Monitoring of Volatile Organic Compounds in urban and rural tropical environments

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Abstract

Rapid urbanization and economic development in South-East Asia in past decades has led to air pollution problems such as excess of particles, nitrogen oxides (NOx), carbon monoxide (CO) and volatile organic compounds (VOCs). The Motor vehicle exhaust, industrial emissions, chemical solvents as well as biogenic emissions are among the major anthropogenic sources of pollutants. The goal of this study is to identify and quantify the types of VOCs in tropical environment and compare the results with data obtained in temperate climate in France, near Bordeaux. Two automated Thermal-Desorber Gas Chromatographs equipped with Flame Ionization Detectors (auto-TDGC-FID) were used to monitor continuously the concentrations of VOCs in May 2014 in three different sites in Thailand and in one site in France. A laboratory study has been carried out to optimize the system before installation in tropical area. One analyzer was dedicated to the monitoring of C2 to C6 and another for C6 to C12. It was possible to adjust the time, gas flow and temperature for the pre-concentration of the sample independently for both analyzers. Columns, pressure and temperature gradient have been optimized to obtain a good separation for more than 100 VOCs. The results of the study show very important pollutant concentrations in the different area in Thailand. BTEX concentration is 10 times higher in Bangkok than on the seaside. Other compounds such as dichlorobenzene and styrene could be measured in industrial area and in Bangkok while very low concentrations were measured in Bordeaux and on the seaside in Thailand.

Keywords: volatile organic compounds, gas analysis, organic aerosol, tropical environment, continuous monitoring

1. Introduction

It has been established that organic aerosol (OA) makes up for a major fraction of fine particulate matter in all region of the atmosphere. This fraction accounts approximately for half of the total PM2.5 dry mass.[1,2] Primary OA is directly emitted in the troposphere from anthropological and natural sources whereas secondary OA (SOA) is formed in-situ in the atmosphere from the oxidation of biogenic or anthropogenic gas-phase precursors and subsequent partitioning of the less volatile products into the particle phase. The current number is that, on a global scale, SOA would represent around 60% of the overall OA.[3] However, recent global mass-balance estimations for the removal of volatile organic compounds (VOCs) suggest that this number could under-predicts SOA production.[4] Recent field measurements in urban locations are also in support of a larger share, indicating that SOA is the dominant fraction of OA, with amounts considerably 20 times greater than models predictions.[2,5,6] To reduce the emission of particles, different countries have implement specific prevention and control action plans which aim to reduce $PM_{2.5}$. For example, the Chinese State Council has decided to reduce the level of $PM_{2.5}$ by up to 25% by 2017 relative to 2012 levels.[7] Achieving this highly ambitious goal requires targeted, optimized emission control strategies.

One of the challenges of this project was to measure continuously the concentrations of specific VOCs emitted in different regions in Thailand and in France. The analytical system must monitor continuously and accurately without perturbation of external condition such as rapid increase or decrease of concentrations, variations of pressure, humidity or temperature. The cycle time must be short enough so that kinetics of emissions can be monitored. Also, the types of VOCs must be identified and quantified accurately. We present in this article the methodology for the on-site measurement of VOCs. First a laboratory study has been carried out to calibrate and check the stability of the instruments. Then the system has been deployed in Thailand and in France. For each campaign, the concentrations have been measured continuously for 3 days.

2. Method

2.1 Sampling and description of analysis sites

The hydrocarbon measurements were conducted in 2014 at different sites. Three measurement campaigns were performed in Thailand: An industrial area in the Rayong province from the 15/05 (DD/MM) to the 18/05 (named in the article as *Industrial area*), in Bangkok from the 20/05 to the 23/05 (named in the article as *Bangkok*) near seaside in the Phetchaburi province from the 24/05 to the 27/05 (named in the article as *seaside*). The other campaign was performed from the 18/05 to the 21/05 in the research laboratory of Chromatotec: 15 km from Bordeaux (France) and located at 300 meters from the motorway (named in the article as *near Bordeaux*). All different locations can be seen on the maps in the Appendix C. Sampling is performed using ¼ PTFE tubing directly connected to the back of the analytical system.

2.2 auto-TDGC-FID for C2 to C6 Monitoring

An automatic gas chromatograph (airmoVOC C2-C6, Chromatotec, France) equipped with a flame ionization detector (FID) has been used for the monitoring of molecules containing from 2 to 6 carbon atoms (Appendix A). For each analysis, 107 ml of ambient air was drawn into the system with a flow rate of 10.7 $ml.min^{-1}$ (air sample is integrated over 10 min). The air sample passed first through a dryer (airmoDry, Chromatotec, France) to remove the humidity and then hydrocarbons were pre-concentrated at -10°C on a trap filled with a mixture of Carboxen and Carbopack. The pre-concentrated air sample was thermally desorbed at 300°C for 4 minutes and directly injected in a 25 m Al2O3/Na2SO4 column (PLOT column, 0.53 mm ID, 10.0 um dF) located inside the heated oven of the GC. Within the first minute of the analytical procedure, the oven temperature rose from 36°C to 38°C. Afterwards a constant heating rate of 15°$C.min^{-1}$ was applied and the temperature reached 202°C. Then the temperature is kept at 202°C for 630 s before cooling. C2–C6 hydrocarbons were detected by FID and the detection limit has been determined to be 0.038 $\mu g.m^{-3}$ for Butane (see 3.1.1). The measurements in Thailand were performed with one analyzer while results in France were obtained with another. The same calibration procedure has been used for both systems.

