Notes on Sulfur Fluxes in Urban Areas with Industrial Activity

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Abstract*– The objective of this study was to evaluate sulfur fluxes in kg/ha/year in the urban area which is located close to oil refinery and the wood industry in Esmeraldas (Ecuador). The fluxes were determined by the turbidimetric method, for this the sulfur concentration was captured using 16 passive samplers located in four monitoring sites categorized by land use during dry and rainy season between 2018 and 2019. For the spatial description of the area of study were used QGIS version 2.18 and Google Earth 2018, monthly wind graphs were generated with the help of the WRPLOT View version 8.0.2 program. The sulfur fluxes were varied between 5,060 and 5,294 kg/ha/year according to monitoring site, the low values of sulfur fluxes were attributed to the rainy season (0.37 kg - 1.60 kg/ha/year) in emission sources such as the Margarita Cortez monitoring site. The atmospheric and orographic conditions which had an influence on concentrations of the sulfur fluxes were varied significantly in a radius smaller than 45 km^2. The results obtained in this study can contribute for the development of policies or legal instruments such as public ordinances and monitoring plans in the industrial area of Esmeraldas.

***Keywords*-- Sulfur fluxes, passive samplers, pollution from refineries.**

I. Introduction

The contribution of greenhouse gas emissions and their predominance in the atmosphere are linked to pollutants of anthropogenic sources [1]. This is a problem which affects both developed and developing countries all over the world [2], gases may be poisonous and have a negative effect on the life of people [3], and the ecosystems. The main source of air anthropogenic pollutants is the burning fossil fuels, an activity which is closely associated with oil refineries [4].

For example the use of heavy oil in Iran generates SO_2 pollution with weight values of 1.55 - 3.5 % as a byproduct of burning oil in steam plants [5], the average of SO_2 emissions was 15.27 g/kWh, which is equivalent to 541,000 mg of this pollutant. In the Middle East, the Abadan refinery produces pollutants with ranges of SO_2 emissions more than 150 tons per year, in comparison with the standards of the permissible limits for refineries in Latin America these indicators are lower [6].

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In Latin America, studies carried out on the Isla del Carmen in Mexico [7], confirmed the negative impact of oil activity. In case of Ecuador, it was determined that the concentrations of SO_2 generated by Esmeralda's refinery is above the Ecuadorian Standard, the values were 350 ug/m^3 in 24 hours and 80 ug/m^3 of annual average [8]. Reference [9] reported that data in Mexico City, Bogotá, Sao Paulo, and Santiago, they have been painstakingly documented during the last two decades to terminate atmospheric pollution. Reference [10] characterized the factors, which are potential elements of the environmental impacts caused by the emissions and generated by refineries.

The inventories and life-cycle emission are the cause-effect chain that linking emissions with damage of ecosystems quality and human health, as well as the entry of these pollutants into life cycles [11]. Reference [12] reported that in Esmeraldas there is a negative effect on the health of people who live in the surrounding area.

The determination of sulfur fluxes using passive samplers as in [13] is an accessible and effective method to compare with others long-term monitoring methods, which are very expensive and have availability problems. Fenn's method made it possible to monitor fluxes during the climatic seasons in the study area to determine the local and regional distribution of sulfur [14]. The monitoring of emission sources allows action to be taken on the limits of pollutants, which are controlled through local ordinances to support international policy on pollution problems that can be managed in the short and medium term [15].

The presence of an oil refinery in Esmeraldas has been scarcely documented regarding to the ambient air quality, the problem is related to the useful life of the refinery [16]. The refinery was built between 1975 and 1977 to produce 110,000 barrels of oil per day [17], and of course this is the factor affecting the city's air quality significantly. The Esmeraldas State Refinery currently emits particles of various sizes, as well as volatile hydrocarbons [18], these emissions come from the different phases of operation [19], in addition to the combustion of products petroleum generates sulfur dioxide (SO2), ultrafine particulate (UFPs), nitrous oxide (N2O), carbon dioxide (CO_2) and carbon monoxide (CO) [20].

