups (Mac Carthy and Rice, 1985, Davis et al., 1999 and Richard et al., 2007), whilst the second band is interpreted as the mixture of the stretching vibrations of C=C aromatic bonds, conjugated carbonyl groups (quinone), carboxylic salt groups and amide groups (Vergnoux et al., 2011). Another crucial feature is characteristic peak of lignin spectrum,

which can be assigned to an aromatic $\nu\text{C}=\text{C}$ stretching vibration in the interval of $1517\text{--}1509\text{ cm}^{-1}$ (Duarte et al., 2007; Tinoco et al., 2006). Apart from the characteristic peaks of kaolinite, HA, FA and lignin observed in zone-2 and zone-3, the sharp peak appears in the interval range of $947\text{--}895\text{ cm}^{-1}$ detected in zone-1 emphasizing the influence of relatively high contribution of silicate mineral in typical marine deposits.

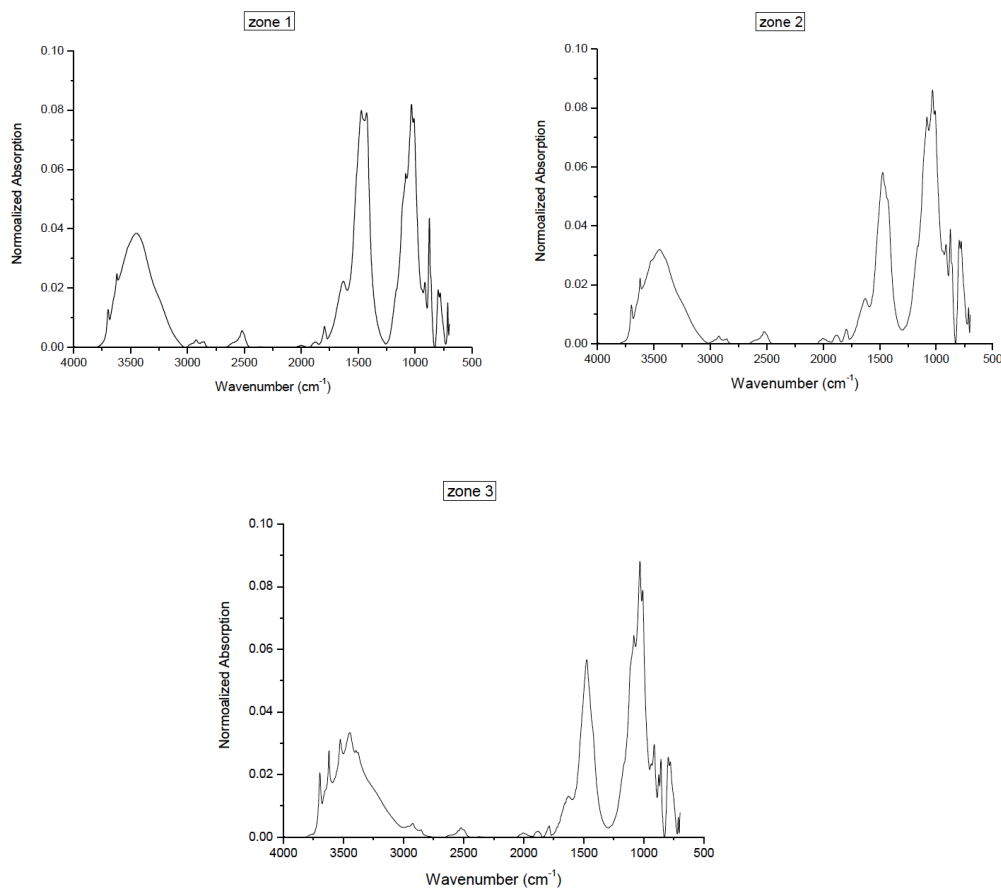


Fig. 2. FTIR spectral of Zone-1, Zone-2 and Zone-3 in $4000\text{--}500\text{ cm}^{-1}$ frequency range.

