

# Evaluation of Nitrogen dioxide, Benzene, Toluene, Ethylbenzene and Xylene concentrations in the urban environment of Meknes city, Morocco

## Abstract

The present study focuses on the monitoring and the evaluation of air quality in the city of Meknes, based on the tracers of pollution of proximity cars (NO<sub>2</sub> (nitrogen dioxide) and BTEX (Benzene, Toluene, Ethylbenzene, and Xylene)). In the absence of a telemetric station and a mobile laboratory within the city, passive diffusion tubes, analyzed offline in the laboratory after exposure, were the most plausible solution. The low cost, ease of implementation of the technique, and the possibility of covering a large geographic area with many samplers all argue for adopting this approach.

The coupling of the results of the measurement campaigns and counting sessions under a geographical information system allowed us to determine the most affected areas by automobile pollution and to carry out cartography at a large scale of spatial resolution of the prospected pollutants.

The deployment of passive sensors at 14 measurement sites revealed the existence of spatio-temporal variability of the pollutants studied. This variability is due to the climatic conditions that prevailed during the measurement campaigns, notably wind and precipitation, the photochemical nature of the said markers, the proximity to the emission sources, the type of measurement site, and the topography and road infrastructure.

The approach developed could be used as a decision-making tool for the competent authorities in this field and adapted for monitoring other types of pollutants (pesticides, tracers generated by industrial units, furan dioxins, etc.).

**Key words:** Passive diffusion tubes, air quality, nitrogen dioxide, BTEX, Meknes

## 1. Introduction

Air is essential for the survival of any living being. On average, humans consume 14 kg of air for 1.5 kg of food and 2 kg of water (Ait Bouh, 2012). Man can subsist for five weeks without eating, five days without drinking, and less than 5 minutes without breathing (Pleil et al., 2021).

The degradation of air quality exerts a substantial impact on human health, manifesting through an increased incidence of cardiovascular and respiratory diseases, premature mortality, and a higher risk of cancer (Almagro et al., 2015; Thurston et al., 2016; Turner et al., 2016; Hamanaka & Mutlu, 2018; WHO, 2019; Manisalidis et al., 2020; Lu et al., 2022). Air pollution has also a significant impact on the environment, leading to a series of adverse effects such as environmental acidification, ecosystem disruption, photochemical pollution, eutrophication, alteration in plant growth patterns, and degradation of the built environment (Smith et al., 2001; Hallquist et al., 2016; Sicard et al., 2017; Manisalidis et al., 2020; Strak et al., 2021; Babu & Aravinth, 2022). While air pollution problems are not new, they only gained momentum with the Industrial Revolution of the 19th century (Caruana, 2017). In the 14th century, being aware of the negative impacts of air pollution, King Edward II of England (1307-1327) took corrective measures against polluters with coal (Aubier and Lambrozo, 2000). Among the dramatic events linked to the degradation of air quality that marked the 20th century and increased interest in the various aspects of air pollution, we can cite the disaster in the Meuse Valley near the city of Liege in Belgium, where sixty people died in

December 1930 as a result of the increase in sulfur dioxide (SO<sub>2</sub>) levels (Aubier and Lambrozo, 2000; Nemery et al., 2001; Nemmar et al., 2003). Exposure to levels of the same tracer ranging from 1400 to 5500 µg/m<sup>3</sup> in 1948 resulted in 20 deaths in Donora, Pennsylvania (Schrenk et al., 1949; Aubier and Lambrozo, 2000; Nemmar et al., 2003). In 1952, nearly 4,000 people succumbed to London smog resulting from increased SO<sub>2</sub> levels (1260 µg/m<sup>3</sup>) combined with particulate matter concentration (2650 µg/m<sup>3</sup>) within 24 hours (Aubier and Lambrozo, 2000; Bell and Davis, 2001; Nemmar et al., 2003; Roussel, 2015). The number of recorded deaths exceeded five times the seasonal average, and two-thirds of the victims were over 65 years of age, 80% of whom had pre-existing cardiorespiratory problems. In 1984, the city of Bhopal in India suffered 3828 deaths following the explosion of a factory specialized in producing phytosanitary products by releasing more than 40 tons of methyl isocyanate into the atmosphere (Kurzman, 1987). To this can be added the explosion of the two nuclear reactors, Chernobyl and Fukushima (Brumfie, 2013; Yajima et al., 2014), whose damage is very difficult to determine so far. In order to prevent the recurrence of such issues that have led to the loss of hundreds or even thousands of lives (Aubier and Lambrozo, 2000; Nemery et al., 2001; Nemmar et al., 2003; Roussel, 2015) and to alleviate the severe consequences of air pollution, the international community has undertaken various initiatives and actions:

- The adoption of renewable energies (hydro, wind, photovoltaic, and geothermal)
- The replacement of fossil fuel vehicles with electric and hybrid cars
- Banning certain chemical compounds (chlorofluorocarbons (CFCs), persistent pesticides,...)
- The creation of low-emission zones, eco-neighborhoods, and the implementation of alternating traffic and urban tolls
- The adoption of environmental protocols such as the Kyoto Protocol, which set the thresholds of atmospheric emissions of each country and which gave birth to CDM projects (clean production mode)

Despite all the actions taken, air pollution still represents a significant public health issue and continues to claim millions of victims. According to the latest WHO report, 7 million deaths are caused each year by ambient and indoor air pollution (WHO, 2018). Among the severe disorders identified are respiratory disorders (asthma, COPD, bronchiolitis, bronchitis, rhinitis, pneumonia...), cardiovascular (stroke, myocardial infarction, ischemic heart disease, arrhythmia, heart failure, hypertension...), reproductive system (decreased male fertility, increased intrauterine mortality and premature births) and cancers (Li et al., 2022; WHO, 2022). The scientific literature on this subject is rich but concerns Europe, North America, and Asia.

In Morocco, there is a lack of comprehensive evaluation of air pollution, and the existing efforts have primarily been ad hoc and often lack the necessary representativeness to provide a thorough assessment (Ministry of Health, 1998; Casa-Airpol, 2000; Mohammedia-Airpol, 2002; Croitoru and Sarraf, 2017). Research studies aimed at characterizing air quality have been carried out in several Moroccan cities in order to fill the existing gaps in air quality (Bounakhla, 1998; Bounakhla et al., 1999; Bounakhla et al., 2003; El Abidi et al., 2000; Ouarzazi, 2003; El Khoukhi et al., 2004; Zaghaid et al., 2009; Zouir, 2009; Ouhakki, 2009; Ait Bouh, 2012; El Ghazi, 2012; Monna et al., 2012; Belhassan, 2013; Tahri et al., 2013; Ouali Alami et al., 2014a; Ouali Alami et al., 2014b; Boularab et al., 2015; El Rhzaoui et al., 2015; Khouddane et al., 2015; Khouddane et al., 2016; Inchaouh et al., 2017; Boularab, 2018 ; Khomsi et al., 2020; Sekmoudi et al., 2020; Sekmoudi et al., 2022 ;Bouchriti et al., 2023; Oujidi et al., 2023; Saidi et al., 2023). At the national scale, air quality monitoring is carried out by a telemetric network of 29 fixed stations distributed in 15 cities in 7 regions. To this

are added two mobile laboratories. In the absence of a telemetric station in the city of Meknes, the use of passive diffusion tubes for air quality monitoring and assessment is justified. In Meknes, the industrial sector is underdeveloped and has a limited capacity for income generation. Despite its modest economic importance and relatively minor social impact, industry stands out as one of the primary sources of environmental pollution. Moreover, the transport sector's emissions also contribute significantly to exacerbating air pollution and the degradation of the urban environment (MRE, 2002; Abdouh et al., 2004; AUM, 2010; ORE, 2012; AUM, 2013; Inchaouh & Tahiri, 2017; Boularab, 2018 ; Dettner & Blohm, 2021; El Hafdaoui et al., 2023). In this context, the present work adopts an interdisciplinary methodological approach that aims at the surveillance and monitoring of ambient air quality in the city of Meknes. The second added value of this study is the elaboration of a database that could be used to assist the competent authorities in making the necessary decisions regarding air pollution mitigation. To achieve these objectives, we adopted the passive sampling technique to collect tracers of vehicular proximity pollution in the absence of an air quality measurement and monitoring station. This easy-to-implement method allows for coverage of a large geographic area with a large number of samplers at a low cost, which allows for high spatial resolution (neighborhood scale) mapping (Brown, 2000; Garcia-Fouqué et al., 2000; Adon et al., 2010; Caballero et al., 2012; Pienaar et al., 2015; Cerón Bretón et al., 2020). We were interested in several types of tracers in this work, including volatile organic compounds, BTEX (Benzene, Toluene, Ethylbenzene, and Xylene), and nitrogen dioxide (NO<sub>2</sub>). Two types of axially symmetric passive diffusion tubes were used at each proximity (transport) and background site. Perkin Elmer tubes for BTEX trapping and Palmes for nitrogen dioxide sampling (Atkins, 1990; Garcia Fouqué et al., 2000; Meybeck et al., 2000; Plaisance, 2004; Laurinavičienė and Dėdelė, 2013; Smith et al., 2015; Gaeta et al., 2016; Heintzelman, 2022; Niepsch et al., 2022). After exposure, the tubes are analyzed off-line in the laboratory. In parallel with the measurement campaigns, motor vehicle counting sessions were carried out on the main roads of the city of Meknes. The results obtained were introduced into a geographical information system (GIS), which could be used as a database in the future. We have adopted the following approach: Identify and quantify the primary sources of air pollution; To determine the share of the transport sector in the air pollution in the city of Meknes through monitoring of the tracers of the automobile pollution (NO<sub>2</sub> and COV) and conducting sessions of counting of the motor vehicles at the principal road axes; To carry out cartography with high spatial resolution of the contents of the prospected pollutants; To compare the results obtained with both national and international air quality standards.

