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Assessment of Ambient Air Particulate Matter in the New Orleans Historic District

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Assessment of Ambient Air Particulate Matter in the
New Orleans Historic District

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Abstract

Particulate matter in the ambient air of down-town New Orleans, LA, is not currently recorded by any government, state, or private organization. This research quantified particulate matter (PM) and its metal concentration in ambient air of the New Orleans Historic District. Both, PM10 (PM less than 10 micron in size) and PM2.5 (PM less than 2.5 micron in size) were quantified by gravimetric analysis using an Andersen Dichotomous Sampler (Series 240). Posterior to gravimetric analysis, the filters were analyzed with a fluorescent test method using an Innov-X Portable XRF Analyzer (Model A-6500).

This study demonstrated that the ambient air of the New Orleans Historic District is in compliance with the National Ambient Air Quality Standards regarding contamination of particulate matter and Lead.

Keywords: Particulate matter (PM), PM10, PM2.5, heavy metals in ambient air, Andersen Dichotomous Sampler, Innov-X XRF Analyzer, air quality of New Orleans Historic District, French Quarter, health risk from metals in ambient air.

List of Abbreviations

AQI: Air Quality Index

CAA: Clear Air Act

CAAA: Clear Air Act Amendments

CDC: Centers for Disease Control and Prevention

CFR: Code of Federal Regulations

EPA: Environmental Protection Agency

FEM: Federal Equivalent Method

FRM: Federal Reference Method

HDVs: Heavy Duty Vehicles

LDEQ: Louisiana Department of Environmental Quality

NAAQSs: National Ambient Air Quality Standards

NIST: National Institute of Standards and Technology

NIOSH: National Institute for the Occupational Safety and Health

NSPSs: New Sources Performance Standards

PSI: Pollution Standards Index

PSD: Prevention of significant deterioration

SIP: State Implementation Plan

SLPM: Standard Liters per Minutes

TEOM: Continuous Sampling Monitor Equipment. Not approved by EPA as FRM.

XRF: X-Ray Fluorescence

Introduction

Particulate matter (PM) is one of the six criteria air pollutants regulated by the Environmental Protection Agency (EPA) through the National Ambient Air Quality Standards (NAAQS). Criteria pollutants are defined as those air pollutants for which NAAQS have been established due to their high potentiality to deteriorate human health and the environment. Particulate matter is formed by suspended particles in the ambient air as a result of aggregation of gaseous pollutant molecules, fragmentation of solid materials (by scrubbing), and/or dust dispersion by wind.

Numerous studies have shown that the PM of major interest for human health is the one formed by particles with aerodynamic diameter equivalent to or smaller than 2.5 µm. Therefore, NAAQS differentiates "coarse", or inhalable, particles suspended in the air from "fine", or respirable, particles. Coarse particles, with an aerodynamic diameter between 2.5 and 10 µm, could be trapped in the mucociliary clearance mechanism of the upper respiratory system epithelia cells. On the other hand, fine particles, might bypass mucociliary clearance mechanism of the upper respiratory system. Those fine particles can reach the deepest respiratory recesses and cause serious damage to pulmonary alveoli. This situation is grimmer when $PM_{2.5}$ present a high concentration of heavy metals because these substances accumulate in body tissues.

Additional to the potential hazardous characteristics of $PM_{2.5/10}$ to human health, these pollutants also affect the human welfare. As stated by the EPA, human welfare air quality standards are those not related to health effects of pollution but to its visual and economic consequences instead, that diminish enjoyment of life. Reduction of visibility due to formation and persistence of

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fog has been demonstrated in relationship with the amount of particulate matter in the ambient air of polluted areas. Moreover, deposition of particles reduces aesthetic appeal of historic national monuments like statues and buildings.

Edifications and artistic artifacts need deeper and more frequent maintenance in polluted areas because some PM specimens can intensify the chemical effect of other pollutants. For instance, corrosion due to acid rain is stronger in areas with ambient air rich in PM with heavy metals. Likewise, previous studies have demonstrated the relationship between rapid deterioration of ambient air quality and high concentrations of heavy metals as $PM_{2.5}$.

A common method to estimate the PM content in ambient air is the gravimetric analysis of the filters from a known volume of sampled ambient air. The Andersen Dichotomous Sampler will collect air containing $PM_{2.5/10}$ when operated correctly. At the end of the collection period, the Dichotomous Sampler will contain two filters, one with fine particles and the other with coarse particle. If the instrument has been calibrated perfectly, it will be easy to determine the volume of air sampled by multiplying the flow rate by the total collection time. PM concentrations are obtained by the gravimetric analysis of the filters. Once PM is collected on Teflon filters, these filters are analyzed with X-Ray Fluorescent Spectroscopy (XRF) to determine fraction of metals in collected PM, as well as it identifies the types of metals in PM.

The present study aims to determine the PM concentration in the ambient air at the Historic District of the City of New Orleans, Louisiana. Additionally, the study focuses on the metals concentrations in the ambient air of the French Quarter area. Previous studies focuses in the PM concentration in the ambient air of the campus of the University of New Orleans using the Anderson Dichotomous Sampler. However, there are not PM sources important enough

at UNO to justify local air sampling and analysis on UNO. Additionally, there is no current ambient PM monitoring in the New Orleans French Quarter area, which presents a confluence of heavily transited streets, vent discharges from several residences and businesses, and close proximity to petrochemical industrial sites that can represent a risk to the general public and the historic monuments of the New Orleans down town area.

The present report was divided in four chapters plus their corresponding appendices sections. Chapters 1 through 3 include various topics of thesis: literature review, methodology and equipment utilized to collect the data, data collected and its analysis. Chapter 5 includes research conclusions.

Objectives

General Objective

Assessment of air quality with respect to particulate matter PM and its metallic composition in ambient air of the Historic District of the City of New Orleans.

Specific Objectives

- Measurement of particulate matter (PM) concentration in Ambient Air of the New Orleans Historic District
- Measurement of the metals and heavy metals concentration in the airborne particulate of the New Orleans Historic District
- Evaluate sampling site's ambient air quality compliance with NAAQS based on PM2.5 and PM10
- Determinate AQI for the sampling site area based on PM2.5 and PM10

Chapter 1: Literature Review

Ambient Air and Meteorology

The Environmental Protection Agency (EPA) is the Federal organization in charge of protecting the quality of the Ambient Air in the United States. The EPA defines ambient air as the section of air not restricted by any means or barriers that can be accessed by the general public. Under this definition, the air outside the walls enclosing a car-body shop, for instance, will be ambient air if there is no fence delimitating the boundaries of the private property beyond the walls.

Another characteristic of the ambient air is that it does not recognize political boundaries. As long as it is outside the area delimitated by a specific property it is ambient air, regardless of whether it is located in Texas, Florida, or Washington State. In fact, currents of air move from county to county inside each state or from state to state across the nation as a consequence of world-wide climate patterns, which ignore city or state limits. Therefore, it is necessary to study environmental issues with a holistic interdisciplinary approach, especially when they are related to the quality of ambient air.

One of the most influencing disciplines in the assessment of ambient air quality is meteorology. Meteorology studies and tries to predict the characteristics of weather changes as consequences of global-scale patterns of air circulation. Meteorology involves the study of micro and macro environment parameters like ambient temperature, wind speed, and wind direction that greatly affect the dispersion or accumulation of anthropogenic pollutants (Cooper, 2002).

One of the greatest contributions made by meteorology to the study of ambient air quality is the determination of atmospheric stability. Atmospheric stability is the resistance of sections of air at different heights to mix with each other vertically. Vertical mixing of parcels, or sections of air, occurs as a consequence of the adiabatic processes undergone by these parcels. On a clear summer day, incoming solar radiation hits the hearth surface and increases its temperature; part of this heat is dissipated to the lower atmospheric layer of air which increases the temperature of the air right above the earth's surface. This hot air dilates adiabatically and becomes less dense than the air above the parcel. As a result, the parcel of air that was in contact with the soil, or right above the earth's surface, elevates by a voyage effect and mixes vertically with its surrounding mass of air. Likewise, vertical mixing of the hot air coming out of a chimney will occur with greater or lesser extent depending on specific characteristics of the atmosphere surrounding the exhaust pipe. The combination of these atmospheric characteristics is known as atmospheric stability and is defined experimentally for each microenvironment (Cooper, 2002).

Environmental Legislation in USA

The intervention of the federal government in ambient air quality and environmental issues has changed greatly in the past five decades. This intervention began in 1955 with the creation and implementation of the Air Pollution Control Act. At that time, the federal government functioned as a mere sponsor for the creation of technology applicable to diminish the amount of pollutants being emitted by industries into the atmosphere. A few years later, federal involvement increased to the point of proposing emissions standards to be achieved by the industries and other sources with the current technology available (Cooper, 2002).

Government involvement in air quality regulation further evolved to the point where federal agencies forced the private sector to develop systems and processes to comply with emerging standards, and, from there, to enforce the utilization of certain air monitoring and pollution control equipment. Table 1 presents a synopsis of the federal legislation evolution regarding air quality in the United States from 1955 to present.

Table 1: Changes of in Air Quality Federal Legislation

Piece of Environmental Legislation		Major Characteristics	Forces Pushing for Legislative Evolution
Air Pollution Control Act (APCA) of 1955 ↓	→	. Only provide funds for research and technical assistance	. No federal intervention in controlling what was understood as local problems
Clean Air Act of 1963 ↓	→	. Replaced APCA of 1995 by presidential request. Provided money for federal research and for outside agencies as well	. Provided, for the first time, federal authority to address interstate air pollution problems
Motor Vehicle Air Pollution Control Act of 1965 ↓	→	. First in establishing a federal plan for the regulation of emissions from new motor vehicles	. Set for 1968 models. The law recognized the need of tighten controls as new technology became available
Air Quality Act of 1967 ↓	→	. Enhanced research and development . It was the first law in articulate federal government to enforce use control equipment	. Required the secretary of HEW department to promulgate air quality criteria (by regions). First law enforcing industry to develop technology in order to meet regulatory standards
Clean Air Act Amendments of 1970 ↓	→	. One of the most powerful pieces of environmental legislation . Together with the National Environmental Policy Act provided the authority to create EPA . Attained clean air by 1975; standards and new time lines were set . Large fines and criminal penalties were authorized for willful violation . Addressed PM10 as one of the criteria pollutants.	. Required EPA to attain NAAQSs . Require states to submit SIP . NSPSs were to be set and implemented by states . Industries must monitor their emissions and make these data available to EPA . Include first attempt to address global air pollution problems

Table 1: Changes of Federal Legislation in Air Quality (Continuation)

Piece of Environmental Legislation		Major Characteristics	Forces Pushing for Legislative Evolution
Clean Air Act Amendments of 1977 ↓	→	. EPA must review and update air quality criteria by 1980, and on five year-interval thereafter . EPA must continue issuing performance standard for new and existing sources . Inclusion of "Emissions offset" for non attained areas	. Still figure of federal management with implementation by states . Inclusion of PSD: Class I (pristine areas, below NAAQSs), Class II (almost all other), and Class III (non attainment areas)
Establishment of PM2.5 NAAQSs 1997 ↓	→	. By the first time, EPA lowers the size of the particulate matter to be monitored and controlled from the previous PM10 to the current PM10 and PM2.5 parameters	. In addition to the standards for PM10, PM2.5 is also ruled by NAAQSs
Revised Standards for PM respect 1997 NAAQSs 2006	→	. 24 hrs Average for PM2.5 are tightened from $65\mu g/m^3$ to $35\mu g/m^3$. 24 hrs Average for PM10 remains $150 \mu g/m^3$	. EPA insists, and wins battle in the Supreme Court, on creating different standards for PM2.5 and PM10 to be attained by the private sector

Air Quality Standards

Historically, environmental laws and regulations regarding air quality have been designed to regulate one of the two aspects of this topic, the amount of pollutant in the ambient air or the amount of pollutant being emitted. Standards related to ambient air fall under the Ambient Air Quality Standards (AAQs) category, and are specified in units of mass of pollutant per volume of ambient air, µg SO_2/m^3 air, for instance. On the other hand, the second group of laws, or environmental standards, concern to the amount of pollutant being emitted by a particular source, and are called performance

standards. These performance standards are measured in unit amount of pollutant emitted by unit amount of raw material processed or by unit amount of product generated (EPA, May 2008).