2.3 auto-TDGC-FID for C6 to C12 Monitoring

For the monitoring of molecules containing from 6 to 12 carbon atoms (Appendix B) an automatic gas chromatograph (airmoVOC C6-C12, Chromatotec, France) equipped with a flame ionization detector (FID) has been used. For each analysis, 440 ml of ambient air was drawn into the system with a flow rate of 44 $ml.min^{-1}$ (air sample is integrated over 10 min). The hydrocarbons were pre-concentrated at room temperature on a trap filled with Carbopack. The pre-concentrated air sample was thermally desorbed at 380°C for 4 minutes and directly injected in a 30 m MXT 1 column (0.28 mm ID, 1.0 um dF) located inside the heated oven of the GC. During the first 7 minutes of the analytical procedure, the oven temperature rose from 36°C to 50°C. Afterwards a constant heating rate of 10 °$C.min^{-1}$ was applied for 3 minutes followed by a heating rate of 15 °C.min-1 for 8 minutes. The temperature reached 200°C by the heating time. Then the temperature is kept at 200°C for 240 s before cooling. C6–C12 hydrocarbons were detected by a FID and the detection limit has been determined to be 0.045 $\mu g.m^{-3}$ for Benzene (see 3.1.2). The measurements in Thailand were performed with one analyzer while results in France were obtained with another. The same calibration procedure has been used for both systems.

2.4 Gas supply

Air generators (airmopure, Chromatotec, France) and Hydrogen generators 99.9999% with dew point below -15°C (Hydroxychrom, Chromatotec, France) were used for the flames of FIDs, valve actuations of the auto-TDGC-FIDs and drying of samples for C2 to C6 analysis. The VOCs content of gas generated by both generators was verified experimentally using auto-TDGC-FID and Non-Methanic Hydrocarbon Concentration (NMTHC) for both analyzers was below 0.1 $\mu g.m^{-3}$.

2.5 Standards used for calibration

Quality controls of the instruments were performed using NIST certified cylinders. National Physical Laboratory cylinder (European list of 30 compounds), TO15 (64 compounds), TO14 (44 compounds) and PAMS 58 (from Takachiho) were used for the calibration of instruments and response factor calculations (in accordance with the requirement of the ISO:17025 for benzene calibration). The relative response factors to benzene were determined experimentally and then values were compared with the theoretical relative response factors obtained using the equivalent number theory. We always obtained less than 10% difference between theoretical and apxerimental values which indicates that the system is suited for such measurement. On-site, permeation tubes of n-butane, n-hexane and benzene were used every 24h to check automatically the calibration of the instruments as well as the stability of the retention times. The permeation tubes are tested for one week to check the stability and quantify precisely the permeation rate using instrument which are certified for the continuous measurement of Benzene (airmoVOC C6-C12 - MCERTS Performance Standards for Continuous Ambient Air Quality Monitoring Systems, Version 8, dated June 2012; EN 15267-1:2009, EN 15267-2:2009 & EN 14662-3:2005).

3. Results

3.1 Calibration and standards analysis

Before the campaigns, the systems were calibrated and tested for two weeks in laboratory. Certified cylinders and permeation tubes were used for calibration and for the verification of retention times and response factors. We describe in the next sections the results obtained with the analysis of the NPL cylinders for both auto-TDGC-FID (Same procedure has been done for TO14, TO15 and PAMS 58).

3.1.1 Calibration of auto-TDGC-FID for C2 to C6 analysis

The chromatogram obtained with the auto-TDGC-FID for the analysis of C2-C6 is displayed in the Figure 1. The NPL cylinder contains 30 compounds at 12 ppb (± 2%). The analytical conditions allow for excellent separation and quantification of all compounds within 30 minutes. As expected using this type of column, the saturated compounds elute faster than the equivalent unsaturated ones. For example, propane and propene elute at 58s and 162s respectively. Also, good separation is obtained with isomers. n-butane and i-butane elutes at 195s and 215s respectively (with peak width of 10s). During the measurement campaign, benzene and n-hexane will be measured on the auto-TDGC-FID for C6-C12 even though they can be analyzed by the C2-C6.

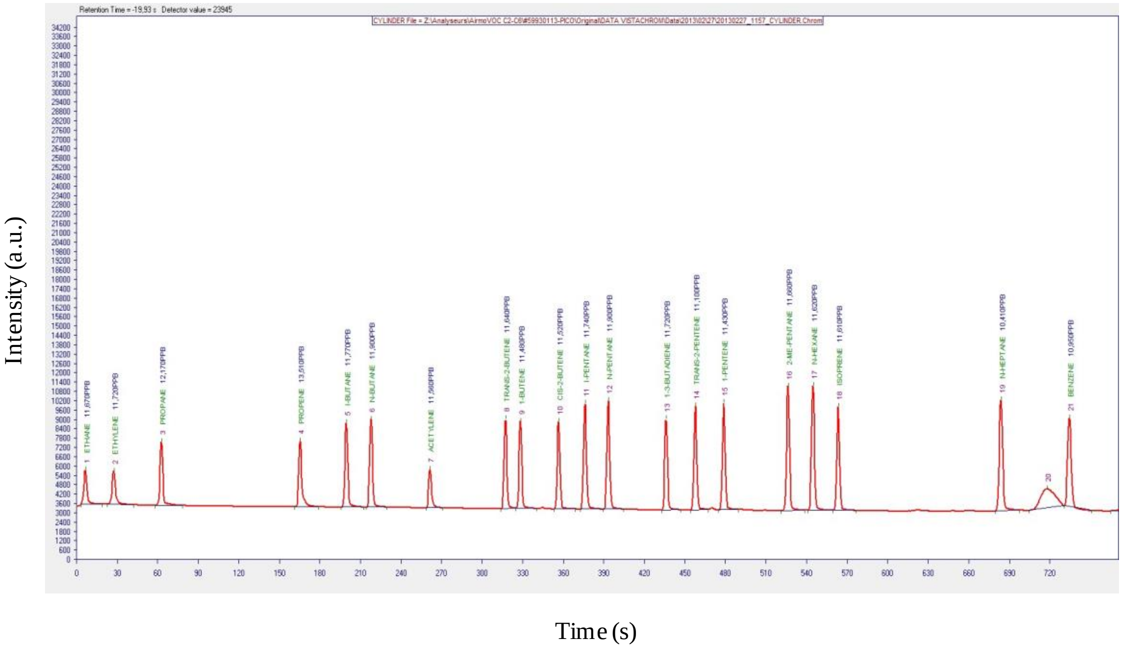

Figure 1: Chromatogram obtained with the NPL cylinder for the analysis of C2-C6.

