UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

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TÍTULO: Comparison of concentration levels of nitrogen dioxide and tropospheric ozone in Ecuador and other latitudes

Trabajo de integración curricular presentado como requisito para la obtención del título de Químico

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DEDICATORIA

A mi familia y amigos,

el mejor regalo que la vida me ha dado

gracias.

Manuel Alejandro Andino Enríquez

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Para empezar quiero darle las gracias a mis padres que son mi luz, mi sustento y mi todo para siempre superarme, para ser una mejor persona, para ser la mejor versión de mí. A mis tutores de tesis, el Dr. Luis Ladino, Ph.D. y la Dra. Sandra Hidalgo, Ph.D. por ayudarme a crecer y creer en el mundo científico y académico. A mis hermanos Lui, Rudy y José Esteban que siempre han sido y serán mi ejemplo a seguir. A mi sobrino Joaquín, que me dio luz y fuerza para no rendirme en los momentos más difíciles. A Nando, mi mejor amigo, gracias por los días de risas, salidas y reflexiones, gracias por ayudarme en los momentos cuando me sentí perdido y desorientado, gracias por ser mi hermano. A Michu, la amiga que siempre estuvo ahí, en las buenas y en las malas, con consejos, con abrazos, no existen palabras para agradecerte todo lo que me has ayudado a crecer.

Manuel Alejandro Andino Enríquez

RESUMEN

En décadas recientes, los problemas relacionados con la actividad antropogénica han generado preocupación debido a la acumulación de contaminantes en el aire. En Ecuador, la contaminación del aire representa un riesgo y una amenaza para la salud y el medio ambiente. Los estudios realizados en Ecuador sobre las emisiones de contaminantes se han llevado a cabo desde 2010. Sin embargo, no se han registrado hasta la fecha comparaciones sobre la concentración de gases de efecto invernadero en el contexto global, lo que conduce a la imposibilidad de hacer una evaluación real de la calidad del aire en el país. De esta manera, el objetivo principal de esta investigación es comparar mediante la recopilación de datos los niveles de concentración de dióxido de nitrógeno y ozono troposférico de Ecuador con diferentes ciudades de todo el mundo para conocer la calidad del aire del país.

El Centro Mundial de Datos para Gases de Efecto Invernadero es un programa de la Organización Meteorológica Mundial. Esta institución proporcionó los datos de concentración de los gases de estudio de las estaciones internacionales. Mientras que los datos atmosféricos (concentracion de dióxido de nitrógeno y ozono troposférico) de las estaciones ecuatorianas provienen del Gobierno Autónomo Descentralizado Municipal del Cantón Ibarra y la Secretaría de Ambiente del Municipio del Distrito Metropolitano Quito.

Como resultado de este trabajo, el valor de concentración de dióxido de nitrógeno en la ciudad de Quito fue mayor que el de las ciudades extranjeras consideradas en este estudio. El valor de concentración de ozono troposférico para las ciudades de Quito e Ibarra es más bajo que la concentración de este gas en las ciudades extranjeras elegidas para el estudio. De acuerdo a los valores guía otorgados por la Organización Mundial de la Salud y el departamento de Calidad del Aire del Ayuntamiento de Madrid, la concentración de los dos gases de estudio está por debajo de los valores ambientales permitidos que determinan que la calidad del aire de Ecuador tiene valores razonables.

Palabras clave:

Contaminación antropogénica, dióxido de nitrógeno, ozono troposférico, concentración de gases atmosféricos.

ABSTRACT

In recent decades, problems related to anthropogenic activity have generated concern due to the accumulation of pollutants in the air, which has generated changes in the concentrations of greenhouse gases and particulate matter. In Ecuador, air pollution represents a risk and a threat to health and the environment. Studies carried out in Ecuador on pollutant emissions have been carried out since 2010. However, until the present date, there are no studies about comparisons of the concentration of greenhouse gases in the global context, which leads to the impossibility of making a real assessment of air quality in the country. In this way, the main objective of this research is to compare by data collection the concentration levels of nitrogen dioxide and tropospheric ozone of Ecuador with different cities around the world in order to know the air quality of the country.

The World Data Centre for Greenhouse Gases, which is a program of the World Meteorological Organization. This institution provided data from international stations. While atmospheric data (concentration of nitrogen dioxide and tropospheric ozone) from Ecuadorian stations came from the Autonomous Decentralized Municipal Government of Ibarra and the Secretariat of the Environment of the Municipality of the Metropolitan District of Quito.

As a result of this work, the concentration value of nitrogen dioxide in the city of Quito was higher than that of the foreign cities considered in this study. The tropospheric ozone concentration value for Quito and Ibarra cities is lower than the concentration of this gas in the foreign cities chosen for the study. According to the guide values granted by The World Health Organization and the Air Quality department of the Madrid City Council, the concentration of the two study gases is below the permitted environmental values which determine that Ecuador's air quality has reasonable values.

Keywords:

Anthropogenic pollution, nitrogen dioxide, tropospheric ozone, concentration of atmospheric gases.

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1. INTRODUCTION – JUSTIFICATION

In recent decades, pollution problems due to the development of human activities have led to an increase in the concentration of greenhouse gases in the planet's atmosphere. Atmospheric pollution implies changes in the physical, chemical, and biological characteristics of atmospheric components, which can impair the health and survival of living beings.[1]

The surface of the Earth has had great natural temperature changes over the last 10,000 years, which even surpasses the current values. However, since the Industrial Revolution in 1750, there has been a continuous and uncontrolled increase in the heating of the surface of the Earth due to the rise of the concentration of greenhouse gases as a result of anthropogenic pollution.[2]

The sun is the greatest source of the radiation that Earth receives, it is transmitted by electromagnetic waves. When solar radiation comes into contact with the Earth's atmosphere, part of this radiation is absorbed by the Earth's surface and then re-emitted as infrared radiation (IR). A fraction of the solar radiation and IR is absorbed by the atmospheric components which results in an increase in the temperature of the planet. Part of the solar radiation is reflected back to space by clouds, aerosol particles, the atmosphere, and by the same terrestrial surface, which results in a cooling of the terrestrial surface.[3] In order to maintain a stable temperature and climate, the Earth must have an energetic balance between the radiation that receives from the sun and the IR that emits into space. This balance is known as effective temperature.[4] When the IR emitted by the Earth is absorbed by greenhouse gases, it is irradiated back to the terrestrial surface, resulting in the heating of the surface. This phenomenon is known as the greenhouse effect.[4] The capture of terrestrial radiation by greenhouse gases is essential to maintain a temperature of the terrestrial surface sustainable for life since. Otherwise, the Earth's temperature would be near freezing point -18 °C.[4] The problem arises due the anthropogenic pollution, as the uncontrolled emission of greenhouse gases can induce a faster heating of the surface of the Earth. Currently, efforts to reduce its speed or magnitude have given moderate results but have failed to reverse adverse environmental changes.[5]

When organic matter is burned, carbon atoms bind with oxygen present in the air, forming carbon dioxide (CO_2). Because of this, an increase in the concentration of this gas, and to such a point of going from 280 parts per million (ppm) to more than 400 in just 150 years.[6] The influence of human beings to burn natural gas, coal and oil in a massive way to give energy to our civilization made evident an anomaly in the planet's temperature, through the greenhouse gas-temperature relationship (see Appendix A).[7]

The greenhouse effect, as already mentioned, relates the concentration factors of greenhouse gases with temperature of the planet. When the evolution of the average temperature of the planet with CO_2 is studied over hundreds of thousands of years, it is appreciated that they are fairly correlated.[8] During the interglacial periods these two factors increase their value, while in the glacial periods their value is reduced (Figure 1).[8]

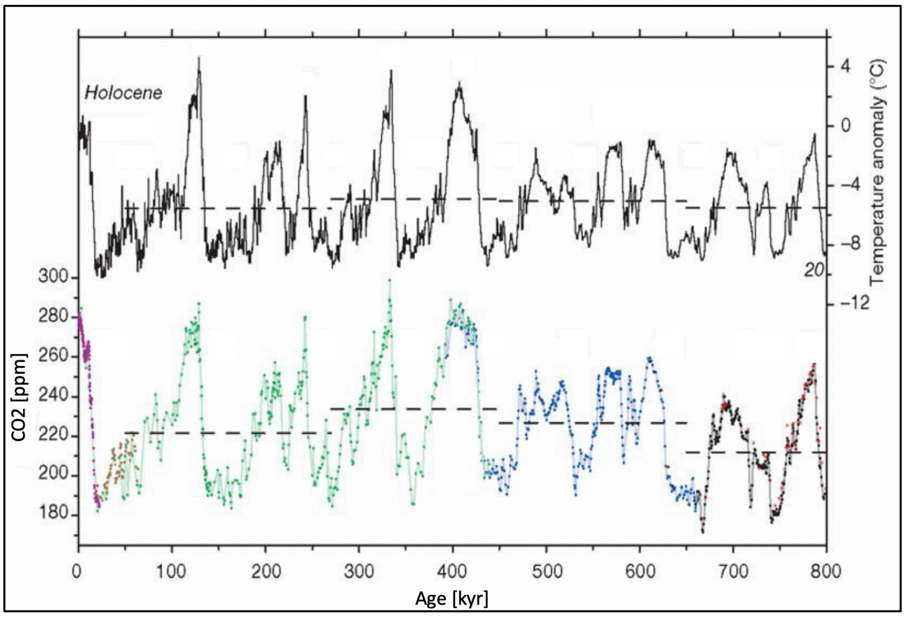


*Figure 1. Compilation of CO2 records and temperature anomaly over the past 800 thousand years. Source: Adapted from Lüthi, D.; Le Floch, M.; Bereiter, B.; Blunier, T.; Barnola, J.-M.; Siegenthaler, U.; Raynaud, D.; Jouzel, J.; Fischer, H.; Kawamura, K.; et al. High-Resolution Carbon Dioxide Concentration Record 650,000–800,000 Years before Present. Nature **2008**, 453 (7193), 379–382. https://doi.org/10.1038/nature06949.*

As already mentioned, the sun is practically the source of all the energy the planet receives, and small variations in its activity can cause changes in the Earth's climate. The star of our solar system has natural variations in the light that emits in cycles of approximately 11 years (see Appendix B).

These changes are so small that the planet does not react to these oscillations because the resistance of the water of the oceans dampens it.[9] The carbon atom has different isotopes (^{12}C, ^{13}C, ^{14}C). From indirect measures, such as the measurement of ^{14}C in the tree rings, it has been possible to determine the solar activity of the last 10 thousand years.[10] It shows oscillations every 200 years, and that is probably the explanation of certain periods of low temperatures on the planet.[10] Similarly, according to this study, the planet should now experience a cold period, but

the evidence shows that the temperature has increased (see Appendix C). This allows eliminating the factor corresponding to solar activity as a cause of the rise of temperature.[11]
Discarding the solar activity factor as responsible for increasing the temperature of the Earth, another possible explanation may come from the Milanković cycles. These cycles describe the changes in Earth's movements that can cause alterations in the climate. Within these movements are highlight the precession, the axial inclination and the orbital eccentricity.[12]

Appendix D shows the different changes that each movement that make up the Milanković cycles have had. The eccentricity determines the glaciations of the last million years, and the existing amount of ice depends on the precession and the axial inclination. But since these periods movements are too slow, they cannot explain an abnormal increase in Earth's temperature nor the increase in CO_2 concentration greater than 400 ppm.[8]

Inside of the planet, there can be an influence of volcanic activity and vegetation since they also emit CO_2. Each of the carbon isotopes has a different atomic weight, being the ^{12}C the most abundant of all, this allows plants and some bacteria to capture more CO_2 with ^{12}C than ^{13}C during photosynthesis, integrating into the tissues and after a while being expelled in the form of CO_2.[13]
Stuiver et al.[13] determined the concentration of the different carbon isotopes in the air, finding that the proportion of ^{12}C concerning to ^{13}C increases when the CO_2 concentration increased. This allowed to determine that the source favors the absorption of ^{12}C over ^{13}C, being the source of living beings, allowing to discard the influence of volcanoes and oceans.[13]

Once a living being dies, the proportion of ^{14}C decrease at a fixed rate. Through the measurement technique of this isotope, applied in the air itself, it was found that the amount of CO_2 with ^{14}C must come from living beings that have been buried thousands of years. This produce the reduction of ^{14}C and that have been returned to the surface to satisfy the needs of society.[14] This indicates that the increase in CO_2 concentration results from an extraction process of organic matter with ^{14}C that subsequently produced an increase in the planet's temperature. The humankind beings being the most likely source of warming the Earth's surface, the importance of the study of greenhouse gases is fundamental to understanding the evolution and importance that these may have in changing the temperature of the planet.

According to the United States Environmental Protection Agency (EPA), the changes in climate due to emissions of contaminants into the air impacts on local air quality because of the atmospheric warming associated with climate change increase the ground-level ozone in many regions. To overcome this problematic, investigations are focus to understand the role that plays the air quality on health and disease and support the development of more sustainable and integrated air quality management strategies.[15] The results from these investigations contribute to support the air quality standards and make improvements in public health.[16]

The most common greenhouse gases are CO_2, tropospheric ozone (tropospheric O_3), water vapor, and methane (CH_4). Due to human activities, their concentrations have been increased.[17] The most tangible example is for CO_2 (Figure 2).