- **National Ambient Air Quality Standards (NAAQSs)**

  The EPA defined six specific pollutants as criteria pollutants due to their high potentiality to deteriorate human health, and set threshold limits for their concentration in the ambient air in order to define a geographic region as an attained or not attained area. Those pollutants are sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), particulate matter (PM_{10} and $PM_{2.5}$), particulate lead (Pb), and ozone (O_3). Those pollutants are further defined as primary or secondary, pollutants depending on whether they are released in its contaminant form or if they are a product of a chemical reaction between released specimens. Four of the primary criteria pollutants are continuously released in the US; these pollutants are SO_2, NO_2, CO, PM. The remaining primary criteria pollutant, Pb, is banned in the US territory. The only secondary criteria pollutant, O_3, is the product of several photon-excited chemical reactions in the lower atmosphere.

  Additionally, two types of NAAQSs are defined, primary and secondary standards. Primary standards were set to protect human health while secondary standards are related to human welfare. Human welfare, or secondary standards, refer to the ability of enjoying life and are related to the safeguarding of artistic monuments, protection of national buildings, maintaining good visibility, preservation of recreational environment, and guaranteeing of successful agricultural activities. Table 2 shows set concentrations for the NAAQSs (EPA, May 2008).

Table 2: National Ambient Air Quality Standards (NAAQS)

Pollutant	Average Time	Primary Standard	Secondary Standard
SO_2	Annual arithmetic mean	0.03 ppm	
	24 hrs average	0.14 ppm	
	3 hrs average		0.50 ppm
NO_2	Annual arithmetic mean	0.053 ppm	Same as primary
CO	1 hrs average	35 ppm	
	8 hrs average	9 ppm	
PM_{10}	Annual arithmetic mean	[*1]	
	24 hrs average	150 $\mu g/m^3$ [*2]	Same as primary
$PM_{2.5}$	Annual arithmetic mean	15 $\mu g/m^3$ [*3]	Same as primary
	24 hrs average	35 $\mu g/m^3$ [*4]	Same as primary
O_3	1 hrs average	0.12 ppm	Same as primary
	8 hr Maximum	0.085 ppm	Same as primary
Lead	Quarterly Average	1.5 $\mu g/m^3$	Same as primary

Notes: [*1] The Annual NAAQS for PM_{10} had not been set by EPA yet. Before December 2006, it was 50$\mu g/m^3$

[*2] Not to be exceeded more than once per year on average over 3 years

[*3] To attain this standard, the 3-year average of the weighted annual mean $PM_{2.5}$ concentrations from single or multiple community-oriented monitors must not exceed 15.0 $\mu g/m^3$

[*4] To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 $\mu g/m^3$ (effective December 17, 2006)

Extracted from EPA NAAQS, October 2008.

- **New Source Performance Standards (NSPSs)**

  Source performance standards are measured as the mass of a specific pollutant emitted per mass of raw material or product for each specific source. The EPA establishes performance standards for a source depending on the date that source was built. If the source was in operation prior to the date of law promulgation, September 18th of 1978, it is considered old source; otherwise, it is a new source (EPA, May 2008).

The EPA states NSPSs for many different pollutants in the code of federal regulations (40 CFR 50), but for practical purposes only a few of them are exemplified in Table 3.

Table 3: Examples of New Source Performance Standards

Type of Source	Pollutant	Performance Standard
Liquid fuel fired Electric Power Plant	Particulate Matter NO_2 SO_2	0.03 lb/million Btu of heat input 0.30 lb/million Btu generated 0.20 lb/million Btu generated
Solid waste Incinerators	Particulate Matter	0.18 g/(dry standard cubic meter) for a 3 hrs average
Sewage Sludge Incinerator	Particulate Matter	0.65 g/kg sludge input With opacity standard of 20%

- **Air Quality Index (AQI) / Pollution Standard Index (PSI)**

  The Pollution Standards Index (PSI) was a numerical resource implemented in the CAAA of 1977 to describing the overall quality of the ambient air. The EPA designed this arbitrary air quality assessment system based on the ambient air concentration of five different pollutants: PM_{10}, SO_2, NO_2, CO, and O_3. Then, the concentration of each of the six subindexes is related to a numerical value, and the highest subindex value is chosen to represent the overall air quality of the ambient air. In July of 1999, the EPA replaced the PSI with the Air Quality Index (AQI) to tighten the regulations, include $PM_{2.5}$ in the standards, and change to a name not related to Polluted Areas, but to Air Quality in general. Table 4, shows the individual AQI subindexes according to the EPA codification (EPA, May 2008).

Table 4: AQI Subindexes for each primary criteria pollutant

I Value	PM$_{10}$ 24-hrs Ave ($\mu g/m^3$)	PM$_{2.5}$ 24-hrs Ave ($\mu g/m^3$)	SO$_2$ 24-hrs Ave (ppm)	NO$_2$ 24-hrs Ave (ppm)	CO 24-hrs Ave (ppm)	O$_3$ 1-hr (ppm)	O$_3$ 8-hr (ppm)
0	0	0	0	N/A	0	N/A	0
50	55	15.5	0.035	N/A	4.5	N/A	0.060
100	155	40.5	0.145	N/A	9.5	0.125	0.076
200	255	65.5	0.225	N/A	12.5	0.165	0.096
300	355	150.5	0.305	0.65	15.5	0.205	0.116
400	425	250.5	0.605	1.25	30.5	0.405	N/A
500	505	305.5	0.805	1.65	40.5	0.505	N/A

N/A= Values bellow threshold limit; do Not Apply standardization.

After choosing the one single index "I" from Table 4 that represents the overall air quality, EPA uses Table 5 to describe "in words" the quality of the ambient air of the monitored zone. As mentioned before, the "I" value chosen is the highest "I" obtained after using Table 4.

Table 5: Description of Ambient air based on AQI values

AQI Value	Air Quality Description
0 – 50	Good
51 – 100	Moderate
101 – 200	Unhealthful
201 – 300	Very Unhealthful
≥ 301	Hazardous

Particulate Matter (PM)

Particulate is the term employed to define airborne solid and liquid elements as aggregation of several molecules. Generally speaking, air borne molecules have a diameter of about 0.0002 μm, while particulates could range from 0.001 μm to up to 500 μm in size. Due to the large range in particulate size, the study of their translational behavior, their effects on the human body, and the effect of these pollutants in the environment has been segregated into different categories depending on the aerodynamic size of the particle in question. The aerodynamic size of a particle is an approximation used to simplify its size description, because it will be impossible to describe the volume of a group of particles with only one value if they are not perfect spheres. In practice, air borne particles rarely have spherical shape. Actually, most particulates have very complex, and sometimes bizarre, morphology. However, when one states that the particulate size of a pollutant is 3.4 μm it does not mean that the particles have diameter of 3.4 μm; It actually means that the one particle of that "dust" accelerates in a free fall at the same rate of a drop of pure water (density = 1 kg/L) with a diameter of 3.4 μm.

Most of the current studies on particles or particle matter fall between the following size distribution: from 0.1 to 1 μm, from 1 to 2.5 μm, from 2.5 to 10 μm, from 10 to 500 μm, and/or from 0.01 to 500 μm.

Likewise, particles are also defined as primary or secondary, depending on their origin or method of formation. Particles that are suspended in the air in the same stage (or form) they were emitted are primary particulates; these particles are usually generated from abrasion and mechanical friction between solid objects. On the other hand, secondary particulates are those formed in the atmosphere as the product of a chemical reaction between released pollutants (EPA, October 2004).

- **Differentiation and Sources of Particulate Matter**

For environmental, regulatory, and toxicological study purposes, fine particles are those with aerodynamic diameter equivalent or smaller than 2.5 µm; this group of pollutants is also known as $PM_{2.5}$ and is mainly generated during combustion of liquid hydrocarbons, coal, and wood. Fine particles are also created by chemical reaction in the atmosphere when gaseous released pollutants, like sulfur dioxide and nitrogen dioxide, are exposed to sunlight. Then, the presence of fine particles in the ambient air is, most of the time, a consequence of anthropogenic activities.

On the other hand, coarse particles are those with an aerodynamic diameter between 2.5 and 10 µm; these bigger particles are related to PM_{10} to some extent because PM_{10} includes all the particles with diameter equal or smaller that 10 µm. PM_{10} refers to the group made by coarse and fine particles together. Common sources of coarse particles include windblown dust, abrasion or fragmentation of solid materials, solid products of incomplete combustion, sea spray, and aerosols (Kavouras, March 2001).

In addition to $PM_{2.5}$ and PM_{10}, there is another group of particulate pollutants that has been studied by the EPA in the past; this is called Total Suspended Particles (TSP); this group includes suspended solids with aerodynamic diameter equal to or smaller than 40 µm. However, several studies have shown that the smaller particles cause more severe effects on the environment and human body, which has shifted the focus of attention away from TSP (Cooper, 2002).

- **Importance and Effects of Particulate Matter in Air**

The size and composition of particulate matter will determine the density and aerodynamics of the particles, then, define the dispersion pattern of these pollutants once they are released. Likewise, size and composition of the particles suspended in the air greatly affect the way these pollutants affect the human body once a population is exposed to polluted air.

The major pathway, or exposure route, for particulate matter in ambient air is the respiratory system. Therefore, the study of PM health effects has been centered on the way these pollutants invade the respiratory tracts. Coarse particles are commonly called inhalable particles because their size and density will allow them to travel through the respiratory system aggravating several respiratory afflictions like asthma. However, coarse particles might be caught by the ciliated stratified epithelium cells lining the inner wall of the trachea, bronchi, and other respiratory airways. On the other hand, it has been demonstrated that the fine particles might travel through the deepest passages of the respiratory system to the pulmonary alveoli blocking them, or, even worse, passing to the blood stream; this is one of the reasons for the commonly observed link between exposure to fine particulate matter and heart and circulatory system afflictions (Klaassen-Watking, 2003).

- **Sensitive Population**

People at either end of the life span, children or the elderly, are more susceptible to particulate matter. Three specific factors make children more susceptible to exposure to suspended particles in the air than adults. The respiratory system of children is still developing and their tissues are more susceptible to irritant agents like sulfuric acids or partially volatile compounds. Additionally, the average school and preschool kids spend more time outdoors than the average young adult of urban areas. Therefore, city kids are directly exposed to particulate pollutants for longer and more frequent periods of time than less sensitive sectors of the population. Finally, children breathe 50 percent more air per pound of body weight than adults.

The elderly are also seriously affected by particulate matter because their tissues are less responsive to irritation and regenerate more slowly than those of young adults. Therefore, it is common to see a senior patient frequently returning to the hospital to be treated for the same respiratory effect when they have been exposed to particulate matter for long periods, even though the dosage exposure is typically low (Klaassen-Watking, 2003).