Once the retention times and response factors have been checked, a linearity test is carried out with another NPL cylinder at 1 ppm (± 5%) using a dilution system equipped with two mass flow controllers (airmoCAL MFC, Chromatotec, France). 5 measurements were performed for each concentration. In the Figure 2 are shown the results obtained varying the concentration from 0 ppb to 150 ppb. The linearity is excellent with $R^2 \geq 0.9996$ for all compounds.

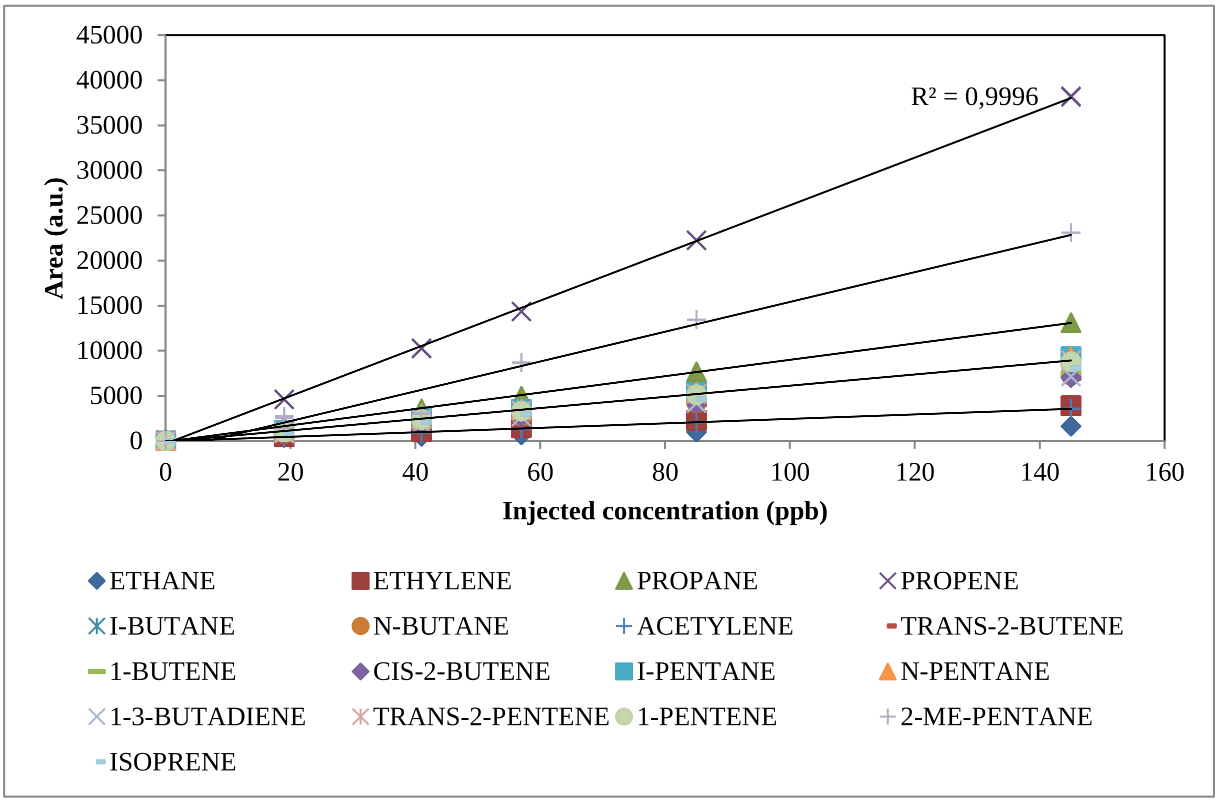

Figure 2: Area measured as a function of the injected concentration (ppb) for each analyzed compound (C2-C6).

3.1.2 Calibration of auto-TDGC-FID for C6 to C12 analysis

The chromatogram obtained with the auto-TDGC-FID for the analysis of C6-C12 is displayed in the Figure 3. The NPL cylinder is the same than the one used for the C2-C6 analysis (30 compounds at 12 ppb ± 2%). All compounds can be identified and quantified separately expect for m-xylene and p-xylene. Therefore the sum of the two compounds will be given. For chlorinated compounds which can be measured in industrial area, the TO14 and TO15 cylinders were used (data not shown). Similar results were obtained with this procedure using PAMS 58 cylinders. Once the retention times and response factors have been checked, a linearity test is carried out with the same procedure as the one used for C2-C6. 5 measurements were performed for each concentration. In the Figure 4 are shown the results obtained varying the concentration from 0 ppb to 150 ppb. The linearity is excellent with $R^2 \geq 0.9996$ for all compounds.