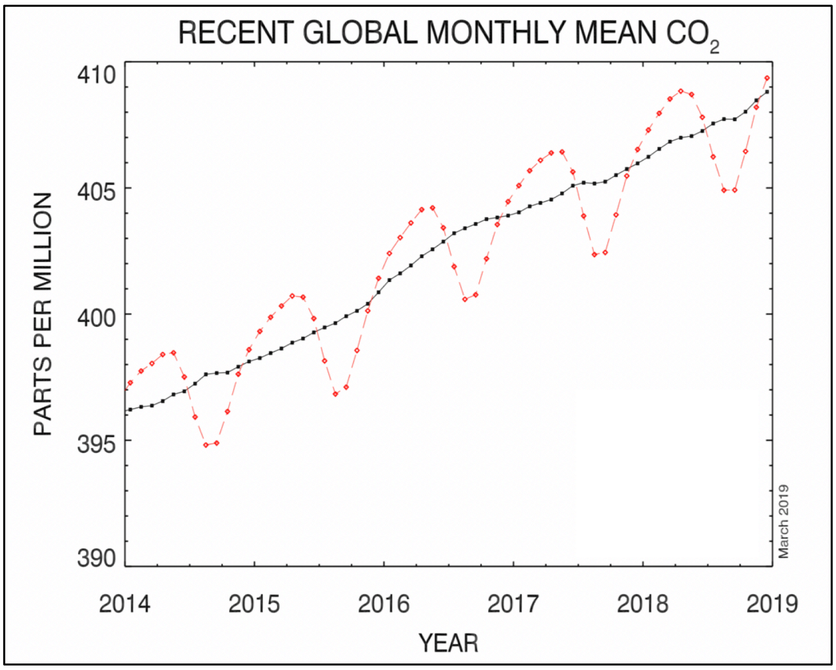


Figure 2. Increase in the concentration of CO_2 in the atmosphere over time.
Source: Adapted from Kubiske, M. E.; Woodall, C. W.; Kern, C. C. Increasing Atmospheric CO_2 Concentration Stand Development in Trembling Aspen Forests: Are Outdated Density Management Guidelines in Need of Revision for All Species? J. For. ***2019****, 117 (1), 38–45. https://doi.org/10.1093/jofore/fvy058.*

1.1. Nitrogen dioxide

Nitrogen dioxide (NO_2) is a poisonous, non-flammable, reddish-colored gas. NO_2 is not a greenhouse gas, but in the atmosphere, it contributes to the photochemical formation of tropospheric O_3. Also, it threatens the health of the inhabitants because it poisons them.[18] Nitrogen oxides (NOx), are created from rays, soil microbial activity, biomass burning, both natural and anthropogenic fires, as well as the combustion of petroleum derivatives. [19]

The NO_2 is generated mainly in the air burning fuel from emissions of cars, trucks, buses, power plants, among others. Along with other NO_X, NO_2 reacts with other chemicals in the air to form both tropospheric O_3 and particulate matter (PM).[20]

Due to the human contamination mentioned above, there has been an increase in the concentrations of NO_2, mainly in the urban and industrial sectors. [21] The daily cycle of NO_2 begins in the first hours of the day, where the maximum concentration is observed between 8 - 9 am in the morning. Then, as this gas is a precursor of tropospheric O_3, it reacts chemically in the presence of solar radiation emitted between $290 \text{ nm} < \lambda < 400 \text{ nm}$ with other gases, reducing its concentration in the atmosphere. As the intensity of solar radiation decreases, the concentration of tropospheric O_3 will decrease, and the concentration of NO_2 will increase again at 8 - 9 pm, but this concentration peak is not as high as the maximum in the early hours of the morning.[22]

NO_2 produces a great risk in the environment, as it is easily oxidized in the vapor of water of the clouds forming nitric acid (HNO_3), one of the main constituents of acid rain.[21] As the raindrops with these acids precipitate, they react with organic and inorganic substances and modify them. This produce destruction or damage to the soil, water, plants, animals and buildings.[23] The precipitation of acid rain manages to subtract essential nutrients from the soil and release aluminum, which makes difficult the absorption of water from trees. Also, they damage the needles of the conifers and the leaves on trees.[24] The detrimental effects of NO_2 on human health are focused on the respiratory system. According to the Department of Health of the Region of Murcia in Spain, it has been found that NO_2 causes damage to the pulmonary parenchyma. In addition, it determines the inhibition of mucociliary purification, phagocytosis and immune response in the lungs, resulting in a decrease in lung resistance to infections.[25]

The World Health Organization (WHO) established the guideline value of 20 parts per billion (ppb) as the annual average of NO_2 to protect the population from the negative effects of this gas in health. Guiding value is a numerical value related to the concentration of particles present in the air indicating that if this is exceeded, there is the possibility of having adverse effects in health. The rationale for this is that most concentration reduction methods are specific to NO_X and are not designed to control other contaminants that accompany them by increasing their emissions.[26]

1.2. Tropospheric ozone

Ozone (O_3) is a colorless gas founded in two layers of the atmosphere: in the stratosphere and the troposphere. O_3 in the stratosphere acts as a protective layer against the negative effects in health and the environment because it is capable of absorbing the ultraviolet radiation from the sun, thus avoiding reaching the Earth's surface.[27] Of the total O_3 concentration present in the atmosphere, less than 10% is found in the troposphere. However, tropospheric O_3 is a greenhouse gas and plays an important role in the environment due to its participation in different chemical processes.

Between the geographic space comprised of the Tropic of Cancer (20 °N) and the Arctic Circle (60 °N). Tropospheric O_3 was the largest contributor to global warming during the twentieth century.[2]

Tropospheric O_3 is a secondary pollutant, which means that it is not emitted directly to the atmosphere, but is the result of chemical reactions, in proper conditions of solar radiation accompanied by other primary pollutants such as volatile organic compounds (VOCs), carbon monoxide (CO), NO_X, and to a lesser extent CH_4. One of the training mechanisms is the interaction between NO_2 and solar radiation between $290 \text{ nm} < \lambda < 400 \text{ nm}$. This interaction produces atomic oxygen (O), which acts as an intermediate in the reaction (I). This chemical species reacts with O_2 and produces tropospheric O_3 (II).[28] Similarly, in its destruction, the tropospheric O_3 reacts with nitrogen monoxide (NO), forming O_2 and NO_2, lowering the concentration of O_3 in the atmosphere (III) (Figure 3).[29]

$$NO_2 + h\nu\ (290 \text{ nm} < \lambda < 400 \text{ nm}) \rightarrow O + NO \qquad \text{(I)}$$

$$O + O_2 \rightarrow O_3 \qquad \text{(II)}$$

$$NO + O_3 \rightarrow O_2 + NO_2 \qquad \text{(III)}$$

Figure 3. Chemical equations for the Chapman cycle.

The daily cycle of this pollutant begins at 6 - 7 am. It is when the anthropogenic activities start emitting mainly NO_X, CH_4, and CO_2. Then, while the planet receives solar radiation, the concentration of O_3 increases according to the presence of the compounds that form it. In the afternoon, solar radiation is not so intense, causing the concentration of tropospheric O_3 to decrease until it returns to its base concentration at 8 pm.[22]

Tropospheric O_3 is mainly originated in urban areas by emission of automobiles and industries. Elevated concentrations of tropospheric O_3 cause this gas to react strongly destroying or altering other molecules. This pollutant cause many problems for human health as respiratory damage and pulmonary, chest pains.[22]

Exposure to tropospheric O_3 has been linked to premature mortality and a range of issues of morbidity and asthma symptoms.[30] WHO established the guide value of tropospheric O_3 concentration at 100 $\mu g/m^3$ for a daily average of 8 hours. The Air Quality department of the Madrid city Council established the guideline value of 60 ppb as an annual average of tropospheric O_3 to protect human health.[31]

1.3. Data collection

The World Data Centre for Greenhouse Gases (WDCGG), which is a program of the World Meteorological Organization (WMO), owns a data center that archives and provides observations of the chemical composition of the atmosphere and its natural change. [32] The WDCGG has more than 400 monitoring stations around the world.[32]

Ibarra is the capital of the province of Imbabura. It is located in northern Ecuador, specifically 115 km northwest of Quito, 125 km south of the city of Tulcán, and with an altitude of 2,225 meters above mean sea level (MAMSL). According to the national population census carried out in 2010, Ibarra has an approximate population of 181,175 inhabitants. This city has a variety of climates with an annual average temperature of 18 ºC, ranging between the cold of the Andean elevations, passing through the warm humid of the area of Lita and Carolina, to the dry tropical of the Chota valley.[33] The city of Ibarra is located within two hydrographic sub-basins: Chorlaví river and Tahuando river. The topography of its soil corresponds to slopes that oscillate between 5% and 15% in the foothills of the Cerro Imbabura.[33] The industrial activity of the city of Ibarra is formed by the manufacturing, construction, mining, and energy industries. The latter focuses on the production of electricity, gas and water.[34] In relation to the vehicular activity, each year there is an increase of 8% to 11% in the number of vehicles.[35]

Quito is the political capital of the Republic of Ecuador, currently with 2,644,145 inhabitants, at a height of 2,850 MAMSL. The city is located mainly on the valley of Quito, forming part of the Hoya of Guayllabamba. Its climate corresponds to the subtropical climate of highlands, ranging from arid and temperate to humid and cold climates. Quito is divided into three zones: south, center, and north. The south is the coldest part in the city as it is the highest, the center is hot showing the highest temperatures, and the north is temperate. Quito is the house of largest number of industries in the country, becoming one of the primary sources of development in the country. This has caused severe environmental impacts in the city and consequently problems in the health of its inhabitants.[36] In 2014, the automotive park of Quito was 468,777 vehicles. The number of people sharing the car decreased from 1.7 people in 2013 to 1.2 people in 2014, representing an increase in vehicular congestion in the city.[37] At this time, there are 10,450 companies installed in the Ecuadorian capital, of which 372 are industries and are located in urban areas. Due to this problem, parks and industrial regions are being reorganized in a specific sector by creating three industrial parks. Industries in Quito are related to structural products, heavy machinery for the electrical sector, the agricultural, construction, textile, metalworking industries.[38]

2. PROBLEM STATEMENT

The analysis and understanding of the air quality of Ecuador allow the development of better knowledge about climate change and the negative consequences on people's health, flora and fauna of the country. All of this, to make responsible and justified decisions for the good of all those who are part of the diversity of the country.

In recent decades, problems related to anthropogenic activity have generated concern due to the accumulation of pollutants in the air, resulting in changes in the concentration of greenhouse gases. In Ecuador, air pollution is based on the study of risks and threats to health and the environment. To carry out an analysis on this topic is necessary to carry out a dynamic process, followed by a permanent effort to improve the quality of pollutant gas data. Studies in Ecuador about emission of pollutants are made since 2010. However, no comparisons on this topic in the global context, which leads that cannot know the real situation of air quality in the country.

3. GENERAL AND SPECIFIC OBJECTIVES

3.1. General objective

To know the quality of the air of Ecuador through a data comparison of NO_2 and tropospheric O_3 concentrations from Ecuadorian and international stations.

3.2. Specific objectives

- To know if the air currents influence NO_2 concentration in a city or region.
- To determine if NO_2 concentration is directly proportional to the increase in the population of a city or region.
- To analyze if as long as the population of a city or region increases, the concentration of tropospheric O_3 will increase.
- To identify if the tropospheric O_3 concentration will be higher in a city or region if it receives higher solar radiation.

4. METHODOLOGY

To develop the bar chart graphics was used OriginPro program. OriginPro is a data analysis and graphing software oriented to academia, commercial industries, and government laboratories worldwide.[39] Among its tools, it integrates data analysis, programming, and scientific plotting.[40]

The Excel program was used to develop the statistical calculation and the different trend line graphs. Excel has capable computing tools developed to solve from routine data analysis to sophisticated optimization problems. It has calculation tools, graphics, spreadsheet interface that combined with its integrated programming language called Visual Basic for Applications, makes it a versatile computing tool.[41]

The WDCGG under the GAW is a program of the WMO provided the data of the concentrations of NO_2 and tropospheric O_3 of the different stations that it possesses. Also, the Autonomous Decentralized Municipal Government of Ibarra and the Secretariat of the Environment of the Municipality of the Metropolitan District of Quito provided the data of their respective cities. The selection of the stations of the WDCGG was carried out to be able to elaborate a direct comparison of the concentration of NO_2 and tropospheric O_3 of the Ecuadorian stations with different cities from around the world covering different latitudes and lengths.

The red marks in Figure 4 represent all NO_2 stations available from the WDCGG. From these, the stations chosen for the study of this gas are marked in blue and the Ecuadorian station is marked in black. Among these selected cities for the analysis for NO_2 are countries such as Latvia, Switzerland, Poland, Hungary, Czech Republic, Slovenia, Malta and Ecuador (Figure 4).