Metals and Heavy Metals

Metals and heavy metals are generally solid substances at ambient temperature that cannot be synthesized or broken down by any biological process. Metals are released into the environment as particulate matter by fragmentation of bigger pieces in industrial processes and can surprisingly travel large distances as airborne particles before settling down to the ground. Heavy metals are, instead released into the atmosphere in small amounts (traces) in the exhaust of combustion processes. Combustion gases can travel even further distances than industrial dusts due to the buoyancy effect generated as a consequence of their high temperature with respect to the surrounding environment (Kavouras, March 2001).

- **Importance and Effects of Metal Pollutants in Human Health**

  Some metals like Iron, Magnesium, and Zinc are required in very small amounts by the human body for its normal physiological activities but will cause a wide range of adverse effects in excess concentration. Additionally, other elements like Lead, Mercury, and Plutonium (heavy metals) are clearly identified as detriments for the human health at any concentration level; These heavy metals exhibit negative inotropic (decrease in the strength of muscular contraction) and dromotropic (impairing of electrical impulses conduction in the heart) effect that can seriously alter normal cardiovascular activities. The Cardiotoxic characteristics of heavy metals are suspected to be related to their ability to form complexes with intracellular macromolecules and to their ability to antagonize calcium mediated metabolic activated and storage mechanism.

Metals and heavy metals can be present in the particulate matter suspended in the ambient air of urban areas. Likewise, metals can be absorbed in the human body through the respiratory system. Therefore, the EPA has set NAAQSs to guard human health in the US (Klaassen-Watking, 2003).

For the specific case of Nickel, several studies have demonstrated its relationship with cardiovascular failure and even premature death, but the biomechanics through which it occurs is still not well understood (Lippmann, 2006). Therefore, it would be interesting to quantify the concentration of Nickel in the ambient air sampled.

- **Importance and Effects of Metal Pollutants in Human Welfare**
  Besides preventing public health from deterioration, the EPA also watches over human welfare. As mentioned in Table 1, air quality standards are set to guarantee normal development of those activities that promote life enjoyment. This means that pollution levels that are not high enough to concern human health might still deteriorate historical monuments, art sculptures, paintings, natural park vegetation, crops, cattle, and recreational water reservoirs (EPA, October 2004).
  Numerous studies have shown the relationship between high gaseous pollutant concentrations in the indoor ambient air of museums and the deterioration of their collections, but few studies have been developed in relationship with airborne particles in the same matter. However, it is known that, once fine particles settle on certain surfaces like feather, fur, unframed tapestries, and unvarnished paintings, they can never be removed without affecting the settling surface. Some big (coarse)

particles can be removed with a current of air, but elemental carbon cannot be blown off with this technique. Additionally, researches on damage to electronic gadgets by nitrate particles suggest that museums' metal collection artifacts might be equally sensitive to deterioration by nitrate. There are also sites of archaeological interest, like the Yungang Caves in China that contain polychromic carvings and are being affected by ambient particulate matter (The Getty Conservation Institute, 1993).

There is a strong desire to precisely assess the effect particulate matter has on historic buildings in the EU because air contaminants of heavily populated areas are the major cause of building deterioration. Keep in mind that for European standards, buildings with historic interest are commonly one thousand, or more, years old. When those buildings were erected, materials used in that time where lest resistant than modern construction materials. Some of the effects directly related to concentration of ambient SO_2, NO_2, PM, heavy metals, and VOC are soiling, corrosion, disruption, and black and white crusts. Furthermore, several European studies have demonstrated that the rate of degradation increases with the humidity and ambient temperature of the zone (Vaccaro, 2002).

Background of the city of New Orleans

New Orleans was founded on May 7th, 1718 under the name of "La Nouvelle-Orléans" by the French empire as a strategically situated commercial port; this beginning defined New Orleans as a conflictive site where marine merchants, privateers, and pirates shared a place on earth. Consequently, New Orleans became part of the Spanish Empire in 1763; period of time when most of the current New Orleans historic architecture was built, from 1763 to 1801. Spanish occupancy ended when New Orleans was re-conquered by Napoleon Bonaparte and became a French colony once more. In 1803, Napoleon sold the Louisiana territory to the United States of America under the "Louisiana Purchase". This transaction was executed for a little more than $23 million and included an area of 828,800 square miles extending from New Orleans to Canada. The Louisiana territory sold to the US covered what are today the states of Arkansas, Missouri, Iowa, Oklahoma, Kansas, Nebraska, part of Minnesota, North Dakota, most of South Dakota, northeastern New Mexico, north Texas, part of Montana, Wyoming, Colorado, and Louisiana (Wikipedia, 2008). Figure 1 shows a map of the sold territory.

Figure 1: Louisiana Territory sold to US in 1803

Courtesy of www.wikipedia.org: Louisiana Purchase, 1803.

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Chapter 2: Methodology

Andersen Dichotomous Sampler

The Dichotomous Sampler used in this study was designed and fabricated by Andersen Sampler Inc. (ASI) in collaboration with General Metal Works (GMW), and was distributed by Thermo Andersen. However, Thermo Andersen was purchased by Thermos Scientific; currently, this last company is the one providing spare parts and technical support for the Anderson Dichotomous Sampler Model 240. Moreover, the Dichotomous Sampler can be used to generate and present data to the Environmental Protection Agency once requirements for the Federal Reference Method (FRM) are fulfilled. Table 6 shows the minimum FRM requirement to use dichotomous data in an EPA report with the serial number of the piece that makes it possible to satisfy FRM the requirements (Thermo Andersen, 1997).

Table 6: FRM requirement for Andersen Dichotomous Sampler 240

Specification	Dichotomous Part Number
Draw a measured quantity of ambient air through a specially designed, particle size discriminating inlet	SA/G 246b
Maintain a constant flow rate within the design specifications of the dichotomous inlet	SA241-CU
Collect the sample on approved filter media	SA240PR100
Have a timing control system within the accuracy limits stipulated by FRM	SA241-CU-M SA241-CU

The Dichotomous Sampler 240 fulfills all the requirements mentioned above.

- **Description of the Andersen Dichotomous Sampler**

The Andersen Dichotomous Sampler consists of two modules: the sampling module and the flow controlling module. The sampling module collects ambient air at specifically 16.7 L/min while selectively admitting suspended particles of aerodynamic diameter equal to or lesser than 10 μm (PM_{10}) through a specially designed inlet.

Inside the sampling module, in the virtual impactor chamber, the inlet flow is further divided in two currents. One current contains only coarse particles and the other contains only fine particles. Each section of the inlet flow is forced through a different 37mm Teflon filter which collects the corresponding sized particulate matter. Figure 2 shows a drawing of the sampling module with the tripod structure on which it is mounted. The whole sampling module is 4 feet tall and weighs 15 pounds.

From the sampling module, two pipes connect the filtration chambers to the flow controlling module, one for coarse particles and the other one for fine particles. In the flow controlling module, there are two rotameters controlling total flow (16.7 L/min) and coarse particles flow (1.67 L/min). Figure 3 shows a drawing of the flow controlling module, which has dimensions 22" x 11" x 16" and weighs 65 pounds (SCARB, 1997).

Figure 2: Sampling Module of the Andersen Dichotomous Sampler

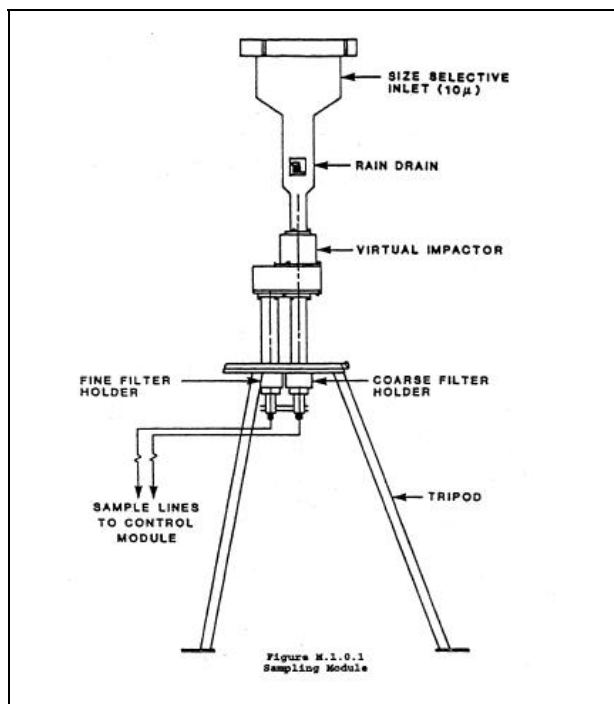Figure M.1.0.1
Sampling Module

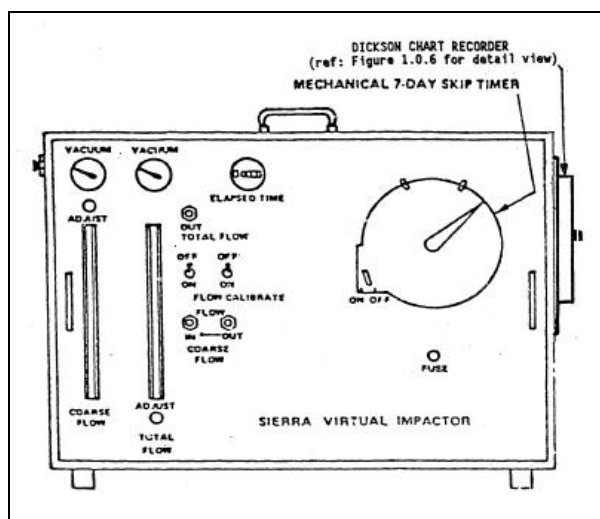**Figure 3: Flow Controller Module of the Andersen Dichotomous Sampler**

Figure 2 and Figure 3 were extracted from the "Standard Operation Procedure for Air Quality Monitoring" SCARB, 1997.

- **Principles of operation of the Dichotomous Sampler**

The Andersen Dichotomous Sampler selectively collects particles suspended in ambient air based on their aerodynamic size and the principle of inertia. At the inlet of the sampling module, ambient air is forced into the equipment at the exactly flow rate of 16.7 L/min. At this flow rate, particles larger than 10μm are not able to make the violent turn of direction, and are, therefore, separated at the inlet point. At a different flow rate, the linear velocity of the sampled particles will be different, and the inertia of those particles will also be different. Therefore, the size of sampled particle depends on the volumetric flow of the instrument.

Particles larger than 10μm in the ambient air will continue their linear trajectory due to their larger mass (larger mass = strong inertia at determinate speed), and they will miss the inlet of the equipment. Further division of the sampled particles occurs in the virtual impactor. A virtual impactor separates particles by striking them against a high speed flowed air rather than striking them against a solid surface.

Flow entering through the virtual impactor nozzle at 16.7 L/min is forced to make a 90° turn to pass to a second chamber which has a flow of 15 L/min. At this point, only particles of aerodynamic size of 2.5μm or smaller will be able to make the violent turn off direction to the fine particle collection chamber, which ends at the fine particles filter, a 37 mm Teflon filter. Particles larger than 2.5μm will not be able to pass to the fine particles chamber due to their inertia, and they will continue a linear trajectory with respect to the one at the virtual impactor nozzle. This linear trajectory will take coarse particles to another 37 mm Teflon filter at the end of this chamber at a flow rate of 1.67 L/min (EPA, 1999).

Figure 4 present a scheme of the virtual impactor in the Andersen Dichotomous Sampler extracted from the 1997 EPA document EPA/600/4-77-027a named Monitoring PM_{10} in Ambient Air Using a Dichotomous Sampler.