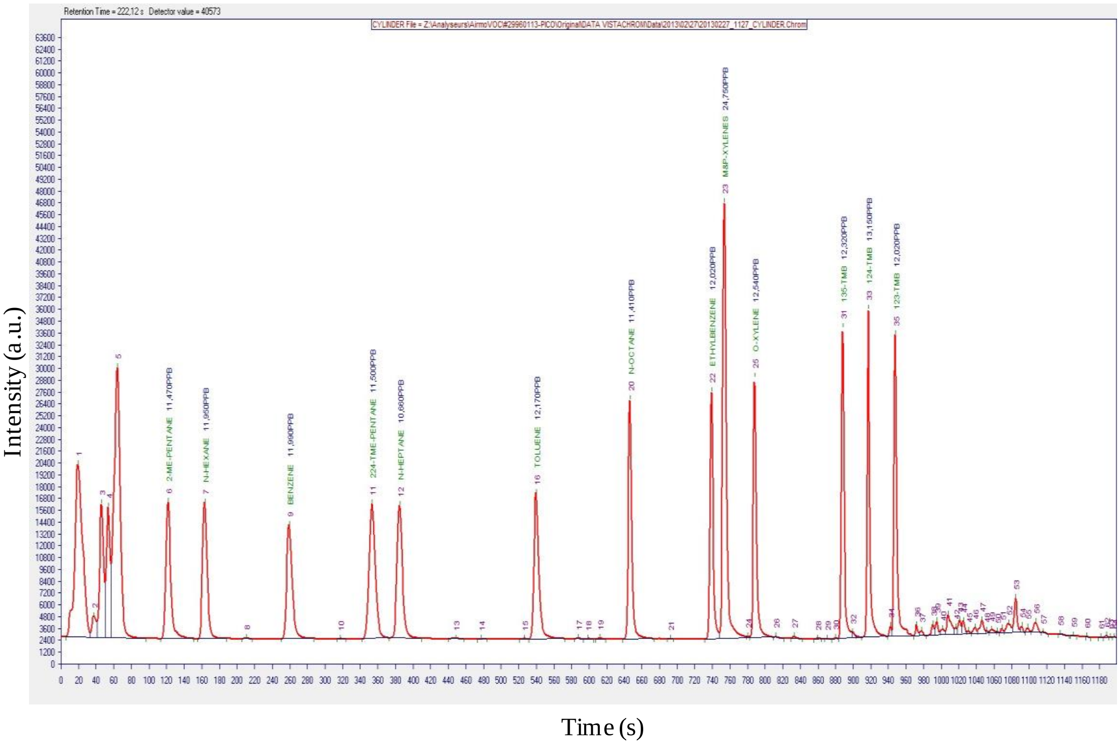

Figure 3: Chromatogram obtained with the NPL cylinder for the analysis of C6-C12.

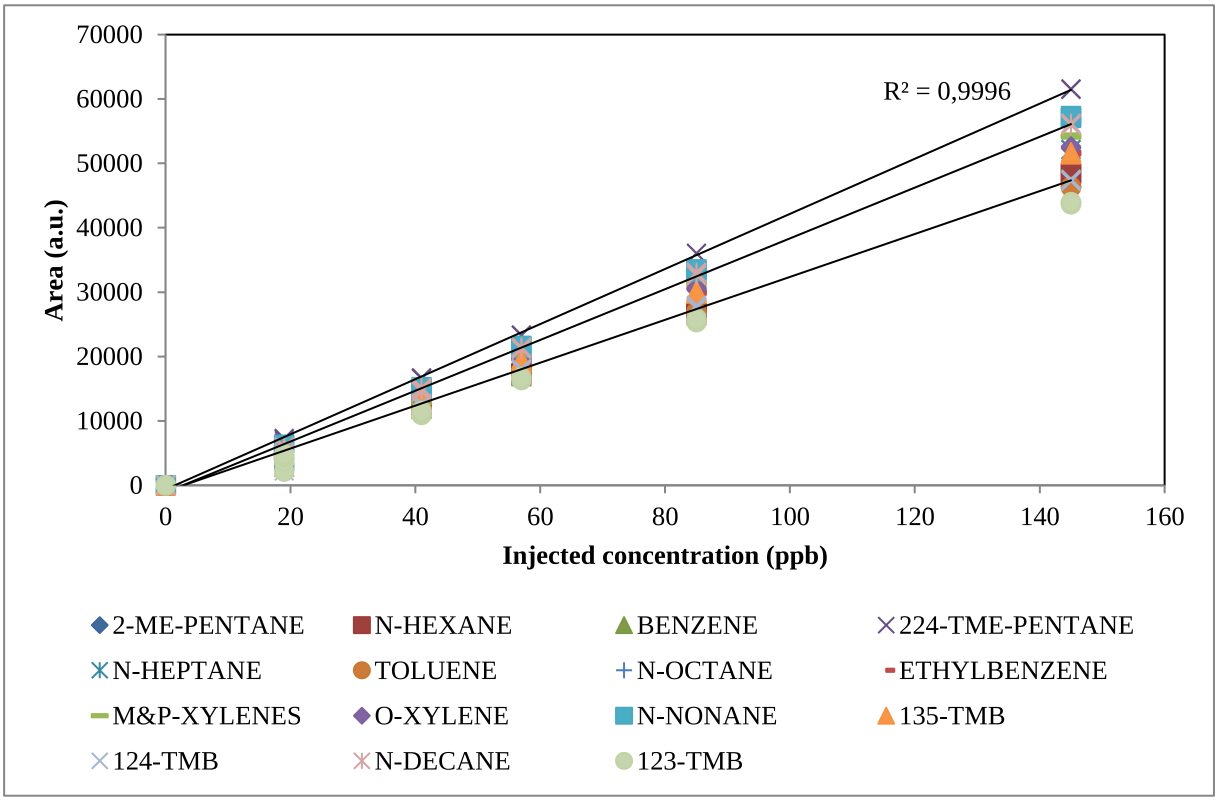

Figure 4: Area measured as a function of the injected concentration (ppb) for each analyzed compound (for C6-C12).

3.2 Statistics and Data Analysis for C2-C6

The C2-C6 monitored at the different sites can be classified in two different categories: i) saturated compounds such as ethane, propane, iso-butane, n-butane, cyclopentane, iso-pentane, n-pentane, 2,2-dimethyl-pentane, methyl-cyclopentane, 2,3-dymethyl-butane, 2-methyl-pentane, ii) unsaturated compounds such as ethylene, propene, acetylene, trans-2-butene, 1-butene, iso-butene, csi-2-butene, 1,3-butadiene, trans-2-pentene, 1-pentene, cis-2-pentene and isoprene. In the Figure 5 and Figure 6 the mean concentrations of each compound are displayed for the saturated and unsaturated compounds respectively. The concentrations vary from below detection limit (0.038 µg.m^{-3}) to 100 µg.m^{-3} in Bangkok (for propane). For saturated and unsaturated hydrocarbons, the highest concentrations are always measured either in Bangkok or in Bordeaux. Surprisingly, the concentrations measured in the industrial area are quite low as compared to the concentrations measured in Bordeaux and Bangkok. For instance the propane concentrations are 12.35 µg.m^{-3} in the industrial area, 106.31 µg.m^{-3} in Bangkok, 0.40 µg.m^{-3} on the seaside and 22.50 µg.m^{-3} near Bordeaux. The level of isoprene, produced and emitted by many species of trees into the atmosphere, is more concentrated in Bordeaux (11.95 µg.m^{-3}) than in the three other sites in Thailand (from 0.7 up to 4 µg.m^{-3}).

