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Etude et caractérisations de la pollution atmosphérique de la région de Ouargla

(Study and Characterizations of atmospheric pollution in Ouargla city)

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Symbols

ACE: acetone

BTEXs: Benzene, toluene, ethyl benzene, Xylenes

CPI: Carbon Preference Indexes

DCM: dichloromethane

D : Home

EC: element of carbon

EU: the *European Union*

GC/MS :Gas chromatography–mass spectrometry

GC/FID: Gas Chromatography – Flame Ionization Detector

H :Hospital

IRAC : International Agency for Research on Cancer

LODs : Limit of detection

LOQs : Limit of quantification

OC: organic carbon

PAHs: polycyclic aromatic hydrocarbons

PAS: Passive Sampler

PCBs: polychlorobiphenyls

PCDD/Fs: polychlorodibenzodioxins and furans

PM: Particulate Matter

PM_{2.5} : Particulate matter with an aerodynamic diameter less than 2.5 micrometers

PM₁₀ : Particulate matter with an aerodynamic diameter less than 10 micrometers

S = Schools

SIM: Selective ion monitoring

TMP: Trimethylpentane

U : University

US: the United States

US EPA: United States Environmental Protection Agency

VOCs: volatile organic compounds

Wax -C_n : Concentration of alkanes biogenic

WHO: *World Health Organization*

DEDICATION

I dedicate this work to my beloved family especially my parents, my brothers and sisters, My neighbors .Second family .The whole family and all my friends

My grandmother God rest her soul

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General Introduction

General Introduction:

Air is made up of 78% nitrogen 21% oxygen, less than 1% carbon dioxide, and trace amounts of other gases .The World Health Organization (WHO) defines air pollution as “substances put into the air by the activity of mankind into concentrations sufficient to cause harmful effects to health”. Air pollution means “the presence or deleterious discharge, from whatever source, of solid, liquid or gaseous matter or any combination thereof, in the ambient air in sufficient quantities and of such characteristics and duration which: injures or threatens to injure human, plant or animal life”.

The world atmospheric pollution problem started as an outcrop of the Industrial Revolution.Many international organizations are studying the reasons for this problem and searching for solutions. In this study, we determined qualitatively and quantitatively organiccompounds in the particulate matter of the gas phase and the dust, and looked for volatile organic compounds in the indoor and outdoor ambient air for different sites in the city of Ouargla, Algeria. This is the first study of its kind in this region.

The thesis comprises five chapters:

The first deals have some generality of pollution atmospheric (type of pollution , definition , sources ,...) , effect health and environment .

The Second chapter we will determine the organic compound by GC/MS (Gas Chromatography /Mass Spectrometry) in gas phase using the sampler PUF-disks indoor and outdoor of university sites, schools and hospitalduring the autumn season 2014. Moreover, we made a sampling collection of dust indoors (room) on the autumn 2014.

The third chapter studies with the same sampling of the PUF- disks at summer season 2015 , indoor /outdoor collecting the dust at autumn 2015 , it compares the levels of organic compounds and sources between the same sites in different times.

In the fourth chapter we detect the BTEX (Benzene, Toluene ,ethyl benzene and Xylene) indoor /outdoor in hospital and university sites ,during the autumn seasons of 2014 and 2015. BTEX considered in volatile organic compounds were collected by means of diffusive samplers and determined through gas chromatography coupled with flame ionization detection (GC-FID).

In the fifth chapter we describe the discovery of volatile organic compounds in hospital and university sites sampled during the autumn 2015. We focus on the PAHs (polycyclic aromatic hydrocarbons), which collected by means of diffusive technique, it determined the PAHs by gas chromatographic - mass spectrometric analysis (GC/MS).

The goal of the present study aims at determining precise concentration and sources of the daily pollutants in homes and work places inside and outside. We also provide tentative solutions for diminishing the damage of these pollutants. Indoor sites especially are effect of human health

Chapter I:

**General information of pollution (definition , sources ,
impact of health...)**

I.1. Introduction:

Pollution is the introduction of contaminants into a natural environment that causes instability, disorder, harm or discomfort to the ecosystem i.e. physical systems or living organisms. Pollution can take the form of chemical substances or energy, such as noise, heat, or light. Pollutants, the elements of pollution, can be foreign substances or energies, or naturally occurring; when naturally occurring, they are considered contaminants when they exceed natural levels. Pollution is often classed as point source or nonpoint source pollution [1]. Pollution may be defined as addition of undesirable material into the environment as a result of human activities. The agents which cause environmental pollution are called pollutants. A pollutant may be defined as a physical, chemical or biological substance released into the environment which is directly or indirectly harmful to humans and other living organisms.

I.2. forms of pollution :

The major forms of pollution are:

I.2.1 Air pollution:

The present-day atmosphere is quite different from the natural atmosphere that existed before the Industrial Revolution, in terms of chemical composition. If the natural atmosphere is considered to be “clean”, then this means that clean air cannot be found anywhere in today’s atmosphere. Air pollution describes the concentrations that cause damage to humans, plant, animal life, human-made materials and structures. According to US EPA the air pollution and air pollutant are defined .An air pollutant is any substance in the air that can cause harm to humans or the environment. Pollutants may be natural or manmade and may take the form of solid particles, liquid droplets or gases. These pollutants are divided into various groups, including particulate matter, volatile organic compounds (VOCs) and halogen compounds. Also included are commonly-known pollutants such as lead, mercury and asbestos.” [1- 4]

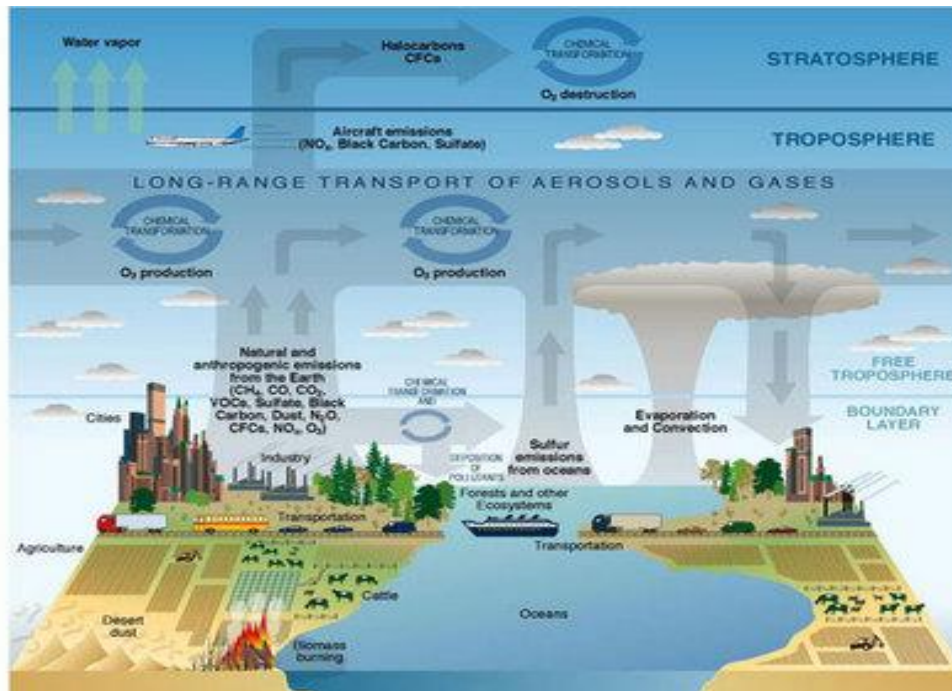


Figure I.1: Processes related to atmospheric composition[11]

I.2.2. Water Pollution:

Water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans and groundwater). Water pollution affects plants and organisms living in these bodies of water; and, in almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities. Water pollution occurs when pollutants are discharged directly or indirectly into waterbodies without adequate treatment to remove harmful compounds.[1]

I.2.3. Soil Pollution:

Soil pollution is caused by the presence of xenobiotic (human-made) chemicals or other alteration in the natural soil environment. This type of contamination typically arises from the rupture of underground storage tanks, application of pesticides, percolation of contaminated surface water to subsurface strata, oil and fuel dumping, leaching of wastes from landfills or direct discharge of industrial wastes to the soil. The most common chemicals involved are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. This occurrence of this phenomenon is correlated with the degree of industrialization and intensities of chemical usage. In addition, fertilizers and pesticides from agricultural use which reach soil as run-off and land filling by municipal waste are growing cause of soil pollution. Acid rain and dry deposition of pollutants on land surface

also contribute to soil pollution. The concern over soil contamination stems primarily from health risks, from direct contact with the contaminated soil. [1]

I.3. Pollutants :

An air pollutant is known as a substance in the air that can cause harm to humans and the environment. Pollutants can be in the form of solid particles, liquid droplets, or gases. In addition, they may be natural or man-made. Pollutants can be classified as either primary or secondary. As shown in figure I.1 [1– 5]

I.3.1. Classified pollutants:

I.3.1.1. Primary Pollutants:

Primary pollutants are substances directly emitted from a process. Major primary pollutants produced by human activity include the main these pollutants the following:

- Carbon compounds, such as CO, CO₂, CH₄, and VOCs [1,5]
- Nitrogen compounds, such as NO, N₂O, and NH₃ [1,5]
- Sulfur compounds, such as H₂S and SO₂ [1,5]
- Heavy metals (Pb, Cd....) [1,5]

I.3.1.2. Secondary pollutants :

Secondary pollutants are not directly emitted from sources, but instead form in the atmosphere from primary pollutants (also called “precursors”). The main secondary pollutants known to cause harm in high enough concentrations are the following :

- NO₂ and HNO₃ formed from NO [1,5]
- Ozone (O₃) formed from photochemical reactions of nitrogen oxides and VOCs [1,5]
- Sulfuric acid droplets formed from SO₂ and nitric acid droplets formed from NO₂ [1,5]

I.3.2 Sources:

Sources of air pollution refer to the various locations, activities or factors which are responsible for the releasing of pollutants in the atmosphere. These sources can be classified into two major categories which are , in table I.1 explained all compound and sources :

I.3.2.1 Anthropogenic sources:

(Human activity) mostly related to burning different kinds of fuel

- "Stationary Sources" include smoke stacks of power plants, manufacturing facilities (factories) and waste incinerators, as well as furnaces and other types of fuel-burning heating devices [1,5]
- "Mobile Sources" include motor vehicles, marine vessels, aircraft and the effect of sound etc.[1,5]
- Chemicals, dust and controlled burn practices in agriculture and forestry management. Controlled or prescribed burning is a technique sometimes used in forest management, farming, prairie restoration or greenhouse gas abatement. [1,5]
- Fumes from paint, hair spray, varnish, aerosol sprays and other solvents [1,5]

I.3.2.2 Natural sources :

- Dust from natural sources, usually large areas of land with little or no vegetation.[1,5]
- Methane, emitted by the digestion of food by animals, for example cattle.[1,5]
- Radon gas from radioactive decay within the Earth's crust. Radon is a colorless, odorless, naturally occurring, [1,5]

radioactive noble gas that is formed from the decay of radium. It is considered to be a health hazard. Radon gas[1,5]

from natural sources can accumulate in buildings, especially in confined areas such as the basement and it is the second most frequent cause of lung cancer, after cigarette smoking.[1,5]

- Smoke and carbon monoxide from wildfires.[1,5]
- Volcanic activity, which produce sulfur, chlorine, and ash particulates.[1,5]

I.3.3 Particulates matter :

PM consists of tiny particles of solids or liquids, suspended in the air. Particles are divided into different classes, depending on their aerodynamic diameter: large particles ($>10\ \mu\text{m}$) and inhalable particles ($< 10\ \mu\text{m}$). The inhalable particles can be further divided into three subcategories: coarse particles ($2.5\text{-}10\ \mu\text{m}$), fine particles ($0.1\text{-}2.5\ \mu\text{m}$) and ultrafine particles ($< 0.1\ \mu\text{m}$). PM_{10} and $\text{PM}_{2.5}$ denote particles with an aerodynamic diameter of less than $10\ \mu\text{m}$ and $2.5\ \mu\text{m}$, respectively. Consequently, $\text{PM}_{2.5}$ is included in PM_{10} . Major source of SPM (suspended particulate matter) are vehicles, power plants, construction activities, oil refinery, railway yard, market place, industries [13] .

Particulate matter (PM) is composed of inert carbonaceous cores with multiple layers of various adsorbed molecules, including metals, organic pollutants, acid salts and biological

elements, such as endotoxins, allergens and pollen fragments. PM is classified in the following types. The extent to which airborne particles penetrate the human respiratory system is determined mainly by size, with possible health effects resulting from the presence of toxic substances (in figure I.2). Visibility degradation is known to be a function of both the size and composition of the airborne particles. A clear distinction is that particles smaller than $2.5\ \mu\text{m}$ penetrate into the alveoli and terminal bronchioles; larger particles of up to $10\ \mu\text{m}$ will deposit primarily in the primary bronchi, and much larger particles (up to $100\ \mu\text{m}$) will deposit in the nasopharynx. These particles are dominated by sulfates, nitrates, organic carbon (OC) and, namely, elemental carbon (EC). Ultrafine particles (UFPs) present a particular health threat in that their small size allows greater lung penetration and onward passage across the air-blood barrier. [5-9]

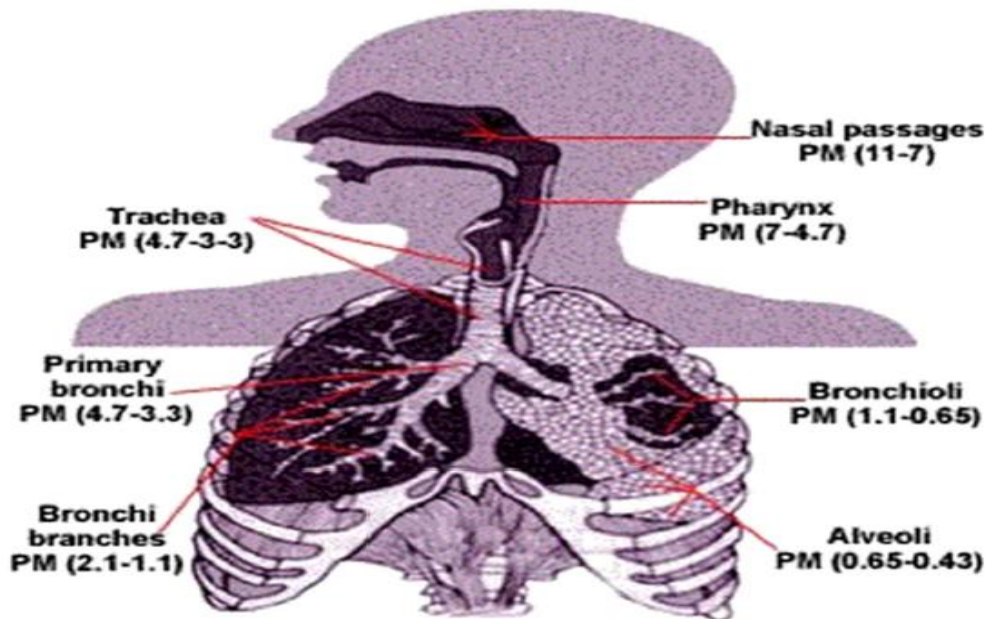


Figure I.2: Deposition potential for particles of varying sizes

[6]

I.3.4 Volatiles organic compounds VOCs:

I.3.4.1 Definitions:

The general definition of VOCs is used in the scientific literature which is consistent with the definition used for indoor air quality of the USEPA. According to USEPA in their regulations for indoor air, Volatile organic compounds or VOCs are organic chemical compounds whose composition makes it possible for them to evaporate under normal indoor atmospheric conditions of temperature and pressure.

Volatility is indicated by a substance's vapor pressure. As the volatility of a compound is generally higher, the lower its boiling point temperature and that's why the volatility of organic compounds are sometimes defined and classified by their boiling points.

The European Union uses the boiling point, rather than its volatility in its definition of VOCs. According to the EU Paint Directive, 2004/42/EC (EU, 2004), defines VOC as an organic compound having an initial boiling point lower than or equal to 250 °C at an atmospheric pressure of 101.3kPa. Similarly, the European Eco-Labeling scheme (2002/739/EC amending 1999/10/EC) for paints and varnishes defines a VOC as an organic compound with a boiling point (or initial boiling point) lower than or equal to 250°C. [9-11].

I.3.4.2 Indoor /outdoor sources:

the meta-analysis of 77 surveys of VOCs in homes in the US found the top ten riskiest indoor air VOCs were Acrolein, Formaldehyde, Benzene, Hexachlorobutadiene, Acetaldehyde, 1,3-butadiene, Benzyl chloride, 1,4-dichlorobenzene, Carbon tetrachloride, acrylonitrile, and Vinyl chloride. These compounds in most homes exceeded health standards . Human activities such as cooking and smoking also contribute to indoor VOCs .Other contributors had been cited which includes, solid fuel combustion , emissions following house renovations , poor ventilation , and insecticide application . Outdoor sources (e.g. industrial emissions, exhaust from vehicles) also contribute to indoor VOCs . In indoor, the main sources of VOCs are building materials, furnishings, cleaning products, dry cleaning agents, paints, varnishes, waxes, solvents, glues, aerosol propellants, refrigerants, fungicides, germicides, cosmetics and textiles, appliances, air fresheners and clothing. Attention to ambient and indoor VOCs has been increased ever since with the growing concern for quality life in safe and clean environment .[4-5,10,12]

I.4. Health effects and environment of air pollution:

Many forms of atmospheric pollution affect human health and the environment at levels from local to global.