Reference [9] in their report described the difficulty of accessing information related to the ambient air quality in Latin America, this information was available only in 24.3 % concerning to all cities in Ecuador, in this case the data were available only for Quito and Cuenca. Reference [21] mention that there was an uncertainty in the expected values of SO_2, which are linearly dependent on the concentration of Sulfur in the fuel produced in Esmeralda's refinery and the sulfur content can vary from 1.3 to 2.3 %.

The main objective of this study was to measure sulfur fluxes in the surrounding areas in Esmeraldas (Ecuador). To do so, it was analyzed and categorizing the incidence of sulfur fluxes according to the land use, in the influence area were placed passive samplers in dry and rainy season from November 2018 to March 2019.

II. Materials And Methods

A. *Study Area*

The city of Esmeraldas is in the province with the same name in the north of Ecuador, its population is 189,400 inhabitants [22]. This province is one of the economic poles of Ecuador, it is located on the border with Colombia and maintains Esmeraldas Port and the Heavy Crude Refinery, managed by Esmeralda's state refinery Petro-Ecuador (Fig. 1).

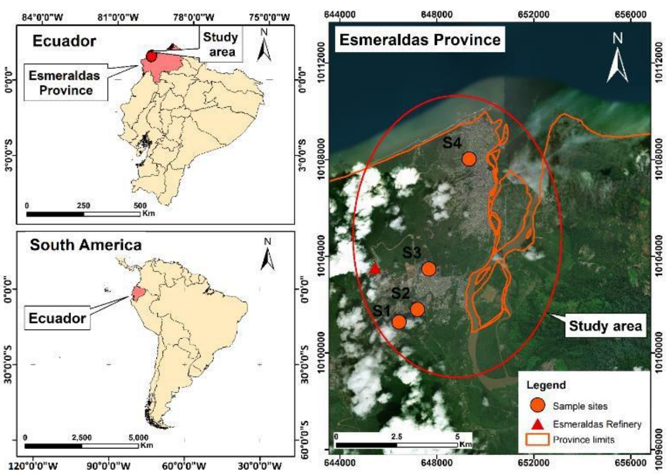

Fig. 1 Geographic location of the study area in city of Esmeraldas, Ecuador.

B. *Design of the investigation*

The sampling sites were randomly selected, according to the land uses in the city of Esmeraldas, which were identified as: food industries, land and shipping transport, and cement.

Passive samplers are used as deposits for sulfate ions from the atmosphere and are ideal for collecting information during dry and rainy seasons. The passive samplers were installed in high places such as on roofs and open spaces free of buildings and vegetation. The samples were collected in dry and rainy seasons, and samplers were changed every 20 - 30 days after being exposed to the environmental conditions, in total 16 samples were obtained [7].

C. *Description of the throughfall*

The passive sampler consisted of a funnel with an approximate diameter of 23 cm, covered with a fine metal mesh to prevent insects and leaves falling, to the funnel was attached a PVC pipe of 20 cm long with a diameter of ¾ inches, inside of each sampler were placed 30 gr of mixed AmberliteTM IRN 150 resin (Fig. 2). Glass wool was placed at the ends of the tube, to support the resin and filter only fine particulate material (PUF). A PVC valve was placed at the lower end of the tube, to which was attached a coupling with different outlet diameters. The sampler is protected from heat with a preferably white Polychloride and vinyl (PVC) tube of 2 inches wide and approximately 30 cm long [13], [23].

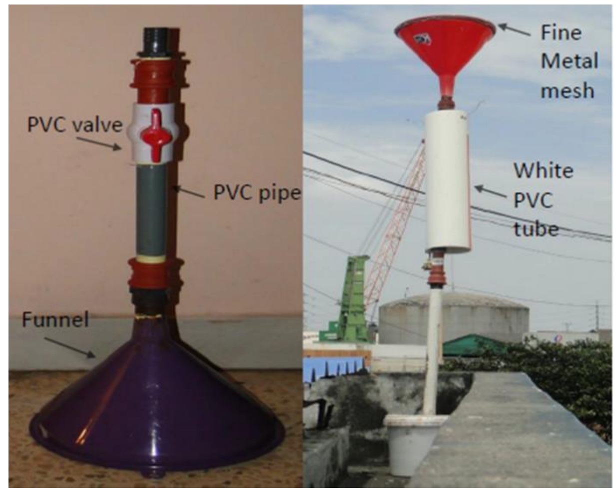

Fig. 2: Passive sampler for assessing sulfur fluxes.