3.2. Comparison of integrated peak area of FTIR

Averages and standard deviations of integrated peak area of FTIR spectra at 12 different absorption bands (i.e. $3715\text{--}3608\text{ cm}^{-1}$, $3608\text{--}3048\text{ cm}^{-1}$, $3020\text{--}2800\text{ cm}^{-1}$, $2660\text{--}2450\text{ cm}^{-1}$, $2066\text{--}1930\text{ cm}^{-1}$, $1930\text{--}1846\text{ cm}^{-1}$, $1832\text{--}1760\text{ cm}^{-1}$, $1756\text{--}1600\text{ cm}^{-1}$, $1600\text{--}1268\text{ cm}^{-1}$, $1270\text{--}895\text{ cm}^{-1}$, $895\text{--}831\text{ cm}^{-1}$, $831\text{--}708\text{ cm}^{-1}$) of all sampling zones were carefully investigated and compared as shown in Fig. 3. A visual comparison reveals fundamental differences between sampling zones observed in the frequency range of $3608\text{--}3048\text{ cm}^{-1}$, $1756\text{--}1600\text{ cm}^{-1}$, $1600\text{--}1268\text{ cm}^{-1}$ and $831\text{--}708\text{ cm}^{-1}$. Significant differences were observed for these four absorption bands based on the analysis of variance (ANOVA). For instance,

zone-1 shows significantly higher integrated peak area observed in the frequency range of 3608-3048 cm^{-1} and 1600-1268 cm^{-1} , which can be explained by relatively larger contribution of OH group organic fractions and calcites as typical chemical components often found in marine sediments (Kovač et al., 2005, 2006). No significant differences of alumino-silicates and carbonate minerals were observed in the interval of 3020-1760 cm^{-1} , highlighting the homogeneity of these chemical substances in sampling sites. Interestingly, zone-3 displays significantly higher contributions of aromatic compounds and alkene double bond in the absorption bands of 1756-1600 cm^{-1} that might represent the existence of HA, FA and lignin in terrestrial soils.

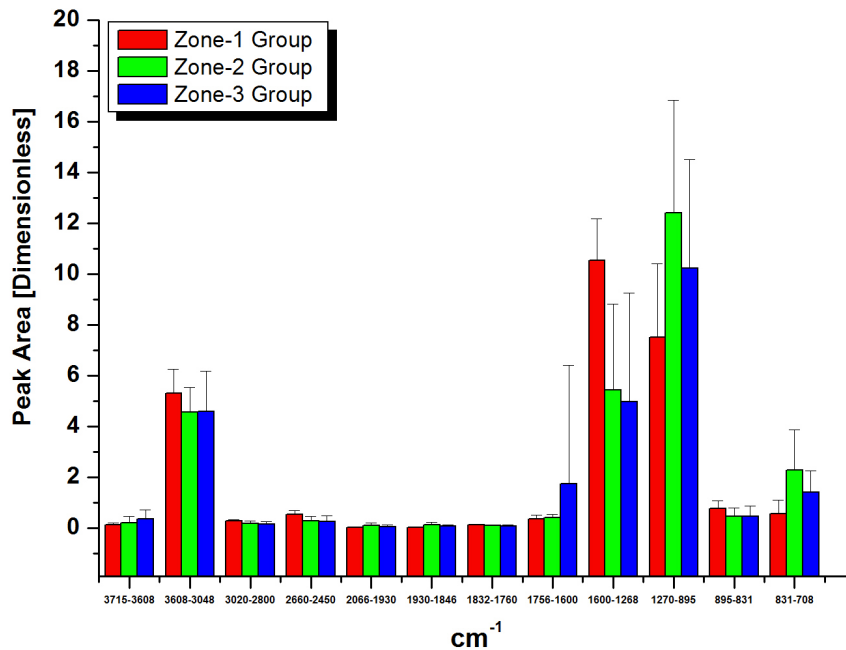


Fig. 3. Integrated peak area of FTIR spectra at 12 different absorption bands for Zone-1, Zone-2 and Zone-3 group.