## **2. Materials and methods**

### **2. 1. Pollutants prospected**

#### **2. 1.1. BTEX**

BTEX are monocyclic aromatic hydrocarbons of the family of volatile organic compounds. They are colorless liquids, slightly soluble in water, flammable, and highly volatile. They are present in many household products (solvents, detergents, paints, glue, inks, pharmaceutical

products, cosmetics, cigarettes, pesticides...). They are emitted by gasoline-powered vehicles as well as in exhaust fumes. They can also be generated by industrial activities such as oil refining, paint production, glue, plastic, nylon, detergents, cosmetics, and drugs (INERIS, 2004). In addition, there are storage and distribution units for petroleum products.

### **2. 1.2. NO<sub>2</sub>**

NO<sub>2</sub> comes mainly from the combustion of fuels (gasoline, petrol, coal, fuel oils). High temperatures catalyze the NO<sub>2</sub> formation reaction by combining nitrogen (atmospheric and contained in fuels) and atmospheric oxygen. The transport sector remains the main contributor to these emissions.

## **2.2 Effects on health and the environment**

### **2.2.1. Toxicological aspect**

By inhalation, BETX can cause a range of health disorders in humans, which depend on the nature, concentration, and duration of exposure but also the sensitivity of the individuals (INRS, 1992; SFSP, 1996).

Depending on the doses of BETX inhaled, the short- and medium-term effects are reflected in various symptoms: irritation of the respiratory tract and eyes, headaches, vision, hearing and memory problems, abdominal pain, convulsions... In the case of highly absorbed doses, these symptoms can lead to a coma or even death.

Numerous studies have been carried out and are underway to identify the complex mechanisms of hematological toxicity and carcinogenicity of benzene (Snyder and Kalf, 1996). The WHO has established risk threshold values for benzene and toluene (WHO, 1996). The mutagenic character of benzene is due to its lipophilic properties, which allow it to penetrate cells where it is oxidized (Zhang et al., 1996; Lovern et al., 1997). The metabolites formed can then insert themselves into DNA molecules (Andreoli et al., 1997) and cause errors in gene transcription, which, in the few cases where they are not corrected, generate undesirable proteins that can lead to a tumor (INRS, 1992; SFSP, 1996).

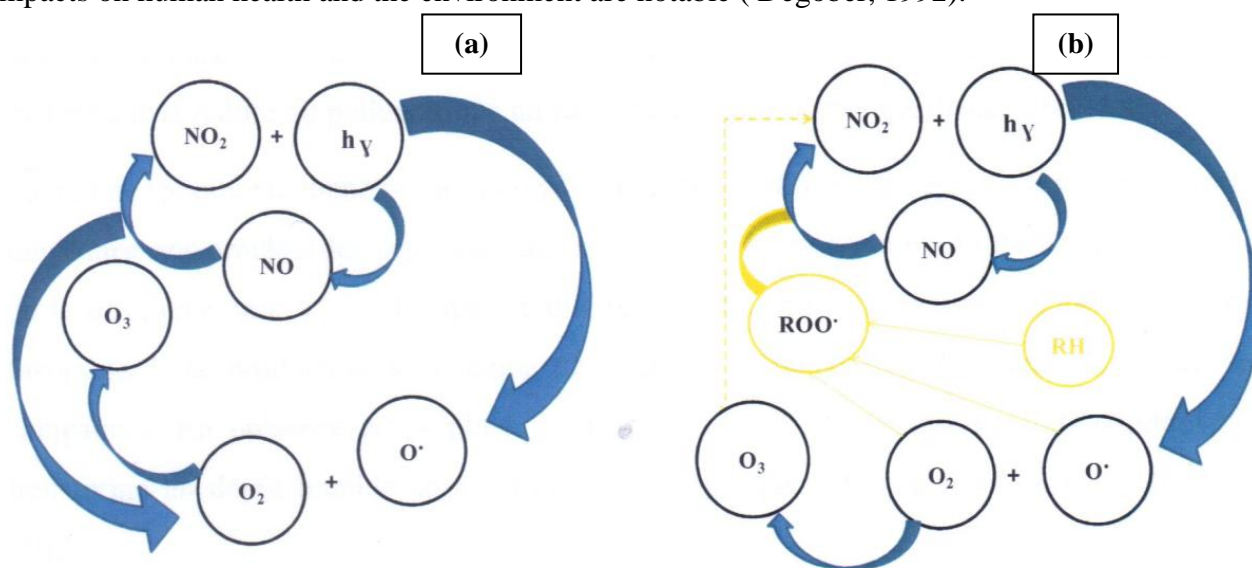
Benzene exposure is associated with benzolism, a condition marked by a decrease in the counts of white and red blood cells and platelets. This reduction in blood cell numbers can lead to symptoms such as headaches, fatigue, dizziness, loss of appetite, and, in severe cases, may progress to hemorrhaging and even fatality. This disease is exceptional in developed countries due to reduced benzene exposure rates. Toluene and xylenes have a lesser impact on health. Their oxidation occurs preferentially on the methyl groups with the formation of an acid function, which confers a hydrophilic character to the molecule that the body will easily eliminate. The compound's ability to penetrate the cell is notably attenuated (SFSP, 1996).

Nitrogen dioxide has an impact on respiratory functions. It penetrates the fine ramifications of the respiratory system and can cause bronchial hyperreactivity in asthmatics (SFSP, 1996).

### **2.2.2. Environmental impact**

In addition to their direct action on humans, BTEX and NO<sub>2</sub> generate, by reaction in the troposphere with free radicals, other so-called secondary pollutants, such as ozone or aldehydes, which have harmful effects on humans and their environment (INRS, 1992; SFSP, 1996). In the troposphere, in the absence of volatile organic compounds, the O<sub>3</sub> content is controlled by the NO-NO<sub>2</sub>-O<sub>3</sub> ozone formation-destruction reaction cycle shown in Figure 1a,

p. 6. Ozone is formed by combining  $O_2$  with an oxygen atom from the dissociation of  $NO_2$  under the effect of radiation of wavelength less than 400 nm. This cycle is completed by the reaction of NO on the ozone previously produced. There is, thus, a photostationary equilibrium between NO,  $NO_2$ , and  $O_3$ . On the other hand, in the presence of VOCs (identified as RH in figure 1b, p. 6), this equilibrium is disturbed by the privileged conversion of NO into  $NO_2$ . The 'OH' radicals react with RH and give rise to alkyl radicals which, by a series of rapid reactions with  $O_2$ , lead to the formation of peroxide radicals  $ROO'$  which, in turn, rapidly oxidize NO to  $NO_2$  with the regeneration of the 'OH' radical;  $O_3$  is thus no longer consumed by NO: the system can become productive in  $O_3$ . It thus follows an increase in tropospheric ozone, and indirect production of aldehydes or nitrated compounds, whose impacts on human health and the environment are notable ( Dégober, 1992).



a. Chapman cycle in the absence of VOCs

b. Chapman cycle in the presence of VOCs

**Figure 1.** Chapman's cycles

## 2.3. Sampling protocol

### 2. 3.1. NO<sub>2</sub> sampling

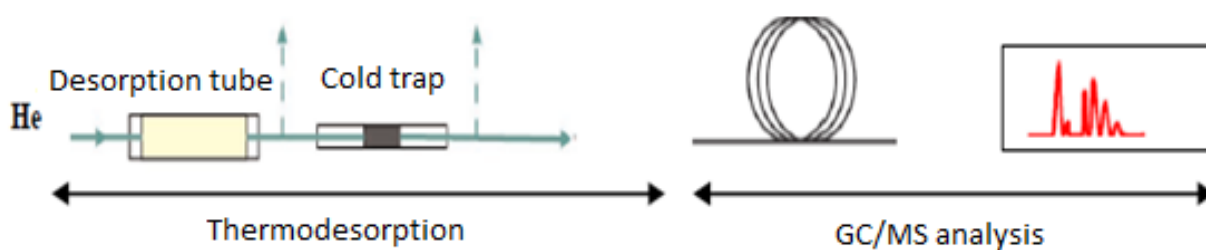
For NO<sub>2</sub> monitoring, passive diffusion tubes with three stainless steel grids impregnated with triethanolamine (Atkins, 1990; NBN EN 16339) were deployed at 14 sampling sites. The choice of passive sampling is based on its practicality, the absence of a need for electrical connections or pump operation, and its capability to cover extensive geographical areas with

numerous samplers at a cost-effective rate. The samplers consist of 74 mm long, 9.5 mm diameter acrylic tubes.

The samplers were fixed vertically to straight supports, 3-4 m above ground level (NBN EN 16339). A specific shelter was used to protect the sampling equipment from weather and wind influence (Plaisance et al., 2004). Following a two-week exposure period, the Palmes tubes were retrieved, and the NO<sub>2</sub> captured in the grids was extracted by adding 3 ml of Saltzman's reagent (as described in Atkins, 1990; NBN EN 16339). Subsequently, the concentration of NO<sub>2</sub> in the extracts was quantified using UV spectrophotometry at a wavelength of 542 nm.