I.4.1. Health Effects:

Air pollution can harm us when it accumulates in the air in high enough concentrations. The toxic pollutants pose serious health concerns. People exposed of short and long term epidemiological studies investigated the effects of air quality changes on human are

usually exposed to pollutant mixtures than to single substances, can lead to diverse impacts on human health. Human health effects can range from:

- * Irritation of the eyes, nose, and throat [13-16,19,21].
- * Wheezing, coughing, chest tightness, and breathing difficulties [13-16,19,21].
- * Worsening of existing lung and heart problems, such as asthma [13-16,19,21] .
- * Increased risk of heart attack [13-16,19,21] .

In addition, long-term exposure to air pollution can cause cancer and damage to the immune, neurological, reproductive, and respiratory systems. In extreme cases, it can even cause death. [13-16,19,21] .

I.4.2. Environmental Effects

Along with harming human health, air pollution can cause a variety of environmental effects table 1 explained al compound and effected of health:

*Acid rain is precipitation containing harmful amounts of nitric and sulfuric acids. These acids are formed primarily by nitrogen oxides and sulfur oxides released into the atmosphere when fossil fuels are burned.[17-18]

*Influence of meteorological conditions (greenhouse effect) [8,17-18]

*Effects on ecosystems: forest, freshwater reserve[17-18]

Table.I.1: Gaseous air pollutants: their sources and effects

Pollutant	Source	Harmful effect
Carbon compound	Automobile exhaust Burning of the wood and coal	– Respiratory problems (CO and CO ₂) Green house effect
Sulphur compounds (SO ₂ and H ₂ S)	Power plants and refineries volcanic eruptions	–Respiratory problems in humans Loss of chlorophyll in plants (chlorosis) – Acid rain
Nitrogen Compound (NO and N ₂ O)	Motor vehicle exhaust atmospheric reaction	– Irritation in eyes and lungs Low productivity in plants – Acid rain damages material (metals and stone)
Hydrocarbons (benzene, ethylene) SPM (Suspended Particulate Matter) (Any soild and liquid) particles suspended in the air, (flush, dust, lead)	Automobiles and petroleum industries Thermal power plants,, Construction activities metallurgical processes and automobiles	– Respiratory problem –Cancer causing properties – Poor visibility; breathing problems -Lead interfere with the development of red blood diseases and cancer -Smog (smoke & fog) formation leads to poor visibility and aggravates asthma in patients

I.5.Reference :

- [1]Shafi . S.M., environmental pollution.2005.copyright Atlantic Publishers and distribution, printed India,p:50,133,260.
- [2] Daly, A. and P. Zannetti. 2007. *An Introduction to Air Pollution –Definitions, Classifications, and History*. Chapter 1 of *ambient air pollution*.
- [3] Fernandes, E. de Oliveira , Characterisation of spaces and sources ENVIE Co-ordination Action on Indoor Air Quality and Health Effects Project no. SSPE-CT-2004-502671 , p 15-28 .
- [4] Proposal for a Regional Action Plan for Intergovernmental Cooperation on Air Pollution for Latin America and the Caribbean, October 2013,UNEP/LAC-IGWG.XIX/7,p18-p31.
- [5] Nsengimana,H., Bizimana,J. P., Sezirahiga,Y.,a study on air pollution in Rwanda with reference to Kigali city and vehicular emission.,Copyright: Rwanda Environment Management Authority., 2011,p 47,49,54,57,75-80.
- [6]Kim, K.H., Kabir ,E., Kabir, S., 2015.A review on the human health impact of airborne particulate matter. *Environment International* 74 , 136–143.
- [7]Araújo ,I. P. S. , Costa ,D. B. , and Rita J. B., 2014. Identification and Characterization of Particulate Matter Concentrations at Construction Jobsites.*Sustainability*, 6, 7666-7688.
- [8] Health effects of particulate matter World Health Organization Regional Office for Europe © World Health Organization 2013 UN City, Copenhagen O, Denmark,.P2-11.
- [9] Vallius, M. Characteristics and sources of fine particulate matter in urban air. National Public Health Institute, Department of Environmental HealthKuopio, Finland. 2005. P 15-21
- [10] Lacour. S., Cours de pollution atmosphérique , Ecole Nationale des Ponts et Chaussées.Centre d’Enseignement et de Recherche sur l’Environnement Atmosphérique. Avenue Blaise Pascal, Cité Descartes, 77455 Champs sur Marne .
- [11] Ladji, R., 2009. Analyse qualitative et quantitative des composés organiques volatils, semi-volatils et particulaires dans l’air. Thèse de doctorat.Universite des sciences et de la technologie Hou ari Boumadienne Faculte de Chimie. p 10 – 13 .

- [12] Yurdakul ,S. ,October 2014 .Temporal variation of volatile organic compound concentration in bursa atmosphere., Ph.D., Department of Environmental Engineering, the graduate school of natural and applied sciences of middle east technical university, p5-17.
- [13] Kampa, M., Castanas, E.,2008. Human health effects of air pollution.Environmental Pollution 151, 362-367.
- [14]Oudin,A.,2009,Short-term and Long-term Exposure to Air pollution andStroke risk Lund University, Faculty of Medicine Doctoral Dissertation, Printed in Sweden, by Media-Tryck, Lund University Lund 2009,p5-10.
- [15]Hansen, A. B., 2012. Challenges in Modern Air Pollution Modeling- Focusing on Transport, Model Evaluation, and Impact on HumanHealth. PhD Thesis, Institute for Environmental Science, Aarhus University,Denmark,p 73-83.
- [16]Patrick,D.,Health& Environmental Effects of Air Pollution , . Commonwealth of Massachusetts, Executive Office of Energy and Environmental Affairs , Department of Environmental Protection One Winter Street Boston,Printed on Recycled Paper .
- [17]Hedegaard, G. B., 2011. Future air pollution levels in the Northern Hemisphere Sensitivity to climate change and projected emissions .The PhD. School of Science Faculty of Science University of CopenhagenDenmark.39-45.
- [18]Brasseur,G. P., Jacob,D., Jürgen Oßenbrügg,Hamburg 2009 , Climate and Air Pollution Modelling in South America with Focus on Megacities , Claas Teichmann aus Wilhelms.
- [19]Powell, H. L.,Estimating Air Pollution and its Relationship with Human Health university of Glasgow,2012 ,P47-P68.
- [20]World Health Organization WHO, 2014. World health statistics. WHO Press, Geneva, Switzerland, pp. 180 .
- [21]Nejjari, C., Filleul, L., Zidouni ,N., Laid ,Y., Atek ,M., El Meziane, A., Tessier, J. F. 2003 .La pollution atmosphérique un nouveau risque respiratoire pour les villes du sud Int J Tuberc Lung Dis7(3) : 223-231 .

Chapter II:

**Analyzing OC in the dust and air of different sites (2014
-2015)**

II.1 Introduction:

Biogenic and anthropogenic sources concur to release huge amounts of chemicals harmful for humans [1]. Toxicants exist both in the particulate form (aerosols and settled dust) and as gases; in particular, most organic substances partition between the two aggregation modes, according to total concentrations they reach and to environmental contour, e.g., ambient temperature and relative humidity, levels and nature of suspended particulate matter, pH, etc. [2 -5]

Organic substances occur everywhere in the world, independently of the features of site investigated, e.g. urban, industrial, remote, rural, and marine.[6-10]The organic mixture comprises a number of compounds such as linear and branched hydrocarbons, *n*-alkanols, *n*-alkanoic acids, polycyclic aromatic hydrocarbons (PAHs), pesticides, halogenated toxicants like polychlorobiphenyls (PCBs), dioxins and furans , phthalate and phosphate esters, licit and illicit drugs [11-13]. These substances affect both internal and external locations, with distinct levels and pathways.[14-16]

Airborne *n*-alkanes originate naturally from living organisms, high plants, and from forest fires. The common process leading to their release into the atmosphere is combustion of organic matter like biomass used for heating or agricultural purposes, petrol-derived mixtures to fuel vehicles, industrial plants, kitchens, power generators. Another relevant source is methane and oil spill from pipelines, tanks and natural deposits. Biogenic and anthropogenic emissions are characterized by distinct *n*-alkane homologue signatures. Particulate exhausts coming from petroleum-derived fuels show a mono-modal percent composition, with the maximum usually centered between C₁₇ and C₂₆, depending on ambient temperature; by contrast, high vegetation emits overall odd-carbon numbered *n*-alkanes, with maximum in the correspondence of C₂₉ or C₃₁. Thus, the relative importance of the two source types can be estimated by means of dedicated indexes, like

Carbon Preference Indexes (CPIs) or Natural Wax Percentage [11,17-19]. The non-polar organic fraction of particulates is also characterized by variable percentages of branched hydrocarbons (e.g., steranes, hopanes), typically associated to fuels and lubricating oils, which further put in the evidence the impact of man's activities [20]

The principal source of airborne polycyclic aromatic hydrocarbons is, by far, combustion of organic matter. Though PAHs are present in petrol formulations and can originate from soil resuspension, brake and tire consumption, and natural synthesis by biota, however most of the total budget outcomes from combustion for transport (automobiles, ships and airplanes) [16,20-23], heating and cooking (natural gas, heating oil), refuse disposal, pipelines [24] industry and power plants [25], as well as from biomass burning (forest fires) [26]. Relatively scarce in terms of global budget, but very important with regards to impact on humans, is the presence of PAHs in tobacco smoke [27]. PAHs have been extensively investigated in open and indoor air [3,28,29,19,30], overall to preserve health and verify the fulfillment of normative [31]. Though depending on meteorology, the PAH concentrations in air are overall regulated by year seasons [28,32] and are over 10 times higher in the winter than in the summer [33,34]. The environmental monitoring of PAHs is oriented by toxicity, which depends drastically on compounds [35]. Indeed, most attention is paid to 4-, 5- and 6- benzene-ring congeners, and benzo[a]pyrene is regarded as the most important one [36] and indicator of the whole group [31].

As key toxicants, halogenated organic substances are studied since long time and extensively monitored in emissions and environment. "Old" and "new" groups of compounds belong to this class; the most important ones are polychlorobiphenyls (PCBs), polychlorodibenzodioxins and furans (PCDD/Fs), halogenated pesticides (e.g., chlordane, DDT, DDE, HBB) and flame retardants (e.g. polybromodiphenyl ethers [PBDSs]) [37,38]. Internal environments are often affected by huge concentrations of

nicotine originated by tobacco smoking, as well as by traces ($\approx\text{ng/m}^3$) of psychotropic substances and emerging contaminants (phthalates, phenols, plasticizers) [39].

Measurements of particulate *n*-alkanes and PAHs have been already performed in Algeria, both in Algiers and in other urban and rural localities. Investigations have been somewhere extended to fatty acids and polar organics [11.40.41.13.7.9]

In this study *n*-alkanes, PAHs and polar organic compounds were monitored at several locations in Ouargla city, Algeria, by collecting settled dust from surfaces, and gas phase contaminants by means of passive sampling devices. The distinct neat concentrations of compounds and the respective distributions between particulate and gas phase could be evaluated. Finally, insights about the impact of natural and anthropogenic sources could be drawn.

II.2. Experimental :

II.2.1. Air sampling sites and protocols:



Figure II. 1: Sampling sites selected for indoor/outdoor measurement of organic contaminants in Ouargla city: U = University ; H = Hospital ;S and D = Schools and Home

Two monitoring networks were implemented in our study; the former was dedicated to dust (sampling points $N = 7$), and the latter to semi-volatile substances ($N = 15$), with some points in common. All sampling points lied in Ouargla city, Algeria, or its neighborhoods (Figure II.1), and belonged to four main environments, i.e., university, hospital, school and home.

Six locations (two outdoors and four indoors including offices and laboratories) were investigated in the university, five in the hospital (patient treatment and service rooms), four in the school (classrooms and common areas), and one in the home (dining room); school and home were not in downtown but in its proximities (at Ain Beida, ca. 10 km E of Ouargla) (Table II.1).

The protocol in-field experiment was conducted between October 2014 and January 2015. To collect dust, horizontal surfaces (in marble or furniture matter, each equal to 0.50 m², located ≥ 1 m above floor and ≥ 1 m from vertical surfaces) were polished with pre-cleaned cotton wads (sterile swab stick, 13*155 mm, purchased from Ningbo Greetmed Medical Instruments Co., Ltd., Ningbo, China R.P.) without using organic solvents or cleaning products, then they were exposed to particle deposition; after 15 or 31 days, surfaces were cleaned again and dust was retained in cotton wads. Before chemically characterizing dusts, the analytical procedure was tested by means of analogous samples collected without exactly recording the deposition times, to draw preliminary information. Dust loaded cottons were wrapped with aluminum foils, sealed into plastic bags and stored at low temperature ($\sim 4^{\circ}\text{C}$) until analysis.

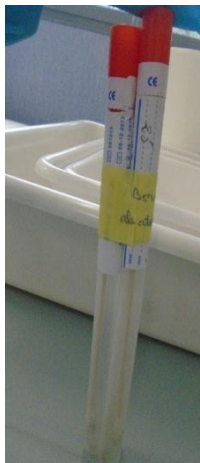
Passive samplers (14 cm diameter; 1.35 cm thick; surface area, 365 cm²; volume, 207 cm³; density, 0.0213 g cm⁻³; purchased from PacWill Environmental, Beamsville, ON, USA) were deployed in interiors 2 m above soil and 1.5 m away from vertical walls, and exposed to ambient contaminants from October 28 to December 28, 2014 (61 days). Afterwards, the devices were removed and PUF cartridges were sealed and stored at low temperature until analysis. Unused cotton wads and PUF cartridges were examined for blank subtraction. (see figure II.2)



Indoor

outdoor

1- PUF – disks



2- Swabs

Figure II.2: the sampler of collected the organic compounds in the dust and gas phase

Table .II.1: Sites and individual locations of dust and air sampling in Ouargla, Algeria.

Locality	Environment	PUF-disks sampling sites	Dust sampling sites
Ouargla	University	U ₁ : office dean U ₂ : secretarial office U ₃ : chemistry lab (1) U ₄ : chemistry lab (2) U ₅ : outdoor playing area (1) U ₆ : outdoor playing area (2)	U ₂ : secretarial office U ₃ : chemistry lab (1)
	Hospital	H ₁ : cancer patient waiting room H ₂ : treatment of infectious patients corridor H ₃ : reception hall H ₄ : hemodialysis room H ₅ : biochemistry lab	H ₆ : hall of the cancer patient rays room. H ₇ : treatment room H ₄ : hemodialysis room
Ain Beida	School	S ₁ : primary class room (1) S ₂ : primary class room (2) S ₃ : SEM classroom S ₄ : school hall	S ₁ : primary class room
	Home		D ₁ : dining room

II.2.2. Sample treatment

The analytical procedures were adapted from the studies of Ladj,2014 and Moussaoui,2010, after testing for quality controls (detector linearity, lack of interferences and matrix effects). LODs for PAH congeners (signal to noise ratio =3) ranged from 0.04 ng/m² (*n*-C₁₈) to 0.08 ng/m² (*n*-C₃₅) for n-alkanes, from 0.015 ng/m² (phenanthrene and fluoranthene) to 0.05 ng/m² (dibenz[a,h]anthracene) for PAHs, and were better than 0.08

ng/m² for phthalates, DEET, nicotine and caffeine. LOQs were set equal to 3 times the respective LODs. Global uncertainty never exceeded 18%.

Briefly, cotton wads were spiked with perdeuterated congeners of analytes that served as internal standards (C₁₆D₃₄, C₁₈D₃₈, C₂₀D₄₂, C₂₄D₅₀ and C₂₈D₅₈*n*-alkanes; naphthalene-D₈, acenaphthylene-D₁₀, phenanthrene-D₁₀, fluoranthene-D₁₀, chrysene-D₁₂, benz[a]pyrene-D₁₂ and dibenz[a,h]anthracene-D₁₄ for PAHs, nicotine-D₄, cocaine-D₃ and caffeine-¹³C₃) and extracted three times, 20 min each, with a dichloromethane:acetone (DCM:ACE) mixture, 4:1 in volume, in ultra-sonic bath (model *18 Digit*, from *Starsonic*, Shenzhen, China). The extracts were reduced close to dryness under ultra-pure nitrogen at room temperature and back dissolved into DCM/trimethylpentane (TMP) (1:4, 200 μL), then they were transferred onto a neutral alumina column (i.d. = 9 mm, h = 80 mm) partly deactivated with water (2.5% in weight). *n*-Alkanes were eluted first, within the non-polar organic fraction, with TMP (8 mL); PAHs were eluted second, with TMP/DCM, 3:2 (10 mL), polar organic compounds comprising drugs were eluted third with DCM/ACE, 1:1 (10 mL). The three extracts were evaporated and dissolved again in cyclohexane, toluene and chloroform, respectively, and brought to instrumental analysis. All solvent were from ROMIL and purchased from Delchimica, Naples, Italy.

Semi-volatile organics were recovered from passive air samplers (PAS) through refluxing in soxhlet using hexane and acetone as extraction mixture (1:1, 16h). Before treatment, PUF disks (the core of PAS) were spiked with the same perdeuterated standard of dusts. After extraction, the solutions were reduced close to dryness, dissolved into TMP:DCM and processed analogously to dust samples. (see figure II.3) .