In order to achieve more comprehensive analysis of FTIR spectra characteristics of each sampling zone, percentage area graphs of 12 absorption bands were plotted and illustrated in Figure 4. Symmetrical triangle shapes of percentage area graphs of all sampling zones appear in the absorption bands from 3715 to 2800 cm^{-1} . However, the dissimilarity between percentage area graphs becomes apparent at the frequency range of 1756-831 cm^{-1} . This discrepancy arises essentially from the fact that zone-2 was more influenced by terrestrial materials of zone-3 in comparison with zone-1. Since the FTIR absorption bands from 1756 to 831 cm^{-1} contain relatively complicated mixture of several organic compounds, mainly HA, FA and lignin, it appears reasonable to interpret the strong similarity of percentage area graphs observed in zone-2 and zone-3 as a consequence of tsunami backwash that

dragged large amounts of terrestrial materials from coastal area into near shore zone.

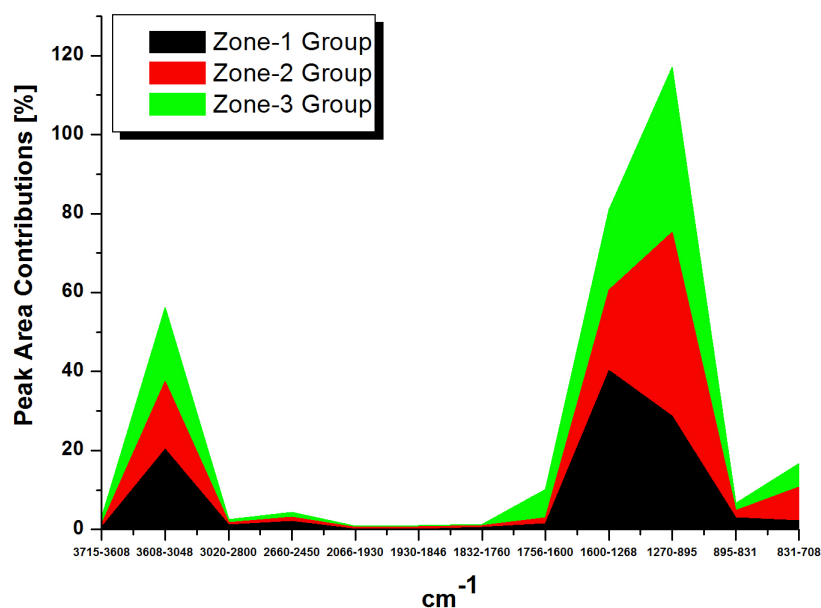


Fig. 4. Percentage contributions of integrated peak areas of FTIR spectra at 12 different absorption bands for Zone-1, Zone-2 and Zone-3 group.

3.3 Probability distribution function (PDF)

The probability distribution function (PDF) was applied to all FTIR spectra at 12 different absorption bands as previously mentioned in section 3.2. PDF is a function that explains the comparative probability for this random variable to take on a given value. The probability for the random variable to fall within a particular region is given by the Gaussian distribution, which can be described as follows:

$$y = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(x - \mu)^2}{2\sigma^2}\right) \quad (1)$$

where y , σ , σ^2 , μ and x represent for probability distribution function, standard deviation, variance, average and peak area of spectrum of each zone respectively. As clearly illustrated in Fig. 5, some characteristic features can be extracted directed from the original images. Firstly, a sharp symmetrical bell-shape curve was observed in zone-1 samples for most absorption bands. Since the measured values of the variable are more concentrated in the middle than in the tails, it appears reasonable to assume this fact is a circumstance of moderately homogeneous spatial distribution of organic functional groups in background marine sediments that were much less affected by the tsunami.