D. *Meteorological aspects*

The spatial distribution of sulfur flux in kg /ha/year was analyzed with QGIS version 2.18 software and with images from Google Earth. The monthly winds were plotted using the WRPLOT View version 8.0.2 software, based on data from the Esmeraldas meteorological station of the Ecuadorian Oceanographic Institute of the Navy (INOCAR). Additionally, to observe the spatial distribution of S flux in the study area with respect to the refinery and other lands around, it was applied an Inverse Distance Weighting (IDW) method, according to it the closest points are similar, which gives more weight and influence on the point which is estimated [24]. The choice of this interpolation method was based on the reduced number of monitoring sampling sites in the present study.

E. *Determination of sulfur*

The samples were washed in the laboratory of the National Institute of Public Health and Research (INSPI). They were proceeded according to the NMX-AA-074-1981 [25], a first wash is carried out with 100 ml of distilled water, the glass wool was removed, after 10 minutes was the second wash, with a solution of 100 ml of Potassium Chloride (ClK). The Turbidimetric Method consists of transferring a 250 ml sample aliquot to a 250 ml Erlenmeyer flask, where 5 ml of conditioning reagent is added and mixed by the stirrer, the content of a teaspoon is added with a few barium chloride crystals (ClBa) for one minute. Immediately part of the solution is poured into the absorption cell of the Visible spectrophotometer Thermo Scientific™ GENESYS 20, where the turbidity (absorbance) is determined at intervals of 30 seconds for 4 minutes at a wavelength of 420 nm sulfur flux were determined using (1).

$$Sulfur\ flux = \frac{Mass\ concentration}{Area * exposure\ period} = \frac{(kg)}{(ha\ year)} \quad (1)$$

D. Principle and Foundation

The turbidimetric method to determine sulfates is based on that the sulfate ion precipitates with barium chloride ($BaCl_2$), in an acid medium (HCl), giving rise to the crystallization of barium Sulfate ($BaSO_4$) of uniform size. The sulfate ion concentration is determined by comparing the reading with a standard curve.

F. Sulfate Standard Solution (Calibration Curve)

Dilute 147.9 mg of sodium sulfate anhydrous (Na_2SO_4) in water and bring it to capacity 1000 ml. Prepare the calibration dissolutions, within the mass concentration range of 0 to 10 mg /L Na_2SO_4; use cells with optical path of light of 1 cm or greater. A minimum of five points are used to construct the calibration curve, additionally to the blank in the range from 0 to 10 mg/L of Na_2SO_4 (1, 3, 5, 7, and 10 ppm). Above 40 mg/L, the accuracy of the method decreases, and barium sulfate suspensions lose stability. A linear regression model $y = mx + b$ was used to determine the sulfur formula, for this it was obtained a slope m of 0.0005 and a coefficient b of 0.0007 for the mass concentrations x, the correlation coefficient was 0.98 using (2).

$$x = \frac{y - b}{m} = \frac{(mg)}{(L)} \quad (2)$$

The mass concentration of the sulfate ion is measured by comparing the reading with an analytical calibration curve.

Aliquot: 0.4 L

Funnel diameter: 23 cm; radio: 11.5 cm

Exposure area = 415.48 cm^2 = $4.15x10^{-6}$ ha

Exposure period: 1 month = 30 days = 0.08219 year.

G. Statistical analysis

The statistical analysis was performed using one-way ANOVA, in addition it was calculated the F test and its meaning. Regarding to the meaning, if the values are less than 0.05, the variables are related and therefore there are significant differences between the groups. On the other hand, the higher is the F value, the more the variables are related. Additionally, box plots were used to observe the dispersion of sulfur fluxes and identify outliers. For the visualization and modelling analysis was used Statgraphics Centurion XVI software.