### 2.3.2 Sampling of BTEX

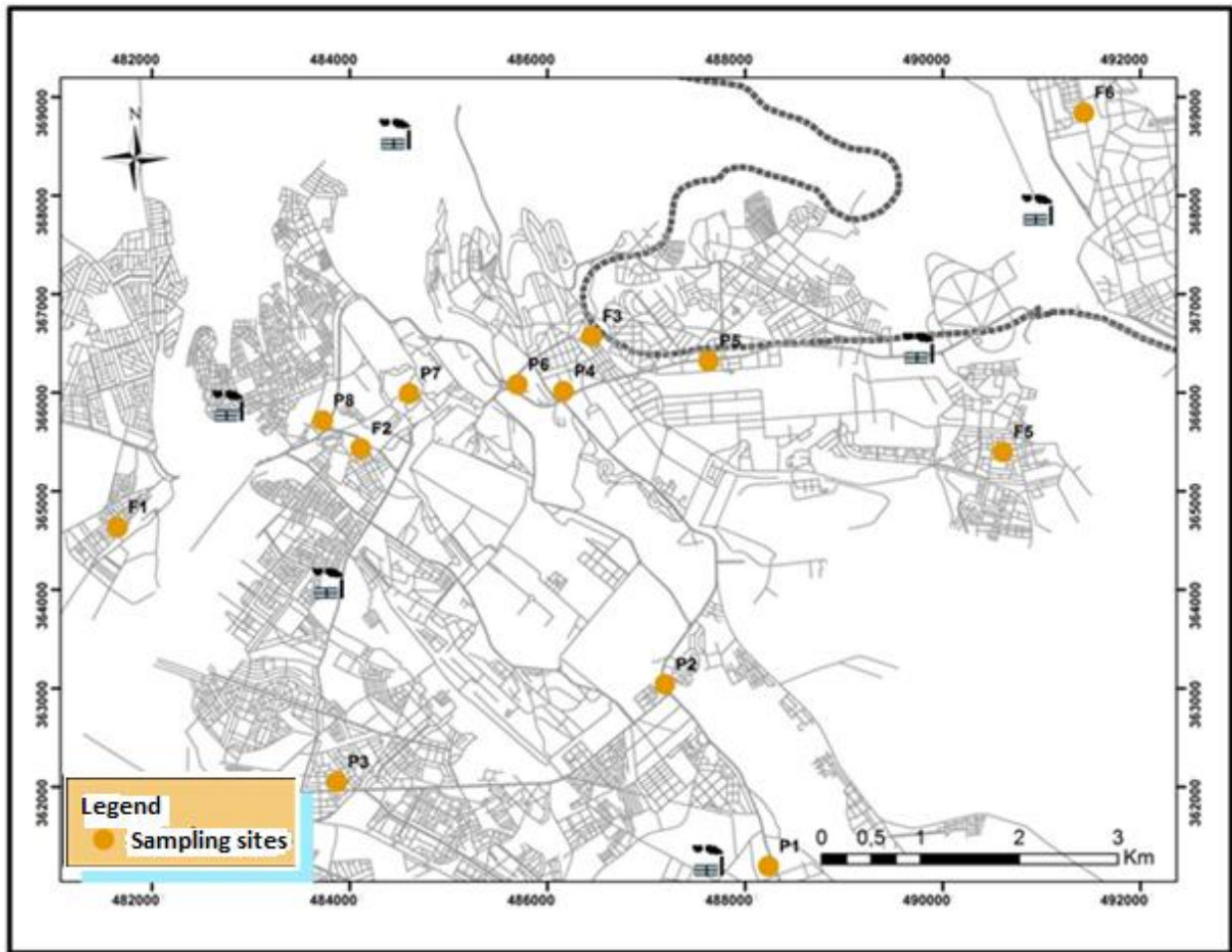
For BTEX, the tubes used are of the Perkin Elmer type. They have a length of 90 mm, an external diameter of 6.35 mm, and an internal diameter of 5 mm. Each tube has a unique identification number engraved. Before and after sampling, they are hermetically sealed with Swagelok® type brass caps, including Teflon ferrules. The exposure time of these tubes is 30 days. Sampling and analysis are performed according to ISO 16017-2: 2003. After sampling, the cartridges are analyzed by thermal desorption followed by gas chromatography with a mass spectrometer as a detector (**Figure 2**).



**Figure 2.** Schematic representation of the analysis steps of a Perkin Elmer tube

## 2. 4. Location of the sampling sites

Passive sensors were deployed at 14 measurement sites divided into automotive proximity (P) and background (F) sites (Figure 3 and Table 1).



**Figure 3.** Location of sampling sites

**Table 1.** Distribution of sampling sites by type and location

points	Lieu	Typologie
P1	Point of intersection between the national road n°13 and the national road n°6	Traffic
P2	Point of intersection of Bair Anzarane Avenue and Zitoune Boulevard	Traffic
P3	Zitoune Avenue (Marjane district)	Traffic
P4	Point of intersection of Bairanzarane Avenue and the Avenue of the Royal Armed Forces	Traffic
P5	Avenue of the Royal Armed Forces near the main railway station	Traffic
P6	Point of intersection of Mohammed VI Avenue and the Avenue of the Royal Armed Forces	Traffic
P7	Daar smane Street, the point where the old Medina meets the new city	Traffic
P8	The bus station of the city of Meknes	Traffic
F1	Toulal	Background
F2	Riad	Background
F3	New city near the station of el Amire Abdelkader	Background
F4	Hacienda	Background
F5	El Bassatine	Background
F6	Wisslane	Background

## 2. 5. Road traffic counts

In parallel with the winter measurement campaign of the tracers of the pollution of proximity cars (NO<sub>2</sub> and BTEX), sessions of counting the road traffic were carried out on the city's main roads. The counting was carried out by operators equipped with manual clickers (Figure 4).



**Figure 4.** Manual clickers used for traffic counting in the city of Meknes

For the study of intraday variations, we focused our census mainly on the peak hours: morning (7:30/9:30), noon (11:30/14:30), and evening (17:30/19:30). The counts were carried out over 15-minute periods.

In order to study inter-day variations and fluctuations in road traffic during working and non-working days, one week of counts per site was required. Twelve traffic sites were selected, and their location was dictated by the nature of the road section and the placement of the passive samplers (**Figure 5**).

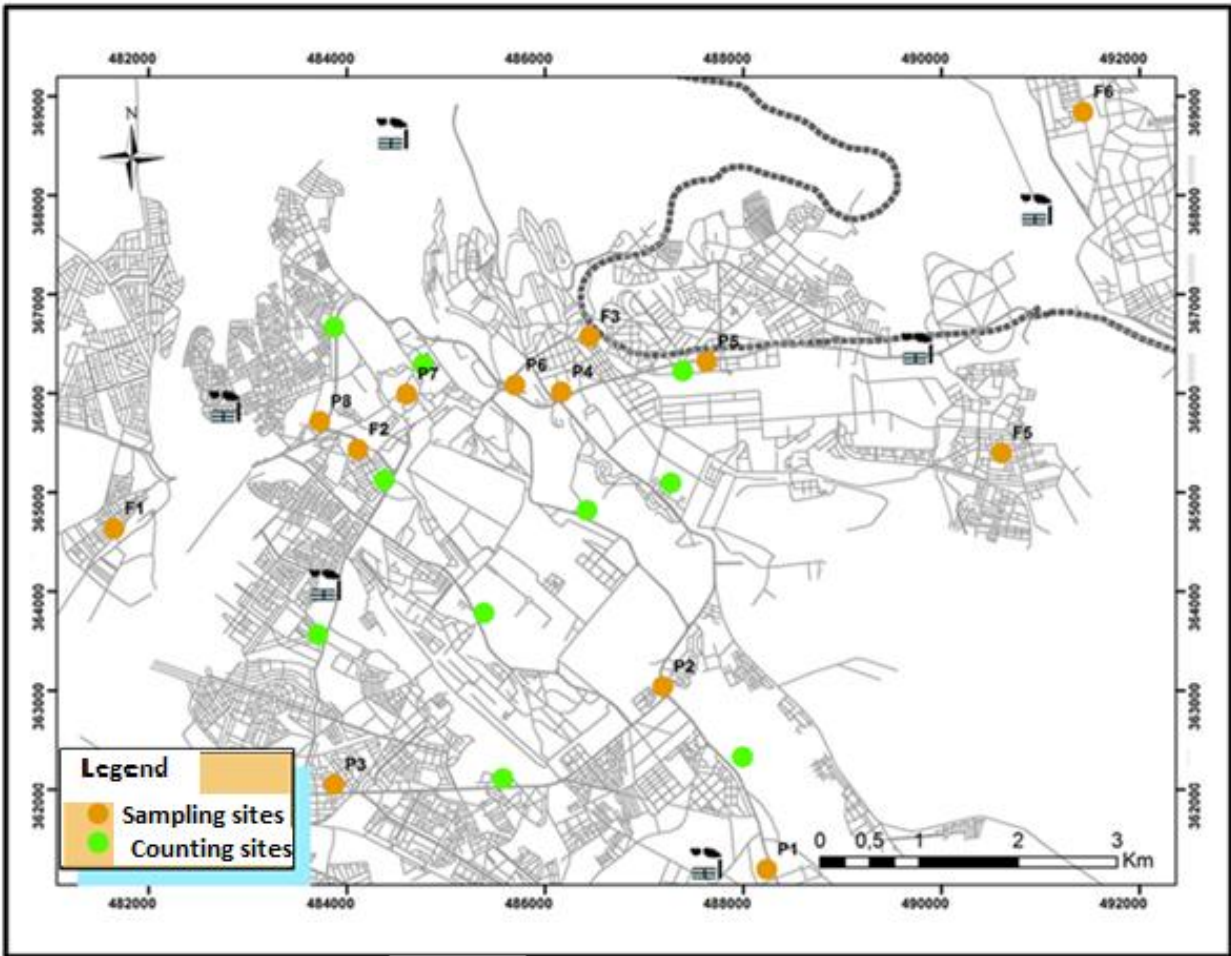


Figure 5. Location of the counting point

## 2.6. Mapping of NO<sub>2</sub> and BTEX levels

Mapping of NO<sub>2</sub> and BTEX concentrations was performed by spatial interpolation using the inverse distance weighting (IDW) method.