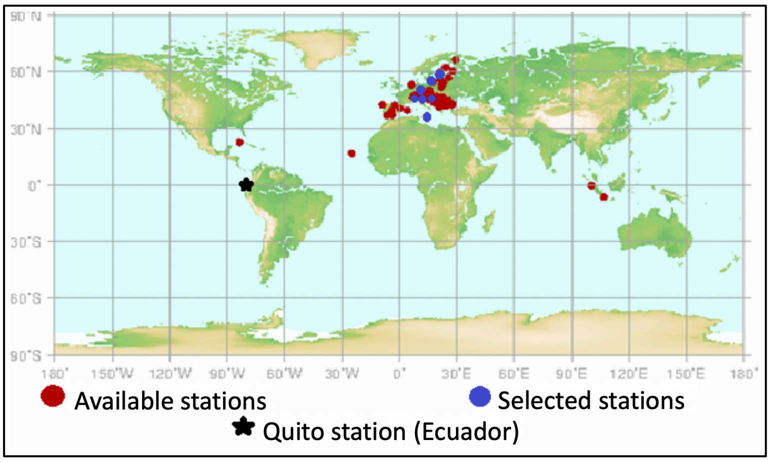


Figure 4. Selected NO_2 stations.
Source: Adapted from World Meteorological Organization. WMO WDCGG DATA SUMMARY, 39th ed.; Japan Meteorological Agency: Tokyo, 2015.

Unlike for NO_2, for the analysis of tropospheric O_3, there was an additional city in Ecuador, Ibarra city. The blue marks in Figure 5 represent the stations that were selected, and the black mark is the Ecuadorian stations. Between the selected stations, there are places as Antarctica, Alaska, United States of America, Japan, Egypt, Argentina, Barbados, New Zealand, and Ecuador.

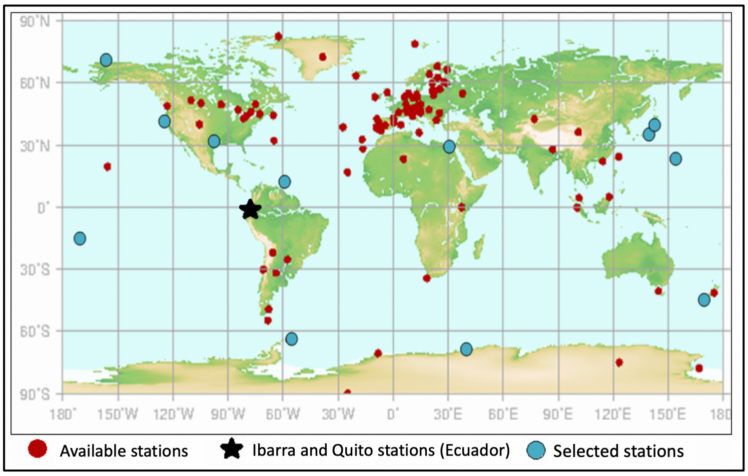


Figure 5. Selected tropospheric O_3 stations.
Source: Adapted from World Meteorological Organization. WMO WDCGG DATA SUMMARY, 39th ed.; Japan Meteorological Agency: Tokyo, 2015.

A selection of the study time was made by a review of the data provided by the different institutions, verifying that in the selected time there are data from Ecuador, the cities of study and have the longest possible duration. The study time for the analysis of NO_2 was from January to December 2013, while for tropospheric O_3, was between April 2013 and September 2014. Once the cities of study and the data of concentrations of gases of interest were obtained, information about their population was collected to have a more general vision of the capacity of emission of atmospheric pollutants.

Figure 6 shows the location of the stations in the city of Ibarra, on the outskirts and in the center of the city. The shortest distance between stations is about 2 km, while the farthest is approximately 4 km. Unfortunately, the data provided by the Autonomous Decentralized Municipal Government of Ibarra do not detail the equipment used for the data taking of tropospheric O_3. Table 1 shows the geographical coordinates of the different stations in the city of Ibarra that were used in this study.

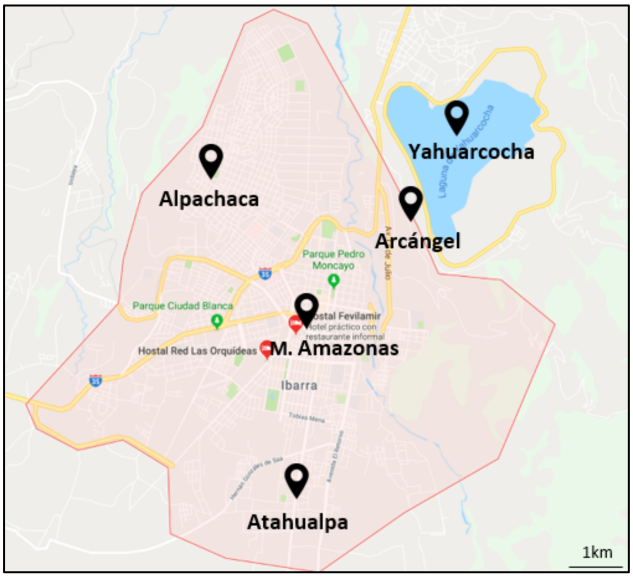


Figure 6. Map of the tropospheric O_3 stations in Ibarra.

Table 1. Geographical coordinates for the different stations in Ibarra city.

Stations	Latitude	Longitude
ALPACHACA	0°21'55.4"N	78°7'56.71"W
ARCANGEL	0°21'5.828"N	78°6'12.934"W
ATAHUALPA	0°19'25.655"N	78°7'22.202"W
MERCADO AMAZONAS	0°20'48.131"N	78°7'18.566"W
YAHUARCOCHA	0°22'20.078"N	78°6'2.03"W

For the treatment of the data, a statistical method called Q-test was used. The Q-test was initially introduced in 1950, it is a statistical method used for the recognition and exclusion of data points that differ notably from other observations.[42] When a value in a series of 3 to 10 measurements seems to deviate from the average ($\bar{x}$) by more than seems reasonable, the Q-value can be calculated as is showed in Equation 1:

$$Q = \frac{(x_i) - (x_{closest})}{x_{highest} - x_{lowest}}$$

Equation 1. Determination of the Q value.

Where x_i is the suspect value, $x_{closest}$ is the closest value to x_i, $x_{highest}$ and x_{lowest} the largest and lowest of the measured values, respectively. After obtaining the Q-value, a comparison should be made, if the measurements are greater than 10, it is suggested that the observation be rejected if its deviation from the average is greater than $2.6 * \sigma$, where σ is its standard deviation.[43]

The vertical velocity method was used to obtain the backward trajectories, which is part of the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, and serves to know the wind speed in a vertical direction. HYSPLIT model is a system that allows calculating simple trajectories of air packages, as well as complex simulations of transport, dispersion, chemical transformation, and deposition. This is done through atmospheric and chemical dispersion models of the air, in addition to studying the atmospheric boundary layer providing high-quality measurements.[44] This model is one of the most used in the community of atmospheric sciences and is developed by the Air Resources Laboratory (ARL), which is an air quality and climate laboratory that collects, develops, and improves atmospheric measurements.[45]

5. RESULTS, INTERPRETATION AND DISCUSSION

5.1. Comparison of levels of concentration of nitrogen dioxide

In most of the selected European cities, the average annual concentration levels of NO_2 are generally below 3 ppb while the highest level exceeds 5 ppb, which corresponds to the town of Kosetice in the Czech Republic (Table 2). The city of Quito shows the highest level of NO_2 concentration of all the cities selected for the study of this gas, 7.935 ppb. As was indicated, population density is directly proportional to the level of NO_2 concentration. Because of this, one of the main reasons for the concentration level of this gas in Quito is the population that it possesses and the pollution it produces, mainly vehicular and industrial.

In general, the cities of study have a directly proportional relationship between the concentration between NO_2 and its population. However, the city of Kecskemét in Hungary has the second-highest population among the study cities (110,000 inhabitants) with a NO_2 concentration value of 1.405 ppb, which is low, comparing it to the town of Rucava in Latvia with 2,013 inhabitants that has a similar concentration value, 1.452 ppb (see Appendix E and Appendix F). In the same way, the town of Kosetice in the Czech Republic has a NO_2 concentration value of 5.142 ppb, which is high despite having a population of just 695 inhabitants (Table 2).

The K-Puszta meteorological station is located in the city of Kecskemét in Hungary. According to this station, during the last five years (2015-2020), the air quality index of tropospheric O_3 was much higher than that of NO_2.[46] This is complemented by the study conducted by Lagzi et al.[47] where at the K-Puszta station, there are a high concentration of tropospheric O_3. Due to NO_2 is a gas precursor of tropospheric O_3, this explains the low concentration value in this city.

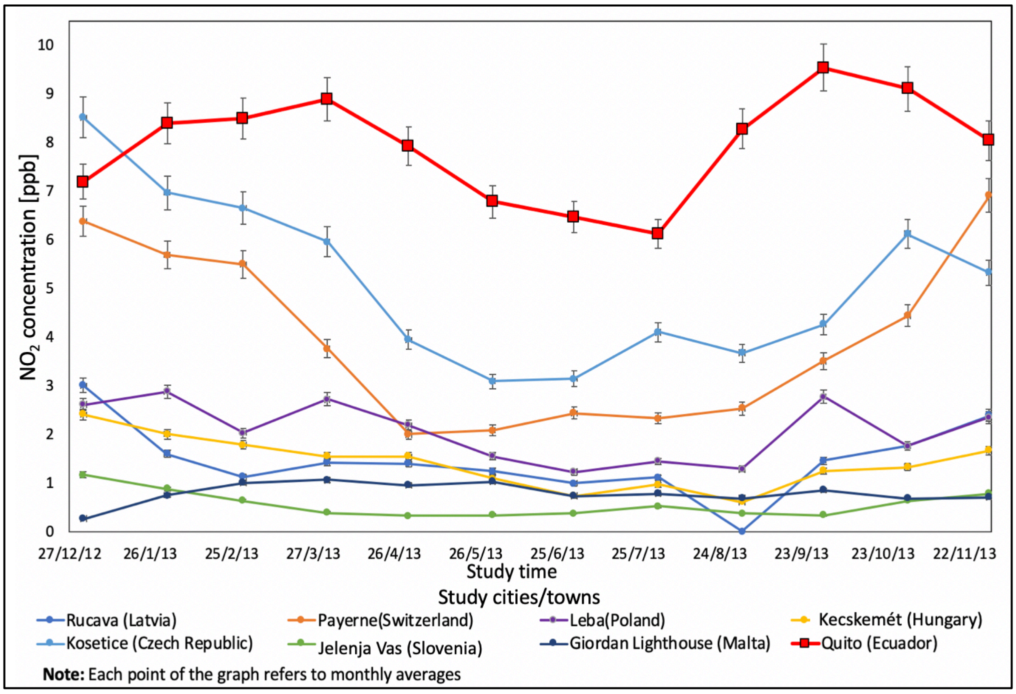
The high concentration of NO_2 in the town of Kosetice in the Czech Republic cannot be related to its population because it is low, so it must come from an external anthropogenic source. The concentration of contaminants is inversely proportional to wind velocity.[48] The direction of the wind influences the dispersion of pollutants in the atmosphere. If the wind direction is constant, the same area will be continuously exposed to relatively high levels of contamination. But if the wind direction varies, the concentrations will be relatively minor due to contaminants being scattered over a larger area.[48] According to Zvyagintsev et al.[49], the high concentrations of NO_2 in the town of Kosetice are explained by the southern transport of air currents, which is repeated throughout the year. These concentrations come from regions with significant emissions of air pollutants and are transported to this town.[49]

The high value of the standard deviation and the margin of error of the city of Payerne (Table 2) is due to the fact that the concentration of NO_2 in this city has an oscillation during the year, which is repeated over time.[50] This causes that when performing the annual average, the error values are noticeable. On the other hand, Kecskemét in Hungary has one of the lowest values of standard deviation and margin of error due the concentrations values of NO_2 were closest to each one over the study time.

Table 2. Population and NO_2 concentration in the different study cities and towns with standard deviation and margin error at 99% confidence values.

City/Town	Population	Average concentration of NO_2 (ppb)	Standard deviation	Margin error at 99% confidence
Rucava (Latvia)	2,013	1.452	0.737	0.549
Payerne (Switzerland)	9,389	3.958	1.779	1.325
Leba (Poland)	3,824	2.061	0.606	0.451
Kecskemét (Hungary)	110,000	1.405	0.528	0.391
Kosetice (Czech Republic)	695	5.142	1.715	1.277
Jelenja Vas (Slovenia)	187	0.556	0.265	0.198
Giordan Lighthouse (Malta)	535	0.786	0.786	0.161
Quito (Ecuador)	2,644,145	7.935	1.080	0.804

During the time of study, the levels of NO_2 for the city of Quito were higher during the majority of months compared to the other cities of study (Figure 7). This shows that the population of that city produces an excessive emission of this gas, which is very alarming. Figure 7 shows the trend line of each study city, presenting the monthly values of NO_2 concentration. If the trend line over the time of study is high, then the city of study produces a considerable emission of NO_2 regardless of the number of its inhabitants. The trend line of Quito city shows lower values mid-year and the highest values at the end and beginning of the year. Because from the autumn equinox, 22/23th September, to the spring equinox, 20/21th March, there is a higher incidence of solar radiation.[51] Lower concentration of NO_2 would be expected as this is a precursor to tropospheric O_3, which is not seen in Figure 7. The precipitation in Quito city usually has a bimodal regimen, where the first rainy period is between March to May, and the second from November to December, in addition to that from July to September there is usually low rainfall.[51] These periods of precipitation explain the reduction of the concentration of NO_2 in this city.