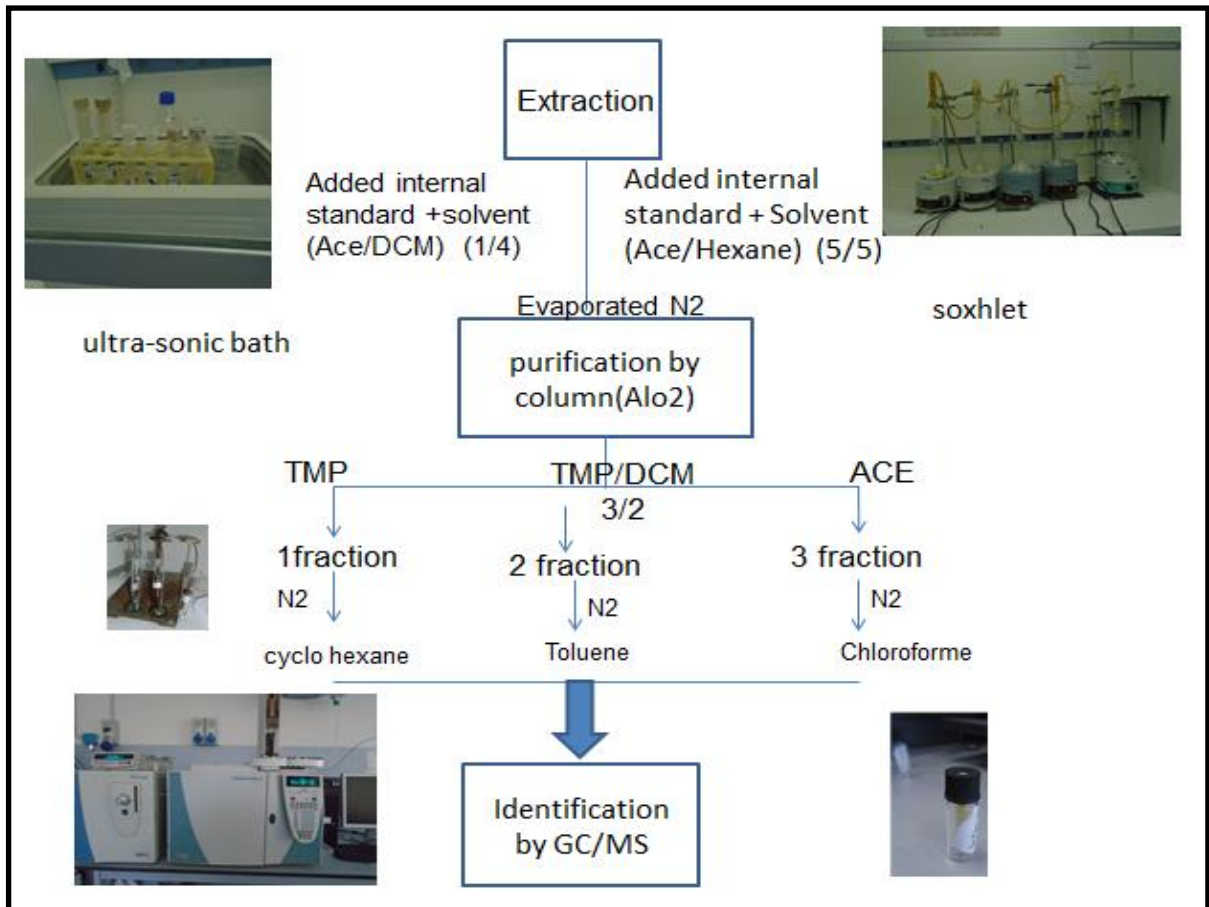
Chemical analyses of extracts were performed by applying the gas chromatography-mass spectrometry procedure set-up by [14] and implemented in recent investigations in Algeria [6.9] Sample aliquots (1 μL) were injected into a GC system (*Trace GC*

Ultrafrom Thermo, Milan, Italy) equipped with a *AS2000* auto-sampler (*Thermo*), and a programmed temperature vaporizer PTV. A DB5-MS type capillary column (30 m, 0.25 mm, 0.25 μm) or was selected to determine *n*-alkanes and polar compounds, while a EUPAH type column (20 m, 0.18 mm, 0.14 μm) was preferred for PAHs, due to its ability to separate benz[a]anthracene from triphenylene and chrysene, and benzofluoranthene isomers; both columns were from *CPS Analitica* (Cinisello Balsamo MI, Italy). The GC system was coupled with a mass spectrometric detector (*Trace DSQ*, from *Thermo*) operating in electron-impact, selected-ion-detection mode. The whole system was managed by a dedicated software (*Excalibur*). Temperature programs from 60 °C or 90 °C up to 280 °C allowed all analytes eluting within 50 min after injection.

The compound identification was based on peak retention times and intensity ratios of characteristic ion current ($[M/Z]^+$) intensities in tables II.2, II.3 and II.4 explained all compounds. For quantification, the ion traces corresponding to molecular or base fragment were compared with those of the closest perdeuterated reference substances in the chromatogram. (See figure II.4 and figure II.5)

When necessary (i.e., for *n*-alkanes) distinct calibration curves, each covering a different range of concentration, were used to quantify the analytes within the linearity range of calibration plot. Mother standard solutions of analytes were purchased from Chemical Research, Rome, Italy; they were: C₁₀-C₄₀*n*-Alkane Mixture, 100 $\mu\text{g/mL}$ each, in cyclohexane; Multi Comp. Std. 18 PAHs, 1000 $\mu\text{g/mL}$ in dichloromethane; Deuterated PAH Surrogate Standard, 1000 $\mu\text{g/mL}$ each in benzene; nicotine-D₃ and native nicotine, 1000 $\mu\text{g/mL}$ in methanol; caffeine-¹³C₃, caffeine, cotinine, cannabinol, cannabidiol, Δ^9 -tetrahydrocannabinol, and heroin, each 100 $\mu\text{g/mL}$ in methanol. Secondary standard mixtures (0.05-1.0 $\mu\text{g/mL}$ or 0.2-10 $\mu\text{g/mL}$) were prepared through dilution with trichloromethane. The blank subtraction was necessary for light *n*-alkanes (up to C₁₈),

PAHs (up to pyrene) and in particular for alkyl phthalates. The effectiveness of the extraction was verified for all classes in both matrices by replicating the procedure on analyzed samples.



FigureII.3: Planned explained party experimental of organic compound in all samplers

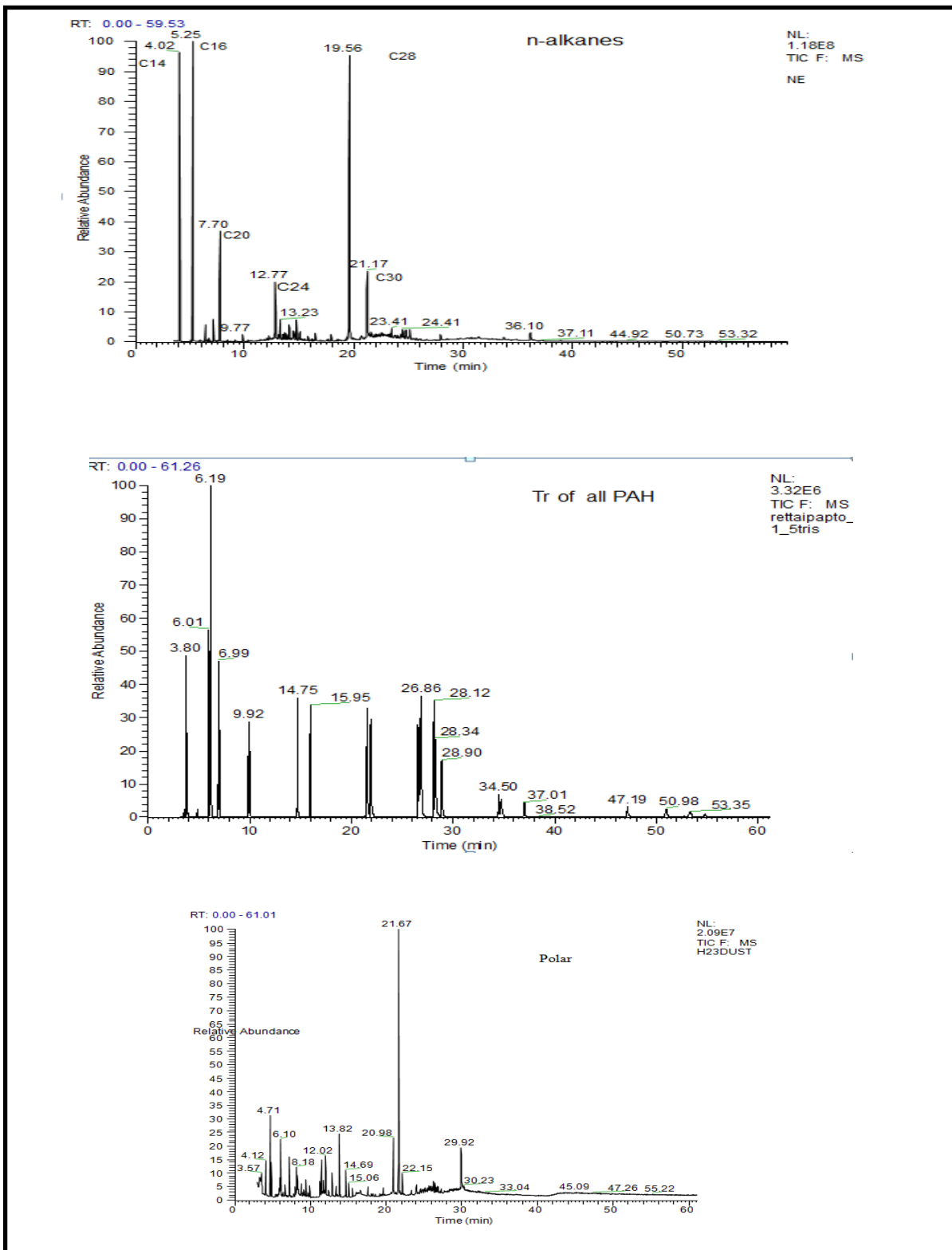


Figure II.4 : Chromatograms of n-Alkanes , PAH and polar compounds in GC/MS in the dust and gas phase

RT: 6.20 - 28.35

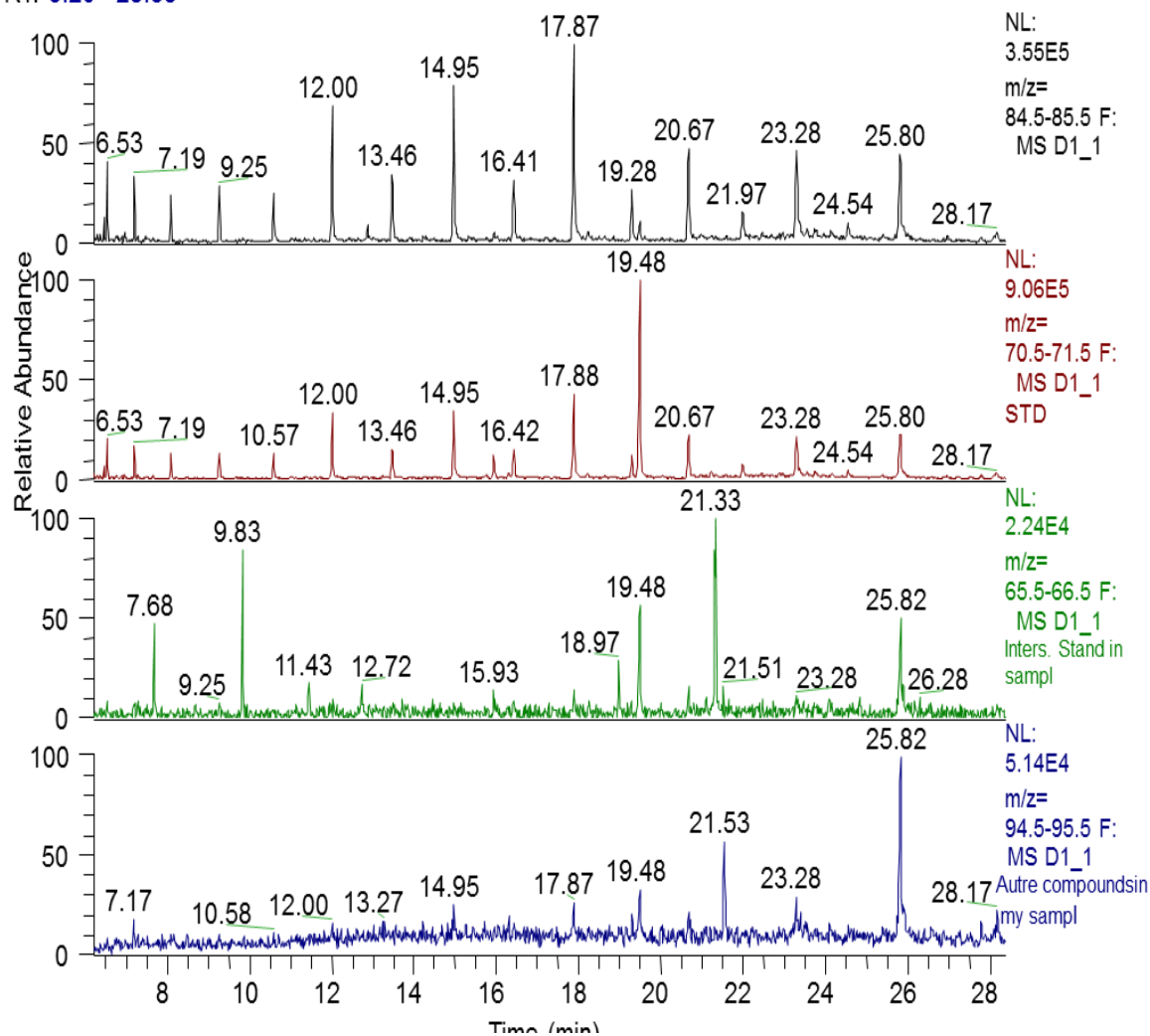


Figure II.5: chromatograms explained the identification Qualitative of n-alkanes in GC/MS

Table.II.2 :Retention time and ion characteristic of n-alkanes

Compound	Symbol	Formula	tr(min)
Tetradecane deuterated	n-C ₁₄ -d	C ₁₄ D ₃₀	4,02
Tetradecane	n-C ₁₄	C ₁₄ H ₃₀	4,81
Pentadecane	n-C ₁₅	C ₁₅ H ₃₂	5,25
Hexadécane deuterated	n-C ₁₆ -d	C ₁₆ D ₃₄	5,41
Haptadecane	n-C ₁₇	C ₁₇ H ₃₆	5,99
Octadecane	n-C ₁₈	C ₁₈ H ₃₈	6,54
Nonadecane	n-C ₁₉	C ₁₉ H ₃₄	7,22
Eicosane deuterated	n-C ₂₀ -d	C ₂₀ D ₄₂	7,70
Eicosane	n-C ₂₀	C ₂₀ H ₄₂	8,09
Heniacosane	n-C ₂₁	C ₂₁ H ₄₄	9,25
Docosane	n-C ₂₂	C ₂₂ H ₄₆	10,59
Tricosane	n-C ₂₃	C ₂₃ H ₄₈	12,09
Tetracosane deuterated	n-C ₂₄ -d	C ₂₄ D ₅₀	12,77
Tetracosane	n-C ₂₄	C ₂₄ H ₅₀	13,59
Pentacosane	n-C ₂₅	C ₂₅ H ₅₀	15,08
Hexacosane	n-C ₂₆	C ₂₆ H ₅₂	16,57
Heptacosane	n-C ₂₇	C ₂₇ H ₅₄	18,06
Octacosane	n-C ₂₈	C ₂₈ H ₅₆	19,55
Nonacosane	n-C ₂₉	C ₂₉ H ₅₈	20,84
Tricontene deuterated	n-C ₃₀ -d	C ₃₀ D ₆₂	21,17
Tricontene	n-C ₃₀	C ₃₀ H ₆₂	22,16
Hentriacontane	n-C ₃₁	C ₃₁ H ₆₄	23,48
Dotriacontane	n-C ₃₂	C ₃₂ H ₆₆	23,48
Tritriacontane	n-C ₃₃	C ₃₃ H ₆₈	24,71
Tetratriacontane	n-C ₃₄	C ₃₄ H ₇₀	25 ,93
Pentatriacontane	n-C ₃₅	C ₃₅ H ₇₂	27,09
Hexatriacontane	n-C ₃₆	C ₃₆ H ₇₄	30,76

Table.II.3:Retention time and ion characteristic of PAH

Compounds	Symbol	Formula	tr(min)
Acenaphthylene	ACY	C12H8	6.11
Acenaphthene- deuterated	ACE-d10	C12D10	6.21
Acenaphthene	ACE	C12H10	6.26
Fluorene – deuterated	FL-d10	C13D10	7.05
Fluorene	FL	C13H10	7.12
Phenanthrene – deuterated	Phe-d10	C14D10	10.03
Phenanthrene	Phe	C14H10	10.12
Anthracene	Ant	C14H10	10.24
Methyle-phenanthrene / anthracene(Σ)	MPA	C15H12	11.63-12.35
Fluoranthene- deuterated	Flu-d10	C16D10	14.90
Fluoranthene	Flu	C16H10	15
Pyrene	Py	C16H10	16.19
Methylefluorathene/pyrene	MFP	C17H12	17.56-18.63
Benzo(ghi)fluorathene	BghiF	C20H12	20.87
Benz(c) phenantherene	BcP	C18H12	21.03
Benzo(a) anthracene	BaA	C18H12	21.74
Chrysene- deuterated	CH-d10	C18D12	22.1
Chrysene	CH	C18H12	22.17
Methlychrysene	MCH	C19H12	23.62-24.53
Benzo(b)fluoranthene	BbF	C20H12	26.10
Benzo(j) fluoranthene	BjP	C20H12	26.22
Benzo(k) fluoranthene	BkP	C20H12	26.33
Benzo(e) pyrene	Bep	C20H12	27.50
Benzo(a) pyrene	Bap	C20H12	27.86
Perylene- deuterated	PE-d10	C20D12	28.28
Perylene	PE	C20H12	28.34
Indeno(1,2,3-cd)pyrene	IP	C22H14	33.50
Dibenzo(a,h)anthracene-deuterated	DBahA-d10	C22D14	34.94
Benzo(ghi)perylene- deuterated	BPE-d10	C22H14	35.25
Dibenzo(ghi)perylene	BPE	C24H14	37.58