Interpolation is a technique that estimates spatially continuous variables at unknown locations from values measured at specified locations.

IDW is one of the most widely used deterministic interpolation methods. The IDW function generates the interpolated surface by estimating NO<sub>2</sub> and BTEX concentrations at unsampled points based on linear combinations of values at sampled points weighted by an inverse function of distance (Shepard, 1968). The assumption of this technique is based on the fact that the difference between the value of the measurement point and the values of the unmeasured points is relative to the distance. The weights ( $w_i$ ) are expressed as follows:

$$w_i = 1/d_i^p / \sum_{i=1}^n 1/d_i^p$$

Where  $d_i$  is the distance between the point of interest  $x_0$  and the sampled point  $x_i$ ,  $p$  is a power parameter, and  $n$  represents the number of sampled points used for estimation.

The main factor affecting the accuracy of the IDW is the power parameter ( $p$ ) value, which expresses the relative importance of nearby points compared to distant points (Li et al., 2008). Indeed, the weight decreases as the distance increases, especially when the value of the power parameter is high so that the neighboring samples have a heavier weight and more influence on the estimation. The selection of the power parameter is arbitrary, but the most common choice is equal to 2, and the resulting method is often called the Inverse Distance-Squared/IDS.

## 2.7. Data processing and statistical analysis

Characterizing the pollution due to NO<sub>2</sub> and BTEX in Meknes requires a spatio-temporal analysis by determining its sources and the possible factors influencing its concentration and dispersion. To achieve this, the data from the field forms and laboratory results were recorded and processed using a spreadsheet in Microsoft Excel. Climatic variables such as Temperature, Precipitation, and Wind were imported from the [www.wunderground](http://www.wunderground) platform for both study periods.

These data were summarized and represented using the basic statistical indicators (Mean, Minimum, and Maximum). The wind directions and speed data were used to develop wind roses using the open-air package of the R statistical software ([www.r-project.org](http://www.r-project.org)).

Finally, a mapping of the dispersion of NO<sub>2</sub> and BTEX at the level of the city of Meknes was carried out by spatial interpolation according to the method of weighting by the IDW. The IDW function generates the interpolated surface by estimating the concentration of NO<sub>2</sub> and BTEX at unsampled points, which is based on linear combinations of values at sampled points weighted by an inverse function of distance (Shepard, 1968).

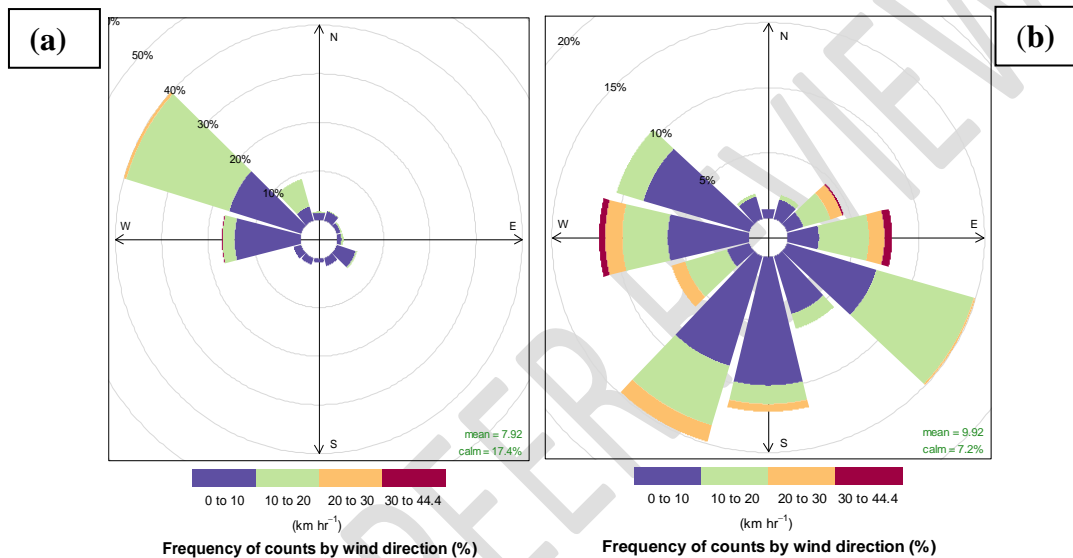
### 3. Results and discussions

#### 3.1. Meteorological conditions

##### Wind directions and speed

Wind distribution affects the spatial spread and distribution of pollutants. In our study, the average wind speed was 7.97 km/h during the summer period, with the dominant directions being northwest and west, with moderate intensities ensuring good pollutant dispersion (**Figure 6a**).

However, the average wind speed during the winter campaign is 9.6 km/h, and almost all directions are recorded. Nevertheless, the most frequent directions are South-East and East, and more violent come from East and North-East with a maximum speed of 37 km/h (**Figure 6b**). Such a multidirectional wind can produce localized pollution and plume deposition, which can be seen clearly in the maps.



**Figure 6.** Frequency distribution of wind direction and speed during (a) The summer period and (b) the winter period

##### Temperature

During the summer, the recorded temperatures show a maximum of 39 C° and a minimum of 15 C° with an average of 24.31 C°. However, the winter period recorded a maximum temperature of 20 C°, a minimum temperature of 1C°, and an average of 9.31 C°. These findings are consistent with the city's weather pattern.

##### Precipitation

Rainfall significantly contributes to the atmospheric leaching process and the removal of pollutants. When interacting with H<sub>2</sub>O, NO<sub>2</sub> reacts to form a mixture of nitrous and nitric acids that can be leached by rain, unlike NO. These effects explain the concentration difference between campaigns conducted in different seasons (Stern, 1968; Hill, 1974).

During both campaigns, no precipitation was recorded except for a few showers on 12/29/2014.

### 3.2 Study of NO<sub>2</sub> concentrations

The sites of car proximity had the highest concentrations of NO<sub>2</sub>. (41.68 µg/m<sup>3</sup>). On the other hand, the lowest levels were recorded at the background sites (20.47 µg/m<sup>3</sup>) (Figure 7).

The average NO<sub>2</sub> concentration measured during the summer campaign (31.96 µg/m<sup>3</sup>) is very close to that reported in winter (31.71 µg/m<sup>3</sup>) (Figure 7).

In winter, the average NO<sub>2</sub> concentration noted at the car proximity sites equals (39.71 µg/m<sup>3</sup>), while that of the background sites is (23.72 µg/m<sup>3</sup>).

In summer, the average NO<sub>2</sub> concentration was (46.71 µg/m<sup>3</sup>) at the car proximity sites and (17.21 µg/m<sup>3</sup>) at the background sites.