III. Results And Discussion

The values of sulfur fluxes in dry and wet season fluctuate depending on the proximity of the samplers to the refinery and industrial zones in terms of distance and meteorological conditions at the time of study (Table II).

TABLE II
Location of the Passive Samplers in the Study Area

Code	District	Sampling sites	Km Distance to refinery	UTM coordinates	Influence area
S*1	Simón	District Las Acacias	1.92	646442 10101277	Refinery, Thermoelectric, CODESA (Contrachapados del Ecuador S.A.)
S2	Plata	District Julio Estupiñan	1.75	647206 10101793	
S3	Torres	Area 15 de Marzo	1.81	647673 10103468	
S4	Bartolomé Ruiz	Area Margarita Cortez	6.02	649334 10108014	Port of Esmeraldas

S*: Sampling sites.

Fig. 3 and Fig. 4, show an asymmetric dispersion of total sulfur flux in kg/ha/year values for the four sampling sites (S1, S2, S3 and S4), in the graph, each sampling site shows four observations corresponding to the months of monitoring. Area 15 de marzo (S3) is the closest sampling site to the refinery and it is approximately 1.8 km far, S3 shows the highest values of sulfur flux, deposited for both dry and rainy seasons with values ranging from 5.06 and 5.29 kg/ha/year, respectively. The sulfur flux for the S3 ranges from 3.42 to 5.29 kg/ha/year. The sampling site of the area Margarita Cortez (S4), which is 6.02 km far away from the refinery has lower sulfur fluxes values, which were between 0.37 and 1.31 kg/ha/year. District Las Acacias (S1) presents a broader distribution of the data with respect to the other sampling sites with values ranging from 1.31 to 4.83 kg/ha/year.

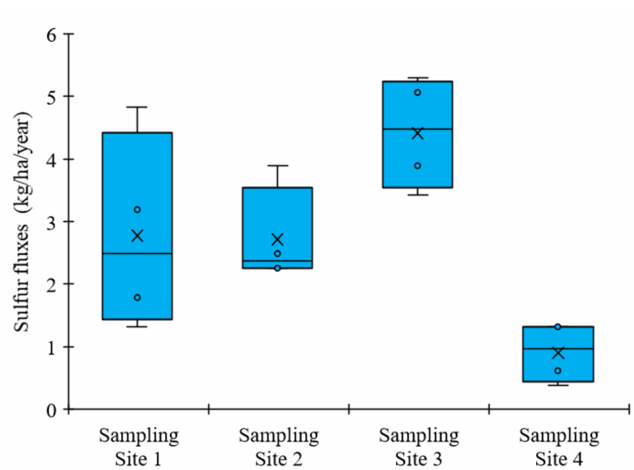

Fig. 3 Sulfur fluxes of sampling sites in the city of Esmeraldas; S1, district Las Acacias; S2, district Julio Estupiñán; S3, area 15 de marzo; and S4, area Margarita Cortéz.