Figure 4: Virtual Impactor. Point of Separation of Fine and Coarse Particles
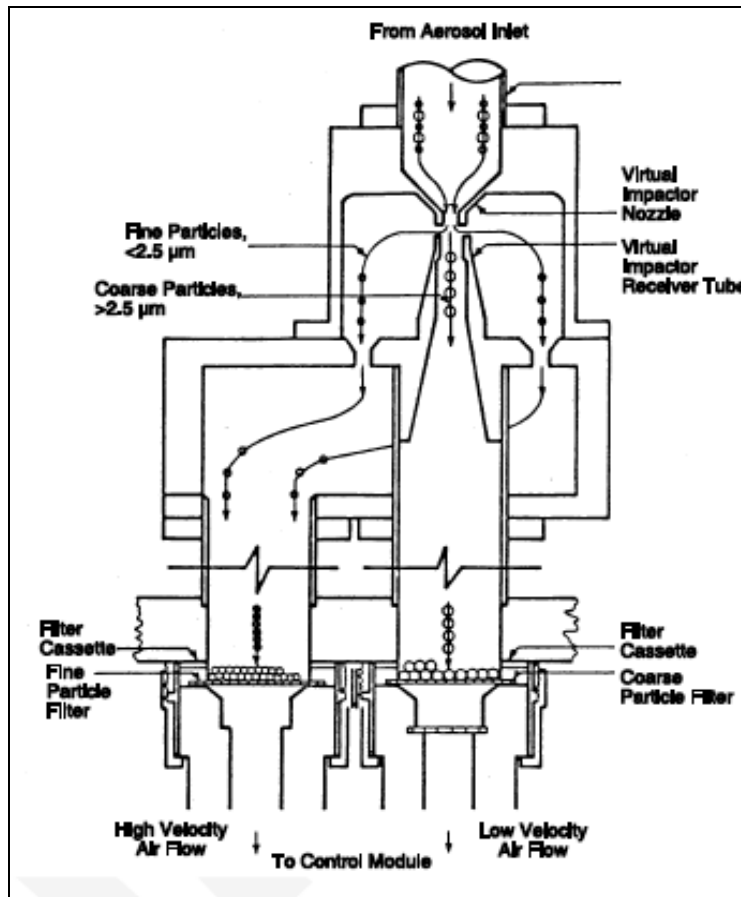
- **Filter handling**

  The only filters approved by the EPA FRM are the 37mm Teflon filters, part number SA240PR25 or SA240PR100. Teflon filters must never be touched with bare hands, since skin oils on the fingertips will affect measurement. Therefore, Teflon filters are to be maintained encapsulated in the polyolefin rings when taken to, and from, the sampling site. Additionally, they must be handled with tweezers in the laboratory. Figure 5 shows one of the Teflon filters inside a tallow ring.

Figure 5: Placing of the Coarse Particles Filter in the Dichotomous Sampler

The water content of the air can also pose another source of error because water trapped in the filter might or might not evaporate causing different reading for filter with the exact amount of pollutant. Additionally, Teflon filters are not-conductive materials and will hold static charges collected on them. For these two reasons, filters must be stabilized in a dissector for 24 hrs prior to and after sampling (in both cases prior to weighting) (Koistinen, 1999).

- **Calibration of the Dichotomous Sampler**

As mentioned before, the Andersen Dichotomous Sampler controls total flow and coarse particles flow of the instrument with two different rotameters. Hence, both rotameters must be calibrated independently. However, it is necessary to check for air leakage before starting calibration. Appendix 1 shows the required precalibration system check. This protocol is to be repeated each time the sampler is transported to or from the sampling site and each time any part or filter is replaced (EPA, 1997).

Rotameters Calibration

A transfer standard flow meter is necessary to calibrate the flow controlling unit of the Dichotomous Sampler (Thermo Anderson, 1997). A dry gas transfer standard with traceable calibrations to EPA standardized equipment is the preferred option for this procedure. However, there was no availability of such equipment during the course of this research. Instead, the following NIST traceable standards equipment was used during rotameters calibration (Chinook Engineering, 2007):

Flow Meter:
Streamline Pro™ Multical™ System
Model M: 0.9 to 19.0 L/min
NIST Traceable standards
Fabricator: Chinook Engineering

The Streamline Flow Meter performance was compared to a dry gas transfer standard owned by the Louisiana Department of Environmental Quality (LDEQ) - Air Quality Monitoring Laboratory of Baton Rouge, LA. The dry gas transfer standard mentioned holds the following EPA certification:

Dry Gas Calibration Transfer Standard
DC-2 Flow Calibrator
Dry Cal/Bios International s/n B833
Certified with EPA equipment Dry Cal s/n 107565

The sampling unit inlet was removed to calibrate the Dichotomous rotameters. The Streamline Flow Meter was connected instead of the sampler inlet. The air feed of the flow meter remained open to ambient. See detailed procedure and picture in Appendix 1.

Innov-X XRF Analyzer

Innov-X XRF Alpha series analyzers offer easy to use equipment for non destructive assays able to identify metals and heavy metals in solid samples, such as soil, solid surfaces, or filters. Additionally, these instruments are able to perform similar tests in liquid samples. Innov-X offers a specific method for the analysis of thin 37mm Teflon filter, which is exactly, the same filters utilized by the Andersen Dichotomous Sampler (Innov-X 2006). XRF Spectrometry is used to identify the atomic elements present in a sample without destruction of material. An element is identified by its characteristic X-

Ray wavelength emission (λ) while the amount of this specific element is determined by quantifying the intensity of the X-Ray emission.

- **Principles of Operation of the XRF Analyzer**

Every element of the periodic table can be identified by the number of protons in its nucleus. In stable state, the number of protons is equal to the total number of electrons located on the different orbits around the nucleus. Energy Dispersion X-Ray Fluorescence (ED-XRF) utilizes the electrons in the three first orbits of an atom because of their low energy level: these orbits are K, L, and M. K orbit is the closer to the nucleus (lower energy level) and M is the third orbit from the nucleus (higher energy level than L and K).

In Energy Dispersion XRF high energy photons emitted from an X-Ray source strike the sample material, displacing the electrons in the orbits with low energy levels. At this point, the atom becomes an Ion (instable), and electrons form orbits of higher energy levels move downward to fill out the empty space in the low orbital, traveling from the outermost orbits to those small, innermost, orbits close to the nucleus. When an electron moves from an outer orbit to an inner orbit, it emits a type of energy known as secondary X-Ray photon, also known as fluorescent energy, which is characteristic of each specific element. This energy is inversely proportional to the wavelength and is related through the following formula:

$$E = hc/\lambda$$

Where: h is the Planck's constant, c is the speed of light, and λ is the wavelength of the emitted photon.

The energy (E) of the emitted fluorescent photon is determined by the difference in energy between the initial and final orbital of the individual

transition. Additionally, the intensity of the fluorescent emission is measured to determine the quantity of the newly identified element. Then, the result of the analysis is presented as a plot of Energy (KeV) vs. X-ray intensity in the interactive screen of the analyzer. Figure 6 shows an example of the plotted spectrum form a sampled material with the Innov-X XRF Analyzer (Innov-X, 2004). Pictures of XRF Analyzer used during this research are presented in Appendix 2.

Figure 6: Example of a XRF outcome from Innov-X Analyzer.
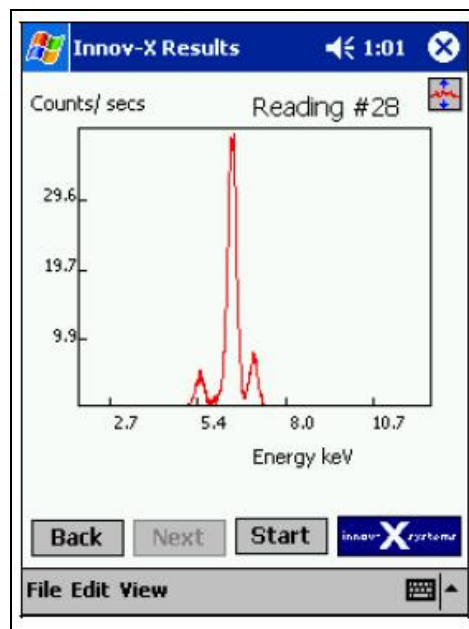
- **Standardization of the XRF Analyzer**

    The standardization of the XRF analyzer must be performed each time the equipment is turned on or every 1 hr in a continuous use. Luckily, it only takes 1 minute. To calibrate the instrument, just select standardization mode and collect the spectrum from a known standard alloy which is provided in the operation kit (Alloy 316) (Innov-X, 2004).

Selection of Sampling Site

Originally, this research aimed to collect ambient air from heavily transited street intersections of the City of New Orleans. The original idea was to measure the concentration of heavy metals in ambient particulate matter of a street where cars, busses, and pedestrians were present at the same time. Then, it was desired to estimate the health effect of those toxic pollutants on the health of the exposed pedestrian. However, it was impossible to coordinate the placement of the collection device with the New Orleans department of transportation on time to meet the dead-line for the present project.

Fortunately, permission was obtained to place the Anderson Dichotomous Sampler on the roof of an antique Creole house located on the intersection of The Cabildo Alley and Pirates Alley, right behind the Saint Louis Cathedral in the New Orleans French Quarter. The sampling point, in the heart of the New Orleans Historic District, permitted collection of PM data in a region of the city that is not currently monitored by the EPA or the Louisiana DEQ.

The Louisiana DEQ permanently monitors the ambient air quality of several points of the state under the Louisiana Ambient Air Monitoring Program. Seven of them are in the Greater New Orleans area, but only four of those seven sites monitor $PM_{2.5}$ and/or PM_{10}. Figure 7 shows the sample points operated by LDEQ in the South-east region of Louisiana, and Table 7 has a list of the sampling sites in the Greater New Orleans area. The sampling points in New Orleans are separated by quite a lot of distance, and it is surprising that LDEQ does not maintain a monitoring site in the New Orleans Historic District to enrich the Louisiana Ambient Air Monitoring Network.