Note: Each point of the graph refers to monthly averages

Figure 7. Comparison of concentration of NO$_2$ in Ecuador with other study cities and towns, year 2013. Note: Each point of the graph refers to monthly averages.

According to WHO, the permissible levels of NO$_2$ concentration correspond to 21.27 ppb, so the concentration of NO$_2$ in the city of Quito is below the limit value. However, according to the data obtained, the concentration of this gas in the city of Quito is the highest of all, so it is recommended to reduce the burning of biomass, prevent the natural and anthropogenic fires, as well the contamination due to pollution from the circulation of vehicles in the city.

5.2. Comparison of levels of concentration of tropospheric ozone

Table 3 shows that the population of Cairo far exceeds the other cities and also that its tropospheric O$_3$ concentration is much lower than expected, considering its high population and its geographical position that is prone to high solar radiation (see Appendix G and Appendix H). As mentioned earlier, atmospheric gas concentrations can be influenced by wind currents. According to Ramadan et al.[52], there was a predominant southward wind flow pattern, providing additional support to say that the emissions in the Cairo area are responsible for the high concentration of tropospheric O$_3$ observed at Helwan city, explaining the low concentration value in Cairo city.

The high standard deviation and margin of error values in Cairo city are justified due the tropospheric O$_3$ concentration is higher during the summer, mid-year months, and lower during the end of the year (Table 3).[52] On the other hand, due to the low dispersion of data of tropospheric

O_3 in the Quito city, its error values are the lowest among the different places taken account for the analysis of this pollutant.

Minami-Tori-shima in Japan has the highest error values among the selected station for tropospheric O_3 (Table 3). These values are associated with a periodical fluctuation of tropospheric O_3 over the years, with high concentration values characteristic of the beginning of the year and low values at mid-year.[53]

Table 3. Population and tropospheric O_3 concentration in the different study cities and towns with standard deviation and margin error at 99% confidence values.

City/Town	Population	Average concentration of tropospheric O_3 (ppb)	Standard deviation	Margin error at 99% confidence
Ibarra (Ecuador)	181,175	8.501	5.404	3.381
Quito (Ecuador)	2,644,145	11.720	2.768	1.732
Syowa Station (Antarctica)	0	25.340	7.521	6.136
Moody (USA)	1,384	31.850	3.598	2.936
Tsukuba (Japan)	226,963	30.476	8.466	5.299
Barrow (Alaska)	4,354	28.480	5.862	4.783
Trinidad Head (USA)	367	23.570	3.985	3.251
El Cairo (Egypt)	8,334,914	17.371	9.696	7.543
Minami-Tori-shima (Japan)	0	27.171	13.545	9.340
Ushuaia (Argentina)	67,600	20.542	4.928	3.671
Ragged Point (Barbados)	284,644	23.418	5.004	3.893
Lauder (New Zealand)	219,200	17.710	3.869	3.156
Tutulia (USA)	55,876	14.360	4.154	3.389

Figure 8 shows the monthly measurements of this greenhouse gas from the stations selected during the study time. However, some stations do not have data from February because they suspended their activities during that time. The tendencies of concentration of tropospheric O_3 of the Ecuadorian cities show the lowest values of the different cities analyzed. This is surprising due Ecuador for its geographical location, receives perpendicular solar radiation to the surface of the equatorial zone [51]. However, solar radiation is not the only necessary component for the formation of tropospheric O_3. Due to the lack of atmospheric data of tropospheric O_3 precursors in the Ecuadorian cities, it can be assumed that the concentration of gas precursors as volatile organic compounds (VOCs), NO_X, and secondary organic aerosols, is very low or that it is much lower than in the other cities of study. Concerning the different stations studied, there is no clear annual trend of tropospheric O_3. In the case of Ecuador, an average-constant concentration of 10 ppb is observed.

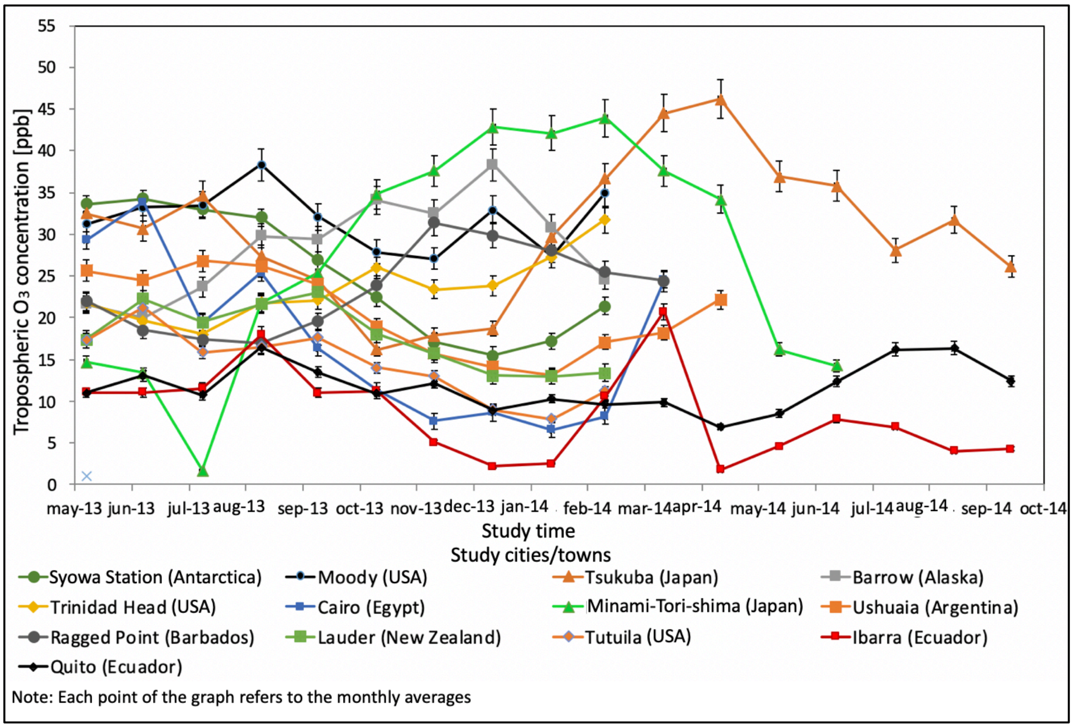


Figure 8. Comparison of concentration of tropospheric O_3 in Ecuador with other study cities and towns, years 2013-2014.
Note: Each point of the graph refers to the monthly averages.

5.2.1. Trends of tropospheric ozone concentration in Ibarra

Figure 9 represents the concentration of tropospheric O_3 in the Ibarra city, where each line represents a station in the town. The tendency of all concentration lines of tropospheric O_3 is closely related. However, some differences can be noted, which may be due to an increase in anthropogenic activity in the sector where the station is located.

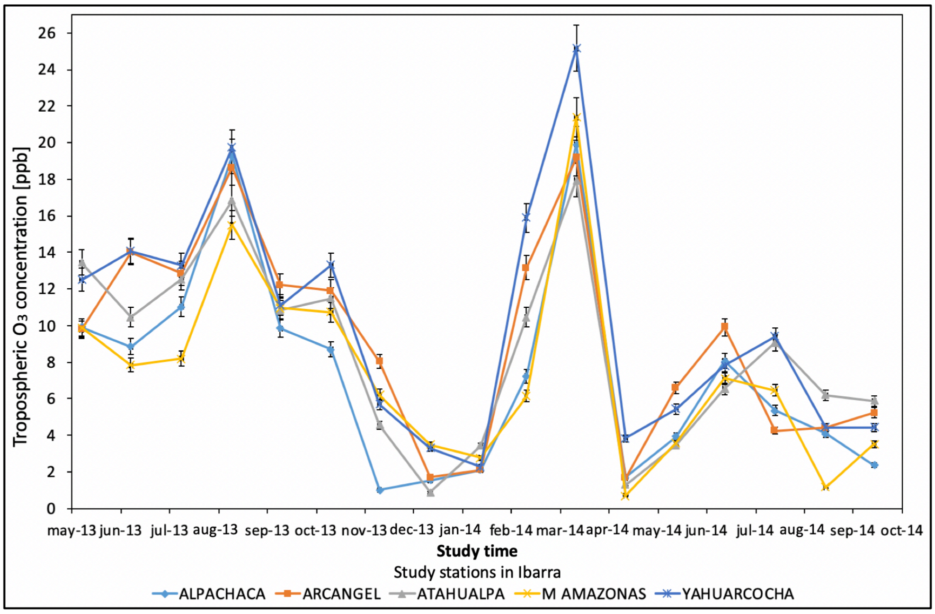


Figure 9. Measurements of tropospheric O_3 concentration in Ibarra city
Note: Each point of the graph refers to the monthly averages.
Source: Gestión ambiental del GAD de Ibarra. Calidad de Aire Ibarra 2013-2014; 2014.

In March 2014, there is an increase in the tropospheric O_3 concentration that generates uncertainty because it seems not to follow the trend line (Figure 9). For that reason, the *Q-test* method was performed to determine the validity of this data. The number of months in Appendix I corresponds to the number of observations (n) that the experiment has, for this reason $n = 17$. Equation 1 was not used, due $N > 0$, but the average $(\bar{x})$ and the standard deviation values of the data were used.

The arithmetic average is developed by adding all the values of the data set, and then they are divided by the total number of values. The following formula will be used to perform the $\bar{x}$ calculation of the data:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Equation 2. Arithmetic average.

Applying Equation 2 to the data of Appendix I, $\bar{x}$ value corresponds to:

$$\bar{x} = 8.5$$

To calculate the standard deviation in a sample, the average of the dataset is first calculated. Then for each number in the dataset, the average is subtracted, and the result is squared. All these values are summed and then divided by the total number of the data minus one. Finally, the square root of the value is taken. The formula to use for the standard deviation in a sample is:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

Equation 3. Standard deviation in a sample.

Occupying the data of Appendix I, is obtained:

$$\sigma = 5.4$$

Multiplying $\sigma * 2.6$

$$\sigma * 2.6 = 5.4 * 2.6 = 14.04$$

Since $\bar{x} = 8.5$ does not exceed the σ value multiplied by 2.6 (14.04). Using this method, the wrong measurement factor of the data for March 2014 is excluded (Figure 9). Once the *Q-test* has been carried out and verifying that the tropospheric O_3 concentration value is correct, a way of explaining this behavior, is through the use of backward trajectories.

The backward trajectories using HYSPLIT model were made considering three different heights 50, 250 and 500 meters above ground level. The time used to run the backward trajectories was 72 hours and for the new trajectory to begin was 12 hours. Thus, making six graphs showing the wind trajectories, each representing a week in order to know and appreciate the evolution of this air pollutant.

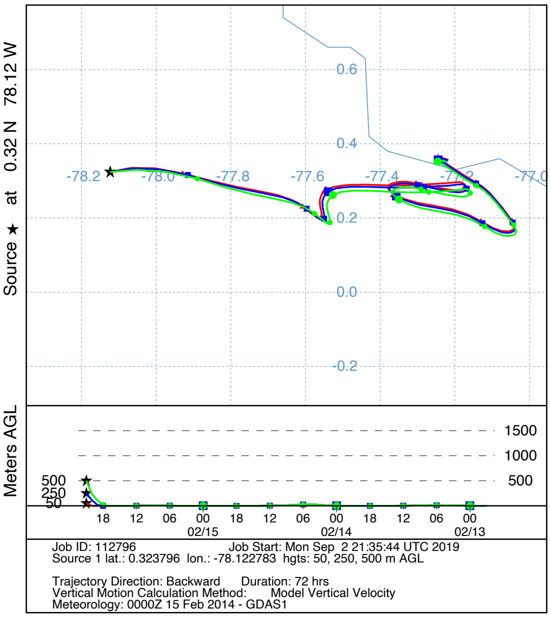


Figure 10. HYSPLIT backward trajectories performed for Ibarra. February 15, 2014.