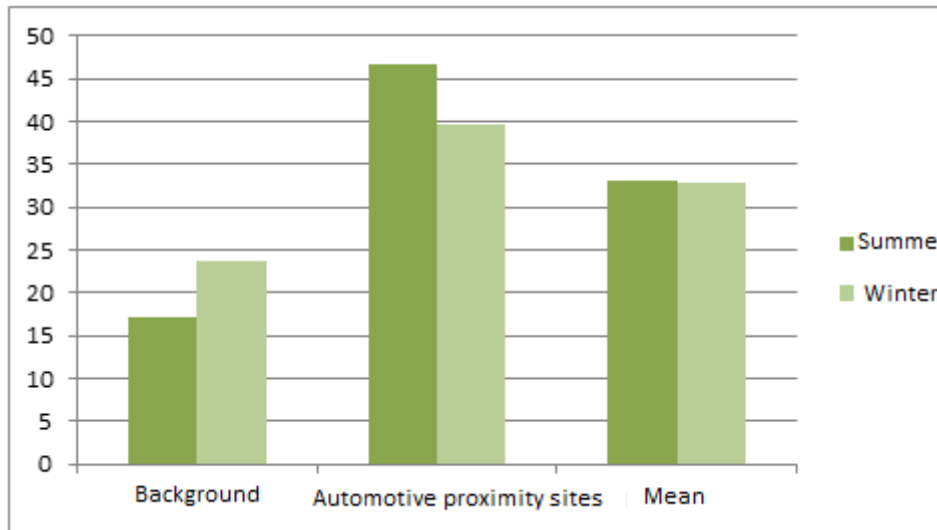
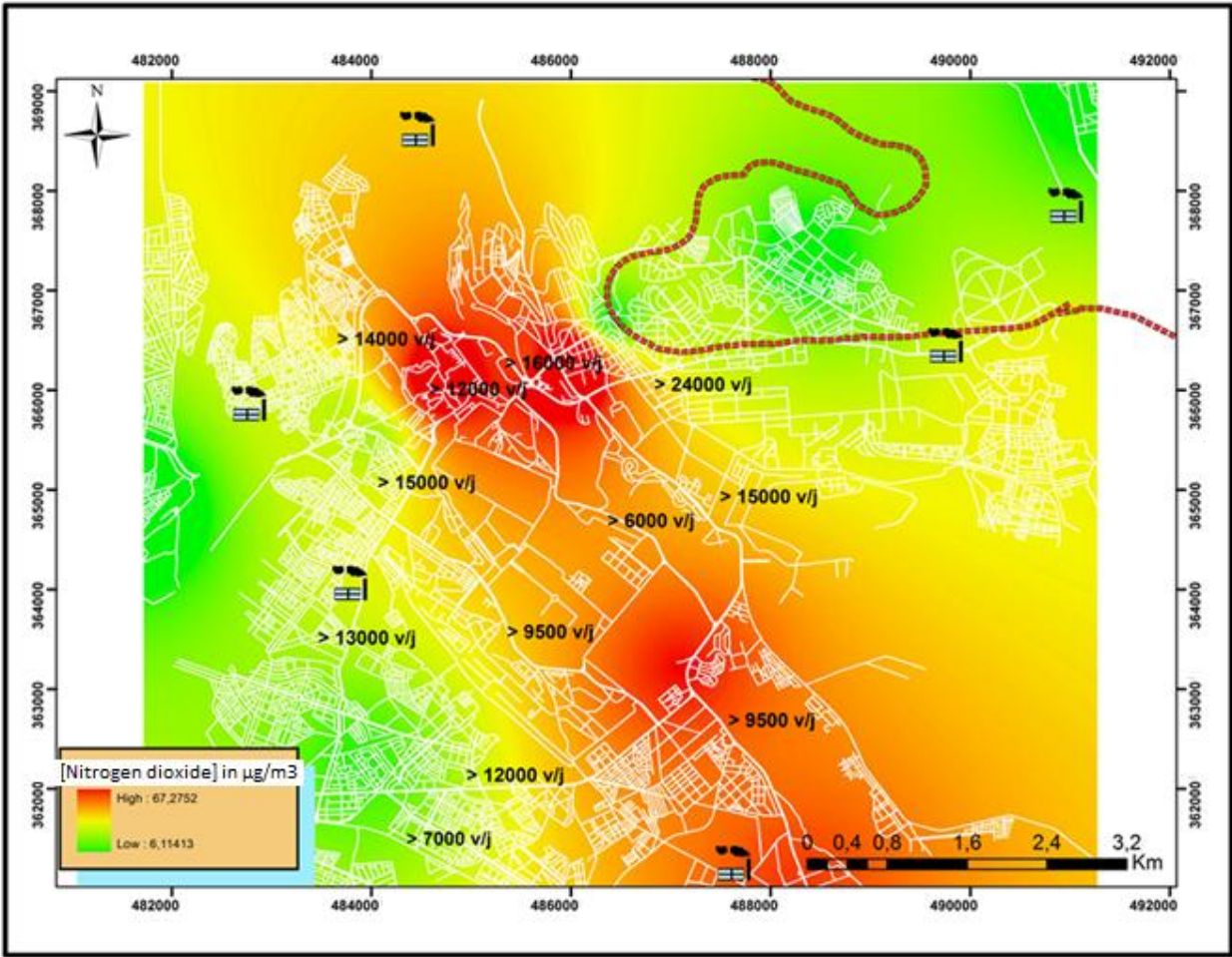


Figure 7. Average NO<sub>2</sub> concentrations

All background sites have NO<sub>2</sub> levels below 40 µg/m<sup>3</sup>, the European limit value (Directive 2008/50/EC). Five out of 8 sites near the car have levels exceeding 40 µg/m<sup>3</sup>. Two of these sites exceed the Moroccan limit value of 50 µg/m<sup>3</sup>.

Atmospheric concentrations of NO<sub>2</sub> reach maximum values in the city center and tend to decrease towards its periphery (Figure 8). The areas with the highest levels of air pollution are located near the city center. Specifically, P7, situated at Dar Smane Street, has a (58.37 µg/m<sup>3</sup>) concentration. P4, the intersection between the Avenue of the Royal Armed Forces and Bir Anzarane Avenue, has a (57.96 µg/m<sup>3</sup>) concentration. Meanwhile, P2, located at the point of intersection of Bir Anzarane Avenue and Zitoune Boulevard, has a concentration of (48.23 µg/m<sup>3</sup>). P6, situated at the intersection of Mohammed VI Avenue and Royal Armed Forces, has a (45.12 µg/m<sup>3</sup>) concentration. Indeed, these roads are characterized by heavy daily traffic, which is the source of a large part of NO<sub>2</sub> emissions (Meybeck et al., 2000; Laurinavičienė et al., 2013). The high levels reported at site P7, located at Dar Smane Street, used by as many as 12000 vehicles per day, exceed those measured at site P4, an intersection point crossed by more than 24000 vehicles per day. This is because the street's structure hinders NO<sub>2</sub> dispersion and favors accumulation. This street's height/width ratio is greater than 1, which allows it to be described as a canyon street (Meybeck et al., 2000). Given their geolocations, the sites with concentrations below 15 µg/m<sup>3</sup> are Wislane (F6) and Toulal (F1). For sites F6 and P1, despite their proximity to the Lafarge cement plant and the industrial district of Sidi Bouzekri, we found that the measured levels are below the permissible limit value. These results agree with those of the surveys carried out by the Moroccan Ministry of the Environment, which showed that road traffic is responsible for 75% of NO<sub>2</sub> emissions and that the industrial sector does not exceed 25% (MRE, 2001). It also rhymes with the study carried out in the city of Toulouse, which showed that the highest NO<sub>2</sub>

levels were reported at the car proximity sites in the city center (Meybeck et al., 2000). Another study conducted at the level of Kaunas, the second largest city in Lithuania, showed that NO<sub>2</sub> emissions strongly correlate with road traffic density (Laurinavičienė et al, 2013).



**Figure 8.** Spatial variations in NO<sub>2</sub> concentrations

“According to this study, the city of Meknes appears moderately polluted compared to other urban sites. The average NO<sub>2</sub> concentrations obtained are very similar to those of Elche (Spain), Edinburgh (United Kingdom), and Granada (Spain), with almost the same population” [132] (Table 2). These concentrations are in the range of large agglomerations with populations over one million, such as Kanpur (India) and Bamako (Mali). On a national scale, a similar passive tube study was conducted in other Moroccan cities, such as Casablanca, Rabat, and Marrakech, where nitrogen dioxide levels are higher than in Meknes (Table 2). However, this average concentration is comparable to Fez's (DSPCT, 2010).

“These observed disparities between cities could be attributed to differences in urban structure, traffic flows, pollutant emitters, and climatic conditions” (Lewné et al., 2004).

The following table shows nitrogen dioxide concentrations measured worldwide by the passive sampling technique and by automatic monitoring networks in some neighboring countries.

**Table 2.** NO<sub>2</sub> results were obtained in the city of Meknes compared with other urban agglomerations worldwide.

Study Area	[NO <sub>2</sub> ] µg/m <sup>3</sup>	Study Period	Country	References
<b>Kocaeli</b>	14	July 2006	Turkey	(Pekey et al., 2013)
<b>Bouni Region</b>	14.8 *	Average of 7 months of measurement in 2011	Algeria	(Fadel et al., 2011).
<b>Windsor</b>	23.31	Average of four 14-day campaigns in February, May, August and October 2004	Canada	(Wheeler et al., 2008)
<b>Malaga</b>	22.8	September 2001 and from December 2001 to February 2002	Spain	(Lozano et al., 2011)
<b>Pampelune</b>	23	From June 2006 to 2007	Spain	(Parra et al., 2009)
<b>Göteborg and Mölndal</b>	23.5	7–20 May 2011	Sweden	(Habermann et al., 2015)
<b>Asturies</b>	23.6	Average of two 7-day campaigns in June and November 2005	Spain	Fernandez-Somoano et al., 2014)
<b>Northern Ireland</b>	24.3	Annual average for 1997	UK	(Stevenson et al., 2001)
<b>Kampala</b>	24.9	From 30 June to 13 July, 2014	Uganda	(Kirenga et al., 2015)
<b>Kocaeli</b>	25	January 2007	Turkey	(Pekey et al., 2013)
<b>Wales</b>	27.26	Annual average for 1997	UK	(Stevenson et al., 2001)
<b>Scotland</b>	27.26	Annual average for 1997	UK	(Stevenson et al., 2001)
<b>Bamako</b>	30.45	From June 2008 to 2009	Mali	(Adon et al., 2010)
<b>Meknes</b>	31.83	From 14 July to 28 July 2014 and from 25 December 2014 to 12 January 2015	Morocco	This study
<b>Elche</b>	32	Average for 2007–2008	Spain	(Caballero et al., 2012)
<b>East Anglia</b>	34.78	Annual average for 1997	UK	Stevenson et al., 2001)
<b>South East England</b>	34.78	Annual average for 1997	UK	Stevenson et al., 2001)
<b>Edimbourg</b>	34	From 2 December 2013 to 13 January 2014	UK	(Lin et al., 2016)
<b>West Midlands</b>	35.72	Annual average for 1997	UK	(Stevenson et al., 2001)
<b>Granada</b>	36.5	Average of two campaigns: from July to September 1999 and from December 1999 to February 2000	Spain	(Lozano et al., 2011)
<b>Kanpur</b>	36.9	February and March 2004	India	(Behera et al., 2015)
<b>Edimbourg</b>	37	From 2 August to 13 September 2013	UK	(Lin et al., 2016)
<b>East Midlands</b>	40.42	Annual average for 1997	UK	(Stevenson et al., 2001)
<b>Yourkshire-and-Humber</b>	42.3	Annual average for 1997	UK	(Stevenson et al., 2001)
<b>London</b>	42.3	Annual average for 1997	UK	(Stevenson et al., 2001)
<b>Agadir</b>	44	From 20 April to 27 April, 2006	Morocco	(Chirmata et al., 2017)
<b>Durban</b>	45.12	Average of one week in summer 2001	South Africa	(Moode et al., 2011)
<b>Rawalpindi</b>	55.74	Annual average for 2008	Pakistan	(Ahmad et al., 2011)
<b>Dakar</b>	59.9	From January 2008 to December 2009	Senegal	(Adon et al., 2010)
<b>Al-ain</b>	59.3	From 21 February 2005 to 20 February 2006	United Arab Emirates	(Salem et al., 2009)
<b>Delhi</b>	68.6	February and March 2004	India	(Behera et al., 2015)
<b>Sfax</b>	Between 37.6 and 112.8 *	Fall 1996, Winter 1997, Spring and Summer 1998	Tunis	(Azri et al., 2008)
<b>Durban</b>	110.92	Average of one week in winter of 2001	South Africa	(Moode et al., 2011)