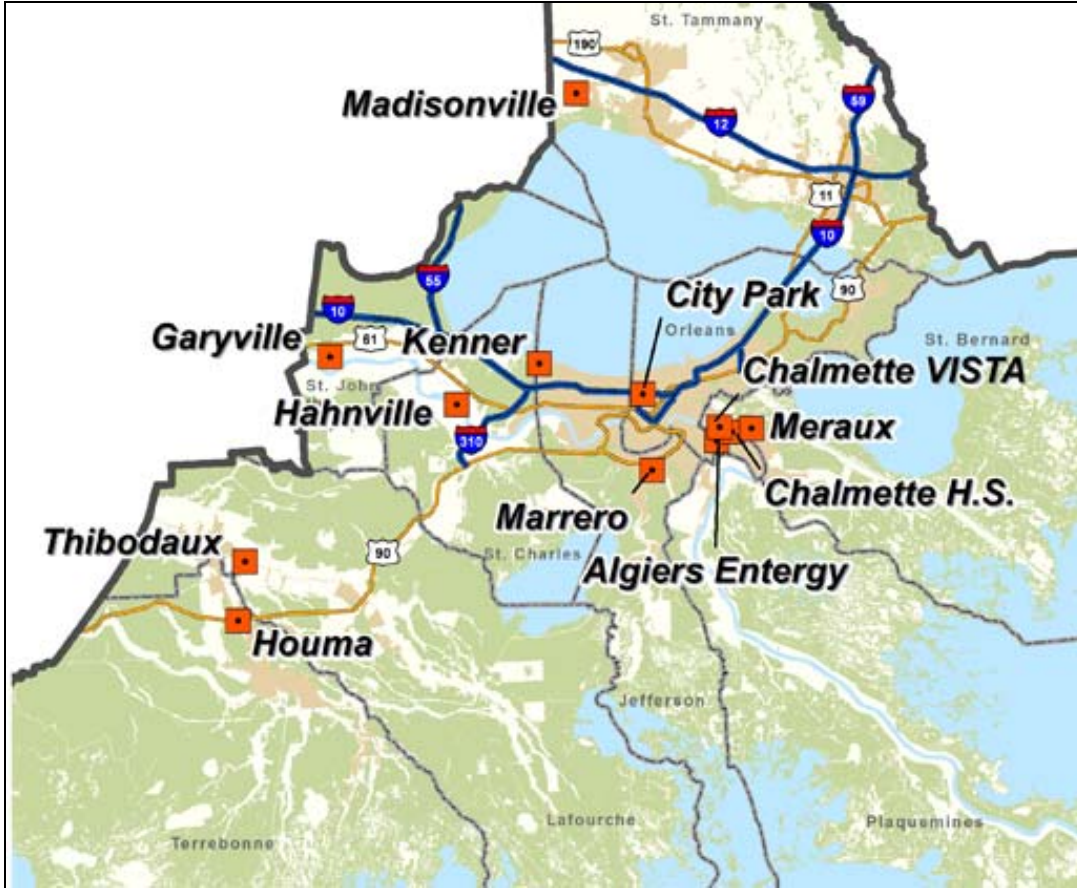**Figure 7: LDEQ Ambient Air Monitoring Sites in South-East of Louisiana**

Image courtesy of LDEQ: http://www.deq.louisiana.gov/portal/tabid/2476/Default.aspx

Table 7: LDEQ Sites in the Greater New Orleans Area and Distance from the St Louis Cathedral

Sampling Site	Address	Distance from the St. Luis Cathedral	Monitoring $PM_{2.5}$ and/or PM_{10}
Algiers Entergy	2456 Ernest. New Orleans, LA	5.5 miles	
Chalmette High School	1100 E Jorge Perez Drive. Chalmette, LA	6.7 miles	
Chalmette Vista	24 E. Chalmette Circle. Chalmette, LA	5.4 miles	Yes
City Park	Florida & Orleans Avenue, New Orleans, LA	3.3 miles	Yes
Kenner	100 West Temple Place, Kenner, LA	13.8 miles	Yes
Marrero	Patriot Street and Allo Street. Marrero, LA	5.4 miles	Yes
Meraux	4101 Mistrot Drive. Meraux, LA	8.5 miles	

Historic Significance of the Pirate's Alley Sampling Point

The ambient air samples were taken from the roof of a coffee shop located at the intersection of The Cabildo Alley and Pirates Alley, in New Orleans, LA. The name of the business is Pirate's Alley Café, and its mailing address is 622 Pirate's Alley, New Orleans, LA. Appendix 3 contains pictures of the ambient air sampling site.

Pirate's Alley Café is located on what was once the former Spanish Colonial Prison of 1769, which was called "El Calabozo". As a curious note, the famous privateer and hero of the Battle of New Orleans (1815), Jean Laffite, was imprisoned in this jail by governor Claiborne. Before coming to New Orleans, Jean Laffite was given the title of Marque by the Venezuelan Spanish war hero Simon Bolivar on 1803 in Cartagena, Grand Colombia (territory today occupied by Colombia, Venezuela, Ecuador, and Panama). Pierre Laffite, Jean's younger

brother, also served several months in the same prison, but he eventually escaped (Seville, 2007).

"El Calabozo" was demolished in 1837 and the land was sold to build the house that still stands today. This historic Creole house was once occupied by the famous southern writer William Faulkner, and it was the place where he wrote his first novel "*Soldiers' Pay*" in 1926. Afterward, Faulkner was awarded the Nobel Prize for Literature in 1949 (Seville, 2007).

Besides the old "Calabozo" and Faulkner's house, the ambient air sampling point on Pirate's Alley is surrounded by some of the most important historic buildings in New Orleans. As a matter of fact, the Pirate's Ally Café is only six feet away from the Cabildo Museum. The Cabildo was built in 1726 and was the place where the French Empire and the USA signed the Louisiana Purchase in 1803. Finally, the Saint Louis Cathedral, probably the most representative landmark of New Orleans, is less than twenty feet away from the Pirate's Alley Café. The Saint Louis Cathedral was built in 1720, rebuilt in 1789, and is the oldest continuously operating church in the US of our days (Seville, 2007).

Data Collection and Recording

The complete study involved the gravimetric analysis of the Dichotomous Sampler filters followed by X-Ray Fluorescence (XRF) analysis of the same filters. Data recorded included:

- The Dichotomous Sampler analysis:
  - Ambient temperature and pressure on the site and date of sampling
  - Weight of the filter prior and after PM collection
- The XRF assay:
  - Metal identified in each filter
  - Concentration of metal by area of filter

As mentioned before, ambient air was sampled from the French Quarter. However, weighting of the filters was always performed in the UNO Wastewater Research Laboratory supervised by Dr. Enrique La Motta. This research laboratory is located at UNO in the CERM building, room 109. The balance used in this procedure is described below.

Balance Maker: OHAUS
Model: GA200
UNO s/n: 528288
Readability: 0.1mg = 100μg

XRF analyses were performed in room EN833 of the UNO engineering building. At the beginning of the research, there was the intention to utilize a UNO property XRF analyzer, but technical problems with the instrument made it impossible to start recording data with this it. The Louisiana DEQ provided a newer version of the analyzer to perform the experiments, and this is the one that was used during the whole research even though the UNO instrument is currently operative. Description of both analyzers is presented in Table 8. In any case, with both XRF analyzers, data is downloaded directly from the instrument to a PC as an MS-Excel sheet.

Table 8: Description of XRF Analyzers Used During the Research

Characteristics	UNO XRF Analyzer	LDEQ XRF Analyzer
Maker	Innov-X	Innov-X
Model	XT-442L	A-6500
Serial No	1001	5660

Data Processing

Most of the data for this research, like the weight of the filters for instance, was used as it was generated, but some calculations were necessary for the calibration and setting of the dichotomous rotameters.

The Ideal Gas Law was used to correct the temperature and pressure of the ambient air at the sampling site because the rotameters were calibrated at different ambient conditions, temperature and pressure.

Ideal Gas Law:

$$P \times V = n \times R \times T$$

Where,

P: Atmospheric Pressure (Atm)
V: Volume of gas (air) sampled (L)
n: moles of gas sampled (gmol)
R: Ideal Gas Law Constant= 0.08206 (atm.L)/(gmol.K)
T: Ambient temperature (K)

Equation 1 was used to relate conditions at the sampling point to the conditions at the calibration site:

$$Q_c = Q_s \times \frac{T_c}{T_s} \times \frac{P_s}{P_c} \qquad \text{(Equation 1)}$$

Where "Q" refers to volumetric flow, "T" to ambient temperature, and "P" to atmospheric pressure. The subscripts "c" and "s" refer to calibration site conditions and sampling site conditions (Wight, 1994).

Chapter 3: Results and Discussions

Particulate Matter Data

The first step in the generation of the PM data was the identification of the correct air flow sampling at the collection site. As mentioned in Chapter 2, the total flow of air collected with the Anderson Dichotomous Sampler model 240 must be 16.7 L/min. Therefore it is necessary to take account on the difference of ambient temperature and pressure between the sampling point and the site of equipment calibration. Following is the calibration data recorder for the coarse and total rotameters of the Dichotomous Sampler.

Table 9: Total Flow Rotameter Calibration. Dichotomous Sampler

Coarse Particles Rotameter fixed to:
Close position
Laboratory Ambient Conditions:
Air T= 18.8 C , P= 1.0006 atm

Dichotomous Total Flow Reading (SLPM)	Corrected Reading from Flow Meter (ALPMC)
21	18.87
20	18.85
18	17.82
17	16.45
16	15.65
15	14.82
13	12.75
10	9.82

Note: SPLM= Standard Liters per Minutes
ALPMC= Actual Liters per Minutes at Calibration Conditions

Figure 8: Relationship between Dichotomous Reading (SLPM) and Calibration Flow Reading (ALPMC) for Total Rotameter
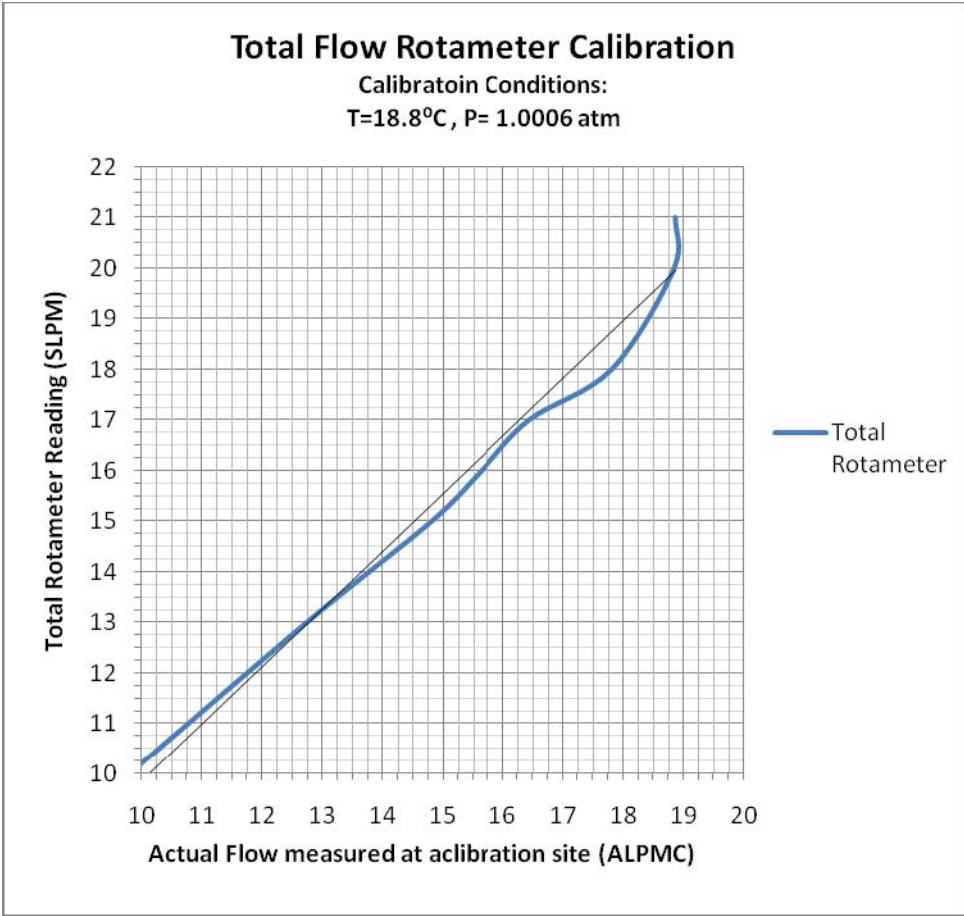
Equation 1, on page 36, was used to relate the conditions on the calibration site (laboratory) with the sampling site (French Quarter) in order to identify correct flow. Total flow was fixed to 16.7 L/min, while flow for coarse particles was 1.67 L/min. Then, Figures 8 and 9 were used to relate corrected flow with the rotameters readings. Table 11 shows the flows chosen at the sampling site for the different experiments.