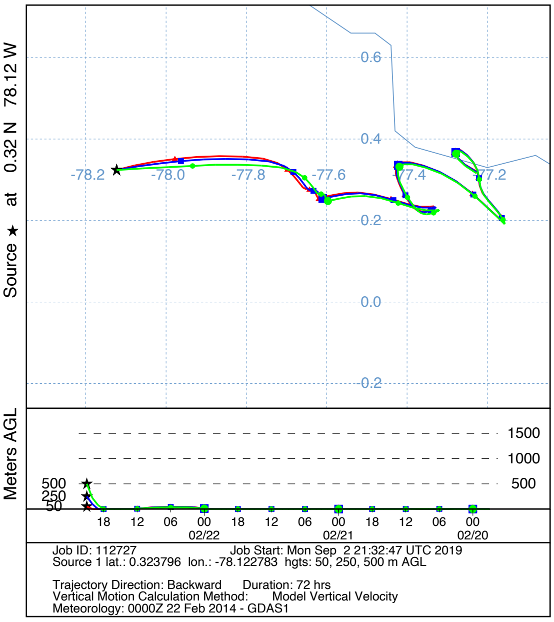


Figure 11. HYSPLIT backward trajectories performed for Ibarra. February 22, 2014.

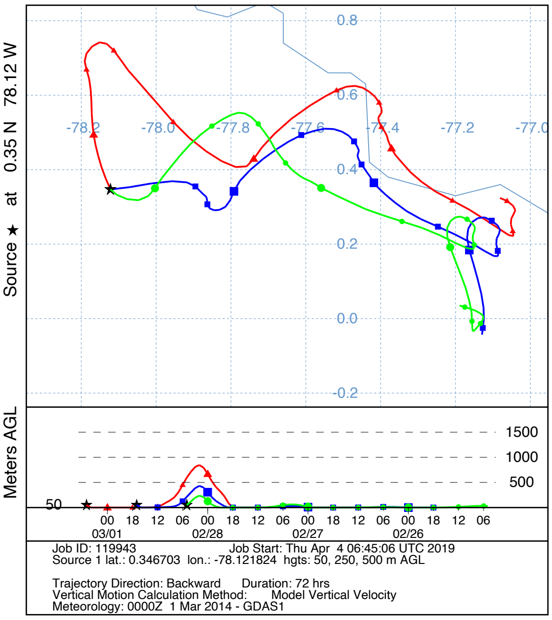


Figure 12. HYSPLIT backward trajectories performed for Ibarra. March 1, 2014.

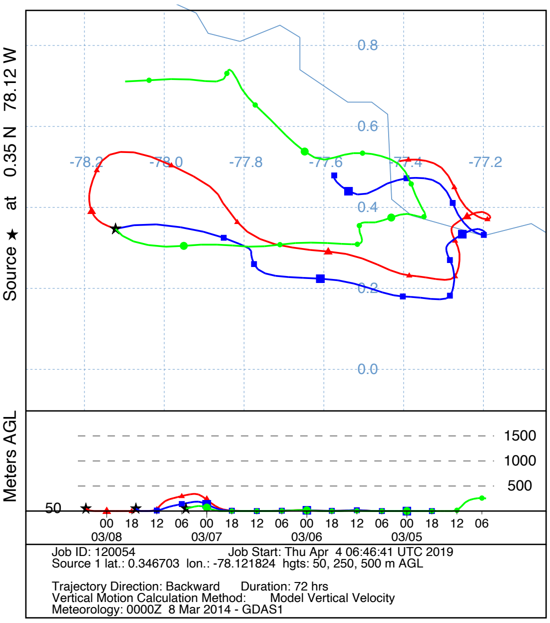


Figure 13. HYSPLIT backward trajectories performed for Ibarra. March 8, 2014.

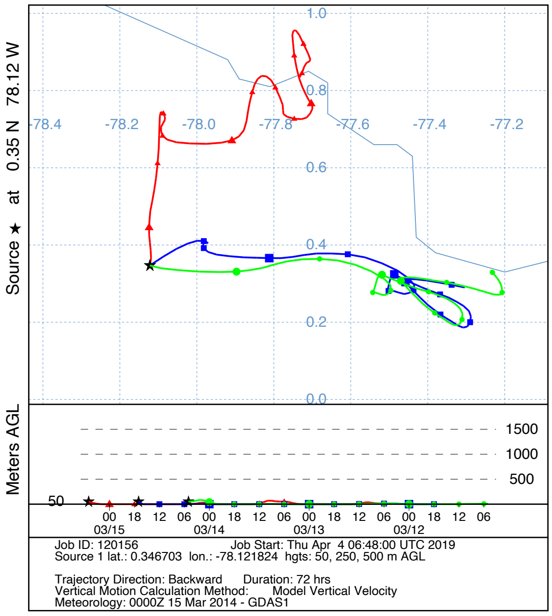


Figure 14. HYSPLIT backward trajectories performed for Ibarra. March 15, 2014.

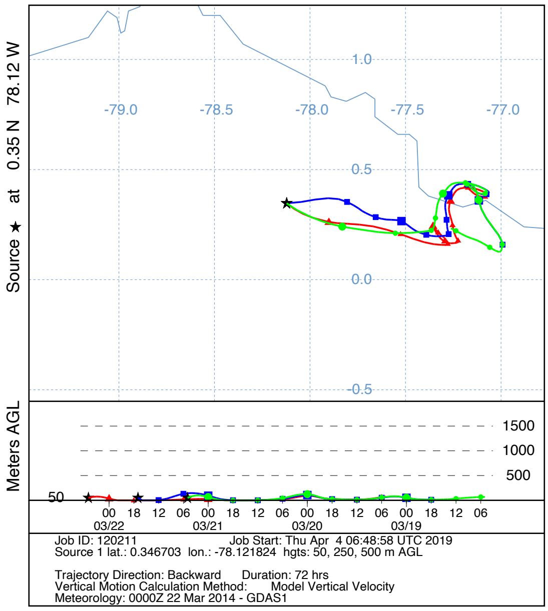


Figure 15. HYSPLIT backward trajectories performed for Ibarra. March 22, 2014.

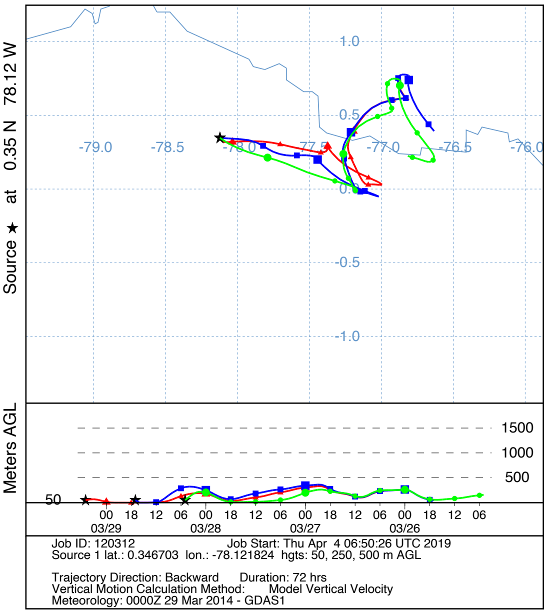


Figure 16. HYSPLIT backward trajectories performed for Ibarra. March 29, 2014.

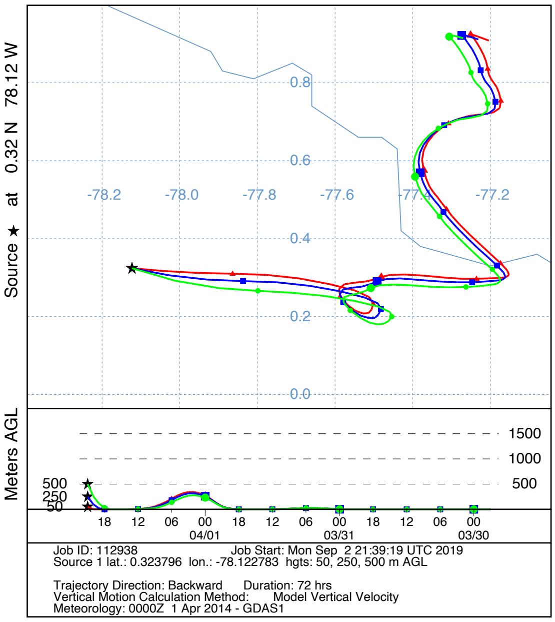


Figure 17. HYSPLIT backward trajectories performed for Ibarra. April 1, 2014.

By obtaining backward trajectories, Figure 10 to Figure 17, is observed that there is an external pollution source, which geographically comes from not very populated villages in southern Colombia (Orito, Victoriano) and in the northeastern of Ecuador (Lumbaqui, Santa Rosa de Sucumbios). These wind currents, coming from cities with small anthropogenic activity, could not explain a high tropospheric O_3 concentration value during March 2014.

Huaca et al.[54], by satellite measurements, carried out the study of UV factor values in the city of Ibarra from January 2010 to December 2016. This study visualizes an oscillation of the UV factor during these six years. Within this time, it can be seen that during March 2014, there is a high value of the UV factor, which explains the high concentration value of tropospheric O_3 in the city of Ibarra (Figure 18).[54]

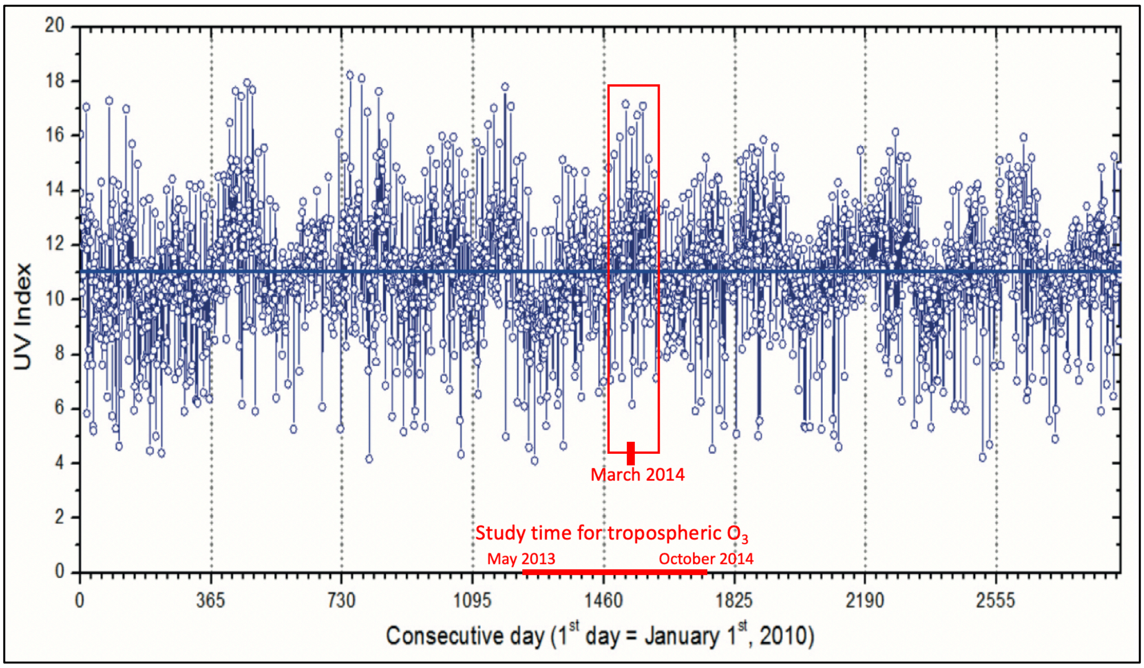


Figure 18. UV Index from January 1st, 2010 to December 31st, 2016 for Ibarra city.
Source: Adapted from Huaca, J.; Salum, G.; Piacentini, R. Solar Erythemal Irradiance in Ibarra, Ecuador (High Altitude Equatorial City). Ground and Satellite Measurements and Model Calculations. Lat. Am. J. Biotechnol. Life Sci. 2018. https://doi.org/10.21931/RB/2018.03.01.3.

5.2.1. Trends of tropospheric ozone concentration in Quito

Generally, the relationship between NO_2 and tropospheric O_3 should be inversely proportional, but for the city of Quito, this is not the case. This is visualized in Appendix J, where the concentration of both gases increases or decreases at the same time. Because this does not explain the trend of tropospheric O_3 in Quito, the solar radiation factor in the mentioned city is analyzed. Figure 19 shows a direct correlation between tropospheric O_3 and solar radiation, suggesting that this precursor explains the tendency of this contaminating gas in the city of Quito. To know how decisive the solar radiation factor is in the concentration of this gas, the coefficient of determination between them was obtained, $r^2 = 0.4793$ (Appendix K). This value shows a questionable relationship of solar radiation in the formation of tropospheric O_3 in the city of Quito, revealing that despite the coupling observed in Figure 19 this is not the main factor that influences the concentration of tropospheric O_3.