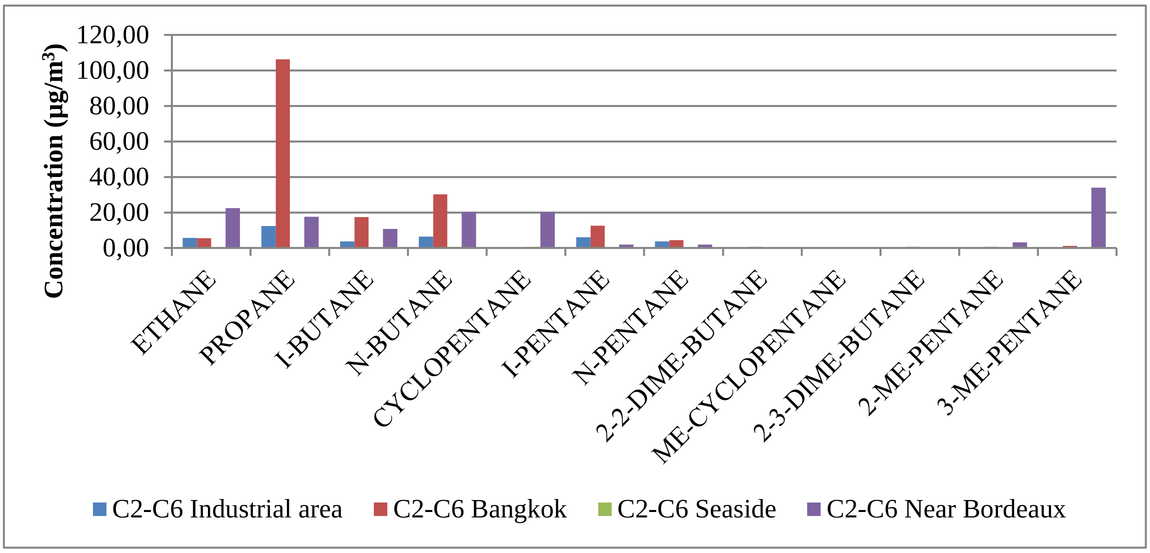

Figure 5: Concentrations (µg/m^3) of saturated hydrocarbons measured in the Industrial area, in Bangkok, on the seaside and near Bordeaux.

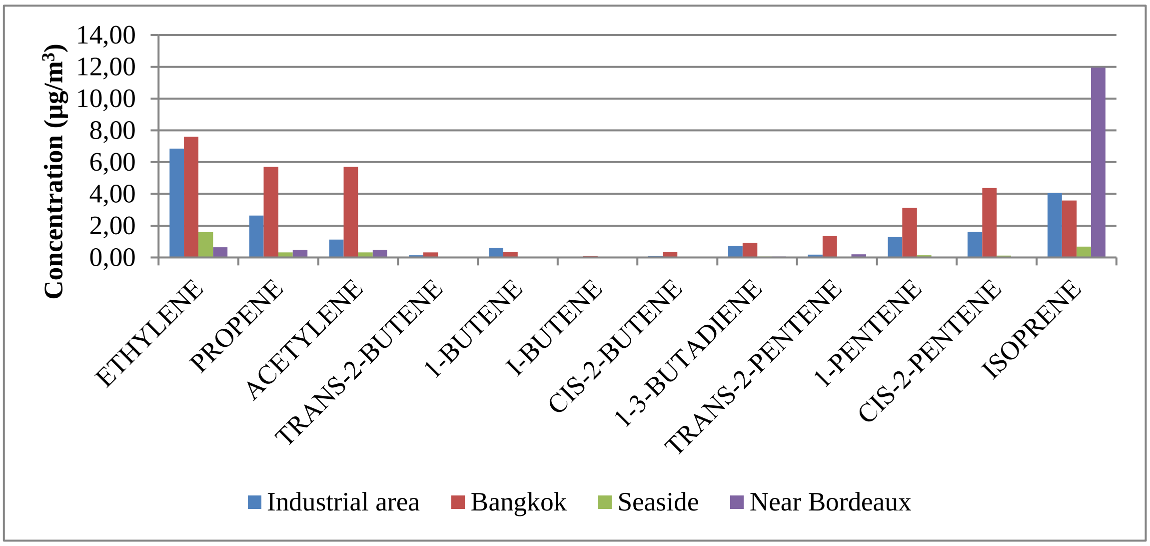

Figure 6: Concentrations (µg/m^3) of unsaturated hydrocarbons measured in the Industrial area, in Bangkok, on the seaside and near Bordeaux.

The trend of propane measured in Bangkok shows that the concentration varies a lot during the three days of measurement from 8.74 µg.m^{-3} up to 599.28 µg.m^{-3} (Figure 7). Three times, plateaus can be observed at 20 µg.m^{-3} followed by very high increase of concentration; Twice the increase of concentrations occurs between 4 and 5 am on the 21st and 22nd respectively.