Table 10: Coarse Flow Rotameter Calibration. Dichotomous Sampler

Total Flow Rotameter fixed to:
90%=21 SLPM position
Laboratory Ambient Conditions:
Air T= 18.8 C , P= 1.0006 atm

Dichotomous Coarse Flow Reading (SLPM)	Corrected Reading from Flow Meter (ALPMC)
2.00	1.98
1.65	1.41
1.50	1.26
1.20	0.93
1.10	0.82
0.80	0.62

Note: SPLM= Standard Liters per Minutes
ALPMC= Actual Liters per Minutes at Calibration Conditions

Figure 9: Relationship between Dichotomous Reading (SLPM) and Calibration Flow Reading (ALPMC) for Coarse Rotameter
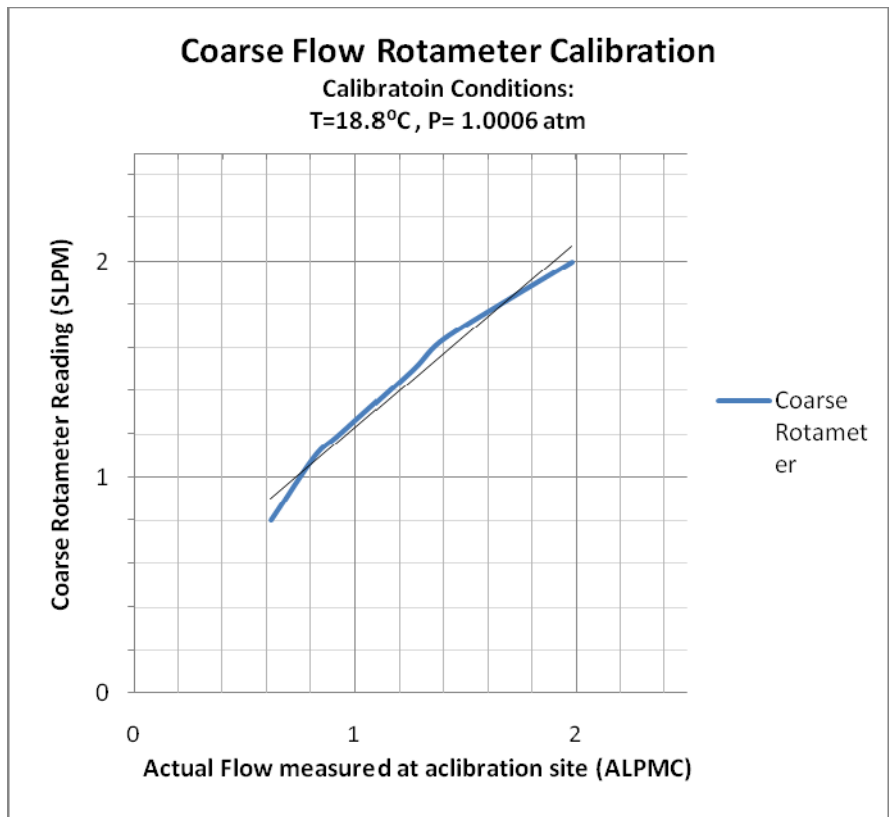
Table 11: Rotameter Corrections at Sampling Site

Exp #	Sampling Site Conditions		Desired Flow at Sampling Site (L/min)		Calibration Site Conditions		Corrected Flow for Calibration T and P (L/min)		Fix Rotameters at : (L/min)	
	T (^{o}C)	P (atm)	Coarse	Total	T (^{o}C)	P (atm)	Coarse	Total	Coarse	Total
1	20	1.007	1.67	16.7	18.8	1.006	1.57	15.71	1.72	16.35
2	19.44	1.006	1.67	16.7	18.8	1.006	1.62	16.15	1.76	16.84
3	18.89	1.006	1.67	16.7	18.8	1.006	1.66	16.62	1.80	17.38
4	21.01	1.007	1.67	16.7	18.8	1.006	1.50	14.96	1.66	15.49
5	20.56	1.008	1.67	16.7	18.8	1.006	1.53	15.30	1.69	15.88

Gravimetric Analysis of the Teflon Filters

Five runs were conducted to sample ambient air and generate the data used for this project. The first two samples (coarse and fine particles) were collected in 24 hrs runs of the Dichotomous Sampler. The last three experiments were performed using longer collection time. The reason for this change in the protocol is that the analytical balance available in the laboratory has a sensitivity of 100 μg. It means that the smallest weight difference accurately measurable with this instrument is 100 μg. Therefore, the collection time was changed to a longer period in order to collect larger amount of PM mass and reduce laboratory error. Appendix 4 presents the gravimetric analysis results for experiments 1 to 5 respectively.

Estimation of PM Concentrations

After gravimetric analysis of the filters, the PM concentration is obtained directly by dividing the net mass of particles sampled (in μg) by the volume of air sampled (in m^3). For the $PM_{2.5}$, the mass used is the one obtained from the analysis of the fine particles filter, and the volume of air will be equal to the collection time (in minutes) multiplied by the sampling flow rate for fine

particles (15.00 L/min = 0.015 m^3/min). On the other hand, the calculations for PM$_{10}$ involved the net mass of all the particles collected (both filters), while volume of air sampled was obtained by multiplying the sampling time (in minutes) times the total flow rate (16.7 L/min = 0.0167 m^3/min). Table 16 shows the PM concentrations found in the New Orleans Historic District during the month of October and November of 2008.

Table 12: Ambient Air PM of the New Orleans Historic District. October-November of 2008

	Ambient Air PM (µg/m^3)	
	PM10	**PM2.5**
Exp # 1	25.00	7.94
2	12.50	4.63
3	15.21	7.25
4	10.20	11.34
5	12.50	4.63
Average	15.08	7.16
EPA NAAQS	150	35

Surprisingly, PM$_{2.5}$ and PM$_{10}$ are both much smaller than expected taking account of the amount of cars and heavy duty vehicles transiting close to the sampled area. Likewise, the proximity to the Mississippi river could represent a source of water vapor which also contributes to the amount of ambient PM$_{10}$. However, the low PM values in the New Orleans Historic District are reasonable explanation of why LDEQ does not monitor ambient air in the French Quarter area. LDEQ usually pay attention to those Louisiana areas with pollution levels above 80% of NAAQS. Appendix 5 shows the a map of Louisiana with the ambient air monitoring sites and also several tables extracted from the 2007 Ambient Air Monitoring Network Annual Report. In

those LDEQ tables PM concentrations for the 24 hrs averages are all higher than the values obtained in the French Quarter because all LDEQ sampling are close to a pollution source. In some case the sampling site are very close of a oil refinery (Chalmette) and in other cases the sampling site are located right in front of a water body (Kenner). Figure 10 shows a plot of the PM concentration found in each of the 5 experiment performed, and Figure 11 shows the same concentration plot with a graphic representation of the NAAQS.

Figure 10: Particulate Matter in the ambient air of the New Orleans Historic District
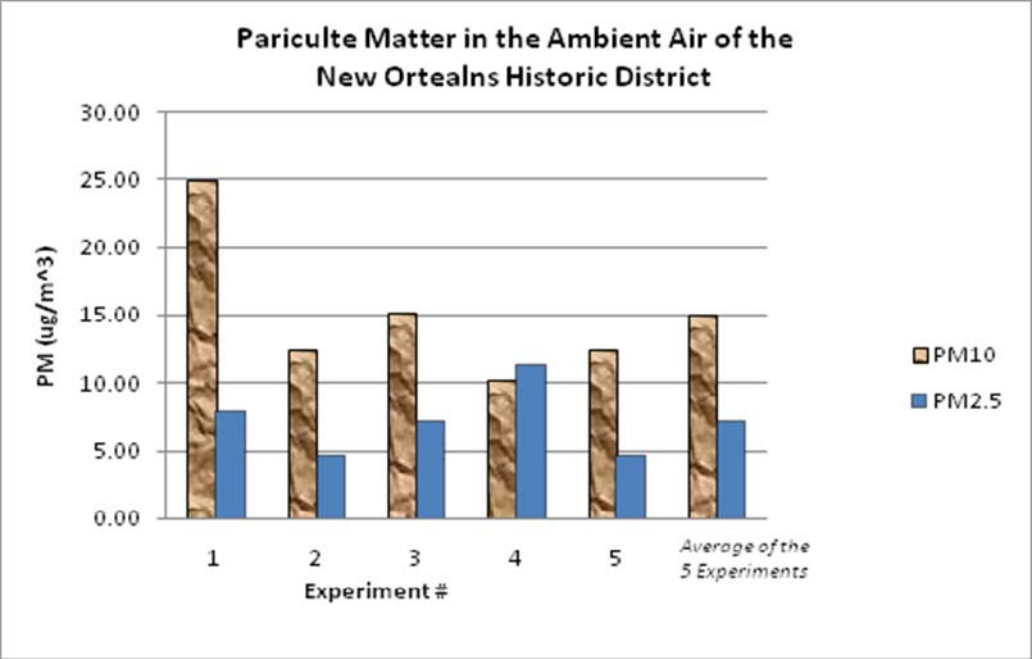
Figure 11: Particulate Matter in the ambient air of the New Orleans Historic District with their corresponding NAAQS
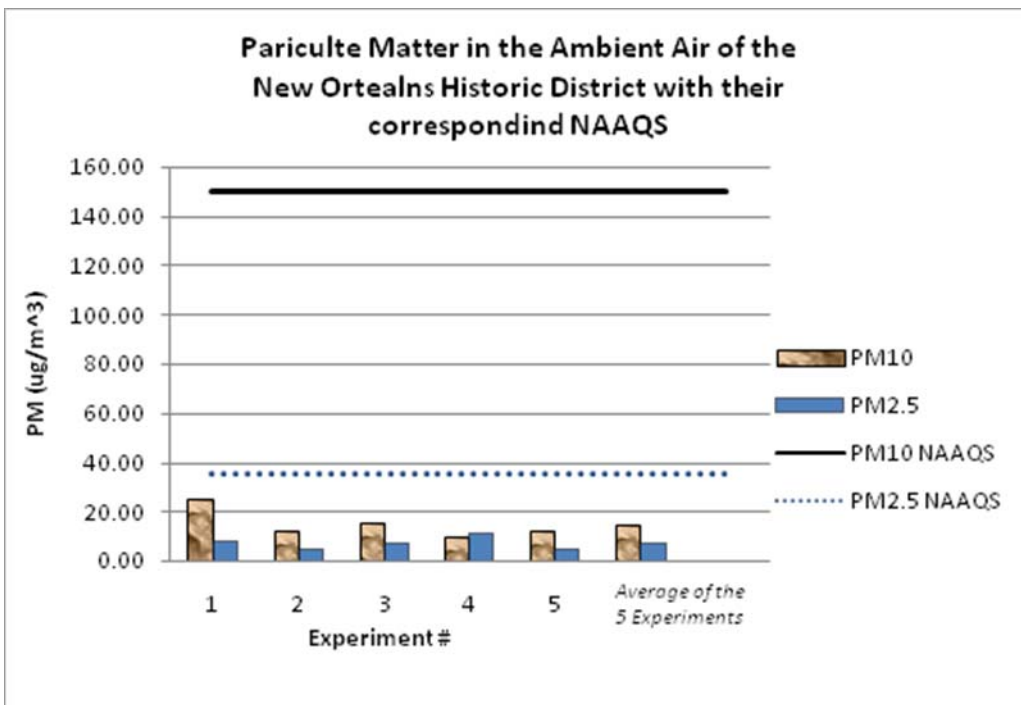
Airborne Metals Data

XRF analyses were performed by exposing the filter with the particles to the X-Ray emitter analyzer. Each sample was recorded three times to allow the XRF analyzer collect data from three different spots of each filter. Innov-X A-6500 series presents the data in MS Excel format, which greatly facilitates processing of the information.