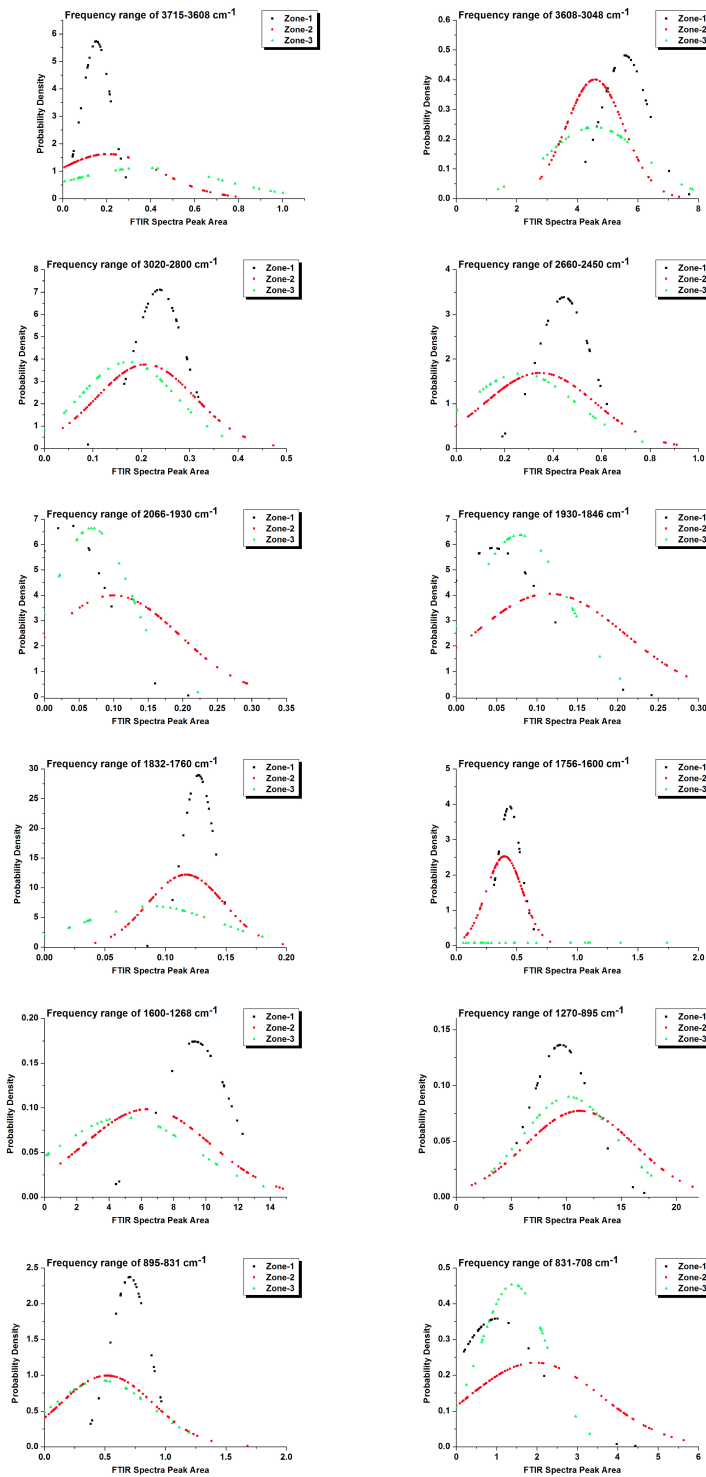


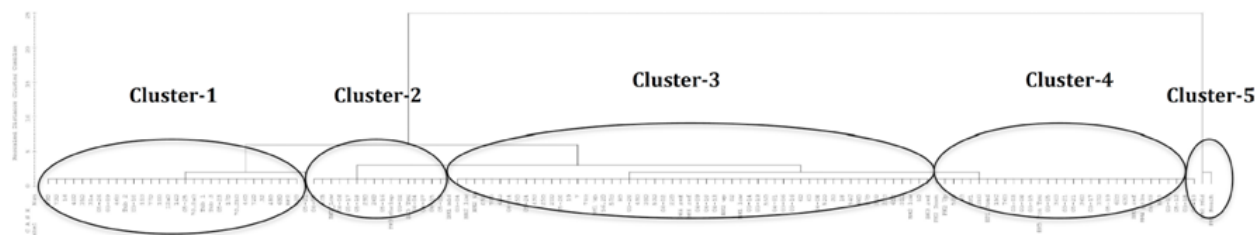
Fig. 5. Probability distribution function graphs of FTIR spectra at 12 different absorption bands of sediment and soil samples collected at zone-1, zone-2 and zone-3.