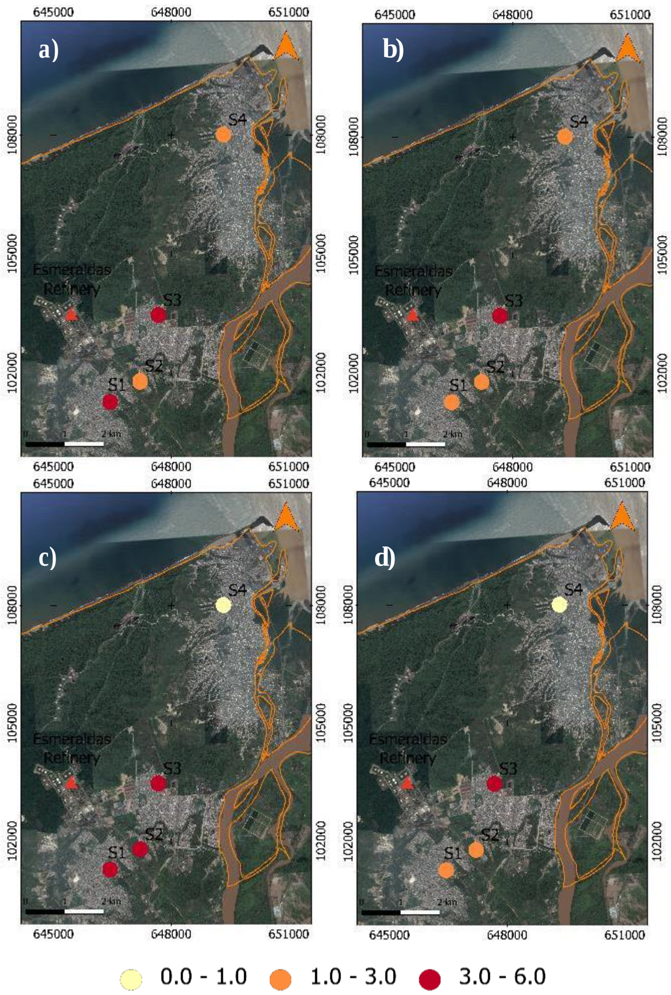

Fig. 4: Sulfur fluxes in kg/ha/year at the sampling sites; a) November 2018; b) December 2018; c) January 2019; d) February 2019).

Fisher's least significant difference (LSD) procedure was used to discriminate between the means based on the variable studied, which then allowed the analysis to be stratified for land uses. The F-ratio, which in this case is equal to 7.90, is the quotient between the estimate between groups and the estimate within groups. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the mean total flux (kg/ha/year) between one sample point level and another, with a level of 95 % confidence (Table III).

TABLE III
ANOVA FOR TOTAL SULFUR FLUX (kg/ha/year)

Source	Sum of squares	df	Middle Square	Reason-F	P-value
Between groups	24,7346	3	8,24488	7,90	0,0036
Intra groups	12,5268	12	1,0439		
Total (Corr.)	37,2615	15			

Calculation of the degrees of freedom (df), which was established in the theory of analysis of Variance, it was considered that (df) between groups is attributed to the calculation of treatments minus one (t-1), which for this case is managed 3 treatments that represented the verification zones in their natural conditions to study their influence and sulfur concentration levels. Thus, for these conditions the value was 2 df, while the intragroup df were attributed to the product of the number of treatments times the difference of the repetitions minus one (t * (n-1)) resulting in 9 df, all this for a total of 11 df in the proposed model.

The P-value of the F-test is less than 0.05, there is a statistically significant difference between the mean total sulfur flux (kg/ha/year) between one level of land use and another, with a 95.0% confidence level (Table IV).

TABLE IV
ANOVA FOR TOTAL SULFUR FLUX BY LAND USE (kg/ha/year).

Source	Sum of squares	df	Middle Square	Reason-F	P-value
Between groups	24,7175	2	12,3587	19,45	0,0005
Intra groups	5,71802	9	0,635336		
Total (Corr.)	30,4355	11			

The analysis of the dry and rainy season showed that there are no significant differences in the sulfur fluxes during both periods since the p value = 0.86 and the F tests is > 0.05. The dry and rainy seasons are represented in eight observations corresponding for each season. The distribution of the sulfur fluxes for the dry season ranges from 1.31 to 5.06 kg/ha/year and for wet season ranges from 0.37 to 5.29 per kg/ha/year. The average sulfur flux values were 2.78 and 2.63 kg/ha/year, for the dry and rainy seasons respectively (Fig. 5).

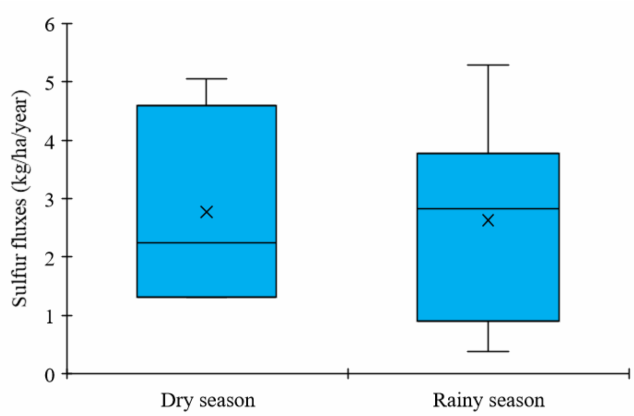

Fig. 5: Seasonality sulfur fluxes in kg/ha/year: dry season (November - December 2018) and rainy season (January - February 2019).