Table.II.4:Retention time and ion characteristic of polar compounds :

Compound	Symbol	Formula	tr(min)
Nicotine -d4	NICD	C10D14N2	6.35
Nicotine	NIC	C10H14N2	6.41
di-methyl-Phthalate	MEP	C10H10O4	7.8
N,N-Diethyl-3-methylbenamide	DEET	C12H17NO	8.64
Di-ethyl-Phthalate	EHP	C12H14O4	8.9
Nonilphenol	NoPH	C15H24O	9.1
Acridine	Ac	C13H9N	12.7
Carbazole	Ca	C12H9N	13.67
Dibutylphthalate	BUP	C16H22O4	13.82
Cafeine	CAF	C8H10N4O2	14.6
Cocaine	COC	C17H21NO4	20.21
Cannabinol	CNB	C21H26O2	21.59
Butylbenzylphthalate	BuBzP	C19H20O4	21.69
Tetrahydrocannabinol	THC	C21H30O2	23.45

II.3. Results and Discussion

II.3.1 n-Alkanes

The non-polar fraction of organic aerosols was dominated by *n*-alkane homologues ranging from C₁₄ to C₃₈. Figure II.6 reports the average *n*-alkane burdens in dusts of interiors at university (U₂ and U₃ sites), school (S₁), hospital (H₆, H₇ and H₄) and home (D₁). Table II.5 reports the *n*-alkane concentrations found in indoor air of university (U₁, U₂, U₃ and U₄ sites), hospital (H₁, H₂, H₃ and H₄ sites) and school (S₁, S₂, S₃ and S₄ sites), as well as outdoors at university (U₅ and U₆ sites) (passive sampling). Total *n*-alkanes (TNAs) ranged 4 - 41 µg /m² in dusts and 0.17-2.4 µg /m³ in air, the maximums being recorded in the home (D₁) and at school (S₂), respectively (Figures II.7-II.8). TNAs measured in this study by means of passive samplers were comparable with those previously recorded in Algiers at Oued Smar landfill (~241 ng /m³) [40], at a fatty manufacture (~914 ng /m³) [41], at Bab-Ezzouar University (~140 ng /m³) [42] at Rouiba, Ouled Moussa and at the Lake of Reghaia (Algeria) in the autumn 2007 (144 - 170 ng /m³) [6], Rouiba in the summer 2007 (82 ng /m³) [6] and in downtown Algiers from 1988 to 1999 (75 ng /m³) [40].

To identify the nature of *n*-alkane source, the approach based on the carbon preference index (CPI) calculation was attempted. Various CPI formulas exist, which differ according to the carbon number range considered. The most commonly used looks as follows [11]:

$$\text{CPI}_{25} = 0.5 * \left(\frac{(\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33} + \text{C}_{35} + \text{C}_{37})}{(\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32} + \text{C}_{34} + \text{C}_{36})} + \frac{(\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33} + \text{C}_{35} + \text{C}_{37})}{(\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32} + \text{C}_{34} + \text{C}_{36} + \text{C}_{38})} \right)$$

and highlights the predominance of odd-numbered *n*-alkanes vs. the even-numbered homologues.

Though whole range of *n*-alkanes existing in the atmosphere is not accounted for, however this formula drastically reduces any possible misinterpretation consequent from the different volatilities of compounds.

The CPI index allows to differentiate biogenic from petrogenic or anthropogenic *n*-alkanes, because values close to 1.0 are indicative of petrol-derived soot, whilst rates >4 are typical of natural emissions [2.43.4]. CPI values ranging from 0.9 to ~1.6 are usually verified in urban or industrial areas, while values between 3 and 10 are typical of rural/forest zones. In our study, the CPI rates ranged from 1.31 to 1.75 for *n*-alkanes associated to the dusts, all coming from interiors. As for gaseous compounds, no differences were found among locations at school (CPI ~1.4), but they were at hospital (CPI = 1.34- 2.51) and overall at university (CPI = 3.6 ± 1.2 in interiors, and 1.7 ± 0.3 outdoors); thus, distinct impacts of biogenic emissions could be detected. Very few data exist concerning alkanes in dust. A comparison was attempted between alkanes measured in Ouargla and values detected by [44] in the organic films on indoor and outdoor glass windows in urban and rural districts of Toronto (Canada). There total *n*-alkanes varied

between 1 and 5 $\mu\text{g}/\text{m}^2$ and in general were higher outdoor, whereas the CPIs in the urban and suburban areas were comparable with this study (CPI=1.1-3.6).

The signature of natural wax *n*-alkanes (WNAs) typical of higher plants, introduced by Simoneit et al. (1990), was calculated for each sample by applying the following formula:

$$\% \text{Wax } C_n = [\sum[C_n - 0.5 * (C_{n-1} + C_{n+1})] / \sum C_n] \times 100 \%,$$

through which the “wax” (i.e., vegetation derived) concentration of each *odd* C_n homologue could be estimated (negative values of C_n were taken equal to zero). According to it, the contribution of the high vegetation emission to dust associated organic material ranged from ca. 16% (home) to 39 % (school). In the gas phase, wax *n*-alkanes accounted for 24-30% at school and 30-58% at university outdoors, 57-82% at university indoors, and ranged between 26% and 67% at the hospital, with maximum in the patient treatment room and minimum in the biochemistry laboratory.

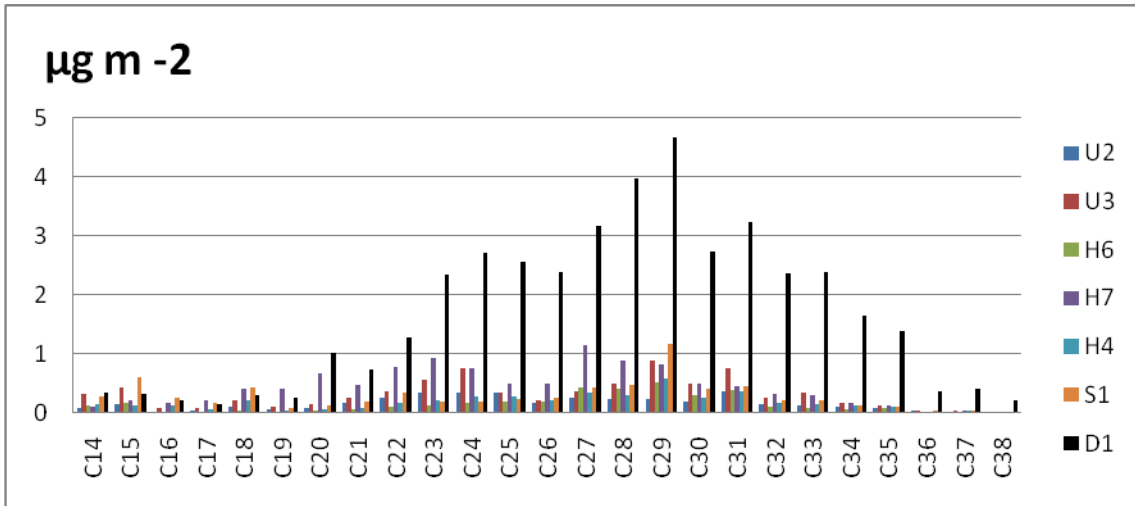


Figure II.6: Concentration of *n*-alkanes ($\mu\text{g}/\text{m}^2$) in indoor dusts collected in Ouargla

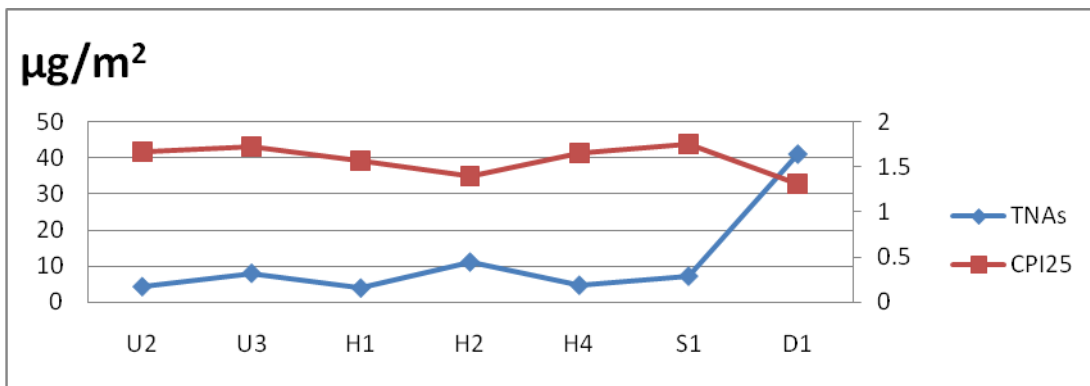


Figure II. 7: Total *n*-alkanes TNAs ($\mu\text{g}/\text{m}^2$) and corresponding carbon preference index CPI₂₅ in indoor dusts collected in Ouargla, Algeria.

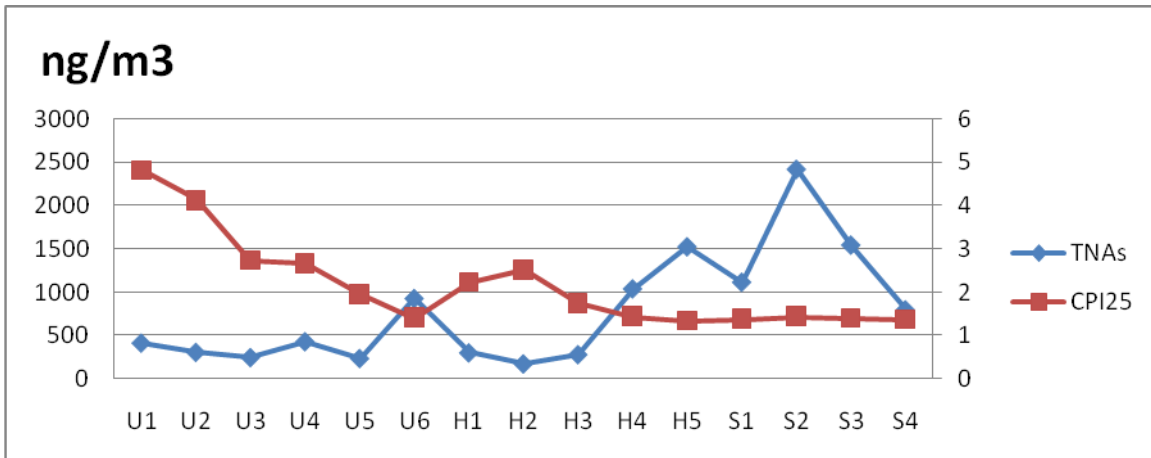


Figure II.8:Total *n*-Alkanes TNAs (ng/m^3) and corresponding CPI₂₅ in the gas phase of Ouargla, Algeria

Table.II.5. Concentrations of *n*-alkanes (ng/m³) affecting the gas phase of interiors in Ouargla

Location	U1	U2	U3	U4	U5	U6	H1	H2	H3	H4	H5	S1	S2	S3	S4
C ₁₄	7.3	8.1	1.6	5.6	1.7	2.0	12	2.3	3.5	11.0	8.4	4.0	3.6	6.4	0.5
C ₁₅	15	17	6.7	8.3	3.0	3.1	11	3.7	5.6	6.8	6.9	6.9	6.2	9.3	4.9
C ₁₆	37	37	24	39	7.8	7.8	13	13	9.3	12	9.7	19	12	13	17
C ₁₇	95	64	67	90	13	13	42	21	15	22	31	35	22	30	41
C ₁₈	90	66	77	114	16	9.5	49	24	17	26	30	36	24	30	32
C ₁₉	60	20	5.4	22	16	8.8	1.8	17	1.4	3.2	2.9	12	16	3.1	3.4
C ₂₀	37	11	3.0	15	13	7.1	1.3	15	1.5	2.7	2.7	7.6	10.7	1.9	2.7
C ₂₁	17	6.2	1.8	6.9	8.8	9.6	0.8	7.2	1.3	3.1	3.1	7.7	14.1	2.3	2.4
C ₂₂	11	6.0	1.3	6.4	9.5	17	0.5	6.6	1.6	3.4	4.3	10.1	26.9	4.6	4.3
C ₂₃	8.5	14	13	17	5.7	32	8.4	6.8	23	35	47	28	56	32	25
C ₂₄	1.2	2.9	7.9	8.3	5.8	72	20	3.2	31	79	115	51	120	80	59
C ₂₅	5.7	13	5.5	12	6.1	68	13	6.0	25	98	99	64	145	77	57
C ₂₆	0.9	1.2	0.4	3.5	4.2	73	8.6	1.8	14	76	102	60	140	76	66
C ₂₇	4.0	8.5	1.3	9.6	6.4	81	6.9	5.4	21	90	120	73	160	88	65
C ₂₈	1.6	2.2	3.2	6.2	8.0	95	23	4.0	15	100	96	84	215	113	69
C ₂₉	13	18	15	33	33	193	43	20	46	213	213	155	482	272	143
C ₃₀	1.6	1.8	0.9	5.0	8.8	59	11	2.7	7.8	58	77	67	153	100	50
C ₃₁	2.9	3.4	2.6	9.0	31	66	14	5.6	13	66	97	81	170	123	52
C ₃₂	1.3	1.1	0.8	3.9	6.8	36	6.8	2.1	5.1	43	83	68	130	93	32
C ₃₃	1.2	0.9	1.2	5.4	12	30	7.7	2.1	6.6	33	89	64	132	96	26
C ₃₄	0.7	0.3	1.0	2.4	5.3	17	3.2	0.8	3.8	20	62	43	89	66	14
C ₃₅	0.3	0.3	0.5	2.9	4.5	12	2.3	0.7	3.2	14	60	43	90	65	13
C ₃₆	0.5	0.0	1.2	1.0	3.3	5.8	2.5	0.0	2.5	8.6	48	30	63	46	7.8
C ₃₇	0.5	0.0	0.3	0.8	3.2	6.1	0.3	0.3	1.6	7.3	60	36	69	59	6.1
C ₃₈	0.0	0.0	1.5	1.0	2.5	2.1	0.0	0.0	3.0	6.3	59	31	70	58	5.0
Total	412	304	244	428	234	927	299	171	278	1,039	1,526	1,116	2,421	1,545	796
CPI ₂₅	4.82	4.13	2.73	2.66	1.95	1.41	2.23	2.51	1.74	1.44	1.34	1.38	1.43	1.39	1.36
% Wax	75	82	57	63	58	30	35	67	45	33	26	24	30	29	27

II.3.2. PAHs :

In dusts, total PAHs ranged from 17 ± 2 ng/m² up to 89 ± 32 ng/m³ (Table II.6 and Figure II.9). Methyl-PAHs (i.e., methyl derivatives of phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene and chrysene, not reported in the figure) accounted for $37\pm 4\%$ of the total independently of site, except in H6 (~16%). The home (89 ± 32 ng/m²) was more PAH-affected than all other sites, which in turn experienced similar contamination rates ($\sim 26\pm 7$ ng/m²).

In the gas phase (Table II.7), total PAHs were equal to 54 ± 7 ng/m³ in the school and 100 ± 22 ng/m³ in the hospital; meanwhile, in the university PAHs reached 141 ± 36 ng/m³ indoors and 145 ± 3 ng/m³ outdoors (unfortunately, no data could be collected in the home). The percentage of methyl-PAHs reached $35\pm 6\%$ at school and hospital, and $43\pm 3\%$ at university, i.e. fairly similar to that found in dust (again, except in H6).

Some caution is needed comparing our data with previous studies, because dust cannot be assimilated to suspended particulate matter in total, nor to its size fractions (PM₁₀, PM_{2.5} and so on); besides, gaseous only PAHs cannot be compared to the sum of vapor and particulate phases. Anyway, some literature data are provided in Table II.8. In Ouargla, fluorene (FL: 3.3-24 ng/m³), phenanthrene (PH: 19-69 ng/m³), fluoranthene (FA: 1.5-11 ng/m³) and pyrene (PY 1.2-10 ng/m³) measured by PUF were, on average, more than those detected in North Carolina and California, USA (5.3-6.7 ng/m³, 9.2-11 ng/m³, 0.5-0.9 ng/m³ and 0.3-0.8 ng/m³, respectively), in Germany (FA: 0.45 ng/m³; PY: 0.34 ng/m³) and in France (FL: 3.7 ng/m³, PH: 7.2 ng/m³, FA: <0.6 ng/m³; PY: <0.6 ng/m³) (et [44.45.46.47]in gas and particulate phases. By contrast, acenaphthene was less (0.0-1.0 ng/m³ vs. 0.8-5.3 ng/m³), and benzo[a]pyrene lied in the common range (0.0-0.36 ng/m³). To draw some insights about the pollution sources, the following concentration ratios between selected congeners were calculated in dust: fluoranthene/pyrene (FA/PY),

indeno[1,2,3-cd]pyrene/benzo[ghi]perylene IP/BPE), benzo(a)pyrene/benzo[ghi]perylene (BaP/BPE), and benzo[a]pyrene/benzo[e]pyrene (BaP/BeP) (Table II.9). The calculated ratios were compared with those provided by scientific literature for the principal PAH sources. The total index TI_{PAH} was also calculated (Tables 6-7) according to the formula:

$$TI_{PAH} = FA/(FA+PY)/0.4 + AN/(AN+PHE)/0.1 + B[a]A/(B[a]A+CH)/0.2 + IP/(IP+BPE)/0.2.$$

This index allowed to discriminate high temperature processes (typical of combustion: $TI_{PAH}>4$) from low temperature sources (petrogenic in particular, $TI_{PAH}< 4$) [49]. According to it, the petrogenic sources were predominant for gaseous PAHs at all sites except H5 and S4; PAHs associated to dust were pyrogenic in U3, H2, S1 and D1, and petrogenic in U2, H1 and H4.