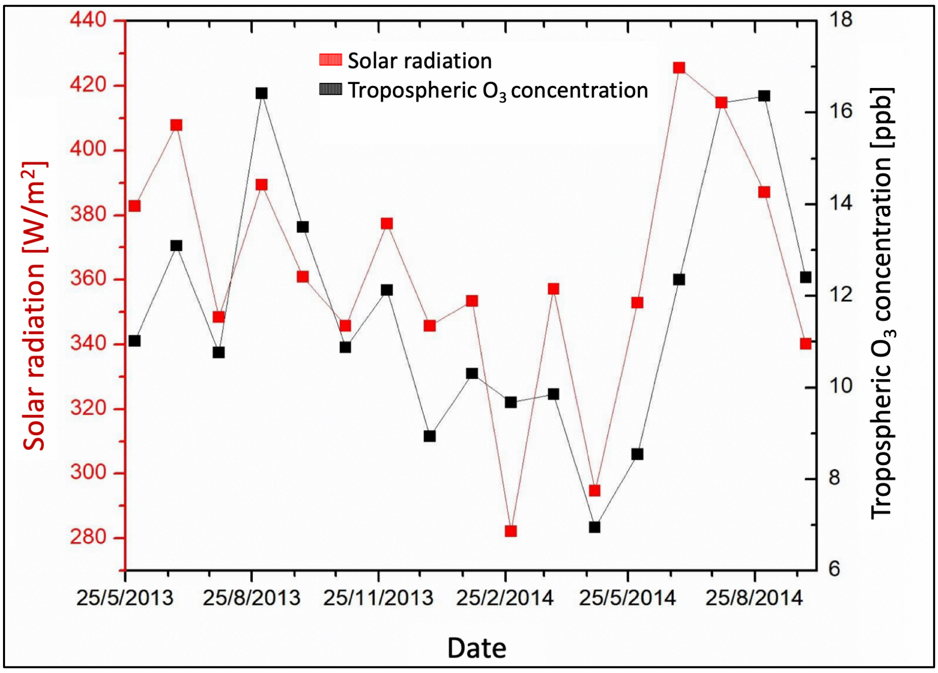


Figure 19. Solar radiation and tropospheric O_3 concentration in Quito during the study time.

According to WHO, there is a fixed value in the tropospheric O_3 guidelines of 100 µg/m^3 of the mean of 8h equivalent to 50 ppb. Unfortunately, there is no annual value reported by WHO for this gas.[55] Despite the absence of this data, the Air Quality department of the Madrid city Council approximate values in which 60 ppb of objective value year should not be exceeded for the protection of human health.[31] Following this data and Appendix H, the tropospheric O_3 concentration of the two cities in Ecuador, Quito and Ibarra, is under the permitted value. However, it is recommended that not only authorities help to reduce the concentration of this gas, but also the community at large because although it is under the authorized value, it can still be detrimental to human health.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

The levels of concentration of NO_2, 7.935 ppb for Quito city, and tropospheric O_3, 8.501 ppb in Ibarra and 11.72 ppb in Quito, have values below those permitted according to the WHO (21.27 ppb for NO_2) and the Air Quality department of the Madrid city Council (60 ppb for tropospheric O_3) respectively.

The air quality of Ecuador has adequate values of NO_2 concentration and tropospheric O_3 compared with the different cities considered for this study and with the guideline values of the atmospheric institutions.

Based on the case of Kosetice town in Hungary and by research carried out, it is proven that there is an influence of the air currents that affect the NO_2 concentration as well as all atmospheric gases.

The population of a city or town and its anthropogenic activities affect the NO_2 concentration, as in the case of the city of Quito. Similarly, the tropospheric O_3 concentration is also affected by the population because the predominant gas of anthropogenic activities is NO_2, which is a precursor of the greenhouse gas studied.

The NO_2 concentration value in the city of Quito was higher than that of the foreign cities considered in this study. The tropospheric O_3 concentration value for Quito and Ibarra cities is lower than the concentration of this gas in the foreign cities chosen for the study.

The anthropogenic activity, NO_2 is the only gas precursor of tropospheric O_3 that is measured in Quito and shows a poor correlation with this greenhouse gas (see Appendix J).

In Quito city, solar radiation showed a good correlation with tropospheric O_3. However, its low coefficient of determination value (0.4793) shows that this is not the main factor that controls the concentration of this gas, concluding that those who control the formation and concentration of tropospheric O_3 are their precursors.

6.2. Recommendations

Based on the knowledge acquired during this investigation, the following recommendations can be drawn to increase the impact of this type of studies:

- To use more than one database to have additional information about the different atmospheric gases to be studied.

- To extend the study time to see if the anomalies found become from normal oscillations of atmospheric gases, meteorological factors, or are due to different anthropogenic activities.

- To use satellite data for the verification of in-situ data, as well as being able to develop a prediction of atmospheric gases and weather factors based on their behavior.

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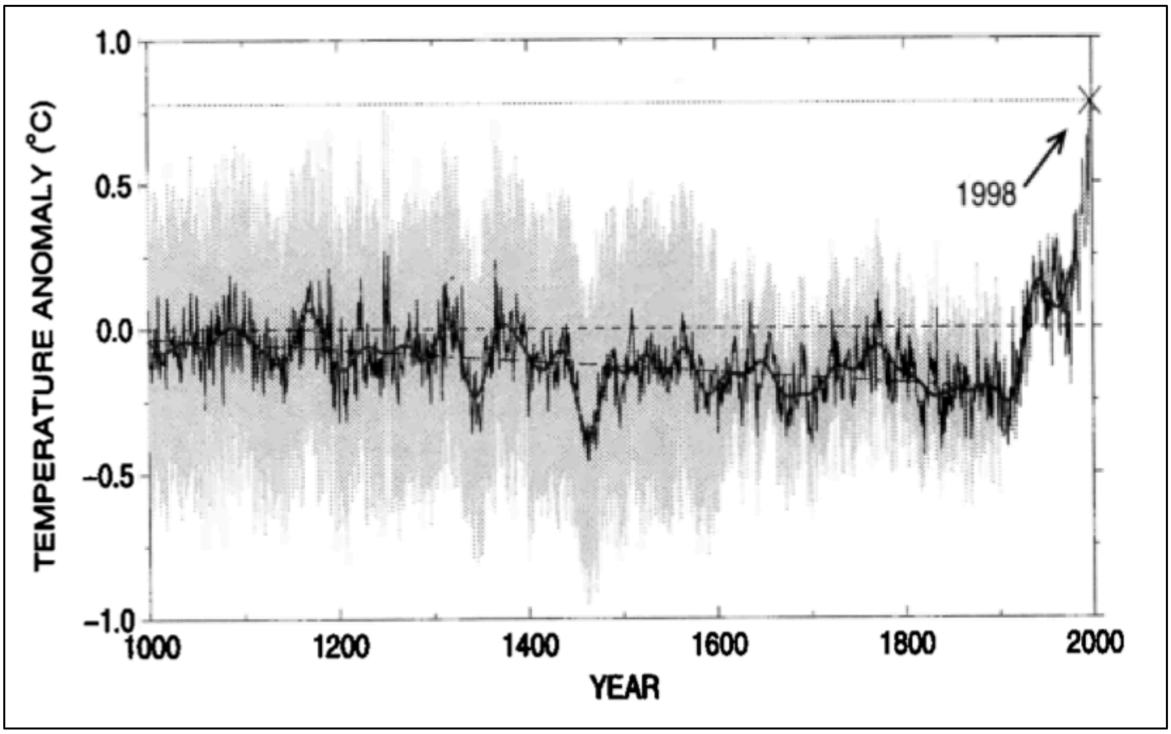
APPENDIXES

Appendix A

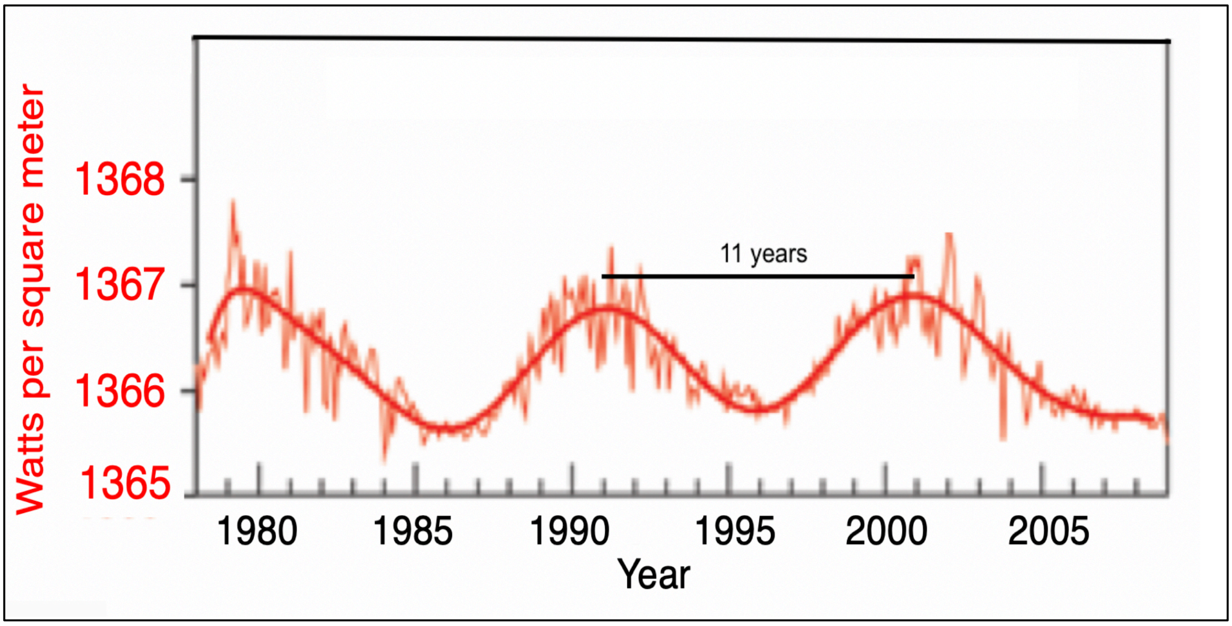
Earth's millennial temperature reconstruction.



Source: Reprinted from Mann, M. E.; Bradley, R. S.; Hughes, M. K. Northern Hemisphere Temperatures during the Past Millennium: Inferences, Uncertainties, and Limitations. Geophys. Res. Lett. ***1999****, 26 (6), 759–762. https://doi.org/10.1029/1999GL900070.*

Appendix B

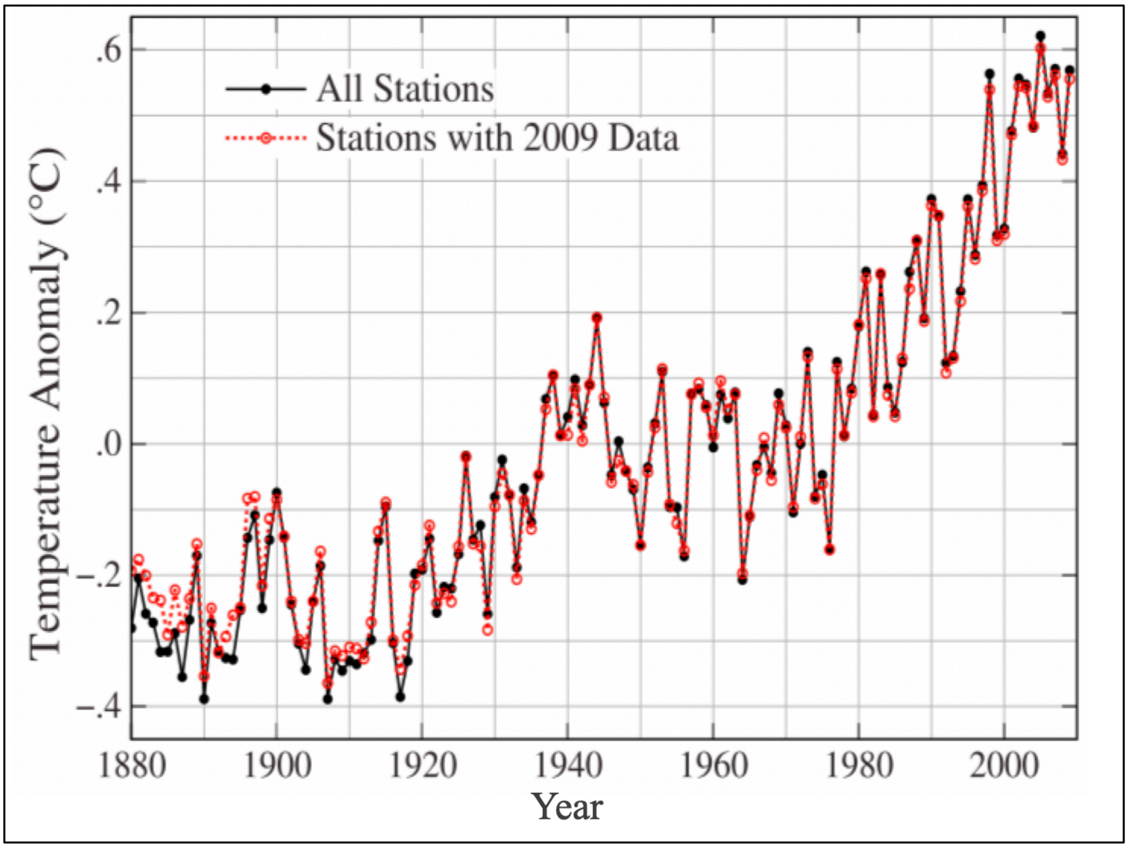
Measurements of sun's energy reaching Earth's top of atmosphere.