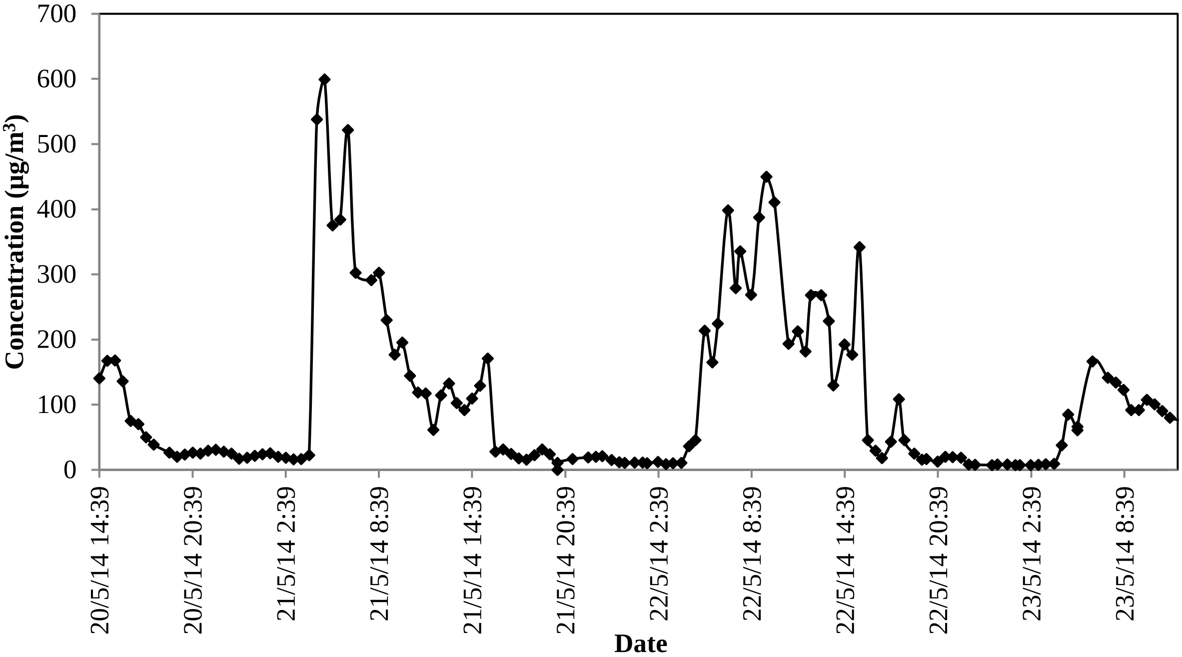

Figure 7: Evolution of propane concentrations (µg.m^{-3}) measured in Bangkok for 3 days.

3.3 Statistics and Data Analysis for C6-C12.

The C6-C12 monitored at the different sites can be classified in 6 different categories: i) The BTEX compounds: benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene, ii) the terpenes: alpha-pinene, beta-pinene and limonene, iii) Alkanes: n-hexane, 2,4-dimethylpentane, 2,3-dimethylpentane, 2-methyl-hexane, 3-methyl-hexane, 2,2,4-trimethyl-pentane, n-heptane, 2,3,4-trimethyl-pentane, 2-methyl-heptane, 3-methyl-heptane, n-octane, n-nonane, n-decane, n-undecane and n-dodecane, iv) Sum of dichlorobenzene: 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, v) cycloalkanes: cyclohexane, methyl-cyclohexane, vi) other: (see list in the appendix B) and two compounds were analyzed separately: Naphthalene and styrene. The concentrations are much higher for the C6-C12 in the three sites in Thailand than near Bordeaux (Figure 8). Particularly, the mean BTEX concentration in Bangkok is nearly 300 µg.m^{-3}. In comparison, the mean BTEX concentration in Bordeaux is 2.33 µg.m^{-3}.

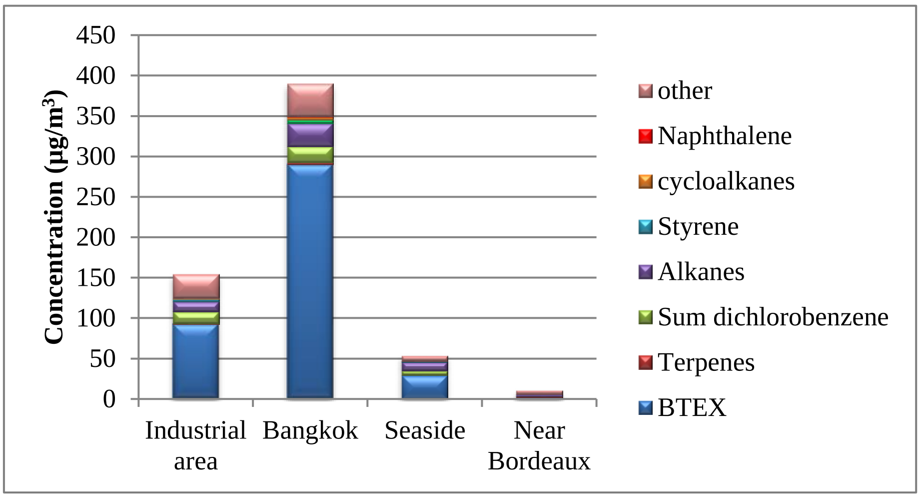

Figure 8: Concentrations of the different compounds measured in the Industrial area, in Bangkok, at the seaside and near Bordeaux.

In order to understand the origin of the BTEX measured in the different area, diagrams have been drawn in the Figure 9. We can see that the proportion is different depending on the measuring site. The percentage of toluene and benzene are very high near Bordeaux (41.6% and 18.7% respectively), while the benzene percentage is very low in the three site in Thailand. Especially in Bangkok we measured only 0.9% of benzene.

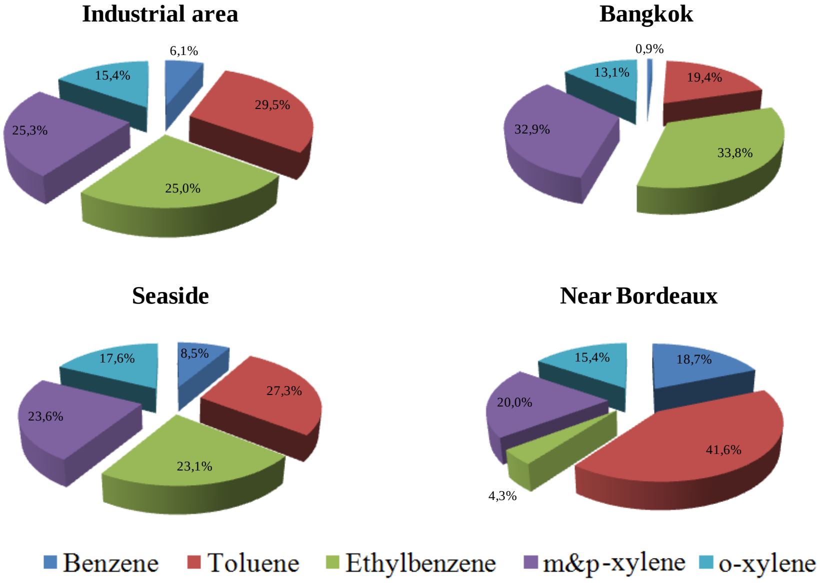

Figure 9: Diagrams of the percentage of benzene, toluene, ethylbenzene, m&p-xylene and o-xylene.