The FA/PY ratios varied between 0.61 and 0.89 for dust particles and 1.18 ± 0.10 for PUF-disks (excluding U6, where it was equal to 1.96), suggesting that vehicles exhausts with mixed and gasoline fuel, particulate from tobacco smoke and fumes from landfill were the principal PAHs sources at indoor/outdoor sites investigated. The BaP/BPE confirm the predominance sources of vehicles exhausts with different fuels kinds, ranging from 0.49 to 0.87. The BaP/BeP ratio ranged 0.27 -0.40, which confirms the PAH degradation on dust confirming the effects of degradation on PAHs content of dust [50]. By contrast, both in dust and air the IPY/BPE ratio changed widely, indicating the distinct PAHs emission sources for the sites. The source diversity was further confirmed by the wide variation of BaP/BPE and BaP/BeP ratios in the air samples.

Table.II.6. average Concentration of PAHs (ng/m^2) in indoor dusts collected in Ouargla.

location	U2	U3	H1	H2	H4	S1	D1
ACE	1.9±1.4	1.2±0.2	3.2±1.5	1.4±0.2	2.1±0.4	1.1±0.1	0.9±0.2
FL	1.8±1.3	2.1±0.5	1.3±0.3	0.4±0.1	1.2±0.1	1.0±0.3	2.5±1.2
PH	5.0±2.8	5.4±0.6	6.5±1.6	2.0±1.0	3.2±0.4	3.8±0.6	9.5±1.7
AN	0.4±0.2	0.4±0.1	0.7±0.0	0.3±0.2	0.3±0.1	0.4±0.6	0.7±0.1
FA	2.2±1.6	2.4±0.3	2.8±2.0	0.7±0.4	1.0±0.2	1.5±0.7	4.0±1.7
PY	2.4±1.3	2.7±0.4	3.7±2.6	1.2±0.7	1.1±0.2	1.9±0.6	7.7±5.5
BaA	0.2±0.1	0.3±0.1	1.5±2.1	0.2±0.1	0.1±0.0	0.2±0.1	1.3±0.4
CH	2.0±1.2	3.4±0.8	3.0±2.8	1.7±1.2	1.5±0.3	2.3±1.0	9.6±1.4
BbF	0.9±0.5	1.5±0.3	2.5±1.8	1.2±0.9	0.7±0.1	1.3±0.5	3.8±0.7
BjF	0.3±0.1	0.5±0.1	0.7±0.5	0.4±0.2	0.2±0.1	0.4±0.1	0.9±0.3
BkF	0.3±0.2	0.4±0.1	0.5±0.4	0.4±0.3	0.2±0.1	0.4±0.1	2.1±1.3
BeP	0.8±0.5	1.2±0.1	3.1±2.2	0.8±0.5	0.5±0.0	1.3±0.4	3.0±1.1
BaP	0.3±0.1	0.4±0.2	0.7±0.5	0.3±0.2	0.1±0.0	0.5±0.3	1.2±0.4
PE	0.0±0.0	0.2±0.3	0.1±0.1	0.0±0.0	0.1±0.0	0.1±0.1	0.1±0.1
IP	0.6±0.4	0.4±0.3	0.6±0.3	0.5±0.3	0.3±0.2	0.3±0.2	1.2±0.7
DBahA	0.0±0.0	0.0±0.1	0.2±0.3	0.0±0.0	0.0±0.0	0.1±0.1	0.0±0.0
BPE	0.5±0.2	0.5±0.4	0.9±0.7	0.5±0.3	0.3±0.1	0.7±0.1	2.0±0.7
MePAHs	8.6±4.4	11.0±3.8	5.3±1.5	7.2±4.0	5.8±1.3	9.5±1.7	40±16
PAHs	26±15	33±7	34±16	18±10	17±2	26±5	89±32
FA/PY	0.85	0.89	0.75	0.61	0.88	0.79	0.63
IP/BPE	1.41	0.77	0.80	1.03	1.15	0.61	0.57
BaP/BPE	0.57	0.74	0.85	0.49	0.61	0.87	0.58
BaP/BeP	0.39	0.38	0.31	0.27	0.29	0.33	0.40
TI _{PAH}	4.43	3.89	4.55	3.97	4.33	3.00	3.25

Symbols: acenaphthene = ACE; fluorene = FL; phenanthrene = PH; anthracene = AN; fluoranthene = FA; pyrene = PY; benz[a]anthracene = BaA; chrysene = CH; benzo[b]fluoranthene = BbF; benzo[j]fluoranthene = BjF; benzo[k]fluoranthene = BkF; benzo[e]pyrene = BeP; benzo[a]pyrene = BaP; perylene = PE; indeno[1,2,3-cd]pyrene = IP; dibenz[a,h]anthracene = DBa,hA; benzo[ghi]perylene = BPE; MePAHs = methylated PAHs (sum); PAHs = total PAHs.; n.e. = not evaluated; 0.00 = below detection limit ; $TI_{PAH} = FA/(FA + PY)/0.4 + AN/(AN + PH)/0.1 + B[a]A/(B[a]A + CH)/0.2 + IP/(IP + BPE)/0.2$.

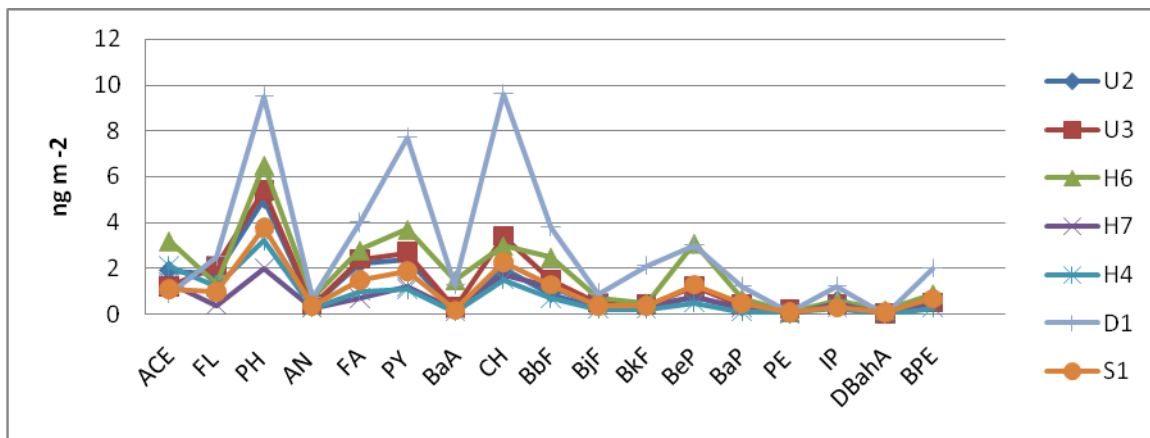


Figure II.9: Concentration of PAHs (ng/m^2) in indoor dusts collected in Ouargla

Table II.7: Average concentrations of PAHs (ng/m^3) in indoor and outdoor air (gaseous phase) in Ouargla, Algeria.

Location	U1	U2	U3	U4	U5	U6	H1	H2	H3	H4	H5	S1	S2	S3	S4
ACE	0.72	0.46	0.01	0.55	0.17	0.00	0.00	1.02	0.00	0.00	0.00	0.00	0.45	0.00	0.00
FL	9.6	6.1	12.2	11.2	5.9	4.1	13.7	6.9	3.3	24	17.0	5.5	5.6	9.7	8.0
PH	56	38	45	69	49	58	45	39	33	56	35	19	22	30	26
AN	1.6	1.8	2.6	3.1	2.1	2.6	1.7	0.75	0.94	1.9	1.7	0.32	0.42	0.78	0.63
FA	5.7	5.5	5.4	9.1	10.8	10.9	3.9	5.9	4.8	3.8	2.2	1.5	2.6	1.7	1.5
PY	4.7	4.8	5.0	8.0	10.1	5.6	3.5	5.0	4.4	2.7	1.7	1.2	2.2	1.4	1.4
BaA	0.22	0.18	0.11	0.16	0.79	0.65	0.10	0.27	0.26	0.06	0.04	0.09	0.16	0.04	0.02
CH	0.55	0.45	0.27	0.45	2.0	1.5	0.41	0.77	0.92	0.25	0.16	0.29	0.43	0.16	0.11
BbF	0.08	0.08	0.12	0.00	1.24	1.00	0.06	0.16	0.26	0.07	0.05	0.07	0.13	0.06	0.02
BjF	0.07	0.05	0.05	0.00	0.52	0.30	0.15	0.06	0.11	0.02	0.01	0.02	0.06	0.01	0.00
BkF	0.04	0.02	0.04	0.00	0.33	0.20	0.05	0.05	0.11	0.03	0.01	0.04	0.07	0.02	0.01
BeP	0.06	0.06	0.01	0.00	0.80	0.94	0.07	0.12	0.20	0.04	0.02	0.00	0.08	0.03	0.00
BaP	0.04	0.03	0.00	0.36	0.23	0.26	0.03	0.04	0.15	0.00	0.00	0.03	0.06	0.02	0.00
PE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
IP	0.01	0.02	0.03	0.09	0.17	0.13	0.03	0.04	0.12	0.01	0.00	0.02	0.04	0.02	0.00
DBahA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BPE	0.01	0.02	0.02	0.04	0.34	0.31	0.03	0.07	0.15	0.01	0.00	0.01	0.02	0.01	0.00
MePAHs	78	45	50	79	58	60	51	42	29	35	22	17	19	19	17
PAHs	158	103	122	182	143	147	120	101	78	124	79	45	54	63	55
FA/PY	1.20	1.15	1.09	1.13	1.06	1.96	1.12	1.18	1.09	1.37	1.31	1.31	1.20	1.28	1.07
IP/BPE	0.71	1.09	1.52	2.45	0.49	0.44	1.20	0.59	0.74	0.92	n.e.	2.27	1.67	3.34	n.e.
BaP/BPE	2.89	2.09	0.27	9.84	0.66	0.85	1.19	0.56	0.98	n.e.	n.e.	2.41	2.62	2.90	n.e.
BaP/BeP	0.71	0.55	0.53	n.e.	0.28	0.28	0.50	0.32	0.75	n.e.	n.e.	n.e.	0.67	0.69	0.75
TI_{PAH}	5.88	5.77	6.76	6.66	4.41	4.47	5.83	4.75	4.67	6.04	3.73	6.73	6.67	6.77	3.13

Symbols: see Table II.6.

Table II.8: Mean PAH concentrations (ng/m³) observed in the air.

country	sampling type	ACE	FL	PH	AN	FA	PY	BaP
U. S. A. ^(a)	QFF/XAD2, GFF/PUF; PM ₁₀ ; 12 m ³	4.9	5.3	9.2	0.65	0.47	0.30	0.09
Germany ^(b)	QFF; PM ₇ ; 28–32 m ³	n.e.	n.e.	n.e.	n.e.	0.45	0.34	0.25
U. S. A. ^(c)	QFF/PUF/XAD2; PM ₁₀ ; 12 m ³	5.3	6.7	11	<0.3	0.9	0.81	<0.3
France ^(d)	QFF/PUF; PM ₁₀ ; 20 m ³	0.8	3.7	7.2	<0.6	<0.6	<0.6	0.07
Algeria (this study)	PAS (ng/m ³)	0.0-1.0	3.3-24	19-69	0.3-3.1	1.5-11	1.2-10	0.0-0.36

References: *a*: [45]; *b*: [46]; *c*: [47]; *d*: [48].

Symbols: GFF = glass fibre filter; QFF = quartz fibre filter; XAD = Divinylbenzene resin; PUF = polyurethane foam; PAS = Passive Sampler.

Table II.9: Anthropogenic PAH sources and typical values of FA/PY, IP/BPE, BaP/BPE, and BaP/BeP diagnostic ratios.

Source	PAH ratio	FA/PY	IP/BPE	BaP/ BPE	BaP/ BeP	References
Vehicles	Mixed	0.60		0.55 0.45		(a), (b)
	Leaded gasoline	0.50	0.37	0.35	0.95	(c), (a) (b), (d)
	Unleaded gasoline	0.54	0.2-0.35	0.8–1.1	0.95	(c), (a) (b), (d)
	Diesel	0.8-1.1	0.65–1.1		0.50	(c), (a) (b), (d) (e)
Domestic heating	Coal		0.9-1.3	1.57		(f)
	Wood, pine	0.78	1.1–1.6	1.94	2.10	(g)
	Wood, oak	0.75	1.2–1.6	1.77	1.77	(g)
	Synthetic fuel	1.19	1.10	1.91		(f)
	Heavy oil	0.83	1.61	0.81	0.52	(f)
Iron/steel plant	Coke (coal)	0.30	1.21	0.78	1.65	(f), (h)
	Power plant (coal)		2.01	0.88	2.57	(f), (h)
Tobacco smoke	Particulate	0.96	0.18	0.23	0.38	(i)
Landfill	Fumes	1.30	0.76	0.70	0.55	(f)
Clay plant	Fumes	~ 2.65	1.82	0.14	0.02	(f)
Urban incinerator	Fumes	~ 17	0.92	~0.12	0.01	(d), (f)
Dusts	U ₂	0.85	1.41	0.57	0.39	This study
	U ₃	0.89	0.77	0.74	0.38	
	S ₁	0.79	0.61	0.87	0.33	
	H ₆	0.75	0.80	0.85	0.31	
	H ₇	0.61	1.03	0.49	0.27	
	H ₄	0.88	1.15	0.61	0.29	
	D ₁	0.63	0.57	0.58	0.40	

References: *a* : [51] , *b* : [52] , *c* : [53], *d* : [54] , *e* : [55] *f* : [56] , *g* : [57] , *h* : [58] , *i* : [59], *n.e.* : note evaluated

PAH symbols: see Table 2

II.3.3. Highly-polar fraction of organic aerosols:

Highly-polar organic compounds are associated to suspended particulates as well as to dust, comprising licit and illicit psychotropic substances i.e., nicotine, caffeine, cocaine and cannabinoids, alkyl phthalates (dimethylphthalate, diethylphthalate, diisobutylphthalate, dibutylphthalate, butylbenzylphthalate and di[2-

ethylhexyl]phthalate), nonylphenols, and insect repellent DEET .[11.60.61.62.6.7.12.63]

The average concentrations of these contaminants are displayed in Table II.10 .

Table II.10: Average concentrations (ng/m²) of highly polar organic compounds in the dusts and gas phase (PUFs) of Ouargla, Algeria.

	Site	NIC	CAF	COC	CBD	THC	CBL	CBs	DEET	NoPh	Aps
Dust	U2	328±198	18±26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1±0.1	15±18
	U3	164±79	173±207	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1±0.2	15±19
	H2	107±57	7±10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1±0.3	15±20
	H1	2,018±1,057	51±29	n.d.	0.5±0.9	3.9±6.8	0.6±0.7	5.2±8.2	n.d.	n.d.	0.9±0.9
	H3	147±148	13±19	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2±0.0	0.6±0.8
	S1	63±58	284±384	n.d.	n.d.	n.d.	n.d.	n.d.	0.1±0.0	1.1±1.4	56±66
	D1	86±89	209±237	n.d.	n.d.	n.d.	0.5±0.7	0.5±0.7	0.4±0.6	0.7±0.3	47±9
PUFs	U1	7.2	6.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.7	10.6
	U2	15	7.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	18.7
	U3	5.4	3.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	11.2	1.2
	U4	5.0	16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.1	n.e.
	U5	21	25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.1	10.9
	U6	n.e.	n.e.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.0	8.8
	H1	95	12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.9	1.1
	H2	54	13	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.3	27.1
	H3	416	60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	0.9
	H4	38	6.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	0.6
	H5	66	3.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.21	3.7
	S2	4.1	9.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	14.6
	S3	15	5.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.28	1.2

Symbols: NIC = nicotine; CAF = caffeine; COC = cocaine; CBD = cannabidiol; CBL = cannabinol; THC = Δ⁹-tetrahydrocannabinol; CBs = CBD+CBL+THC; DEET = N,N-diethyl,*meta*-toluamide; NoPh = nonylphenols; APs = sum of dimethylphthalate, diethylphthalate, diisobutylphthalate, dibutylphthalate, butylbenzylphthalate and di(2ethylhexyl)phthalate; n.d. = not detected; n.e. = not evaluated.

In general, high variability of concentration was found for each substance and at all locations. This could depend either on random use of substances, or on ease decomposition in the presence of air. Despite quite volatile, nicotine and caffeine exhibited rather high concentrations in dusts coming from all sites (63-2,018 ng/m² and 7-284 ng/m², respectively), often resulting as predominant in the polar organic fraction and comparable with *n*-alkanes (Table II.10 and Figure II.6). Traces of DEET and

nonylphenols, both peaking in the school (S₁) and home, could be ascribed to use of mosquito repellants (Autan ®) and disinfectant agents, respectively [64.65.66] while phthalate esters are ubiquitous contaminants as typical components of plastic materials [59]. Cocaine was absent from dusts, however cannabinol was found both in the home and overall at H1 site in the hospital (0.5 ± 0.7 and 0.6 ± 0.7 ng/m² respectively). Cannabinol is a typical by-product of psychoactive Δ^9 -tetrahydrocannabinol (THC), the principal component of marijuana. H1 site seemed to be also affected by native THC (3.9 ± 6.8 ng/m²) and cannabidiol (0.5 ± 0.9 ng/m²).