\* Measurements made with an automatic monitoring network

Nitrogen dioxide is a photo-reactive product whose content is controlled by the NO-NO<sub>2</sub>-O<sub>3</sub> formation-destruction reaction cycle under the effect of a radiation of wavelength lower than 400 nm schematized in figure 1, p.6. This cycle ensures a photostationary equilibrium between NO, NO<sub>2</sub>, and O<sub>3</sub>, which is disturbed in the presence of other pollutants, such as the VOCs identified RH in figure 1, p. 6, by bringing benefit to the conversion of NO into NO<sub>2</sub>. The OH radicals react with RH and give rise to alkyls, leading to the formation of peroxide radicals through rapid reactions with O<sub>2</sub>. These peroxides promote the rapid oxidation of NO to NO<sub>2</sub>, increasing nitrogen dioxide near the emission source and ozone at more distant locations (Azri et al., 2008).

These reactions explain the low concentrations detected in the peri-urban site and the concentrations that exceed the limit values in the sites of road proximity and the sites of industrial proximity juxtaposed to the roads, revealing the presence of spatial variability due to the impact of the type of sites on the concentrations obtained of nitrogen dioxide. The revealed results were proved by a statistical analysis of variance ( $p < 0.05$ ).

The map displays a pollution gradient that represents the significant spatial variability. The city center, areas near roads, and intersections with high traffic loads have higher pollution concentrations. The pollution gradually deteriorates towards the outskirts of the city.

Net spatial gradients of NO<sub>2</sub> are the common element in the different studies of nitrogen dioxide as a pollutant in urban environments (Lozano et al., 2011; Matte et al., 2013). These gradients are attributed to the location of pollution sources, type of measurement site, topography, and road infrastructure (Jerrett et al., 2005). For example, high NO<sub>2</sub> concentrations at high-traffic sites can be attributed to traffic congestion and high NO emissions that rapidly oxidize to NO<sub>2</sub> near emission sources. Nevertheless, some NO is oxidized before reaching the tailpipe (Short et al., 2006; Behera et al., 2015). In urban areas, some air pollutants can exhibit higher spatial variability than others (Parra et al., 2009; Smith et al., 2006), showing that nature plays a crucial role in tracing these gradients.

The photo-reactive nature of nitrogen dioxide also explains the similar average concentrations of the two campaigns; 75% of the days in the first campaign and 58% in the second are the clear sky, representing a similar meteorological profile favorable to NO<sub>2</sub> production in the absence of rain in both campaigns. In the presence of rain, nitrogen dioxide leaches from the atmosphere and is transformed into wet deposition as nitric acid according to the following reaction (Defra, 2012):



The effects of meteorology on nitrogen dioxide concentration and dispersion have been revealed in many studies. Like our case study, some confirm the absence of significant differences in average NO<sub>2</sub> concentration between different study periods (Caballero et al., 2012; Lin et al., 2016). In contrast, other studies have revealed periodic variability attributed primarily to differences in the meteorological profiles of these periods (Wheeler et al., 2008; Moodle et al., 2011; Jang et al., 2016).

Nevertheless, the difference between the two periods of the present study is more apparent in the dispersion of the pollutants in the urban fabric. During the summer campaign, the dispersion of NO<sub>2</sub> is characterized by a plume shape spread towards the southeast of the city

of Meknes and influenced by a dominant wind of moderate intensity coming from the northwest and West, ensuring a good pollutant dispersion.

During the winter campaign, the dispersion of the pollutant is characterized by localized pollution near the sources due to the multidirectional winds and/or to a layer of inversion of the temperature at a few hundred meters of the ground. This phenomenon is present during this time of the year, which slows down the diffusion of pollutants (Ait Bouh, 2012).

Chemical reactions and dilution processes are not only responsible for the spatial and temporal variations of the studied concentrations but also the short lifetime of NO<sub>2</sub>. Therefore, the highest concentrations are found in areas close to the emission source, which decreases with distance, contributing to a heterogeneous dispersion pattern in space (Pekey et al., 2013).

### 3.3. Study of BTEX concentrations

The average concentrations of BTEX noted at the automotive proximity sites exceed those of the background stations (**Table 3**). This result is consistent with the one obtained in the city of Toulouse, where the calculation of toluene/benzene, m, p xylene/xylene, and o-xylene/benzene ratios, known as vehicular pollution indicators, showed that BTEX mainly originates from road traffic.

The average concentrations of BTEX measured during the winter campaign are higher than those in the summer (**Table 3**).

In winter, benzene, toluene, p+m-xylene, o-xylene, and ethylbenzene are characterized by average concentrations of 2.59, 23.415, 27.705, 15.3, 5.69 and 3.95  $\mu\text{g}/\text{m}^3$  respectively.

During the summer campaign, the average concentrations recorded were 1.01 for benzene, 14.21 for toluene, 6.5 for p+m-xylene, 4.58 for O-xylene, and 1.65  $\mu\text{g}/\text{m}^3$  for ethylbenzene.

**Table 3.** Variations saisonnières des teneurs des BTEX

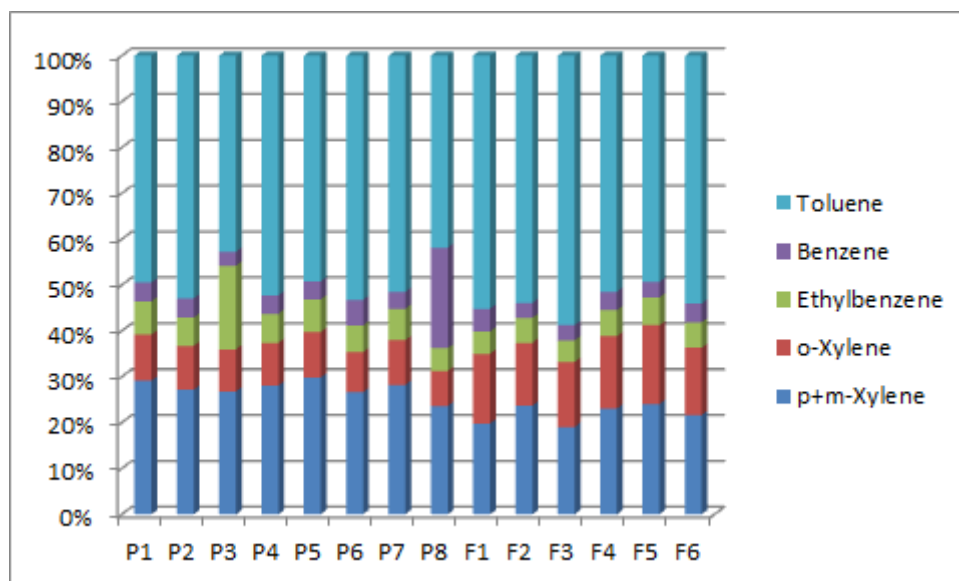
Saison	Type de site	Benzène	Toluène	o-Xylène	p+m Xylène	Ethylbenzène
Hiver	<b>Fond</b>	1,01	15,07	3,09	9,61	2,2
	<b>Proximité Automobile</b>	3,01	31,76	8,29	20,99	5,7
	<b>Moyenne</b>	2,66	23,45	5,69	15,3	3,95
été	<b>Fond</b>	0,62	9,94	2,05	6,03	1,86
	<b>Proximité Automobile</b>	1,01	18,48	7,11	6,97	1,45
	<b>Moyenne</b>	0,83	14,21	4,58	6,5	1,65
Moyenne	<b>Fond</b>	1,40	12,50	2,57	7,82	2,03
	<b>Proximité Automobile</b>	2,04	25,12	7,70	13,98	3,57

The increase in BTEX levels measured in winter can be explained by:

- The degradation and transformation processes of BTEX, which are less important in winter;
- A greater stability of the atmosphere's lower layers limits the dispersion phenomena (winter anticyclone).

The increase in temperature catalyzes the reaction of ozone formation from VOCs and the decrease in BTEX emissions from automobiles resulting from the drop in the number of vehicles circulating in the city during the summer period (vacations) (Meybeck et al. 2000).

Toluene remains the main pollutant for all exposed tubes, followed by m, p- xylene, o-xylenes, ethylbenzene and benzene (Figure 9). A similar result was observed in Tangier (Zouir, 2009).



**Figure 9.** Comparison of the average concentration of each compound versus the sum of BTEX at each sampling site

Atmospheric concentrations of BTEX reach maximum values in the city center and tend to decrease towards its periphery (**Figure 10**).

The site at Daar Smane Street (P7) exhibited the highest BTEX levels, reaching a  $90.76 \mu\text{g}/\text{m}^3$  peak. Following closely, the P5 site, at the FAR avenue recorded BTEX concentrations of  $82.445 \mu\text{g}/\text{m}^3$ . These results are reasonable as Daar Smane Street features a canyon-like structure that impedes the efficient dispersion of BTEX, leading to their accumulation. Similar results were observed for  $\text{NO}_2$  and  $\text{C}_6\text{H}_6$  on this street.