backwash. For instance, the subtle differences between zone-1 and other zones were detected at the frequency range of 3715-3608 cm^{-1} , 3020-2800 cm^{-1} , 2660-2450 cm^{-1} , 1832-1760 cm^{-1} and 895-831 cm^{-1} . This can be inferred as a result of fairly harmonized spatial distribution of kaolinites, CH-stretching mode compounds, carbonates and silicates observed in marine sediments. Secondly, zone-3 shows extremely broad peaks with flat tops at the interval range of 3715-3608 cm^{-1} , 1832-1760 cm^{-1} and 1756-1600 cm^{-1} , emphasizing the high degree of chemical diversity of kaolinite mineral silicates, carbonate minerals, aromatics and alkene double bond components in terrestrial soils. Thirdly, zone-2 demonstrates positive skews in the frequency range of 3715-3608 cm^{-1} , 2660-2450 cm^{-1} , 2066-1930 cm^{-1} and 1930-1846 cm^{-1} , 895-831 cm^{-1} and 831-708 cm^{-1} , indicating that the bulk of spectra peak areas lie to the left of the mean. These asymmetrical distribution curves also reveal the fact that the mean is generally higher than the median and thus underlining the importance of tsunami backwash that dragged large amount of terrestrial materials out to zone-2.

3.4 Hierarchical cluster analysis (HCA)

Hierarchical clustering allows users to select a definition of distance, then select a linking method of forming clusters, then determine how many clusters best suit the data. *Hierarchical clustering* methods do not require present knowledge of the number of groups. There are three general approaches to clustering FTIR spectra, namely “*Hierarchical Cluster Analysis*”, “*K-means Cluster Analysis*” and “*Two-Step Cluster Analysis*”. In both *K-means clustering* and *two-step clustering*, researchers have to specify the number of clusters in advance, and then calculate how to assign cases to the *K* clusters. Furthermore, these two clustering techniques require a very large scale of data set (e.g. $n > 1,000$). On the contrary, *Hierarchical Cluster Analysis* (HCA) is appropriate for smaller samples (e.g. $n < 200$) and can be carried out without any data pre-treatment (Dach *et al.*, 1999). Therefore, classification of FTIR spectra according to spectral similarity was conducted with the assistance of hierarchical cluster analysis (Fig. 6).

To test the hypothesis that zone-2 contains more tsunami backwash deposits in comparison with those of zone-1, HCA had been conducted on the 12 variables (i.e. 12 different absorption bands as previously mentioned in section 3.2). The HCA revealed the presence of two main clusters with five different sub-clusters. The first major cluster consists of all zone samples with the average percentage contribution of 24%, 56% and 20% for zone-1, zone-2 and zone-3 respectively. This cluster can be divided into four subgroups; the first consists of zone-1 (0%), zone-2 (87%), zone-3 (13%), and the second is composed of zone-1 (47%), zone-2 (29%), zone-3 (24%), the third contains zone-1 (41%), zone-2 (43%), zone-3 (16%) and the fourth constructs zone-1 (10%), zone-2 (64%), zone-3 (26%). According to dendrogram, the members present in the first subgroup can be considered to be a mixture of “tsunami-backwash deposits” and “terrestrial components” with the percentage contribution of 22% ($n = 30$) to all samples ($n = 136$). Cluster-5 is another key-feature in dendrogram, which illustrates the strong presence of terrestrial components namely PK1 and BM2. Since these two samples represent the terrestrial components, it appears reasonable to assume the disagreement of cluster-5 in comparison with other sub-clusters is a consequence of relatively high contribution of HA, FA and lignin.