With regards to for vapor phase, highly polar substances could not be determined at S₁ and S₄ sites, where neither illicit drugs nor DEET occurred. The concentrations of nicotine ranged from 4.1-15 ng/m³ at school, up to 38-416 ng/m³ in the hospital. Caffeine was as high as 3.5-16 ng/m³ at school, hospital and university indoors, but exceeded 25 ng/m³ at university outdoors and 60 ng/m³ in H3. Nonylphenols were, on the average, equal to ~4 ng/m³ at university, to 11.2 ng/m³ in U3, ~ 1 ng/m³ at hospital, and ~0.5 ng/m³ at school. Phthalate esters ranged from 1.2 to 18.7-ng/m³ at university, 1.2 to 14.2 ng/m³ at school and 0.9-3.7 at hospital, except in H2 where they reached the maximum of 27.1 ng/m³.

No links seemed to exist between nicotine and caffeine in dusts and gas phase, highlighting that local consumption rather than the population presence was the source of contamination. Analogous behaviors were followed by phthalates and nonylphenols.

The concentrations of nicotine and caffeine at all sites were of the same order of magnitude previously recorded in Algiers and its surrounding during the summer 2006. There, 31-268 ng/m³ were found of nicotine, and 39-414 ng/m³ of caffeine [6.7] in PM₁₀. Abroad, extensive measurements were performed both indoors and outdoors in Italy at sites of different typologies, using both high and low volume PM₁₀ samplers [14]. Levels

of nicotine and caffeine were compared in the hot and cold seasons. Values as high as 537 ng/m³ of nicotine and 9.3 ng/m³ of caffeine were detected inside a coffee bar in winter [67].

As for APs, the indoor concentrations in Ouargla were low compared with those recorded in Massachusetts, USA (1099 ng/m³, [68]), in California, USA (725 ng/m³, [47]), in Norway (111 ng/m³, [69]), in Japan (638 ng/m³, [70]), in Sweden (2,666 ng/m³, [71]), and in France (756 ng/m³, [48]).

4. Conclusion

n-Alkanes, PAHs and polar compounds, were characterized in dusts and in air (vapor phase) in Ouargla city, South-Eastern Algeria.

According to molecular signatures, particulate from tobacco smoke and fumes from landfill sources were identified as the main pollution sources at the indoor/outdoor sites. The contribution from the natural sources was important, exceeding 40% of total in dust particles and reaching 50 % in the gas phase; this finding was confirmed by the high values of the Carbon Preference Index.

Among polar compounds, nicotine and caffeine occurred at quite high concentrations; meanwhile, two locations (one in the hospital) were affected by psychoactive cannabinoids. By contrast, cocaine was always absent, in accordance with previous investigations in Algiers. Phthalate esters were less than elsewhere, while traces of nonylphenols were detected.

At the university, the light alkanes burdens looked as higher indoors than outdoors, suggesting the use of petrol derived solvents was an important source of this group. By contrast, PAHs were less indoors, suggesting that intrusion of substances released from vehicle traffic was the principal responsible for pollution of interiors.

II.5.References :

- [1] World Health Organization WHO, 2014. World health statistics.WHO Press, Geneva, Switzerland, pp. 180 (ISBN 978-92-4-156471-7, ISBN 978-92-4-069267-1 [PDF]).
- [2] Simoneit, B.R.T., 1989. Organic Matter of the Troposphere- V:Application of Molecular Marker Analysis to Biogenic Emissions into the Troposphere for Source Reconciliations. *Journal of Atmospheric Chemistry* 8, 251-275.
- [3] Pio, C., Alves, C., Duarte, A.C., 2001. Identification, abundance and origin of atmospheric organic particulate matter in a Portuguese rural area. *Atmospheric Environment* 35, 1365-1375.
- [4] Alves, C., Vicente, A., Pio, C., Kiss, G., Hoffer, A., Decesari, S., Prevot, A.S.H., Minguillón, M.C., Querol, X., Hillamo, R., Spindler, G., Swietlicki, E., 2012. Organic compounds in aerosols from selected European sites – biogenic versus anthropogenic sources. *Atmospheric Environment* 59, 243-255.
- [5] Balducci, C., Ladji, R., Muto, V., Romagnoli, P., Yassaa, N., Cecinato, A., 2014. Biogenic and anthropogenic organic components of Saharan sands. *Chemosphere* 107, 129–135.
- [6] Moussaoui, Y., Balducci, C., Cecinato, A., Meklati, B.Y., 2010. Chemical composition of extractable organic matter of airborne particles in urban and rural atmospheres of Northern Algeria. *Fresen. Environ. Bull.* 19, 2497-2508.
- [7] Moussaoui, Y., Balducci, C., Cecinato, A., Meklati, B.Y., 2013. Atmospheric particulate organic matter at urban and forest sites of Northern Algeria. *Urban Climate* 4, 85-101
- [8] Canha, N., Almeida, S.M., Freitas M.d.C., Trancoso, M., Sousa, A., Mouro, M., Wolterbeek, H.T., 2014. Particulate matter analysis in indoor environments of urban and

rural primary schools using passive sampling methodology, *Atmospheric Environment* 83, 21-34.

[9] Ladji, R., Yassaa, N., Balducci, C., Cecinato, A., 2014. Particle size distribution of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) in urban and industrial aerosol of Algiers, Algeria. *Environmental Science and Pollution Research* 21, 1819–1832.

[10] Xie, M., Hannigan, P., Barsanti, K.C., 2014. Gas/particle partitioning of *n*-alkanes, PAHs and oxygenated PAHs in urban Denver, Portland, *Atmospheric Environment* 95, 355-362.

[11] Yassaa, N., Meklati, B.Y., Cecinato, A., Marino, F., 2001a. Particulate *n*-alkanes, *n*-alkanoic acids and polycyclic aromatic hydrocarbons in the atmosphere of Algiers City Area. *Atmospheric Environment* 35, 1843-1851.

[12] Ladji, R., Yassaa, N., Balducci, C., Cecinato, A., 2010. Organic components of Algerian desert dusts, *Chemosphere* 81, 925-931.

[13] Moussaoui, Y., Tuduri, L., Kerchich, Y., Meklati, M.B., Eppe, G., 2012. Atmospheric concentrations of PCDD/Fs, dl-PCBs and some pesticides in northern Algeria using passive air sampling. *Chemosphere* 88, 270-277.

[14] Cecinato, A., Balducci, C., Nervegna, G., 2009. Occurrence of cocaine in the air of the World's cities an emerging problem, A new tool to investigate the social incidence of drugs. *Sci. Total Environ.* 407, 1683–1690

[15] Sangiorgi, G., Ferrero, L., Ferrini, B.S., Lo Porto, C., Perrone, M.G., Zangrando, R., Gambaro, A., Lazzati, Z., Bolzacchini, E., 2013. Indoor airborne particle sources and semi-volatile partitioning effect of outdoor fine PM in offices. *Atmospheric Environment* 65, 205-214.

[16] Kliucininkas, L., Krugly, E., Stasiulaitiene, I., Radziuniene, I., Prasauskas, T., Jonusas, A., Kauneliene, V., Martuzevicius, D., 2014. Indoor outdoor levels of size

segregated particulate matter and mono/polycyclic aromatic hydrocarbons among urban areas using solid fuels for heating. *Atmospheric Environment* 97, 83-93.

[17]Wang, Z., Yang, C., Kelly-Hooper, F., Hollebhone, B.P., Peng, X., Brown, C.E., Landriault, M., Sun, J., Yang, Z., 2009. Forensic differentiation of biogenic organic compounds from petroleum hydrocarbons in biogenic and petrogenic compounds cross-contaminated soils and sediments, *Journal of Chromatography A* 1216, 1174–1191.

[18]Wingfors, H., Hägglund, L., Magnusson, R., 2011. Characterization of the size-distribution of aerosols and particle-bound content of oxygenated PAHs, PAHs, and *n*-alkanes in urban environments in Afghanistan. *Atmospheric Environment* 45, 4360 – 4369.

[19]Chen, Y., Cao, J., Zha, J., Xu, H.H., Arimoto, R., Wang, G., Han, Y., Shen, Z., Li, G., 2014. *n*-Alkanes and polycyclic aromatic hydrocarbons in total suspended particulates from the southeastern Tibetan Plateau: Concentrations, seasonal variations, and sources, China. *Science of the Total Environment*. 470-471, 9-18.

[20]Perrone, M.G., Carbone, C., Faedo, D., Ferrero, L., Maggioni, A., Sangiorgi, E., Bolzacchini, E., 2014. Exhaust emissions of polycyclic aromatic hydrocarbons, *n*-alkanes and phenols from vehicles coming within different European classes. *Atmospheric Environment* 82, 391-400.

[21]Fromme, H., Oddoy, A., Piloty, M., Krausec, M., Lahrz, T., 1998. Polycyclic aromatic hydrocarbons PAH and diesel engine emission elemental carbon inside a car and a subway train. *The Science of the Total Environment* 217, 165-173.

[22]Cecinato, A., 2014. Indoor PAHs at schools, homes and offices in Rome, Italy. *Atmospheric Environment* 92, 51-59.

[23]Vojtisek-Lom, M., Pechout, M., Dittrich, L., Beranek, V., Kotek, M., Schwarz, J., Vodicka, P., Milcova, A., Rossnerova, A., Ambroz, A., Topinka, J., 2015. Polycyclic

aromatic hydrocarbons (PAH) and their genotoxicity in exhaust emissions from a diesel engine during extended low-load operation on diesel and biodiesel fuels. *Atmospheric Environment* 109, 9-18.

[24]Orecchio, S., 2010.Assessment of polycyclic aromatic hydrocarbons (PAHs) in soil of a Natural Reserve (Isola delle Femmine) (Italy) located in front of a plant for the production of cement. *Journal of Hazardous Materials* 173 ,358–368.

[25]Alam, M.S., Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2013.Using atmospheric measurements of PAH and quinone compounds at roadside and urban background sites to assess sources and reactivity. *Atmospheric Environment* 77, 24-35.

[26]Cecinato, A., Guerriero, E., Balducci, C., Muto, V., 2014. Use of the PAH fingerprints for identifying pollution sources. *Urban Climate* 10, 630-643.

Dong, M., Hoffmann, D., Locke, D.C., Ferrand, E., 1977.The occurrence of caffeine in the air of New York City. *Atmos. Environ.* 11, 651–653.

[27]Hoh, E., Hunt, R.N., Quintana, P.J.E., Zakarian, J.M., Chatfield, D.A., Wittry, B.C., Rodriguez, R., Matt, G.E., 2012.Environmental Tobacco Smoke as a Source of Polycyclic Aromatic Hydrocarbons in Settled Household Dust, *American Chemical Society* 46, 4174-4183.

[28]Boonyatumanond, R., Murakami, M., Wattayakorn, G, Togo, A., Takada, H., 2007. Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. *Science of the Total Environment* 384, 420-432.

[29]Lu, H., Zhu, L., Chen, S., 2008. Pollution level, phase distribution and health risk of polycyclic aromatic hydrocarbons in indoor air at public places of Hangzhou. *Environmental Pollution* 152, 569-575.

- [30]Romagnoli, P., Balducci, C., Perilli, M., Gherardi, M., Gordiani, A., Gariazzo, C., Gatto, M.P., Cecinato, A., 2014. Indoor PAHs at schools, homes and offices in Rome, Italy . *Atmospheric Environment* 92, 51-59.
- [31]European Commission EC, 2008. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on Ambient air quality and cleaner air for Europe. See: [3](#).
- [32]Sklorz, M., Schnelle-Kreis, J., Liu, Y., Orasche, J., Zimmermann, R., 2007. Daytime resolved analysis of polycyclic aromatic hydrocarbons in urban aerosol samples – Impact of sources and meteorological conditions. *Chemosphere* 67, 934–943.
- [33]Castellano, A.V., Cancio, J.L., Alemàn, P.S., Rodriguez, S., 2003. Polycyclic aromatic hydrocarbons in ambient air particles in the city of Las Palmas de Gran Canaria. *Environment International* 29, 475-480.
- [34]Agudelo-Castañeda, D.M., Teixeira E.C., 2014. Seasonal changes, identification and source apportionment of PAH in PM₁₀. *Atmospheric Environment* 96, 186-200.
- [35]Slezakova, K., Castro, D., Pereira, M.C., Morais, S., Delerue-Matos, C., Alvim-Ferraz, M.C., 2009. Influence of tobacco smoke on carcinogenic PAH composition in indoor PM₁₀ and PM_{2.5}. *Atmospheric Environment* 43, 6376–6382.
- [36]International Agency of Research on Cancer IARC, 2014. Diesel and gasoline engine exhausts and some nitroarenes. IARC Monographs on the evaluation of carcinogenic risks to humans, Volume 105. Lyon, France, pp. 714 (ISBN 978-92-832-01434, ISSN 1017-1606).
- [37]Montone, R.C., Taniguchi, S., Weber, R.R., 2002. PCBs in the atmosphere of King George Island, Antarctica. *The Science of the Total Environment* 308, 167–173.
- [38]Zhu, C., Li, Y., Wang, P., Chen, Z., Ren, D., Ssebugere, P., Zhang, Q., Jiang, G., 2015. Polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs) in

environmental samples from Ny-Alesund and London Island, Svalbard, the Arctic. *Chemosphere* 126, 40-46.

[39]Fromme, H., Schober, W., 2014. Waterpipes and e-cigarettes: Impact of alternative smoking techniques on indoor air quality and health. *Atmospheric Environment* 106, 429-441.

[40]Yassaa, N., Meklati, B.Y., Cecinato, A., Marino, F., 2001b. Organic aerosols in urban and waste landfill of Algiers metropolitan area: occurrence and sources. *Environ. Sci. Technol.* 35, 306-311.

[41]Yassaa, N., Meklati, B.Y., Cecinato, A., 2001c. Chemical characteristics of organic aerosols in Algiers city area: influence of a fat manufacture plant. *Atmos. Environ.* 35, 6003-6013.

[42]Yassaa, N., Meklati, B.Y., Cecinato, A., Marino, F., 2001d. Chemical characteristics of organic aerosol in Bab-Ezzouar (Algiers). Contribution of bituminous product manufacture. *Chemosphere.* 45, 315-322.

[43]Gogou, A., Stephanou, E.G., Stratigakis, N., Grimalt, J.O., Simo, R., Aceves, M., Albaiges, J., 1994. Differences in lipid and organic salt constituents of aerosols from Eastern and Western Mediterranean coastal cities. *Atmos. Environ.* 28, 1301–1310.

[44]Liu, Q.T., Chen, R., Mccarry, B., Diamond, M., and Bahavar, B., 2003. Characterization of Polar Organic Compounds in the Organic Film on Indoor and Outdoor Glass Windows. *Environ. Sci. Technol.* 37, 2340-2349 .

Simoneit, B.R.T., Cardoso, J.N., Robinson, N., 1990. An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. *Chemosphere* 21, 1285-1301.

[45]Wilson, N. K., Chuang, J. C., Lyu, C., Menton, R., Morgan, M. K., 2003. Aggregate exposures of nine preschool children to persistent organic pollutants at day care and at home. *J. Expo. Anal. Environ. Epidemiol.* 13 (3), 187–202.

- [46]Fromme, H., Lahrz, T., Piloty, M., Gebhardt, H., Oddoy, A., Rüden, H., 2004. Polycyclic aromatic hydrocarbons inside and outside of apartments in an urban area. *Sci. Total Environ.* 326 (1–3), 143–149.
- [47]Rudel, R. A., Dodson, R. E., Perovich, L. J., Morello-Frosch, R., Camann, D. E., Zuniga, M. M., Yau, A. Y., Just, A. C., Brody, J. G., 2010. Semivolatile Endocrine-Disrupting Compounds in Paired Indoor and Outdoor Air in Two Northern California Communities. *Environ. Sci. Technol.* 44 (17), 6583–6590.
- [48]Blanchard, O., Philippe, G.F., Mercier, N., Bonvallot., C, Chevrier., O, Ramalho., C, Mandin., B, Le Bot., 2014. Semivolatile Organic Compounds in Indoor Air and Settled Dust in 30 French Dwellings, *American Chemical Society* 48, 3959-3969.
- [49]Orecchio, S., Cannata, S., Culotta, L, 2010. How building an underwater pipeline connecting Libya to Sicilian coast is affecting environment: polycyclic aromatic hydrocarbons (PAHs) in sediments; monitoring the evolution of the shore approach area of the Gulf of Gela (Italy). *Journal of Hazardous Materials* 181, 647–658.
- Orecchio, S., 2011. Polycyclic aromatic hydrocarbons (PAHs) in indoor emission from decorative candles. *Atmos. Environ.* 45 (10), 1888–1895.
- [50]Tobiszewski, M., Namieśnik, J., PAH diagnostic ratios for the identification of pollution emission sources, *Environ. pollut.* **162**, 2012, 110-119.
- [51] Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos. Environ.* 42, 2895-2921.
- [52]Rotatori, M., Cecinato, A., Sbrilli, A., Guerriero, E., Bianchini, M., Colamonici, V., Gigliucci, P., Tamburro, D., Tomasi Sciano, M.C., 2005. Benzene, Idrocarburi policiclici aromatici e polveri sottili. New Press Publ., Como (Italy).