The distribution of sulfur fluxes shows asymmetric distribution in the area around the Esmeraldas refinery, the p value = 0.76 it is more than the ratio of F, therefore, there are no significant differences between the months under study. Each month represents the observations corresponding to the four different sampling sites. February is the month that shows the lowest values of sulfur fluxes which ranges from 0.61 to 3.42 kg/ha/year. The month of January presents a wide distribution of the sulfur fluxes with respect to the other months of monitoring, these values range from 0.37 to 5.29 kg/ha/year. The mean values of fluxes of S of 3.07, 2.48, 3.19 and 2.07 kg/ha/year for the months of November - December 2018, and January - February 2019 respectively (Fig. 6).

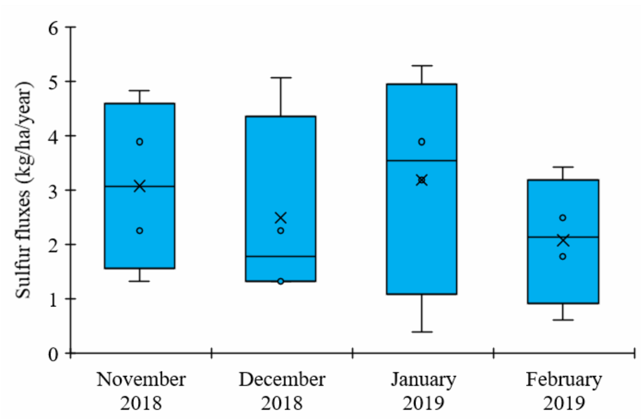

Fig. 6: Average monthly sulfur fluxes in kg/ha/year

The Land Use classes as industrial, urban, and shipping port, are anthropogenic activities which are developed throughout all monitoring sites close to the refinery in a radius of 30 km. The area 15 de Marzo (S3) is directly affected by such industries as Refinery, Thermoelectric and Contrachapados de Esmeraldas S.A. (CODESA). Area Margarita Cortez (S4) is the farthest monitoring site, but it is part of Esmeraldas Shipping Port.

Regarding the methodological aspects, it is important to mention that the trade winds in Ecuador are manifested from August when the cold Humbolt current enters equatorial waters, in the dates of study Equatorial current dissipates the Humbolt current and advances to the north. Because of these conditions, the wind speed shows that in January and February (rainy season) there are prevailing winds in the range of 5.7 - 8.8 m/s with 45.2 and 75 % respectively and in a lower percentage in the interval of 8.8 - 11.1 m/s with 38.7 and 21.4 % respectively (Fig. 7). The spatial representation of wind speed and direction shows a predominance of the South-West direction for all study monitoring months.