Source: Adapted from Karl, T.; Melillo, J.; Peterson, T. Global Climate Change Impacts in the United States; ***2009****.*

Appendix C

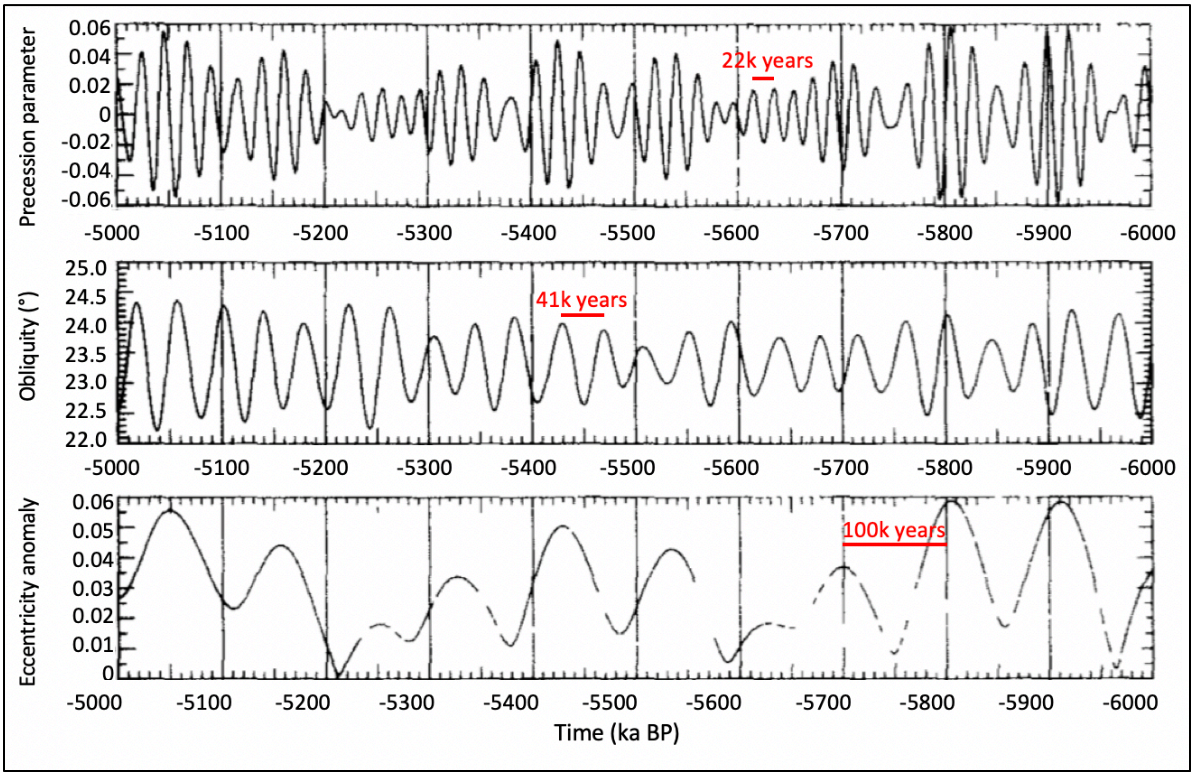
Temperature reconstruction for the past 130 years.



Source: Reprinted from Hansen, J.; Ruedy, R.; Sato, M.; Lo, K. Global Surface Temperature Change. Rev. Geophys ***2010****, 48, 4004. https://doi.org/10.1029/2010RG000345.*

Appendix D

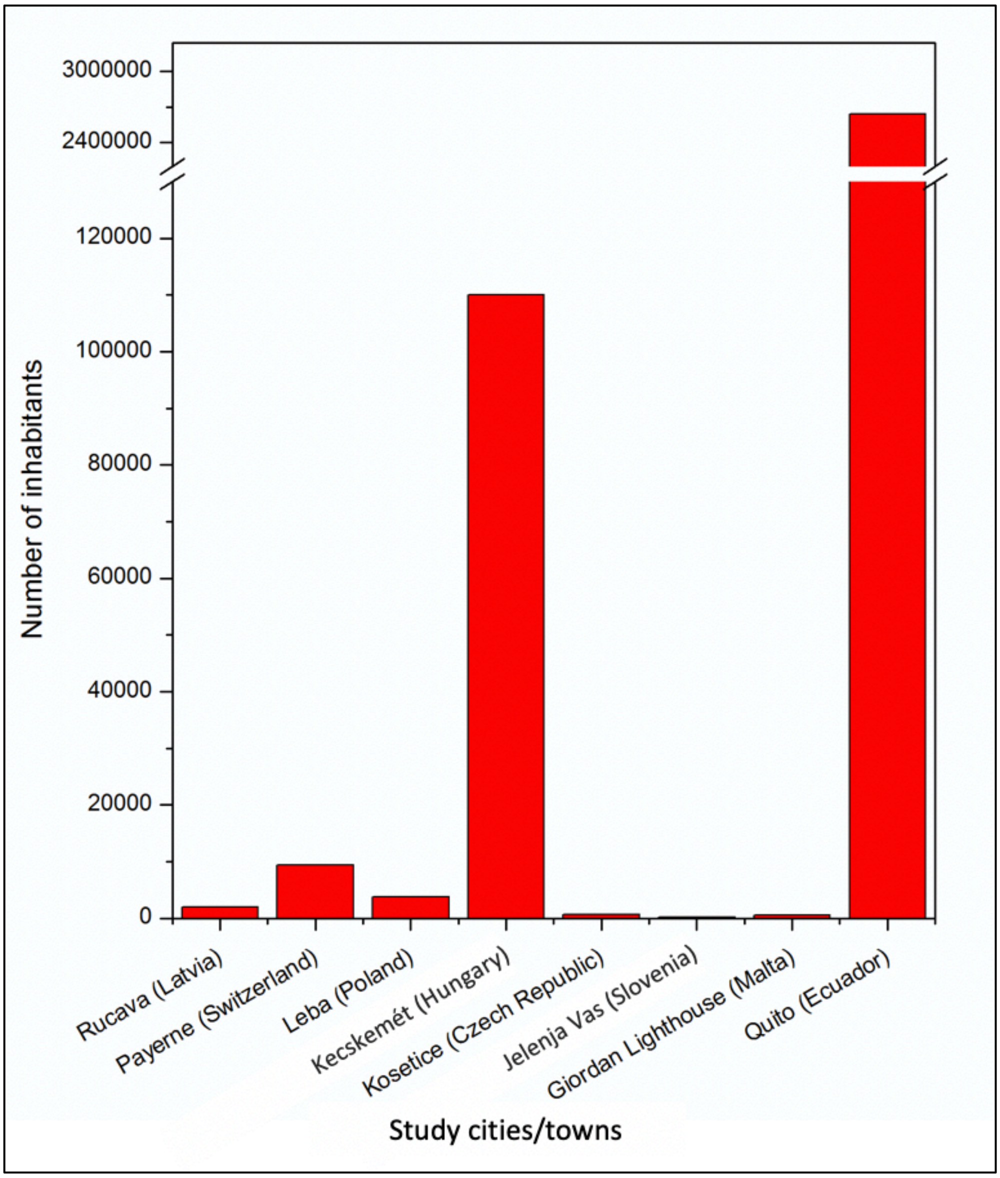
Milanković cycles.



Source: Adapted from Berger, A.; Loutre, M. F. Insolation Values for the Climate of the Last 10 Million Years. Quat. Sci. Rev. ***1991****, 10 (4), 297–317. https://doi.org/10.1016/0277-3791(91)90033-Q.*

Appendix E

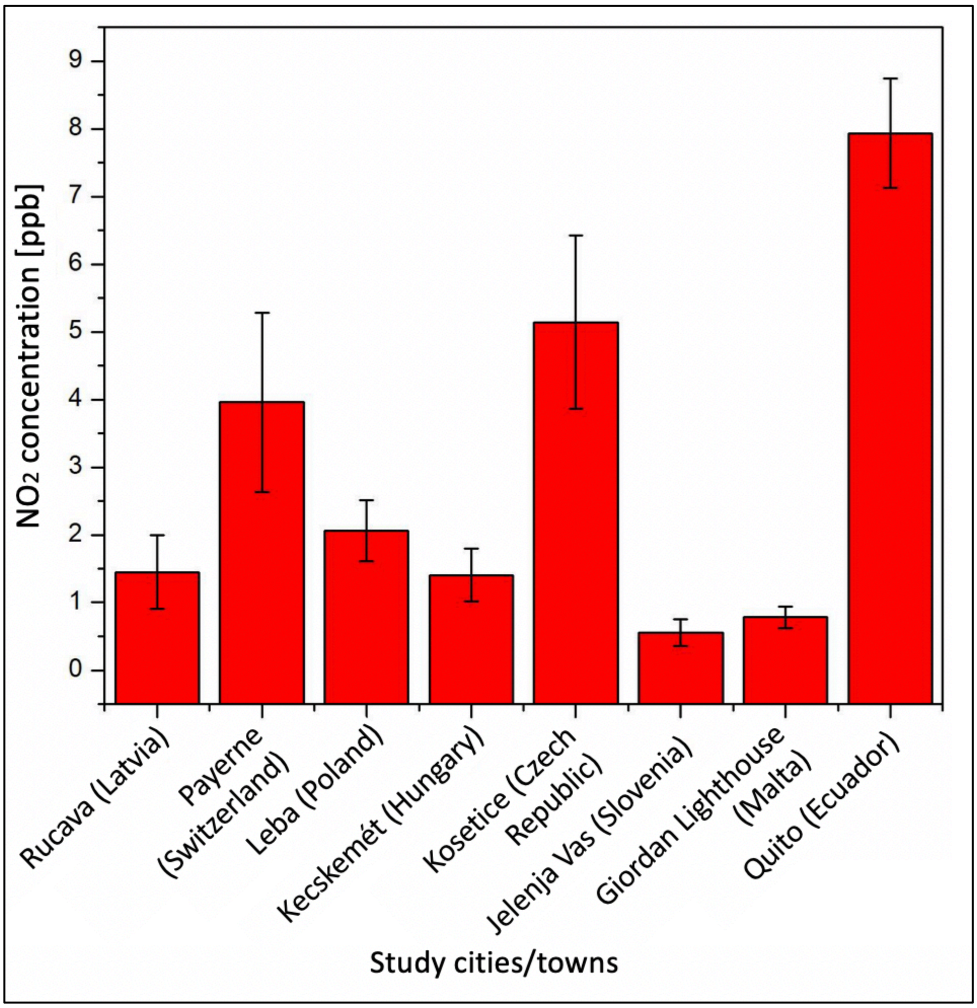
Population in the different study locations for the analysis of NO_2.



Source: Population.City. City populations worldwide http://population.city (accessed Mar 2, 2018).

Appendix F

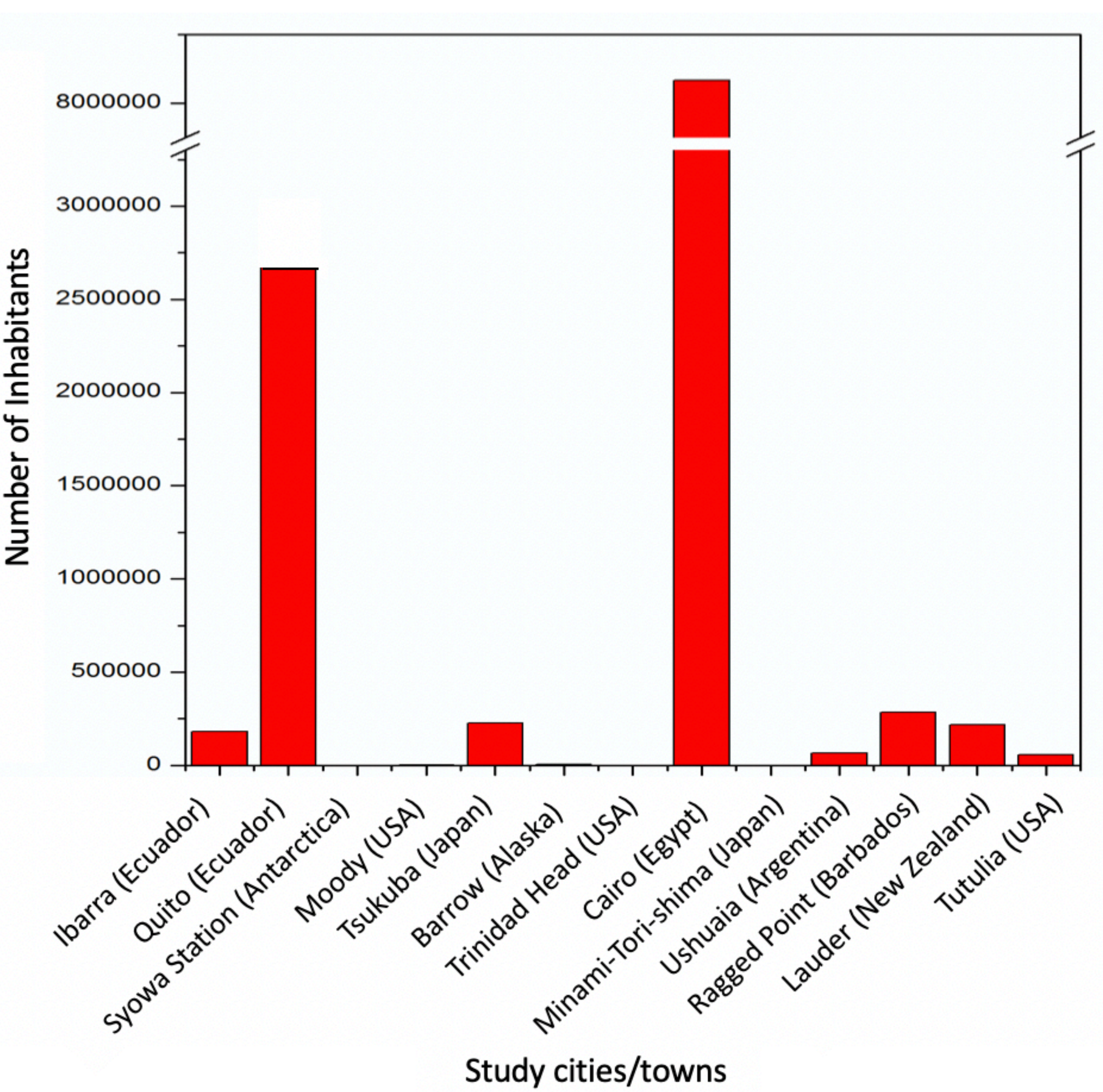
Comparison of NO_2 concentration in the study cities and towns.