- [53]Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1993a. Sources of fine organic aerosol. 2. Noncatalyst and catalyst equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 27, 636–651.
- [54]Bourotte, C., Forti, M.C., Taniguchi, S., Caruso Bicego, C., Lotufo, P.A., 2005. A wintertime study of PAHs in fine and coarse aerosols in Sao Paulo city, Brazil. *Atmos. Environ.* 39, 3799-3811.
- [55]Salzano, R., Mabilia, R., Salvatori, R., Sciano, M.C., Garcia, F.V., 2008. Spectro-radiometric and PAH chemical characterization of vehicle particulate emissions at the chassis dynamometer. *Fresen. Environ. Bull.* 17, 1711–1716.
- [56]Cecinato, A., Mabilia, R., Tomasi Sciano, M.C., Brachetti, A., 2005. Benzene, Idrocarburi policiclici aromatici e polveri sottili. New Press Publ., Como (Italy).
- [57]Schmidl, C., Bauer, H., Dattler, A., Hitzenberger, R., Weissenbroeck, G., 2008. Chemical characterisation of particle emissions from burning leaves. *Atmos. Environ.* 42, 9070–9079.
- [58]Yang, H.H., Lee, W.J., Chen, S.J., Lai, S.O., 1998. PAH emission from various industrial stacks. *J. Hazard. Mater.* 60, 159–174.
- [59]Lu, H., Zhu, L., 2007. Removal of bromophenols from water using industrial wastes as low cost adsorbents. *J. Hazard. Mater.* 139, 193–198.
- [60]Wang, P., Wang, S.L., Fan, C.Q., 2008. Atmospheric distribution of particulate- and gas-phase phthalic esters (PAEs) in a Metropolitan City, Nanjing, East China. *Chemosphere* 72, 1567–1572.
- [61]Abb, M., Heinrich, T., Sorkau, E., Lorenz, W., 2009. Phthalates in house dust, *Environment International* 35, 965–970.
- [62]Balducci, C., Nervegna, G., Cecinato, A., 2009. Evaluation of principal cannabinoids in airborne particulates. *Analytica Chimica Acta* 641, 89–94.

- [63]Souza, K. F., Carvalho, L. R.F., Allen, A. G. , Cardoso, A. A .,2014.Diurnal and nocturnal measurements of PAH, nitro-PAH, and oxy-PAH compounds in atmospheric particulate matter of a sugar cane burning region.*Atmospheric Environment* 83 , 193-201
- [64]Quednow, K ., Püttmann, W.,2009.Temporal concentration changes of DEET, TCEP, terbutryn, and nonylphenols in freshwater streams of Hesse, Germany: possible influence of mandatory regulations and voluntary environmental agreements.*Environ Sci Pollut Res* 16,630–640.
- [65]Balducci,C., Perilli,M.,Romagnoli.P., Cecinato,A.,2012. New developments on emerging organic pollutants in the atmosphere , *Environ Sci Pollut Res* 19,1875–1884.
- [66]Li,J.,Wang,G.,2015.Airborne particulate endocrine disrupting compounds in China: Compositions, size distributions and seasonal variations of phthalate esters and bisphenol A.*Atmospheric Research* 154 , 138–145.
- [67]Cecinato, A., Balducci, C., Perilli,P.,2016. Illicit psychotropic substances in the air: The state-of-art. *Science of the Total Environment* 539 ,1–6.
- [68]Rudel, R. A., Camann, D. E., Spengler, J. D., Korn, L. R., Brody, J. G., 2003. Phthalates, Alkylphenols, Pesticides, Polybrominated Diphenyl Ethers, and Other Endocrine-Disrupting Compounds in Indoor Air and Dust. *Environ. Sci. Technol.* 37 (20), 4543–4553.
- [69]Rakkestad, K. E.,Dye, C. J., Yttri, K. E.,Holme, J. A., Hongslo, J. K., Schwarze, P. E., Becher, R. 2007. Phthalate levels in Norwegian indoor air related to particle size fraction. *J. Environ. Monit.*9 (12), 1419– 1425.
- [70]Kanazawa, A., Saito, I., Araki, A., Takeda, M., Ma, M., Saijo, Y., Kishi, R., 2010.Association between indoor exposure to semi-volatile organic compounds and building-related symptoms among the occupants of residential dwellings.*Indoor Air*, 20 (1), 72–84.

[71]Kubwabo, C., Rasmussen, P. E., Fan, X., Kosarac, I., Wu, F., Zidek, A., Kuchta, S. L., 2013. Analysis of selected phthalates in Canadian indoor dust collected using household vacuum and standardized sampling techniques. *Indoor Air*, 23 (6), 506–514.

Chapter V:

Detecting VOCs (PAH) in hospital and university

V.1.Introduction:

Numerous studies have been implemented with the goal of determining the impact of air quality of interiors on the human health [1- 4], because indoor air is affected by a lot of substances such as volatile organic compounds (VOCs), which display toxic for humans and harmful for the environment; besides, these toxicants are often more indoors than outdoors, due to existence of internal sources as well as to a reduced presence of ozone and other oxidants [5,6]. Among the contaminants there are hydrocarbons and their derivatives, e.g. aliphatics, alkyl benzenes, ketones, polycyclic aromatics, chlorinated hydrocarbons, organic acids [7,8]. Tobacco smoke, use of cleaning products, domestic heating, cooking, construction materials, furnishings, paints, varnishes and solvents, office equipment, and consumer products have been recognized as the principal internal sources of VOCs affecting interiors, though a key role can be played by external sources like vehicular exhausts and industrial emissions [7,9,10]. The indoor/outdoor concentration ratio (I/O) of VOCs looks as a simple tool for understanding whereas internal or external sources prevail, overall combined with the fingerprint of VOC in the air (i.e., the percent composition of groups and the presence of peculiar source markers [11-13]). To investigate the indoor air composition, a suitable way is the application of diffusive sampling methods/devices, since they do not perturb the study locations, nor require electric power; finally, the loss of measurement time frequency is well compensated by the opportunity of examining with high space resolution. Three principal types of diffusive models are *Radiello*, *Analyst* and *SPME* for low-volumes, and *PAS* for high volume sampling [14,15]; alternatively, gases are collected by means of active sampling on traps or in canisters. Particulate air contaminants require filtering air to collect substrate where they are adsorbed, and mechanical cleaning or dedicated collectors for surfaces on which they are deposited [12,16,17]. Various types of indoor

environment have been investigated till now, including schools, offices, hospitals, homes and work places [18-21]. This paper documents the results of indoor and outdoor air monitoring at the hospital and university of Ouargla city, Algeria, conducted during the autumn 2015. The focus were PAHs, collected by means of diffusive technique, and the internal/external nature of pollution sources investigated by calculating the I/O ratio.

V.2. Experimental :

V.2.1 Sites of sampling :

The passive sampling devices were exposed to indoor/outdoor air over two months, from October to December (Figure V.1). Three locations were selected at university, two indoors (U1, U2) and one outdoors (U3); meanwhile, two locations (H1, indoors, and H2, outdoors) were investigated at hospital.

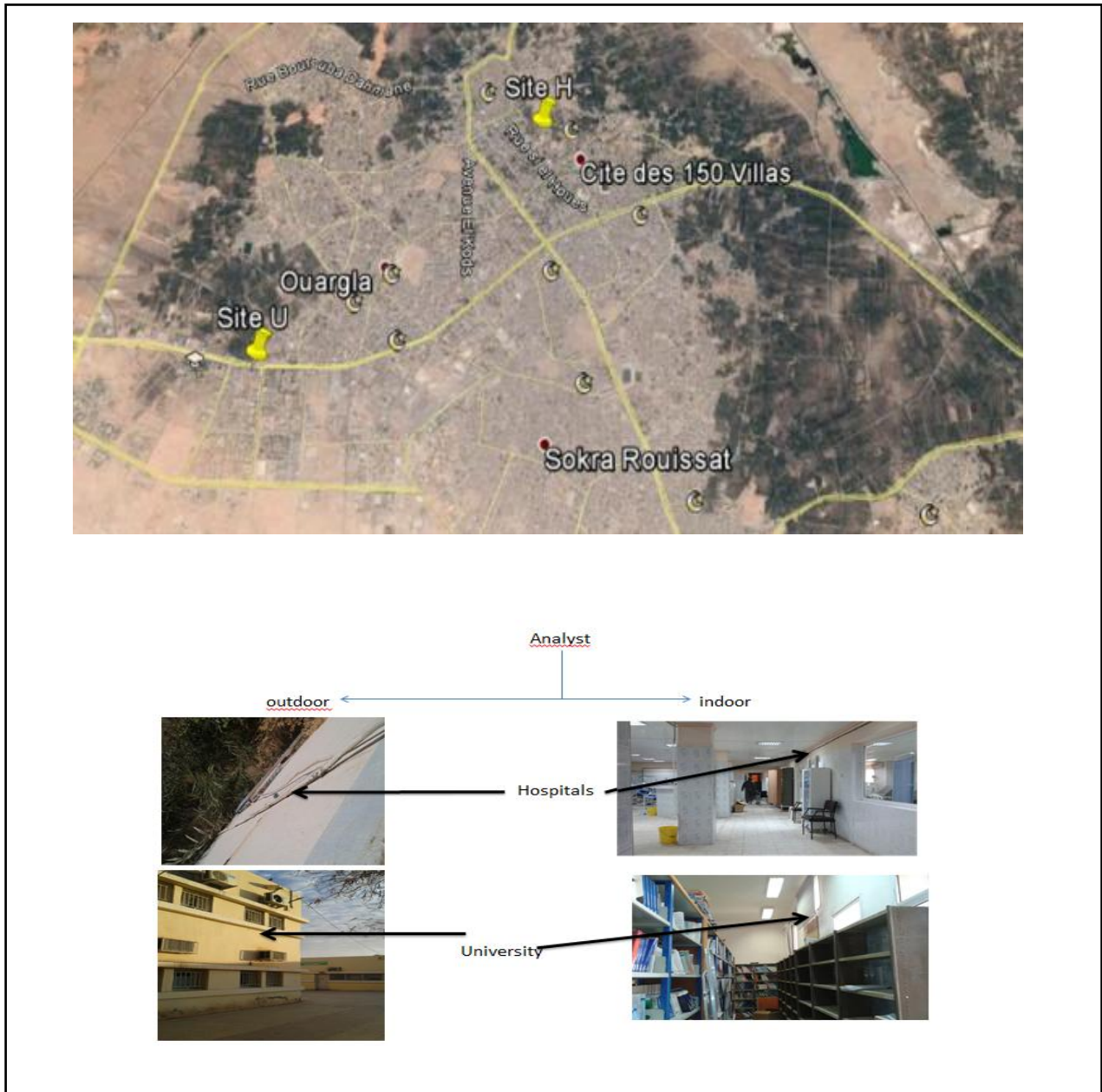


Figure.V.1:Sampling sites selected for indoor and outdoor measurement of semi-volatile PAHs (gaseous fraction) in Ouargla city: U = University (31°56'29.76"N, 5°18'12.77"E); H = Hospital (31°57'44.28"N, 5°19'56.35"E).

V.2.2 Sample treatment:

The analytical procedures were adapted from the studies of (Bertoni,2001)and Romagnoli,2016). Analyst-II samplers have been optimized for working time intervals of some months (two to six; seeBertoni,2001)and look fine for PAHs not exceeding 202 of molecular weight. Unlike of active sampling based on cartridges, these samplers are not

affected by soot collection or by blow off. After collection, PAHs are extracted from the adsorbent with toluene fortified with perdeuterated homologues acting as internal standards, and directly analyzed through GC-MS detection without any further sample treatment(see figure 2). In our case, the MS module (*Trace and Trace DSQ*, both from *Thermo*, Rodano MI, Italy) was operated in electron-impact, selected-ion-detection mode, and the whole system was managed by a dedicated software (*Excalibur*). GC temperature programs from 60 °C or 90 °C up to 280 °C allowed all analytes eluting within 50 min. The compound identification was based on peak retention times and intensity ratios of characteristic ion current ($[M/Z]^+$) intensities. For quantification, the ion traces corresponding to molecular or base fragment were compared with those of the closest perdeuterated reference substances in the chromatogram. (FigureV.3)

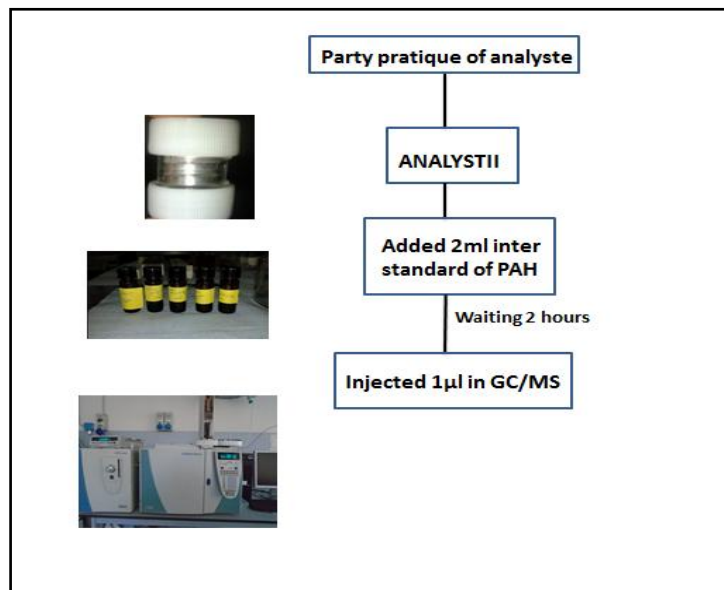


Figure.V.2: Planned party experimental of ANALYSTII

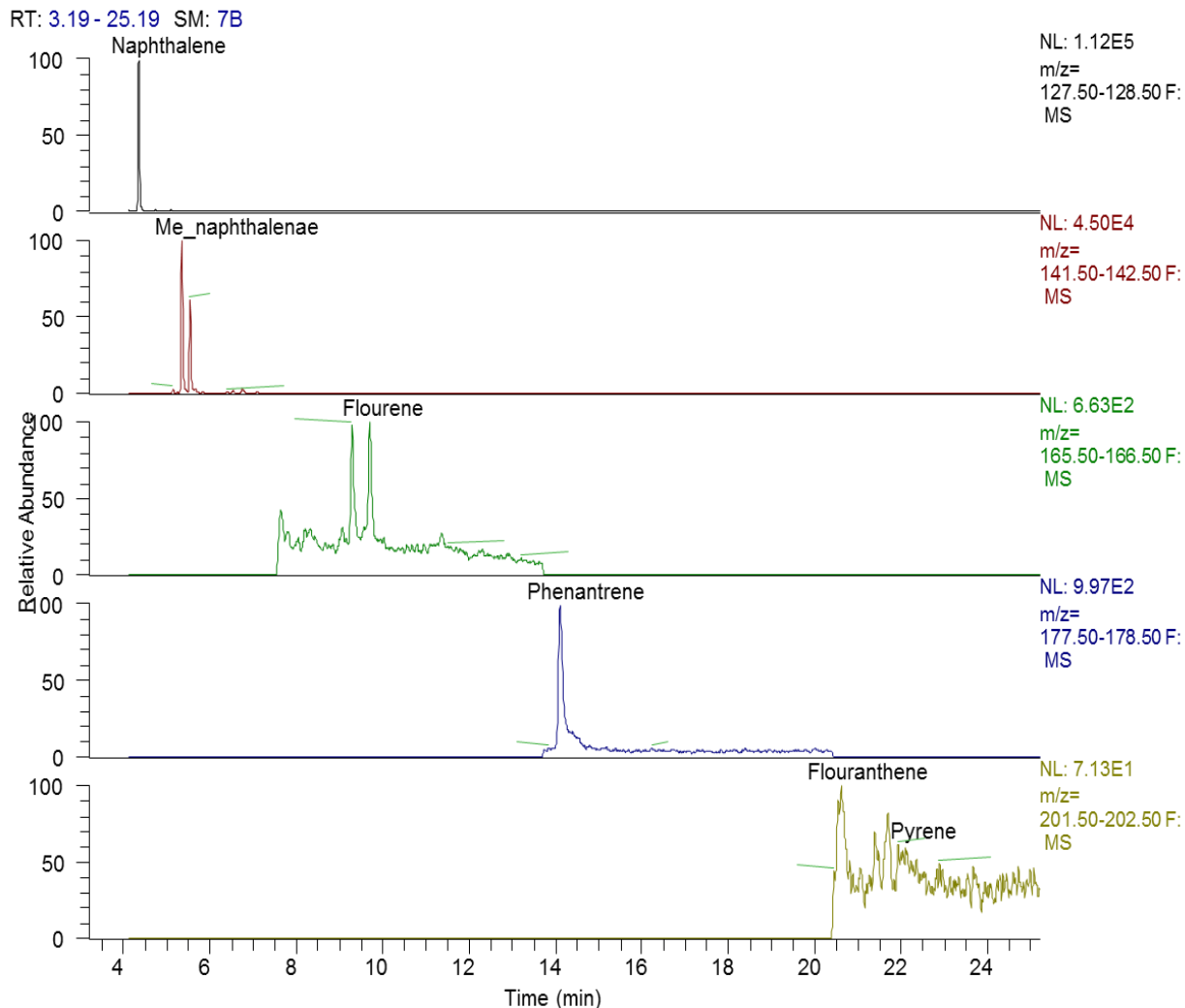


Figure.V.3: chromatogram of VOCs identified in the sampler

V.3. Results and discussions:

Seven individual PAHs and the dimethyl-naphthalene subgroup were identified and characterized in the atmospheric samples. They were: naphthalene (NA), 1-methylnaphthalene (1-MNA), 2-methylnaphthalene (2-MNA), dimethyl/ethylnaphthalene mixture (DMNA), fluorene (FL), phenanthrene (PH), fluoranthene (FA) and pyrene (PY). The concentrations detected at the sites are reported in Table V.1 and figure V.4. Total PAHs (Σ PAHs) ranged from 8,681 to 1,848 ng/m³ indoors and from 823 to 661 ng/m³ outdoors. Naphthalene and its methyl derivatives were confirmed as the most abundant

individual congeners. It is worth to note that the PAH pattern was similar at the two external sites (although university was affected at a 25% higher rate), while the three interiors investigated were distinct not only due to total PAH amounts, but also to the percent distributions; looking to total concentrations, the maximum was recorded at U2, and the minimum at H1.