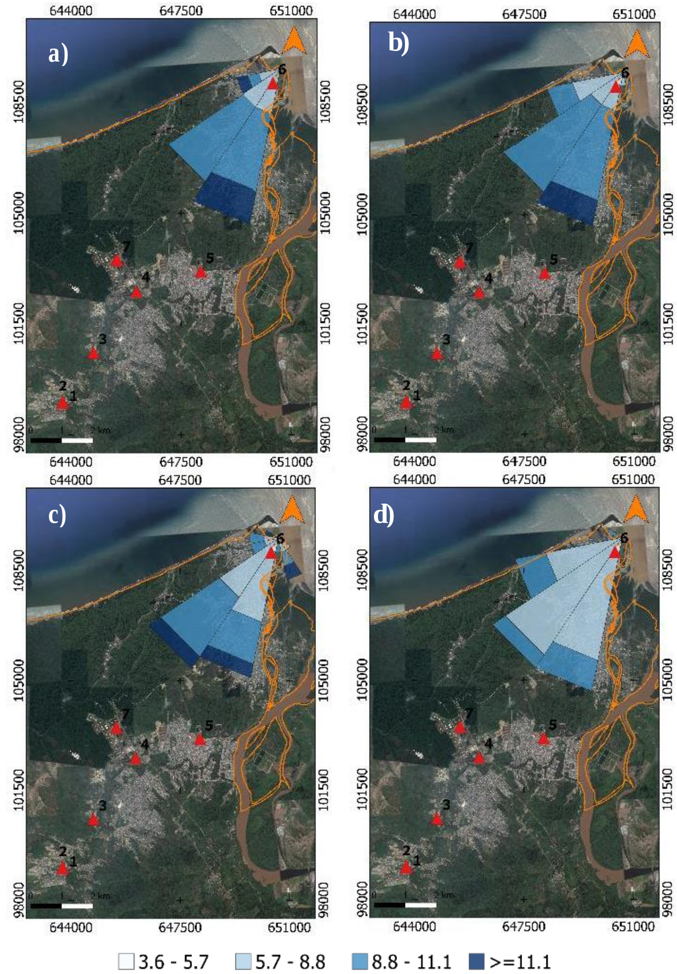

Fig. 7: Wind direction m/s in the study area; a) November 2018; b) December 2018; c) January 2019; d) February 2019. The red triangles represent the polluting places with respect to the sampling sites. 1, Oliojoyas Oil Industry; 2, Romserr (ready-mixed concrete, stone material); 3, Hormigonera Esmeraldas, 4; Thermoelectric; 5, CODESA; 6, Port of Esmeraldas; 7, Esmeraldas Refinery.

The frequency analysis of wind shows that in November and December, the wind speed had a high frequency in the range from 8.8 to 11.1 m/s with 53.3 and 58.1 % respectively and to a lesser extent with 33.3 and 32.3 % in the range of 5.7 - 8.8 m/s. However, winds stronger than 11.1 m/s also happened during both months, although with less frequency (Table IV).

TABLE IV
FREQUENCY OF WIND SPEED (m/s)

Wind speed	November	December	January	February
Calms	-	-	-	-
0.5 - 2.1	-	-	-	-
2.1 - 3.6	-	-	-	-
3.6 - 5.7	-	3.2	3.2	3.6
5.7 - 8.8	33.3	32.3	45.2	75.0
8.8 - 11.1	53.3	58.1	38.7	21.4
>= 11.1	13.3	6.5	12.9	-
Total (%)	100	100	100	100

According to the sampling sites, it is observed that the land use with the highest values of sulfur fluxes in the city of Esmeraldas were Thermoelectric, CODESA and Esmeraldas refinery, particularly in the months of December and January (Fig. 8).