As the BTEX concentrations were very important compared to the other compounds, another graph showing the other important pollutants has been displayed in the Figure 10. The alkane concentration is much higher in Bangkok than in the three other sites. On the other hand, styrene is only monitored in Thailand and particularly in the industrial area (3.29 µg.m^{-3}) and in Bangkok (4.26 µg.m^{-3}). Near Bordeaux, the mean styrene concentration is 0.020 µg.m^{-3}. Cycloalkanes such as cyclohexane and methyl cyclohexane are one order of magnitude higher in Bangkok than in the other places. Finally, Naphthalene has been recorded has a marker of the polycyclic aromatic hydrocarbons (PAHs) pollution. We observe that the concentration is higher in Bangkok (0.4 µg.m^{-3}) than in the other places (0.13 µg.m^{-3} for seaside).

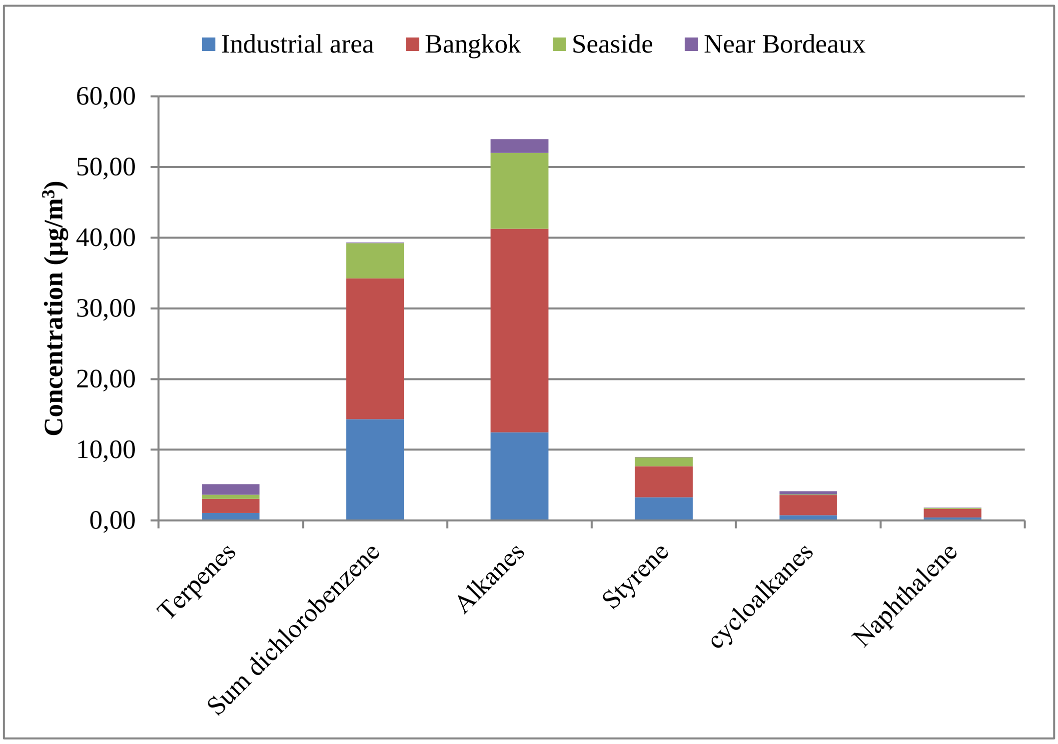

Figure 10: Concentrations of terpenes, sum of dichlorobenzene, alkanes, styrene, cycloalkanes, and naphthalene measured in the Industrial area, in Bangkok, at the seaside and near Bordeaux.

4. Discussion

The calibration procedure and stability tests carried out before the measurements on site are of utmost importance. The certified cylinders allow for the verification of instrument stability and performance for the different compounds. Few compounds such as n-hexane or benzene can be measured by both instruments, allowing inter-comparison of concentrations. If both analyzers do not have the same response for such compounds, it indicates either a coelution or a problem with the instrument. For the measurement on site, the permeation tubes allow for verification of retention time and quantification stability.

Liakakou et *al.*[8] reported in 2009 the seasonal variation of C2-C8 NMTHC in the rural environment in Greece and compared the results with already published data. The measured concentrations are lower than the ones measured in France and Thailand. Ethane concentration in Greece was 1.653 µg.m^{-3} while we measured near Bordeaux 15.50 µg.m^{-3}. For propane, the difference is very important between the levels measured in Bangkok and in the industrial area as compared to the concentrations measured in France, on the seaside in Thailand and in Greece. As it can be seen in the Figure 7, important variations of propane concentrations can be recorded and could be explained by punctual industrial uses of propane gas.

As expected, very high concentrations of BTEX are monitored in Bangkok due to the very important traffic. Barletta et *al.*[9] reported in 2005 the VOCs concentrations, including BTEX, in 43 Chinese cities. The benzene concentration was similar to the one measured in Bangkok and in the industrial area. For Toluene, ethylbenzene, m&p-xylene and o-xylene, the concentrations measured in Bangkok are 10 times higher than the values reported by Barletta et *al.*[9] Also, the trend of concentrations shows that the TEX values measured in Bangkok are always high. We cannot see important concentration variations during the three days of measurement (data not shown) which indicates that the pollutant are emitted at a similar level constantly.