Note: The bar graph represents an average of concentration from January 2013 to the month of December of the same year.

Appendix G

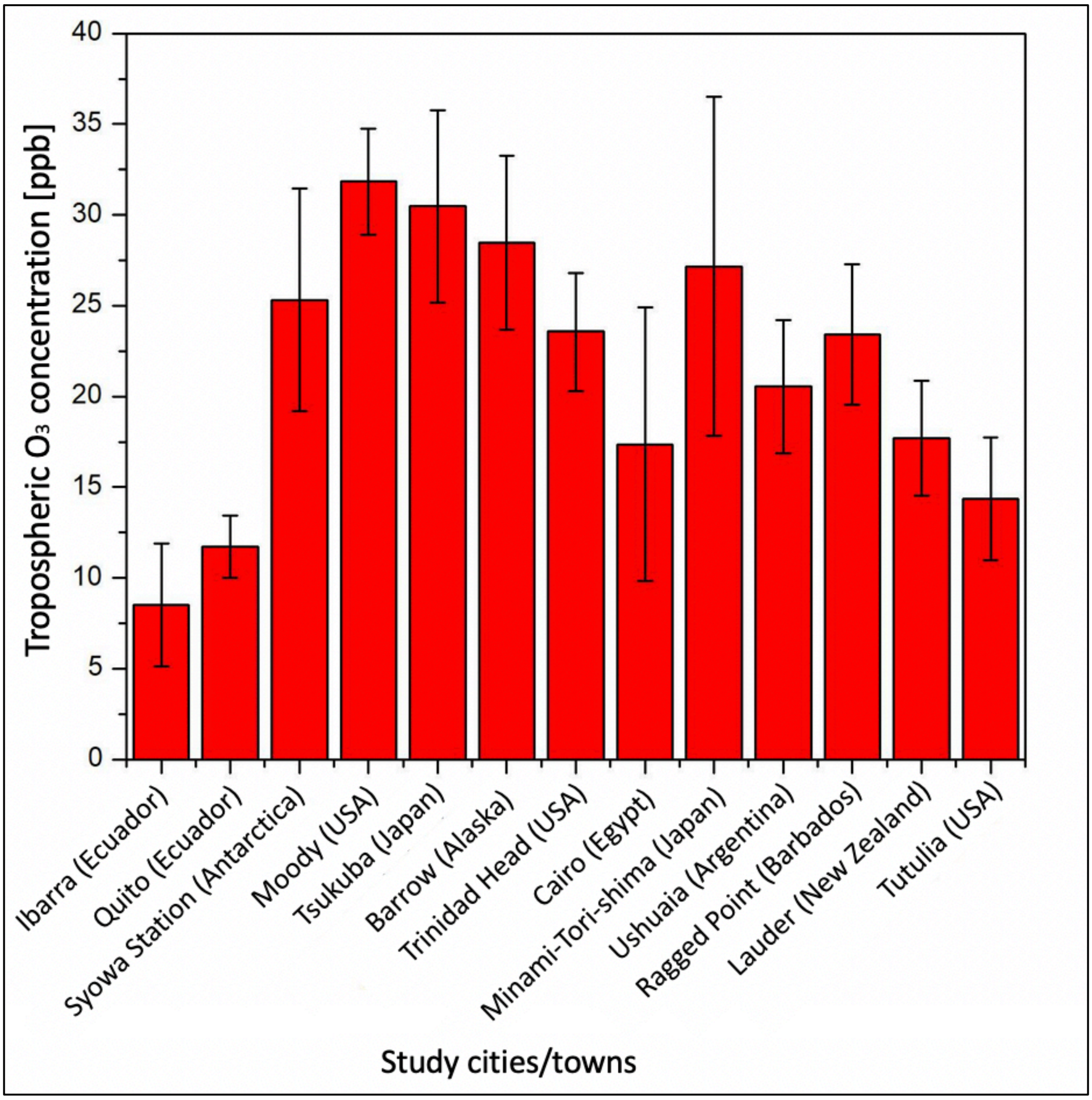
Populations in the different study cities and towns for the analysis of tropospheric O_3.



Source: Population.City. City populations worldwide http://population.city (accessed Mar 2, 2018).

Appendix H

Average concentration of tropospheric O_3 in the study cities and towns.



Note: The bar graph represents an average of concentration from May 2013 to October 2014.

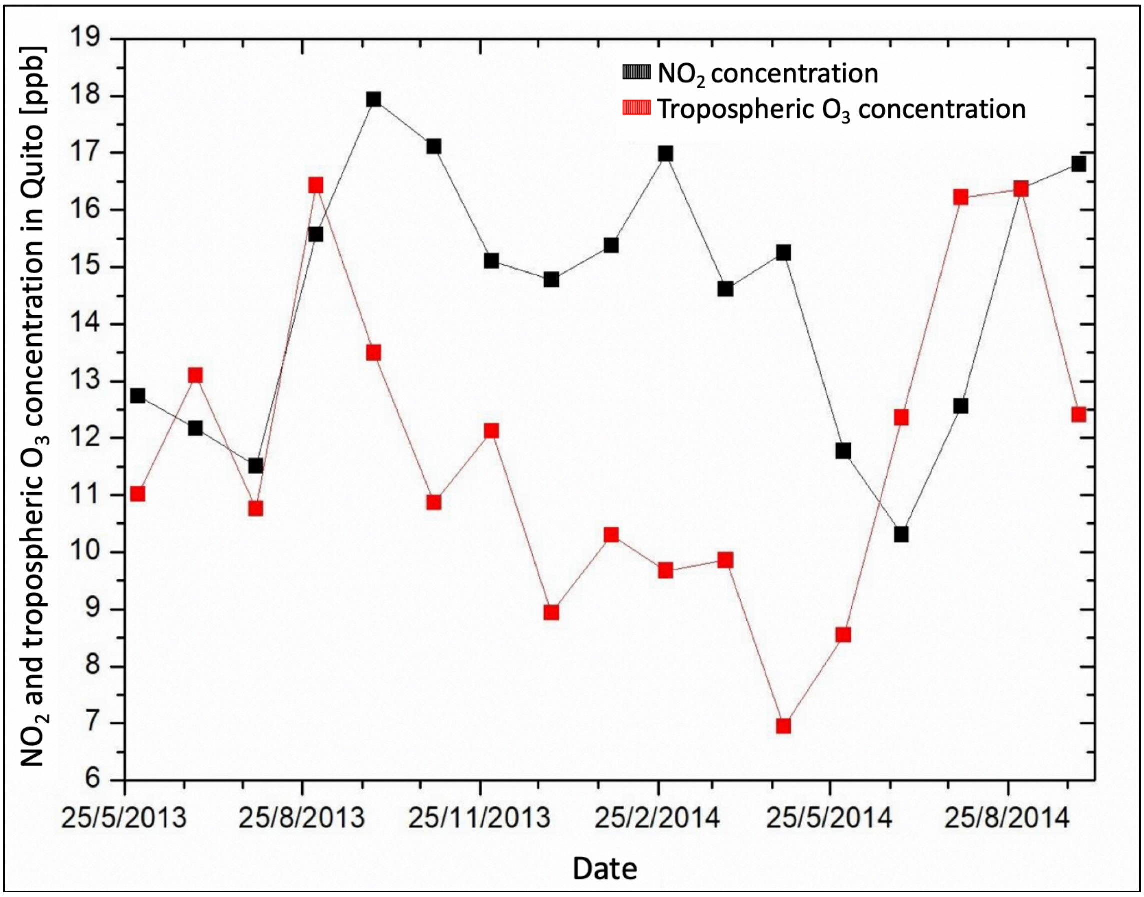
Appendix I

Data obtained from the monthly measurements of tropospheric O_3 concentration in Ibarra city.

Study time	[O_3] tropospheric in Ibarra (ppb)
jun-13	11.101
jul-13	11.045
aug-13	11.576
sep-13	17.986
oct-13	10.985
nov-13	11.223
dec-13	5.098
jan-14	2.168
feb-14	2.529
mar-14	10.572
apr-14	20.707
may-14	1.825
jun-14	4.597
jul-14	7.878
aug-14	6.902
sep-14	4.051
oct-14	4.284

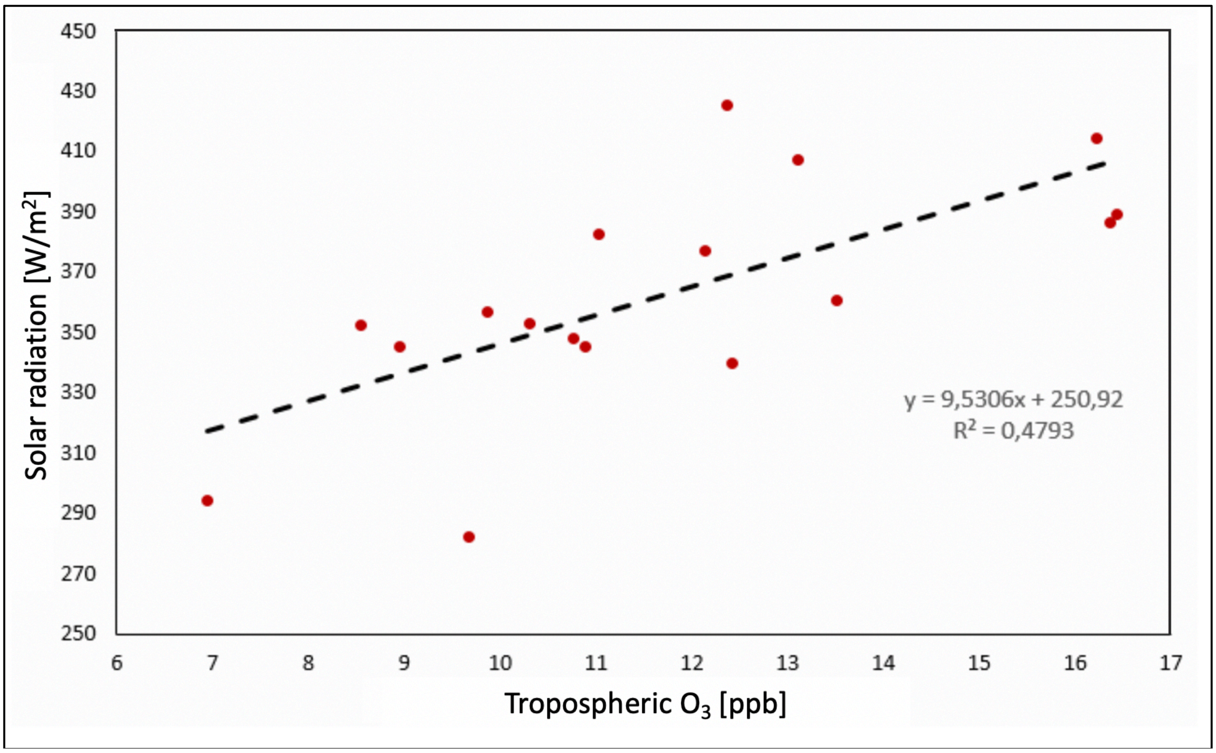
Appendix J

Comparison of the tropospheric O_3 and NO_2 concentration in Quito during the study time.



Appendix K

Correlation of tropospheric O_3 concentration with registered solar radiation in Quito city.



Appendix L

Article

It is annexed the scientific paper named *Comparison of tropospheric ozone and nitrogen dioxide concentration levels in Ecuador and other latitudes* published on March 2, 2018 in the Latin American Journal of Biotechnology and Life Sciences, doi.10.21931/RB/2018.03.02.5