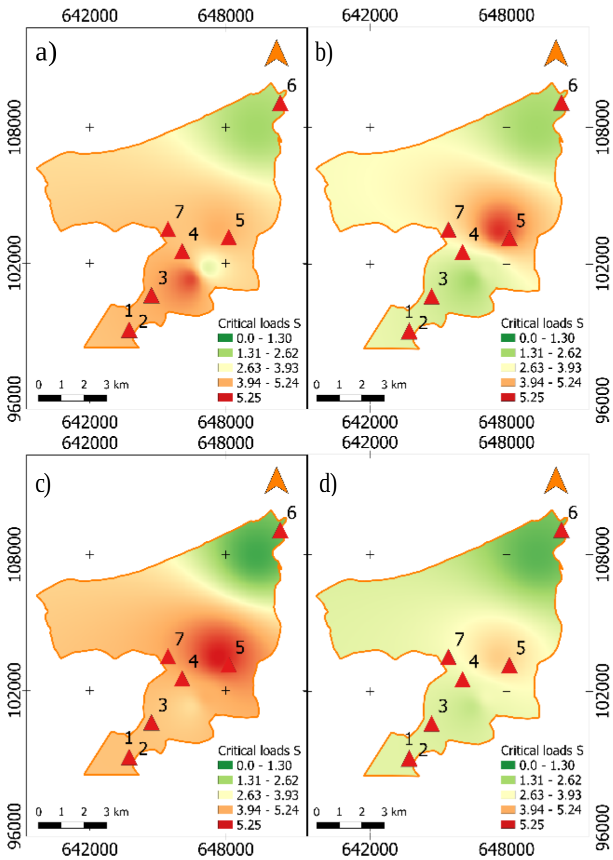

Fig. 8: Spatial distribution of the average sulfur fluxes in kg/ha/year in Esmeraldas. a) November 2018; b) December 2018; c) January 2019; d) February 2019. The red triangles represent the polluted places with respect to the sampling points: 1, Oliojoyas Oil Industry; 2, Romserr (Premixed concrete, stone material); 3, Esmeraldas Concrete Mixer; 4, Thermoelectric; 5, CODESA; 6, port; 7, Esmeraldas´ refinery.

The sulfur fluxes obtained in Esmeraldas can not only be attributed to the Esmeraldas Refinery, because in the areas where the samplers were set there are other companies such as: the shipping port of Esmeraldas, CODESA and Thermoelectric. In the four sampling sites in the city of Esmeraldas described according to land use, the values vary from the lowest in the Port of Esmeraldas with 0.375 S kg/ha/year, to the highest (4.41 kg/ha/year) in the area 15 de marzo, which is closely located to the Refinery, Thermoelectric and CODESA, because of the "industrial" category of the land use. High sulfur fluxes affect sensitive areas like natural forests in values of 2 and 5 kg/ha/year [26].

The sulfur fluxes in the proximity areas of the Esmeraldas refinery varied from 5.06 to 5.29 kg/ha/year, which is mostly received by the forested area surrounding the refinery. Reference [27] argued that these sulfur fluxes content nutrients and contaminants which are incorporated into the soil. Reference [28] found that in the understory layer of the New Hampshire Forest in the United States, the sulfur fluxes from the soil pH, they were less than 2 kg/ha/year among the three study sites.

In the port of Esmeraldas and thermoelectric power station (Barrio Margarita Cortéz), the average sulfur fluxes were 0.90 kg/ha/year. These fluxes data are not comparable with ones in Guayaquil port and Trinipuerto [29], which present values of 8.92 and 7.12 kg/ha/year respectively, thus may be influenced by the direction of the winds from the ocean or sulfur fluxes fluctuate by orography [30], [31].

In the seasonality of the data, it was obtained that the sulfur fluxes do not vary significantly between the climatic stations, they present average values of 2.78 and 2.63 kg/ha/year for the dry and rainy seasons, respectively. However, the monthly values show that the fluxes are linked to rainfall and marine aerosols given the proximity to the Pacific Ocean, thus obtained lower values during the rainy season in the areas of the emission sources [32], [33].

According to the land use, the radius of influence of the sulfur fluxes was 45km, as in [34], the distribution of the sulfur fluxes covers a radius of not more than 100 km. The four months of study reported a southwest wind direction (Figs. 7 and 8), which coincides with maximum wind speed ranges from 8.8 to 11.1 m/s in November and December, and minimum values range from 3.6 to 5.7 m/s in January and February [35].

IV. Conclusions

The sulfur fluxes from the four sampling sites in the city of Esmeraldas show that industrial activities are related to their spatial distribution, mainly in the areas near the refinery, where the highest values are recorded (area 15 de Marzo). The distribution of sulfur fluxes close to the refinery is limited to a radius of 5 km. The climatic seasonality in the sampling sites reflects a change in the values of sulfur fluxes, this explains the high values in the dry season and low in the rainy season. The analysis of the wind through the four months of study shows that the highest values of wind speed were in November and December, and the values were decreased in the months of January and February. The wind direction reported in the four months of study was southwest. The use of passive samplers to determine sulfur fluxes was economically accessible and facilitates fieldwork activities, in addition they can be reused because the PVC material is very resistant to the local environmental conditions such as air temperature, relative humidity and precipitations. It is the first time that sulfur fluxes in Esmeraldas have been referenced. Research like these could also include studies about the quality of life of the population surrounding the Esmeraldas refinery.

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