Cluster-1 (n = 30; Percentage contribution 22%)										
9	73	16	40	35	31	5-26	3-09	46	Tub 2	3-10
11	77	10	13	14	5-25	78	Tub 1	Tub 3	5-23	17
68	44	72	32	48	69	BP2	42			
Cluster-2 (n = 17; Percentage contribution 13%)										
5-21	4-05	47	BK1 low	4-06	5-17	29	26	05-16	PK3	3-02
BK5 Tsu	4-04	4-07	4-15	5-22	BM1 mid					
Cluster-3 (n = 56; Percentage contribution 41%)										
3-04	BN2 low	BM2 up	5	70	64	4-14	45	5-24	43	25
20	5-20	19	7	71	BM1 up	58	57	8	3-20	49
39	53	4-02	22	PK4	BK4	4-09	4-10	4-13	BN2 up	2
BM1 low	3-14	3-19	55	4-01	3-06	3-16	6	42	4-08	52
3	18	54	66	27	30	23	61	41	BM2 low	5
BK3										
Cluster-4 (n = 31; Percentage contribution 23%)										
PK2 down	PK2up	50	4	BN1	33	BP1	15	76	3-03	3-08
3-15	BK5 pre Tsu	3-05	34	3-21	5-21	36	3-17	37	5-19	62
63	BM3	BM4	4-03	BP3	3-07	5-12	3-18	3-13		
Cluster-5 (n = 2; Percentage contribution 1%)										
BM2 mid	PK1									

Fig. 6. Hierarchical cluster analysis of FTIR spectra of terrestrial soils and coastal sediments in the 2004 tsunami-affected Khao Lak area.

3.5 Principal component analysis (PCA)

Factor analysis offers the advantages of not requiring prior knowledge of the chemical composition and size distribution of emissions from specific sources (source profiles) but has the drawback of being mathematically indeterminate, allowing a wide range of possible solutions even when it is applied to relatively simple simulated data sets. In natural soils and sediments, which are composed by many potential and diverse sources, principal component analysis (PCA) has been chosen by many researchers for source apportionment of chemical contaminants such as polycyclic aromatic hydrocarbons (Liu et al., 2009; Yunker et al., 2011; Zhang et al., 2012). This technique has also been widely applied to FTIR spectra as main purposes for classifications of biological and chemical materials (Bombalska et al., 2011; Cotrim et al., 1999). In this study, Varimax rotation was selected to maximize the sum of the variances of the squared loadings and thus enable us to seek the similarity of chemical components in sediment and soil samples. FTIR spectra of the samples listed in Table 1 were analyzed by PCA. The principal component patterns for Varimax rotated components of 136 samples composed of three PC, which account for 91.75 %, 6.69 % and 1.47 % for the total of variances of PC1, PC2 and PC3 respectively. The contribution of PC1 and PC2 explains 98.44 % of total variance, and moreover PC1 is 13.7 and 62.4 times higher than PC2 and PC3 respectively.

A plot of the scores of the first two PCs is presented in Fig. 7. It can be easily seen that the full black squares (zone-1) constitute a very broad group along the positive values of PC2 (y-axis) adjacent to 1.0 and then gently decrease exponentially to positive side of PC1 (x-axis). On the contrary, the full black triangle (zone-2) and full black circle (zone-3) resemble each other with a quarter circle curve from north to east, indicating that these samples might share similar organic functional groups. Three possibilities can be considered to be responsible for this phenomenon; *i*) the tsunami inundation might uplift bottom marine sediments to onshore area, *ii*) the tsunami backwash conveyed terrestrial components to marine environment and *iii*) both tsunami inundation and backwash account for the similarity of two-dimensional plots of PCA appearing in Fig. 7. Another key feature is horizontally deviated samples namely 31, 3-9, 5-21, 5-25, 5-26, 10, 14, 42, BK3, BM3, BP2, Tub3 and PK2, which are located parallel to *x*-axis. Since these samples are representative of onshore soils and coastal sediments adjacent to shoreline, it appears reasonable to conclude that the application of PCA on FTIR spectra can successfully discriminate typical marine sediments from terrestrial components and tsunami backwash deposits in near shore and coastal waters of Thailand.