The density of road traffic at P5 is the origin of this increase. A slight increase in the levels of xylene isomers and ethylbenzene was noted at the background sites near the industrial areas (F6, F2, and F5). These results agree with those observed in the city of Toulouse, where the lowest ratios of toluene/benzene concentrations were noted at the background sites most isolated from the Toulouse agglomeration. At the same time, the maximum values occurred at the sites most frequented by the means of transportation in the city. In addition, BTEX concentrations were highest in the center of Toulouse and tended to decrease towards the outskirts (Meybeck et al., 2000). In Tangier, the highest BTEX concentrations were recorded at the municipal landfill site with a total BTEX sum of  $166.7 \mu\text{g}/\text{m}^3$ , followed by an industrial proximity site with a value of  $111.7 \mu\text{g}/\text{m}^3$ . Toluene was the dominant pollutant, followed by m-p xylene, benzene, and o-Xylene, with a slight increase in the levels of xylene and ethylbenzene isomers at the automotive proximity sites (Zouir, 2009).

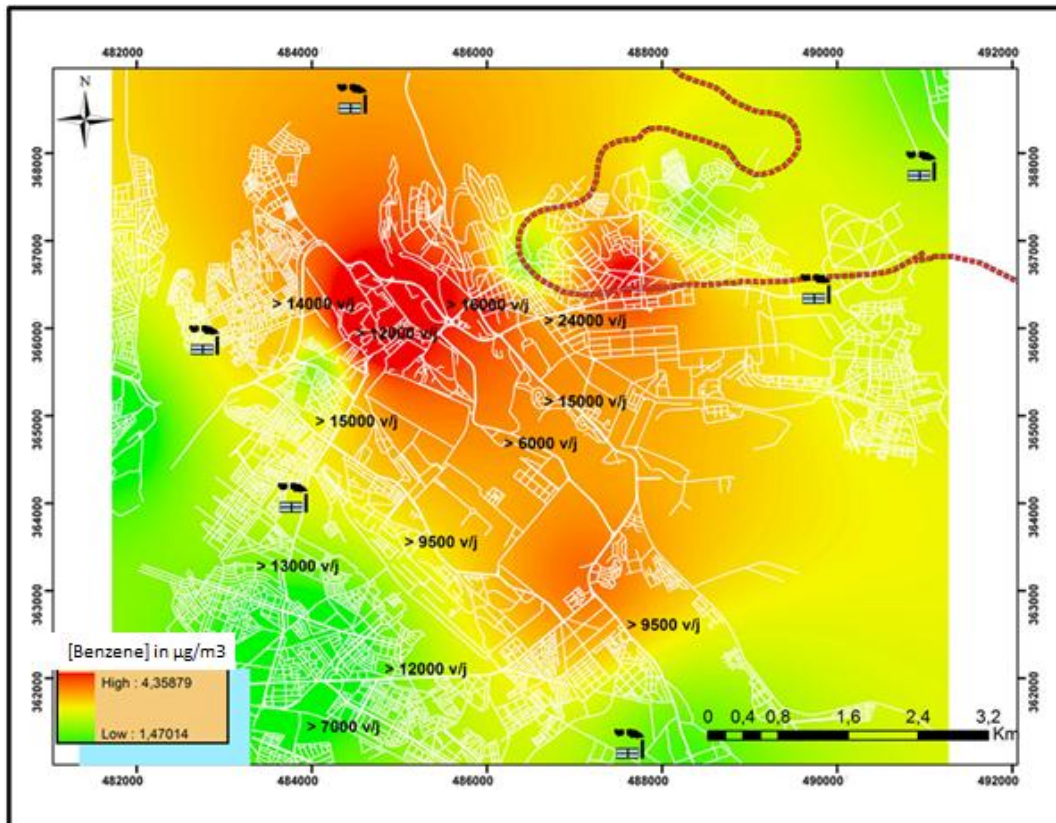


Figure 10(a). Spatial variations of  $C_6H_6$  concentrations

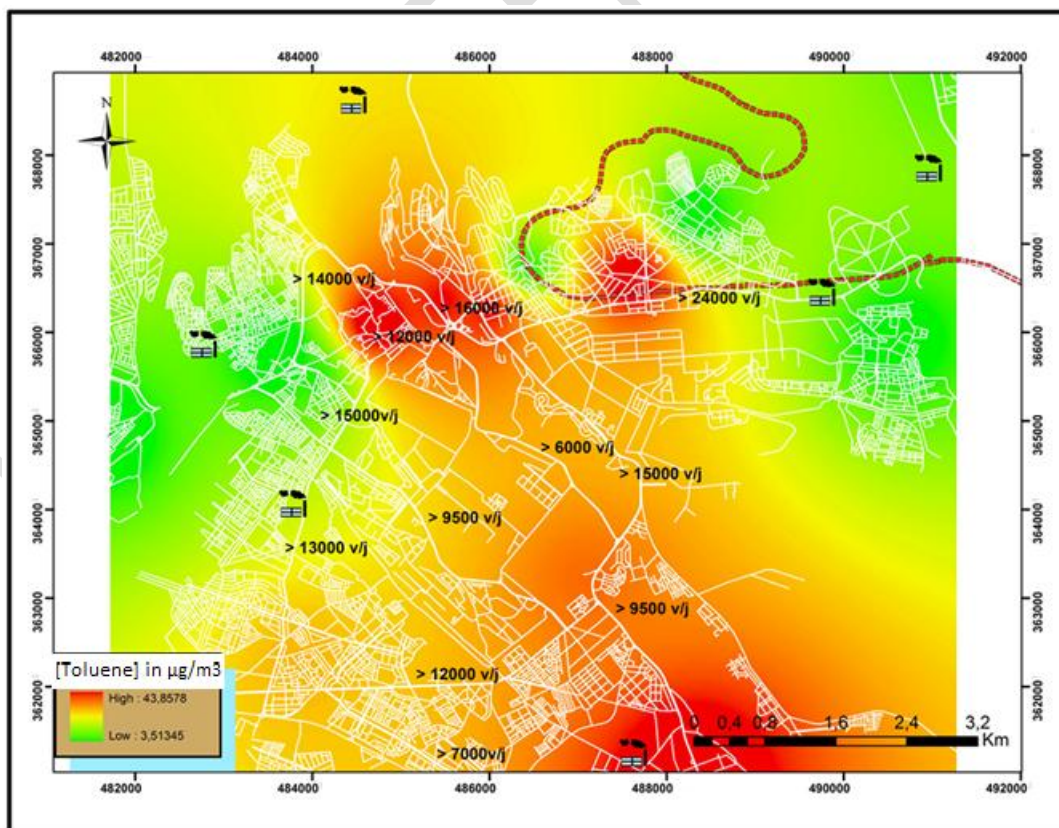


Figure 10(b). Spatial variations in toluene concentrations

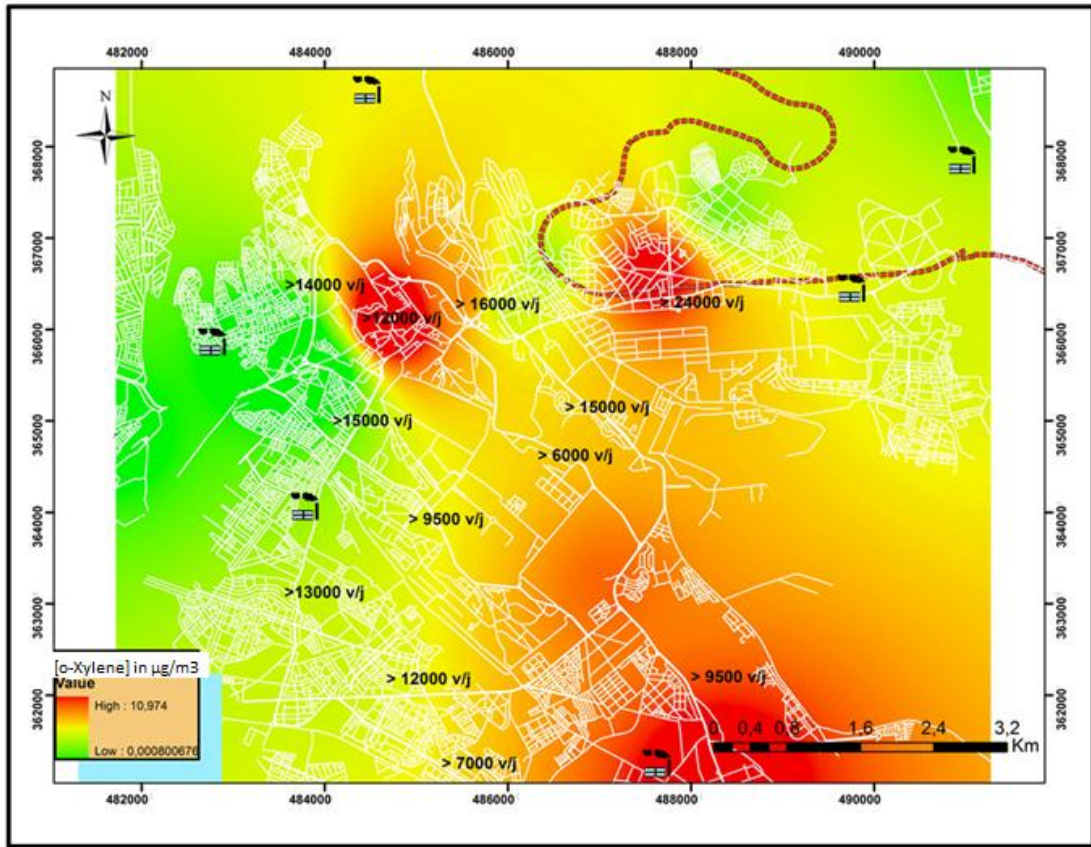


Figure 10 (c). Spatial variations in o-Xylene concentrations

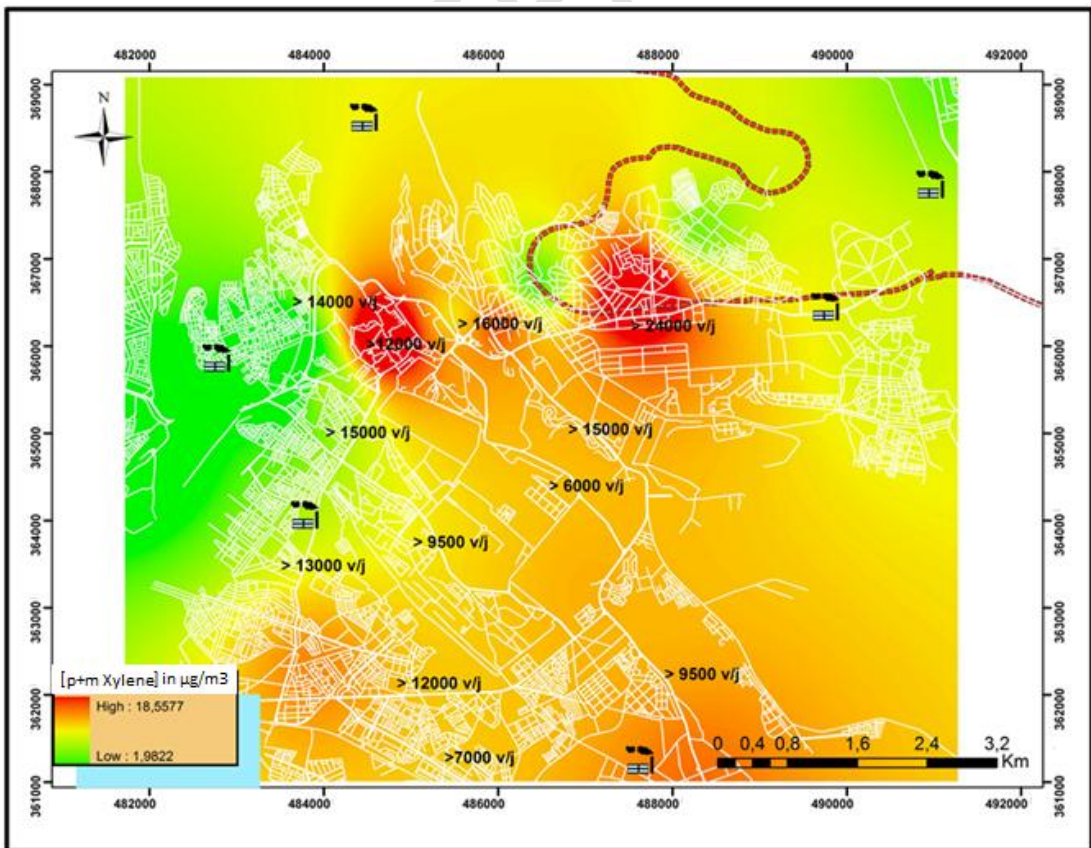
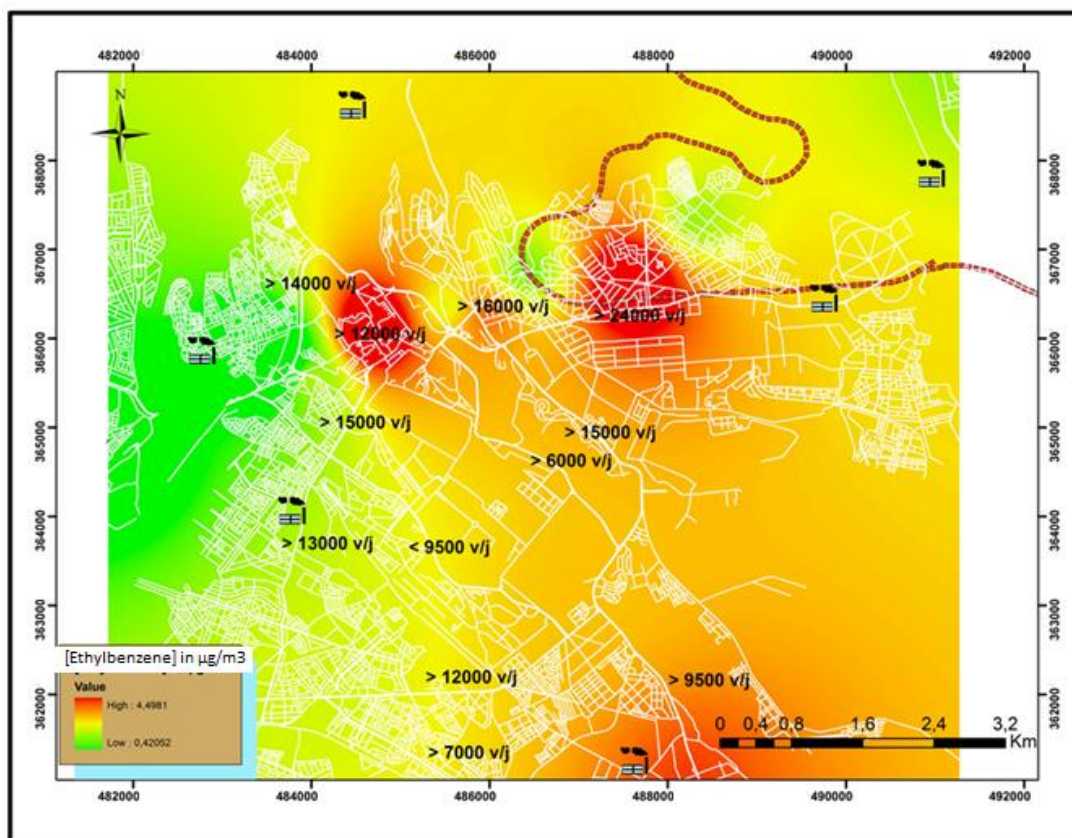


Figure 10(d). Spatial variations in p+m Xylene concentrations



**Figure 10 (e).** Spatial variations in ethylbenzene concentrations

The Moroccan threshold for  $C_6H_6$  is set at  $10 \mu\text{g}/\text{m}^3$ , and this limit was adhered to across all the monitored sites. However, four out of the fourteen sites exceeded the quality objective established by the European Union ( $2 \mu\text{g}/\text{m}^3$ ). Notably, all background sites registered  $C_6H_6$  levels below  $2 \mu\text{g}/\text{m}^3$ , which aligns with the permissible limit in Europe (Directive 2008/50/EC).

Toluene is not currently subject to specific regulations. However, the World Health Organization (WHO) recommends not exceeding  $260 \mu\text{g}/\text{m}^3$  on average over seven days. In Meknes, the recorded toluene levels are considerably lower than this recommended threshold. Despite the highest recorded toluene concentration reaching  $18.81 \mu\text{g}/\text{m}^3$ , it is only 1/15 of the health-recommended value.

The WHO recommends  $4800 \mu\text{g}/\text{m}^3$  over 24 h of xylene in ambient air (WHO, 2000). The results of our monthly measurement campaigns do not allow a real comparison with this standard. For o-xylene and p+m xylene, none of the measured values exceeded this value.