Table.V. 1: Average concentrations of VOCs (ng/m³) in indoor and outdoor air in Ouargla, Algeria.

Compound	U1	U2	U3	H1	H2
NA	609	2908	402	1020	339
1-MNA	370	2390	168	291	123
2-MNA	233	1473	90	155	70
DMNA	792	1881	138	325	107
FL	66	8.1	3.8	10.8	3.4
PH	16	8.8	8.8	32	6.2
FA	6.7	6.5	6.9	7.5	6.8
PY	5.0	4.8	4.9	5.5	5.0
∑PAHs	20,389	8,681	823	1848	661

Symbols: U1: University library, indoors; U2: university photocopier center, indoors; U3: university, outdoors; H1: hospital, hemodialysis room; H2: hospital, outdoors. NA:naphthalene ,1-MNA: 1-methylnaphthalene .2 -MNA : 2-methylnaphthalene . DMNA: dimethylnaphthalenes (sum) .FL: fluorene .PH: phenanthrene .FA: fluoranthene; PY :pyrene.

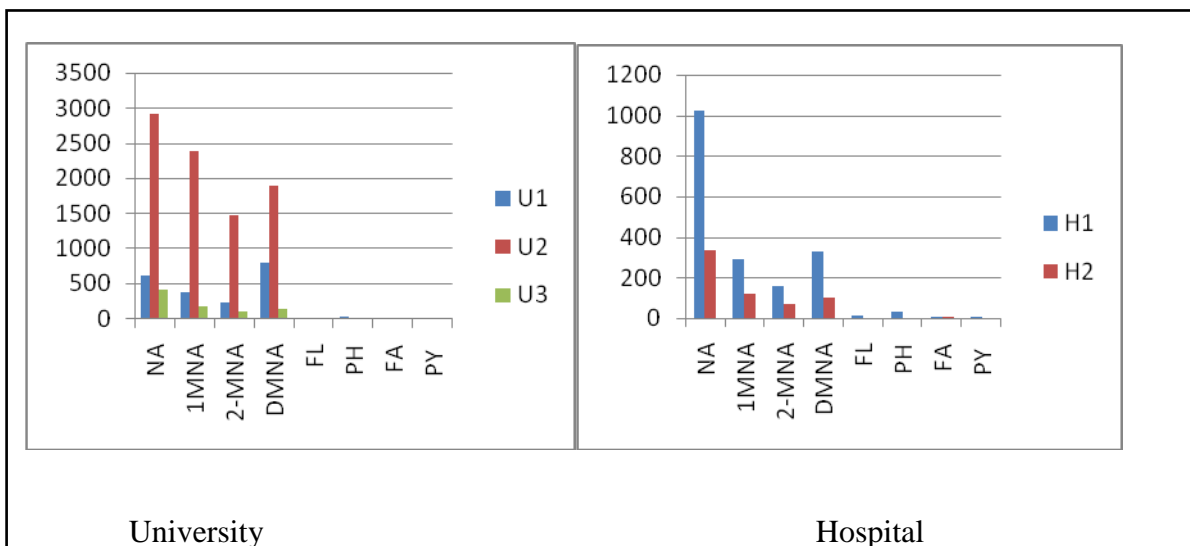


Figure .V.4 :average concentration in hospital and university of VOCs

The I/O ratios equal to 1.0-5.7 in U1 and H1, and >10 in U2 (Table V.2) show that internal sources were predominant [11.13]; the PAH occurrence there could be related to solvent evaporation, to use of printers and photocopiers as well as of cleaning and house products, to tobacco smoke, to cooking and domestic heating [22.10]. Nevertheless, the least volatile PAH compounds studied (FA and PY) were equally occurring indoors and outdoors, which means internal sources were unimportant for them.

Though considered weak carcinogens, naphthalene and its methyl derivatives could be a risk source for population exposed, due to high concentrations recorded [23], which suggests remediation measures must be implemented to abate the PAH loads in both sites investigated.

Table .V.2 :RI/Ovalue of VOCs between indoor and outdoor air

RI/O	U1/U3	U2/U3	H1/H2
NA	1.5	7.2	3.0
1MNA	2.2	14.2	2.4
2-MNA	2.5	16.3	2.2
DMNA	5.7	13.6	3.0
FL	1.7	2.1	3.2
PH	1.8	0.9	5.2
FA	0.9	0.9	1.1
PY	1.0	0.9	1.1

Symbols: see Table V.1.

V.4. Conclusion:

Gaseous PAHs were investigated indoors and outdoors at university and hospital of Ouargla city, Algeria, in the autumn 2015, by means of diffusive sampling technique. High PAH concentrations were detected at the sites, overall of naphthalene and its methyl derivatives, and indoors. The photocopier room in the university was the most contaminated site. The air was more affected by PAHs at university than at hospital.

V.5. references :

- [1] Godoi, R. H.M ., Godoi, A. F.L., Junior ,S. J. G., Paralovo, S. L., Borillo ,G. C., Barbosa ,G. G. C., Arantes ,M. G., Charello ,R. C., Filho, N. A. R., Grassi ,M. T., Yamamoto, C. I., Potgieter-Vermaak, S., Rotondo, G. G., Wael,K. D., van Grieken, R (2013).Healthy environment — indoor air quality of Brazilian elementary schools nearby petrochemical industry .*Science of the TotalEnvironment* 463–464 ,639–646
- [2] Lu, H., Zhu, L., Chen, S(2008).Pollution level, phase distribution and health risk of polycyclic aromatic hydrocarbons in indoor air at public places of Hangzhou, China. *Environment alPollution*152 , 569-575 .
- [3] Colman Lerner ,J.E., Sanchez ,E.Y., Sambeth, J.E., Porta A.A., 2012 . Characterization and health risk assessment of VOCs in occupational environments in Buenos Aires, Argentina .*Atmospheric Environment*55 ,440-447.
- [4] Kampa, M., Castanas, E(2008). Human health effects of air pollution. *Environmental Pollution* 151, 362-367.
- [5] Jones, A.P(1999) . Indoor air quality and health .*Atmospheric Environment*33, 4535–4564.
- [6] Villanueva,F.,Tapia,A.,Amo-Salas, M ., Notario,A., Cabañas,B.,Martínez ,E(2015).Levels and sources of volatile organic compounds including carbonyls in indoor air of homes of Puertollano, the most industrialized city in central Iberian Peninsula.Estimation of health risk.*Environmental Health* 218, 522–534.
- [7] Shi, J., Deng, H., Bai, Z., Kong ,S., Wang, X., Hao, J., Han, X., Ning ,P(2015). Emission and profile characteristic of volatile organic compounds emitted from coke production, iron smelt, heating station and power plant in Liaoning Province, China .*Science of the Total Environment* 515, 101–108.

- [8]Sona ,B., Breysse , P., Yang,W(2003). Volatile organic compounds concentrations in residential indoor and outdoor and its personal exposure in Korea.*Environment International*29 , 79 – 85.
- [9]He, Q., Yan ,Y., Li, H., Zhang, Y., Chen, L., Wang, Y(2015). Characteristics and reactivity of volatile organic compounds from non-coal emission sources in China. *Atmospheric Environment* 115, 153-162
- [10]Rösch ,c., Kohajda, T.,Röder,S., Bergen ,M., [Schlink](#) ,U(2014). Relationship between sources and patterns of VOCs in indoor air.*Atmospheric Pollution Research* 5, 129–137.
- [11]Kliucininkas, L., Martuzevicius, D ., Krugly, E., Prasauskas, T., Kauneliene, V., Molnar, P., Strandberg, B(2011). Indoor and outdoor concentrations of fine particles, particle-bound PAHs and volatile organic compounds in Kaunas, Lithuania.*Environ. Monit* 13, 182 –191.
- [12]Mishra, N., Bartsch ,J., Ayoko, G. A., Salthammer, T., Morawska, L(2015). Volatile Organic Compounds: Characteristics, distribution and sources in urban schools. *AtmosphericEnvironment* 106, 485-491
- [13]Xu,J.,Szyszkowicz,M.,Jovic,B.,Cakmak,S.,Austin,C.C.,Zhu,J(2016).Estimation of indoor and outdoor ratios of selected volatile organic compounds in Canada.*Atmospheric Environment* 141, 523–531.
- [14] Moussaoui,Y.,Cecinato,A.,Assami,K.,and Meklati,B.Y(2012).Indoor and Outdoor VOC emissions in urban areas of northern Algeria. *Fresenius Environmental Bulletin* 21, 1090-1098 .

- [15] Bertoni, G., Tappa, R., Cecinato, A., 2001. Environmental Monitoring of Semi-Volatile Polycyclic Aromatic Hydrocarbons by Means of Diffusive Sampling Devices and GC-MS Analysis. *Chromatographia Supplement* 53, 312- 316 .
- [16] Romagnoli, P., Balducci, C., Perilli, M., Vichi, F., Imperiali, A., Cecinato, A (2016) . Indoor air quality at life and work environments in Rome, Italy . *Environ Sci Pollut Res* 23,3503-3516 .
- [17] Liu, Q.T., Chen, R., Mccarry, B., Diamond, M., and Bahavar, B (2003). Characterization of Polar Organic Compounds in the Organic Film on Indoor and Outdoor Glass Windows. *Environ. Sci. Technol.* 37, 2340-2349 .
- [18] Sarkhosh, M., Mahvi, A. H., Zare, M. R., Fakhri, Y., Shamsolahi, H.R (2012). Indoor contaminants from Hardcopy Devices: Characteristics of VOCs in photocopy centers . *Atmospheric Environment* 63 , 307-312.
- [19] Parra, M.A., Elustondo, D., Bermejo, R., Santamaría, J.M (2008) . Quantification of indoor and outdoor volatile organic compounds (VOCs) in pubs and cafe's in Pamplona, Spain. *Atmospheric Environment* 42 , 6647–6654.
- [20] Dodson, Robin E., Levy, J. I., Spengler, J. D., Shine, J. P., Bennett, D. H. , 2008 . Influence of basements, garages, and common hallways on indoor residential volatile organic compound concentrations . *Atmospheric Environment* 42, 1569–1581 .
- [21] Jovanovic, M., Vucicevic, B., Turanjanin, V., Zivkovic, M., Spasojevic, V (2014). Investigation of indoor and outdoor air quality of the classrooms at a school in Serbia. *Energy*. 1-7
- [22] Batterman, S., Chin, J.-Y., Jia, C., Godwin, C., Parker, Edith., Robins, Thomas., Max, P., and Lewis, Toby., 2012. Sources, Concentrations and Risks of Naphthalene in Indoor and Outdoor Air. *Indoor Air* 22(4): 266–278.

[23]Sarigiannis,D.A.,Karakitsion,S.P.,Gotti,A.,Liakos.I.L.,Katsoyiannis,A(2011)

Exposure to major volatile organic compounds and carbonyls in European indoor environments and associated health risk. *Environment International* 37,743-765.

General conclusion

General conclusion:

In this thesis, we focused our study on the passive sampling method and quantitative qualitative analysis of particulate organic compounds in gas phase, dust and volatile organic compounds, by different chromatographic techniques in several sites of Ouargla city, located in South-Eastern Algeria in hospitals, schools, university sites, and in homes indoors and outdoors.

n-Alkanes, PAHs and polar compounds, were found in dusts and in air (vapor phase) of (hospital, school, university, home) indoor /outdoor.

In the first results of 2014, particulate were released from tobacco smoke, fumes from landfill sources. The contribution from the natural sources was important in dust particles and in the gas phase; this outcome was confirmed by the high values of Carbon Preference Index.

Among polar compounds there are nicotine, caffeine, Phthalate esters and nonylphenols were detected. At the university the light alkanes burdens were observed as higher indoors than outdoors. In this group suggesting of using petrol derived solvents was an important source. By contrast, PAHs were less indoors, suggesting that intrusion of substances released from vehicle traffic was the principal responsible for pollution of interiors.

In the second results of 2015 the organic compounds were in particulate matter from the dust and gas phase, we compared distribution and sources of *n*-alkanes when calculating the CPI and wax% between autumn 2014 and summer 2015 on gas phase indoor /outdoor. Also we applied the same process on the dust in same sites at 2014 and 2015. Generally the sources of *n*-alkanes were anthropogenic (school, hospital, university and home), and they were also internal or external, By contrast, the natural contribution

of organic particulates was low, independently on the site, the same results of n-alkanes gas phase had anthropogenic sources (fuel combustion, domestic solvent, industrial sources, vehicles exhaust), Polycyclic aromatic hydrocarbon PAHs and polar compounds.

The diffusive sampling method indoor /outdoor of hospital and university had detected BTEXs. Toluene has high levels in all sites indoor and outdoor at autumn of 2014, 2015. Benzene was carcinogenic compound, it has high concentration in indoor of hemodialysis in hospital and its sources were indoor. Gaseous PAHs diffusive sampling techniques were investigated indoors and outdoors at university and hospital. High PAH concentrations were detected in the autumn of 2015, overall of naphthalene and its methyl derivatives were high in indoors. The photocopier room in the university was the most contaminated site. The air was more affected by PAHs at university than at hospital.

Most organic compounds found inside and outside in several sites has anthropogenic nature. They have bad effect on health when inhalation for long-term. The proposed solutions for work sites in order to minimize this damage, such as opening the windows and doors for ventilation, diminishing the use of domestic solvent, taking the rubbish outside the cities, reducing the use of industrial materials which cause emissions build, the factories outside the cities and traffic regulation.

Finally, we will continue on this work with using active sampling method in order to determine the exact day of the organic pollutants and especially which effect human health.

Abstract :

Indoor environments are affected by a number of organic contaminants, whose concentration and magnitude are different in external air. In this research, polycyclic aromatic hydrocarbons (PAHs) received a special concern. PAHs occur in the air, are in the form of gaseous and particulate forms; they are associated to fine aerosols and soil dust. PAHs were first investigated in dust of interiors in Ouargla (part of the Algerian Sahara), concurrently with n-alkanes and polar organic compounds and also in the gas phase contained the same fraction. Volatile organic compounds are generally mono cyclic of PAHs (BTEXs) and low molecular mass collected by the diffusive sampling. All contaminants were determined from gas chromatographic - mass spectrometric analysis (GC/MS) performed at CNR laboratory – Italy. We conclude from our results that the air of our living places (school, hospital, university and home) is affected by organic compounds which, effected human health when exposed long time in indoor.

Key Words: Indoor /outdoor pollution; n-Alkanes ; Polycyclic aromatic hydrocarbons; polar organic compounds; VOCs; Passive sampling ; Ouargla city.

Résumé :

Les environnements intérieurs sont affectés par un certain nombre de contaminants organiques, dont les concentrations peuvent dépasser d'ordres de grandeur ceux trouvés à dans l'air extérieur. À cet égard, les hydrocarbures aromatiques polycycliques (HAP) méritent une attention particulière. Les HAP se produisent dans l'air à la fois sous forme gazeuse et particulaire; Ils sont associés aux aérosols fins et aux poussières de sol. Les HAP ont d'abord été étudiés dans les poussières d'intérieurs à Ouargla (Algérie saharienne), en même temps que les n-alcane et les composés organiques polaires concernant à la phase gazeuse contenait également la même fraction et les composés organiques volatils généralement mono cycliques des HAP (BTEX) Recueillies par l'échantillonnage diffusif. Tous les contaminants ont été déterminés par analyse chromatographique en phase gazeuse - spectrométrie de masse (GC / MS) effectuées au CNR - Italie. Nous avons conclu après nos résultats, que l'air de nos lieux de vie (école, hôpital, université et une maison) est affecté par ces composés organiques, ce qui influe sur la santé de l'homme quand il y est longuement exposé à l'intérieur.

Les mots clés : intérieur /extérieur pollution ; n-alcanes ; Hydrocarbures aromatiques polycycliques ; les composées polaires ; COVs ; l'échantillonnages passive ; Vile de Ouargla.

الملخص :

تتأثر البيئات المغلقة من ملوثات عضوية، تختلف من حيث الحجم والتركيز في الهواء الخارج والداخلي، الهيدروكربونات العطرية متعددة الحلقات بصفة خاصة تتواجد في الهواء على شكل غاز وجسيمات في الهباء الدقيق وغبار التربة . حددت الهيدروكربونات العطرية متعددة الحلقات في الغبار الداخلي على أنها الدراسة الأول لفيورقلة (صحراء الجزائر)، بالإضافة إلى الألكانات والمركبات العطرية القطبية المتواجدة في الطور الغازي بنسبة المركبات العضوية المتطايرة أحادية الحلقة العطرية (BTEXs) ذات الكتلة الجزيئية المنخفضة جمععت بواسطة تقنية أخذ العينات الانتشار . جميع الملوثات تحلل بكميات غازية الغاز - طيف الكتلة (GC / MS). في مختبر CNR - إيطاليا. استخلصنا من النتائج التي حصلنا عليها أن الهواء يتأثر من الأماكن التي يعيش فيها بسبب المركبات العضوية المتواجدة في (المدرسة والمستشفى والجامعة والمنزل) التي تؤثر على صحة الإنسان عند التعرض لفترة طويلة لها في الأماكن المغلقة.

الكلمات المفتاحية: التلوث في الأماكن الداخلية والخارجية، الهيدروكربونات العطرية متعددة الحلقات ، المركبات العطرية، المركبات العضوية المتطايرة، أخذ العينات بطريقة سلبية ، ولاية ورقلة.