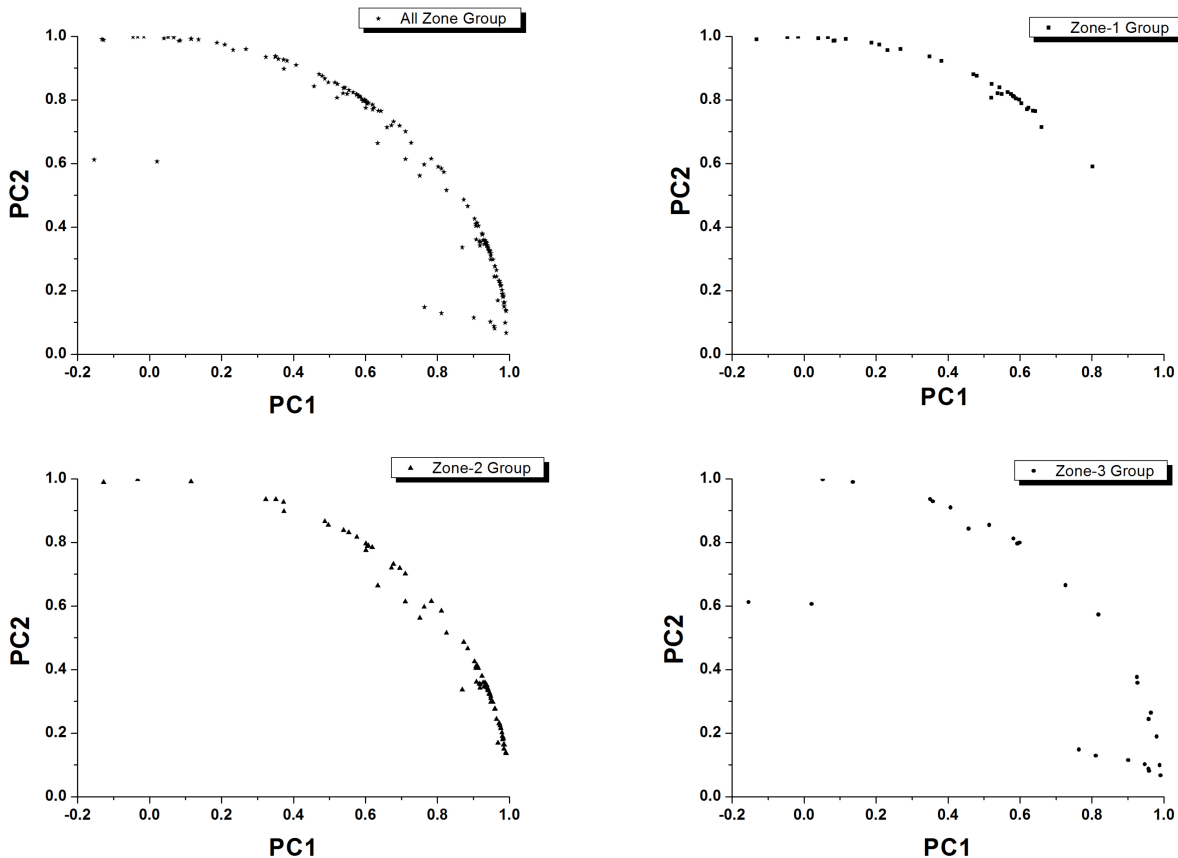


Fig. 7. Two-dimensional plots of PC1 and PC2 using FTIR spectra of terrestrial soils and coastal sediments in the 2004 tsunami-affected Khao Lak area.