For ethylbenzene, the WHO recommends an annual limit of  $22\,000 \mu\text{g}/\text{m}^3$  of ethylbenzene in ambient air (WHO, 2000). However, the average ethylbenzene level observed throughout the study period is only  $2.80 \mu\text{g}/\text{m}^3$ , well below this recommended threshold.

#### 4. Conclusion

The present study focuses on monitoring and evaluating air quality in the city of Meknes, based on two tracers of vehicular proximity pollution (VOC and NO<sub>2</sub>) emanating from road traffic. Given the absence of a telemetric station and a mobile laboratory within the city, the most practical approach involved passive diffusion tubes analyzed offline after exposure. The choice of this technique was driven by its cost-effectiveness, ease of implementation, and the ability to deploy multiple samplers across a wide geographic area, making it a favorable option for our research.

The coupling of the results of the measurement campaigns and the counting sessions under GIS made it possible to determine the zones most affected by automobile pollution and to carry out cartography with a high spatial resolution of the prospected pollutants.

The deployment of passive sensors at 14 measurement sites revealed the existence of a spatio-temporal variability of the pollutants surveyed. This variability can be attributed to several factors, including prevailing climatic conditions such as wind and precipitation, the photochemical properties of these markers, proximity to emission sources, the specific measurement site characteristics, and the local topography and road infrastructure.

The results of our study show that the air concentrations of NO<sub>2</sub> and BTEX reach maximum values in the city center and decrease towards its periphery. NO<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> levels in the winter campaign exceed those in the summer.

A slight increase in the levels of xylene isomers and ethylbenzene was noted at the background sites near the industrial areas.

Some sampling sites showed levels of these pollutants exceeding acceptable limits, which prompted us to investigate the possible link between exposure to these substances and the aggravation of respiratory and cardiovascular diseases in Meknes.

The developed approach could be used as a decision-making tool for the competent authorities in this field and adapted for monitoring various pollutant types (pesticides, tracers generated by industrial units, dioxins furans...).

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