No data for heavy metal was recorded, which might mean that the amount of heavy metal suspended in the sampled air is just too low to be detected by the instrument. Table 16 shows the average metal concentration found in each filter. The data presented in this table has units of μg of metal per cm^2 of filter. Remember filter is circular and has diameter of 0.37 cm (37mm).

Table 13: Metal Concentration found in Teflon filters after Gravimetric Analysis

Exp #	Cr (ug/cm^2)		Fe (ug/cm^2)		Ni (ug/cm^2)		Au (ug/cm^2)	
	Fine PM Filter	Coarse PM Filter	Fine PM Filter	Coarse PM Filter	Fine PM Filter	Coarse PM Filter	Fine PM Filter	Coarse PM Filter
Blank	0.99	0.99	1.46	1.46	0.1	0.1	<LOD	<LOD
1	0.82	0.94	1.32	2.28	0.08	0.14	<LOD	<LOD
2	0.87	0.92	1.5	2.29	0.1	0.12	<LOD	0.32
3	0.75	0.82	1.34	2.56	0.12	<LOD	<LOD	<LOD
4	0.91	0.81	1.21	2.84	<LOD	0.09	<LOD	<LOD
5	0.52	0.56	0.99	2.25	<LOD	<LOD	<LOD	<LOD

<LOD: below limit of detection

Following the XRF analysis it was estimated the concentration of metals on the fractions of particulate matter studied. As noted in table 17, the data collected from the XRF analysis is presented in μg of pollutant per unit area of the filter analyzed. Then, it was necessary to correct that information to μg of pollutant per volume of air, but there were samples taken in 24hrs runs (Experiments 1 and 2) and other taken in 48 hrs runs (Experiments 3, 4, and 5). Therefore, only data from Experiments 3, 4, and 5 were used in the following calculations. It was done through the following conversion factors:

$$Mass\ of\ metal\ per\ filter = \frac{ug\ metal}{cm^2 of\ filter} \times \frac{\pi \times \left(\frac{fd}{2}\right)^2}{1\ filter}$$

Where *fd* means filter diameter, which is in this case 0.37cm

The calculations of the concentration of metal per volume were performed separately for each fraction of particulate size, and Table 18 shows the results of those calculations.

Metal Concentration per mass of $PM_{2.5}$ sampled.

$$Metal\ in\ PM_{2.5} = \frac{ug\ Metal}{filter} \times \frac{1\ filter}{ug\ PM_{2.5}}$$

Where "*µg PM2.5*" is the net mass of fine particles collected.

$$ug\ PM_{2.5} = \frac{7.16\frac{ug}{m^3}}{15\frac{L}{min\square} \times 48\ hr \times 60\frac{min}{hr} \times \frac{1\ m^3}{1000\ L}}$$

Metal Concentration per mass of PM_{10} sampled.

$$Metal\ in\ PM_{10} = \frac{ug\ Metal}{filter} \times \frac{1\ filter}{ug\ PM_{10}}$$

Where "*µg PM10*" is the net mass of fine particles collected.

$$ug\ PM_{10} = \frac{15.08\frac{ug}{m^3}}{16.7\frac{L}{min\square} \times 48\ hr \times 60\frac{min}{hr} \times \frac{1\ m^3}{1000\ L}}$$

Finally, metal concentration per volume of air was calculated as it follows.

$$C\ metal\ \left(\frac{ug\ Metal}{m^3\ ambient\ air}\right)$$

$$= \frac{ug\ Metal\ in\ fine\ particles\ filter\ +\ ug\ Metal\ in\ coarse\ particles\ filter}{16.7\ \frac{L}{min\ \square}\times 40\ hr\ \times 60\ \frac{min}{hr}\times \frac{1\ m^3}{1000\ L}}$$

Table 14: Metal Concentration in ambient air PM of the New Orleans Historic District

	(µg Metal/cm^2)		(µg Metal/filter)		Mass fraction (Metal/PM)		Concentration (µg Metal
	PM$_{2.5}$	PM$_{2.5-10}$	PM$_{2.5}$	PM$_{2.5-10}$	PM$_{2.5}$	PM$_{10}$	/ m^3 air)
Cr	0.73	0.73	0.08	0.08	2.53E-04	2.54E-04	3.26E-03
Fe	1.18	2.55	0.13	0.27	4.10E-04	8.86E-04	8.34E-03
Ni	0.04	0.03	4.30E-03	3.23E-03	1.39E-05	1.04E-05	1.56E-04

Estimation of Ambient Quality Index

With the information in Tables 4 and 5 it was possible to estimate the Air Quality Index (AQI) and the Air Quality Description for the New Orleans Historic District.

$$\text{With: } PM_{10} = 15.08 \ \mu g/m^3$$

$$\text{Interpolating from Table 4: } PM_{10} \ AQI = 13.71$$

$$\text{With: } PM_{2.5} = 7.16 \ \mu g/m^3$$

$$\text{Interpolating from Table 4: } PM_{2.5} \ AQI = 23.10$$

Finally, if the Indicator values for the rest of the pollutant on Table 4 are all lower than "13.10", the ambient air of the New Orleans Historic District could be described as "Good" regarding parameter of Table 5.

Chapter 4: Conclusions

Ambient quality monitoring assays must be designed, initiated, performed, and concluded with a specific intention in mind. Likewise, the principal objective of most environmental assessments is to protect human health through the determination of ambient quality. Therefore, the focus of this research was to estimate the concentration of pollutants that have been identified as detriments to public health in a heavily populated area. Additionally to the stimulus of watching over public health, it was intended to help in the assessment of pollution concentration high enough to deteriorate historic monuments and art artifact even though this concentration of pollutants is too low to be considered a threat to human health. Following are the specific conclusions found as a consequence of this research.

- The concentration of particulate matter with aerodynamic diameter equivalent or lower than 2.5 µm in the New Orleans Historic District, Louisiana, during the months of October and November of 2008 is found to be of 7.16 µg/m^3.

- The concentration of particulate matter with aerodynamic diameter equivalent or lower than 10 µm in the New Orleans Historic District, Louisiana, during the months of October and November of 2008 in found to be of 15.08 µg/m^3.

- The New Orleans Historic District present an Quality Ambient Index of 23.10, which helps to describe the ambient air of that region as presenting "Good" standard according to the Environmental Protection Agency.

- The concentrations of metals suspended in the ambient air of the down town area of the City of New Orleans is too low to be measured by the instruments utilized during this research with the except of Cr, Fe, and Ni, which concentrations were identified as 3.26×10^{-3}, 8.34×10^{-3}, and 1.56×10^{-4} respectively.

- The concentration of heavy metals in the ambient Air of the New Orleans Historic District is too low to be detected by the XRF Analyzer used in this research.

- The Andersen Dichotomous Sampler Model 240 has demonstrated to be a reliable and easy operative piece of equipment once it is correctly calibrated. Moreover, it could be used to collect data to be used in environmental report to be presented to the EPA according to the Federal Reference Methods (FMR).

- It will be very convenient to count on an analytical balance with accuracy of 1μg for further ambient air experiments to be developed at the University of New Orleans.

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Appendix 1:

Calibration of the Dichotomous Sampler

Precalibration System Check

1. Place a pair of 37mm Teflon filters into two polyolefin ring filter holders. Coarse and fine particles are collected in the same type of filter, but yellow rings are used to differentiate coarse particles filters, while white rings are used for fine particles filters. Filters used in this precalibration procedure should not be used for analysis.

2. Using the ring holders, place the filters directly on the filter holder screen of the Dichotomous Sampler. The filter must be placed so that the Teflon membrane is closer to the screen. Again, yellow color indicates the coarse and white indicates the fine particles filters. Figure 5 shows a picture of the coarse filter placing process.

3. Turn on the Sampler and allow it to run for 5 to 10 minutes to warm up. Turn of the optional pressure switch.

4. Remove the sample inlet, and open both rotameters completely.

5. Seal the sample module inlet tube with your palm, and watch the vacuum gauge. After few seconds, the vacuum gauge will reach maximum reading (23 to 27 inHg).

6. When maximum vacuum is achieved turn off the pump and measure the time it takes the pressure to drop below 5 inHg.
   Note: Leak free systems should indicate maximum vacuum of 23 inHg or more, and it should take more than 60 second for the vacuum pressure to drop below 5 inHg.

7. If leakage is identified make necessary adjustment and repeat precalibration system check.

Total Rotameter Calibration Procedure

1. Connect flow meter to the inlet of the collection module tube.

2. Turn on sampler pump and open both (total and coarse) rotameters to maximum. Wait 5 minutes for the equipment to reach normal operating temperature.

3. Close coarse rotameter valve completely.

4. Adjust total rotameter valve to 21 SLPM.

5. Read the following parameters: ambient temperature, barometric pressure, and flow meter corrected reading.

6. Repeat steps 5 and 6, at least 5 times, changing total rotameter valve to values between 20 to 10 SLPM.

Coarse Rotameter Calibration Procedure

1. Connect flow meter to the inlet of the collection module tube.

2. Turn on sampler pump and open both (total and coarse) rotameters to maximum. Wait 5 minutes for the equipment to reach normal operating temperature.

3. Adjust total rotameter valve to 21 SLPM.

4. Adjust coarse rotameter valve to 2.0 SLPM.

5. Read the following parameters: ambient temperature, barometric pressure, flow meter corrected reading.

6. Subtract corrected value for 21 SLPM of the total rotameter calibration minus flow meter corrected reading, and record corrected value for coarse rotameter calibration.

7. Repeat steps 5 and 7, at least 5 times, changing coarse rotameter valve to values between 2.0 to 0.8 SLPM.

Appendix 2:

X-Ray Fluorescence Analyzer
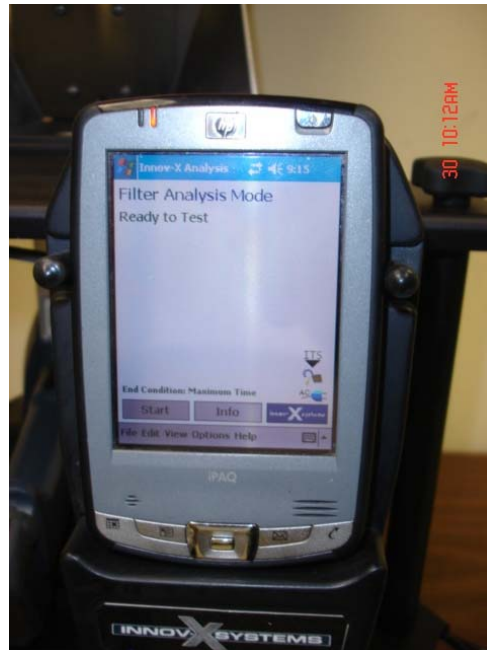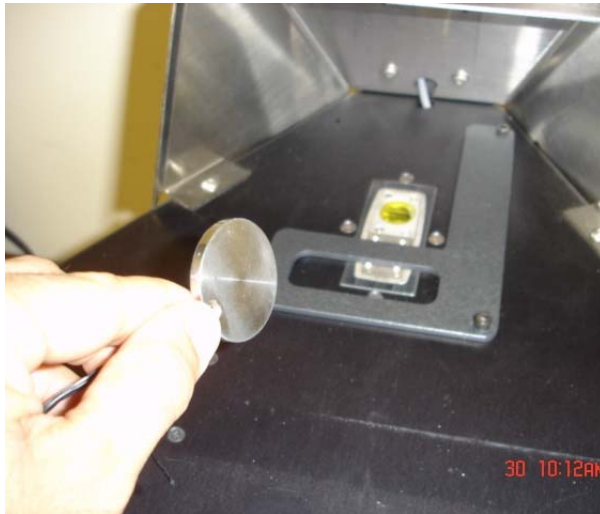
Appendix 3:

Ambient Air Sampling Site

Appendix 4:

Gravimetric Analysis for Experiments 1 to 5

Gravimetric Analysis for Experiment 1

Experiment 1   10/27-28/08 : 28hrs

Filter #	Weight Clean Filer (g)	Ring	Particles size	Weight PM + Filer (g)	Start Collection time 10/27/08	End Collection time 10/28/08	Sampling time (min)	Volume of Air Sampled (m^3)
1	0.1234	yellow	Coarse	0.1239	12:00 n	4:00pm	1680	2.81
2	0.1230	white	Fine	0.1232	12:00 n	4:00pm	1680	25.20

Gravimetric Analysis for Experiment 2

Experiment 2   10/28-29/08 : 24hrs

Filter #	Weight Clean Filer (g)	Ring	Particles size	Weight PM + Filer (g)	Start Collection time 10/27/08	End Collection time 10/28/08	Sampling time (min)	Volume of Air Sampled (m^3)
Y5	0.1253	yellow	Coarse	0.1255	4:00pm	4:00pm	1440	2.40
W6	0.1210	white	Fine	0.1211	4:00pm	4:00pm	1440	21.60

Gravimetric Analysis for Experiment 3

Experiment 3   10/29-31/08 : 46hrs

Filter #	Weight Clean Filer (g)	Ring	Particles size	Weight PM + Filer (g)	Start Collection time 10/27/08	End Collection time 10/28/08	Sampling time (min)	Volume of Air Sampled (m^3)
Y7	0.1223	yellow	Coarse	0.1227	4:00pm	2:00pm	2760	4.61
W8	0.1221	white	Fine	0.1224	4:00pm	2:00pm	2760	41.40

Gravimetric Analysis for Experiment 4

Experiment 4   10/31/08 11/02/08 : 49hrs

Filter #	Weight Clean Filer (g)	Ring	Particles size	Weight PM + Filer (g)	Start Collection time 10/27/08	End Collection time 10/28/08	Sampling time (min)	Volume of Air Sampled (m^3)
Y7	0.1241	yellow	Coarse	0.1244	2:00pm	3:00pm	2940	4.91
W8	0.1229	white	Fine	0.1234	2:00pm	3:00pm	2940	44.10

Gravimetric Analysis for Experiment 5

Experiment 5   11/02 - 04/08 : 48hrs

| Filter #	Weight Clean Filer (g)	Ring	Particles size	Weight PM + Filer (g)	Start Collection time 10/27/08	End Collection time 10/28/08	Sampling time (min)	Volume of Air Sampled (m^3)
Y7	0.1235	yellow	Coarse	0.1239	3:00pm	3:00pm	2880	4.81
W8	0.1225	white	Fine	0.1227	3:00pm	3:00pm	2880	43.20

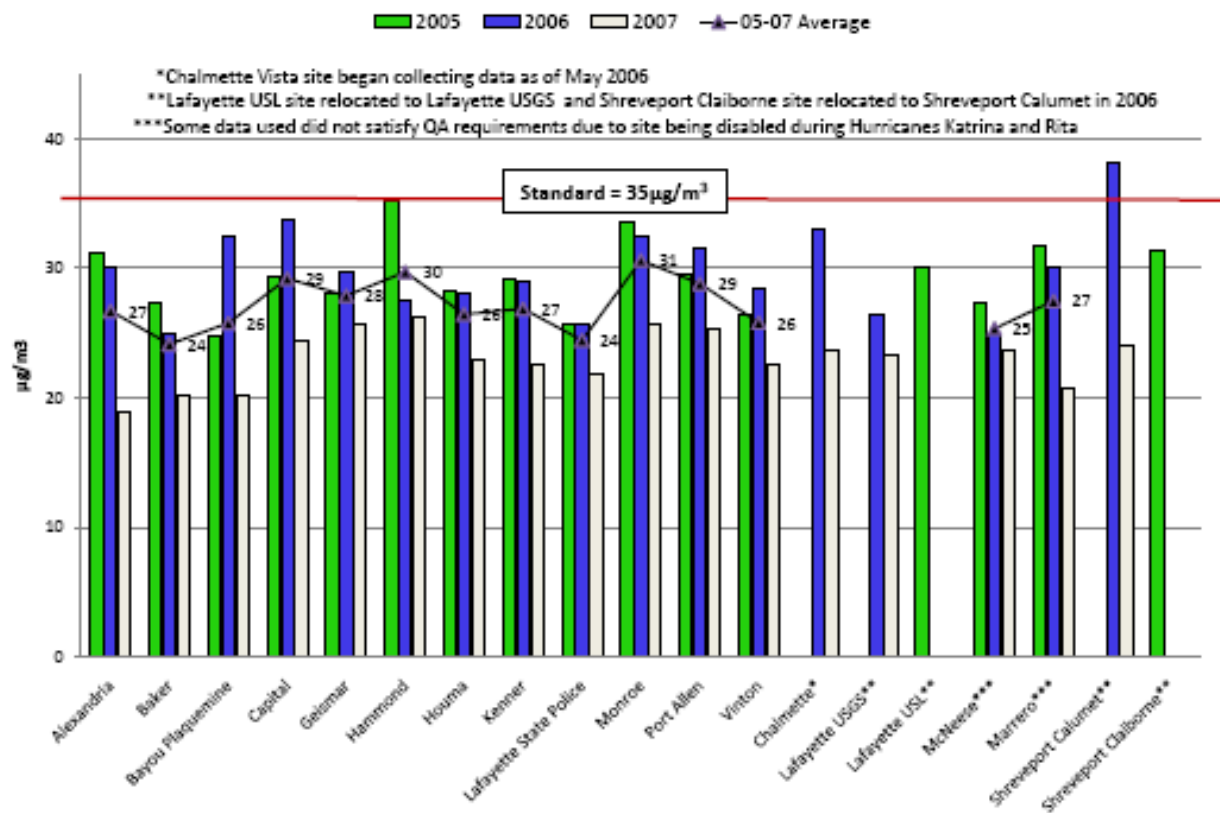**Appendix 5:**

LDEQ PM Data

LDEQ sampling sites

Courtesy of LDEQ. Extracted from the "2007 Louisiana Ambient Air Monitoring Network Annual Report". Baton Rouge, LA. 2007.

Maximum 24-hrs PM10 Concentration in the Ambient Air of Louisiana
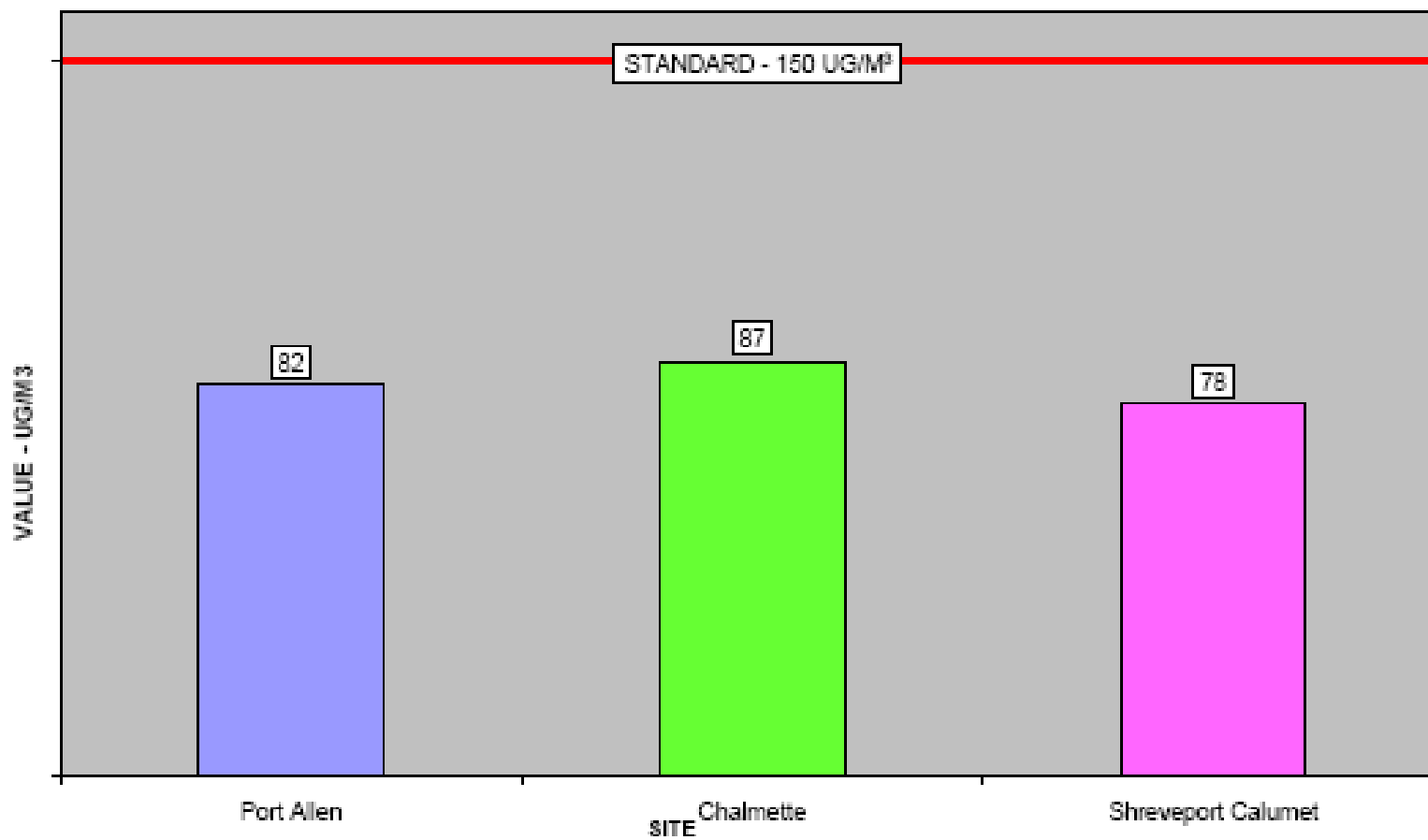
Courtesy of LDEQ. Extracted from the "2007 Louisiana Ambient Air Monitoring Network Annual Report". Baton Rouge, LA. 2007.

PM$_{2.5}$ 24-hrs Values (2005-2007)

Courtesy of LDEQ. Extracted from the "2007 Louisiana Ambient Air Monitoring Network Annual Report". Baton Rouge, LA. 2007.

Vita

Federico Portillo was born in Venezuela where he earned a Bachelor's Degree in Chemical Engineering from the UNEXPO University of Barquisimeto, Lara, in 2003. During his undergraduate studies, Portillo performed two internships in two different oil refineries of PDVSA and developed his undergraduate thesis research in a local Rum distillery. In March of 2003, Portillo began to work as a process engineer in "El Palito", an oil refinery belonging to the Venezuelan oil estate company, PDVSA.

At the end of 2003, Portillo moved to Gainesville, Florida, where he earned an Associate in Sciences degree in Microbiology from the Santa Fe College of Gainesville in 2005. Portillo began to work as a research assistant in the department of medicinal chemistry of the University of Florida in 2005 until he was admitted in the graduate school at the University of New Orleans.

In fall of 2007, Portillo started his master studies in environmental engineering, and began to conduct researches on ambient air quality under the direction of Dr Bhaskar Kura at the University of New Orleans, and finished his MS in December of 2008 with the present research on Particulate Matter in Ambient Air.