Terpene concentrations can be a very important source of VOCs where the vegetation is very dense. Near Bordeaux, due to the Landes forest, important concentration of terpenes can be monitored. This Landes forest is located in the south-west of France and is one of the largest forest in Europe (1 million ha), relatively homogeneous with more than 90 % of maritime pines (pinus pinaster) and few anthropogenic inputs. The measurement of monoterpenes (MT) and MT precursors have already been reported to study seasonal variations of Mediterranean Sea emissions[10] and for the characterization of plant-specific VOC emission rates.[11] Isoprene, alpha-pinene, beta-pinene and limonene have been monitored for all sites. We observe that terpenes concentrations for all sites are quite similar (between 0.6 µg.m^{-3}and 1.98 µg.m^{-3}) but the ratios are very different (14.1% of total C6-C12 near Bordeaux and 0.5% of total C6-C12 in Bangkok).

Cyclohexane can be emitted in large quantities by motorcycles.[12] This can explain the important concentration measured in Bangkok where this mean of transportation is very much used. In the other places, cycloalkane concentrations are very low. Sum of dichlorobenzene and styrene come from anthropogenic emissions and can be used as marker for industrial activity. They are logically measured at high concentration in Bangkok and in the industrial area. Other compounds could be seen but not identified with the auto-TDGC-FID technology. Therefore further studies will be conducted with an auto-TD-GC-FID/MS to identify all compounds emitted in cities and by the industries. Naphthalene was also recorded as a marker of the PAHs variations but the levels measured in all places were relatively low, i.e. between 0.1 and 0.5 µg.m^{-3}.

The systems used for the study were suited for VOCs monitoring in temperate and tropical climate. Also, the system allows for measurement over a wide range of concentrations allowing the monitoring in rural and urban regions (from 0.02 to 500 µg.m^{-3}). The obtained data gives a clear overview of the pollutants and allows for identifying the possible emission sources.

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Appendix A

Type	Compound	Industrial area (µg/m^3)	Bangkok (µg/m^3)	Seaside (µg/m^3)	Near Bordeaux (µg/m^3)
Saturated	ETHANE	5,32	6,43	0,51	15,50
	PROPANE	6,87	132,49	0,96	12,05
	I-BUTANE	1,39	18,17	0,31	7,93
	N-BUTANE	4,68	29,25	0,56	16,50
	CYCLOPENTANE	1,17	0,00	0,56	16,50
	I-PENTANE	13,30	17,72	0,67	8,82
	N-PENTANE	8,99	0,00	0,18	4,39
	2-2-DIME-BUTANE	0,00	0,00	0,00	0,00
	ME-CYCLOPENTANE	0,00	1,94	0,00	0,00
	2-3-DIME-BUTANE	0,57	0,00	0,00	0,00
	2-ME-PENTANE	0,00	0,78	0,00	0,00
	3-ME-PENTANE	0,00	0,00	0,00	27,13
Unsaturated	ETHYLENE	9,89	6,63	1,77	0,65
	PROPENE	5,21	5,88	0,28	0,54
	ACETYLENE	1,63	5,88	0,28	0,54
	TRANS-2-BUTENE	0,29	0,00	0,00	0,00
	1-BUTENE	0,55	0,00	0,00	0,18
	I-BUTENE	0,00	0,00	0,00	0,00
	CIS-2-BUTENE	0,37	1,43	0,00	0,13
	1-3-BUTADIENE	1,16	0,26	0,00	0,39
	TRANS-2-PENTENE	0,27	3,80	0,00	0,62
	1-PENTENE	1,96	0,00	0,17	0,22
	CIS-2-PENTENE	2,54	9,35	0,14	0,19
	ISOPRENE	4,14	8,96	0,18	11,99

Table 1: Mean concentrations measured with the TDGC-FID dedicated to the measurement of C2-C6.

Appendix B

	Industrial area (µg/m3)	Bangkok (µg/m3)	Seaside (µg/m3)	Near Bordeaux (µg/m3)
BTEX	92,75	290,75	29,44	2,33
Terpenes	1,06	1,98	0,61	1,46
Sum dichlorobenzene	14,34	19,90	4,96	0,09
Alkanes	12,48	28,80	10,72	1,95
Styrene	3,29	4,36	1,26	0,02
cycloalkanes	0,73	2,87	0,10	0,43
Naphthalene	0,42	1,22	0,13	0,07
other	29,30	40,05	6,13	4,00

Table 2: Mean concentrations measured with the TDGC-FID dedicated to the measurement of C6-C12.

Appendix C

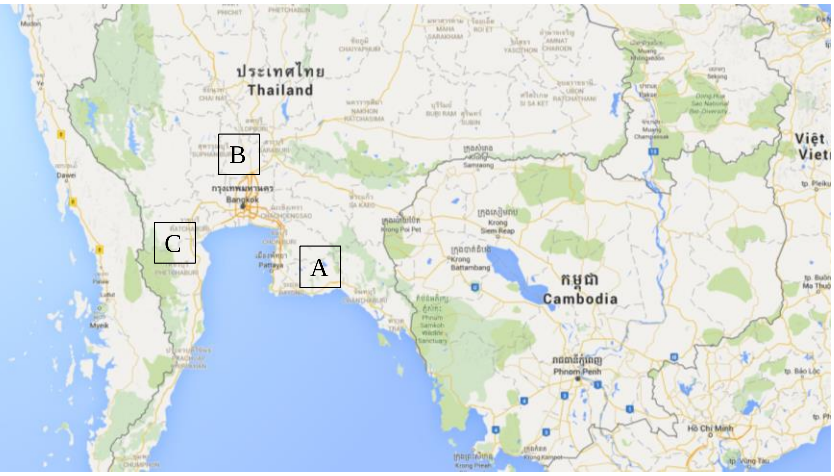

Figure 11: Different sites in Thailand where measurement has been carried out.

Figure 12: Site in France where measurement has been carried out.