3.6 Implications for the identification of tsunami deposits

HCA, PDF and PCA analysis of FTIR spectra are able to discriminate terrestrial material in the marine environment. Offshore Khao Lak, tsunami deposits are preserved within fine-grained sediments that were found to be transported towards offshore during normal conditions during the monsoon without the influence of strong events (Feldens et al., 2012). The proxies discussed in this study are thus not able to differentiate between different processes transporting material from on-towards offshore. Nevertheless, they show great potential for the recognition of (paleo) tsunami events: Depending on the local setting, the identification monsoon-generated deposits is possible (e.g., Kempf et al., 2003, Hanebuth and Stattegger, 2004, Schettler et al., 2006) thus allowing to differentiate tsunami and from sediment deposited under normal conditions. In contrast, one of the most discussed concerns in tsunami research is the differentiation between storm and tsunami deposits (e.g., Phantuwongraj and Choowong, 2011, Chagué-Goff et al., 2011, Switzer et al., 2009, Kortekaas and Dawson, 2007, Nott, 2003), especially offshore. No reliable criteria have been developed so far, with rip-up clasts and antidunes being the most characteristic sedimentological differentiation between tsunami and storm deposits in Thailand (Phantuwongraj and Choowong, 2011). However, in general, storms tend to erode the beach and the coastline, and thus transport less material from onshore towards offshore compared to tsunami waves that inundate the hinterland. Thus, when event-layers of uncertain origin are encountered, frequently partly reworked due to erosion or bioturbation, the determination of the terrestrial input within the layer can be a decisive factor for their interpretation. This is especially true for paleotsunamis for which no historical information is available, as the organic functional groups are expected to be preserved within the sediment for at least 12,500 years (Silliman et al., 1996).

Table 3. IR absorptions for representative functional groups

Functional Group & Molecular Motion	Wave number (cm ⁻¹)*,**
OH vibration of hydroxyl groups in alumino-silicates (Kaolinite mineral silicates)	3715-3608
OH vibration of water and OH groups organic fraction of sediments	3608-3048
CH stretching mode	3020-2800
Carbonate (CO ₃ ²⁻) sediment	2660-2450
	2066-1930
Carbonate (CO ₃ ²⁻) minerals	1930-1846
	1832-1760
Free water, C-C Stretching of aromatics and alkene double bonds, C=O Stretch of secondary amides corresponding NH, COO asymmetric stretching of metal carboxylates	1756-1600
Carbonate minerals (calcite)	1600-1268
Silicate mineral (Si-O)	1270-951
	947-895
Other carbonates (Li ⁺ , K ⁺ , Na ⁺)/Other silicate (Overlapping bands)	895-831
	831-708

*Ramasamy et al., 2009

**Kotoky et al., 2006

4. CONCLUSIONS

The current study showed the high potential of FTIR spectroscopy coupled with hierarchical cluster analysis (HCA) and principal component analysis (PCA) for the discrimination of tsunami backwash deposits and typical marine sediments. According to our best knowledge, this has been the first time that the appropriateness of FTIR spectroscopy for classification of tsunami backwash deposits has been demonstrated. The dissimilarities between the FTIR spectra of all sampling zones were particularly noticeable in the OH vibration of water and OH group organic fraction associated absorption bands from 3608 to 3048 cm^{-1} , C-C stretching of aromatics and alkene double bonds related frequency range of 1756-1600 cm^{-1} , calcite linked interval of 1600-1268 cm^{-1} and other carbonates (Li^+ , K^+ , Na^+) and silicates at the absorption bands from 831 to 708 cm^{-1} . Some considerable discrimination of terrestrial components and tsunami backwash deposits was possible with the assistance of HCA, although the separation in some sub-clusters still remain ambiguous and thus reveals a high degree of similarity in FTIR spectra and chemical composition of natural samples in tsunami-affected area. Two-dimensional plots of PCA highlight the similarities of a quarter circle curve from north to east detected in zone-2 and zone-3, which can be explained by the relatively strong influence of terrestrial components dragged by tsunami backwash within 12 km from the shoreline.

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