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Radiocarbon Concentration Measurements in Tree Leaves near SOCOCIM (Rufisque, Senegal), A Cement Factory

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Abstract

Radiocarbon content in biogenic samples is widely used to study the variation of atmospheric CO_2 due to anthropogenic activities. A total of 20 samples of several types of tree leaves, were analyzed for this study. Sampling was carried out at the end of the rainy season in 2017 from the surrounding of the SOCOCIM cement factory in Rufisque town. Rufisque is located on the peninsula of Cape Verde, 25 km east of Dakar, where it is the «south gate» of the agglomeration. Reference samples of five different species were collected during the same period (2017) from a clean zone. The ^{14}C method was used for the determination of $\Delta^{14}C$ values. The data show that the ^{14}C concentration in the studied sites was significantly lower than the clean area, due to the release of anthropogenic CO_2. To estimate the Suess effect, the fossil fuel fraction was determined based on equations of mass balance for CO_2 concentration, stable isotopic composition of carbon, and ^{14}C concentration. The results show that selected locations are affected differently according to their distance from the factory and the wind direction.

Keywords

Radiocarbon Concentration, Fossil Fuel Fraction, Tree Leaves, Cement Factory

1. Introduction

Radiocarbon (^{14}C) is produced in the atmosphere by a reaction of neutrons with atmospheric ^{14}N that produces ^{14}C, which is rapidly oxidized into CO_2 and then exchanges with different carbon reservoirs. Natural processes such as solar activity, Earth's magnetic field, ocean circulation, and rates of exchange between carbon reservoirs all affect the ^{14}C content. Besides these natural variations, human activities also have an impact on atmospheric ^{14}C concentration. Two anthropogenic effects are recorded by atmospheric ^{14}C: first, the Suess effect, which is the addition of carbon dioxide by fossil fuel combustion; and secondly, the increase in ^{14}C concentration in the atmosphere because of atmospheric nuclear weapons testing [1]. Both anthropogenic factors occur on a global scale, however there are also local Suess effects due to local fossil-fuel sources. So, there are regional discrepancies that are related to the emission zone proximity as well as geographic location [2]. If we compare the global ^{14}C atmospheric record to regional or local signals, then it is possible to relate this to regional and local changes in human activities such as industrial activity, traffic, domestic use, and land use. [3] highlighted an example of traffic-derived CO_2 in the atmosphere of an urban forest. In this context, the ^{14}C method has been widely used during the last decades, in various applications such as archaeology [4], forensic studies [5], hydrology [6] [7], and geology, and has gained great interest in ecology and environmental studies [8] [9]. During photosynthesis, tree rings, leaves, and short-lived plants assimilate carbon from the air, and provide changes in atmospheric ^{14}C concentration. Due to high dead carbon emissions in industrialized and urban areas, ^{14}C concentrations are diluted [10] [11]. The determination of the ^{14}C content in atmospheric CO_2 or from biosphere materials makes it possible to estimate the excess CO_2 or the total emission of carbon dioxide of fossil origin [12]. This is based on the differences between radiocarbon concentration in a reference site supposed "clean area" and industrial or urban area. In Senegal we are interested in determining the local variations of ^{14}C concentration due to fossil fuel combustion caused by the different sources of pollution, such as the transport sector, energy stations, and industries. This work aims to calculate the pollution data obtained in the vicinity of a cement factory (SOCOCIM) situated in Rufisque (33˚37'54"N, 35˚26'70"E). In mining, quarrying, crushing, grinding, and calcining generate large amounts of pollutants, mainly CO_2 [13]. This cement factory located general the cement plant undertakes various processes such as in the town of Rufisque and is created in the 1948's (before independence) however with the expansion of the city the dwellings have moved closer to the site so this could represent a risk to the environment and therefore to the local population. To evaluate this potential pollution a reference site has been chosen in a rural Village of Ngazobil (14˚12'N, 16˚52'W) which is far away from the cement factory and should not be affected by the CO_2 emissions. Accelerator Mass Spectrometry (AMS) was used to quantify the ^{14}C concentration of the sample material. Measurements have been performed at the ETH Zurich Laboratory of Ion Beam Physics (Switzerland) using a MICADAS instrument. The radiocarbon isotopic ratio ($\Delta^{14}C$) and $\delta^{13}C$ were determined in 20 samples of several species from tree leaves collected at the two sites. Estimation of the fossil fuel fraction was carried out based on equations of mass balance for CO_2 concentration, stable isotopic composition of carbon, and ^{14}C concentration [14].

2. Materials and Methods

2.1. Samples

For this study a total of 20 samples were collected around the cement factory of Rufisque (**Figure 1**). In the Colobane district, leaves from *Azadirachta indica*, Albicia le bec and *Calotropis procera* were collected. Leaves from *Prosopis chilensis* were collected opposite the factory, 50 m from the beach. In a salad field in front of the plant, leaves from *Prosopis chilensis*, peltiferum, *Arkin sonia*, cordial, Khay, Lecenia were collected. In a distance of only 10 m from the cement factory samples of Pocéa, aubergine and Goumelia leaves were collected.

These species were chosen because they are widely grown in this region. Thus, the data obtained from this study can be compared to other $\Delta^{14}C$ determined in different zones in the region. All samples were collected in the same period, at the end of the vegetation season in 2017, to avoid possible seasonal variations of ^{14}C concentration [15]. As reference, leaves from Ngazobil (**Figure 1**) a site 101.82 km away from the cement factory located in the municipality of Joal-Fadiouth, in the department of Mbour have been chosen. Five tree leaves samples (Kaya Senegalaisis, *Ziziphus mucronata*, Albizia, *Terminalia catapa*, *Faderbia albidia*) were collected from this clean zone in the same sampling period.

2.2. Sampling Site

The climate of the study sites is characterized by the maritime trade winds from the Azores high, from north to north-east, it is constantly humid in winter. The sea trade winds are constantly wet, cool, or even cold in winter. Also, the 'harmattan, of direction East dominant, finishing branch of the continental trade-wind Sahelian, is characterized by a great drought linked to its long continental course, at last the monsoon, comes from the trade-wind resulting from the Anticyclone of Saint Helena in the South Atlantic. It enters the country during the summer in a south-east - north-west direction. It is marked by a low thermal amplitude, but with temperatures generally higher than those of the maritime trade-winds. The rains that fall come from weakened grain lines. They are very weakened. They are very localized in time, usually occur from July to October. However the times when they start and stop are very fluctuating [16] [17].

Samples were collected from rural areas distributed in the vicinity of a cement factory. The selected sites are distinguished by low population density and agricultural land. They are relatively far from large urban cities, about 25 km from the capital Dakar. The Suess effect could thus be attributed to the potential influence of the cement factory. The first location is situated to the west of the cement factory, while the others are distributed to the north and northeast. **Figure 1** presents a map of Senegal showing the location of the studied region and the selected reference zones. **Table 1** lists the coordinates of sampling locations, including reference areas, as well as their distance from the factory.

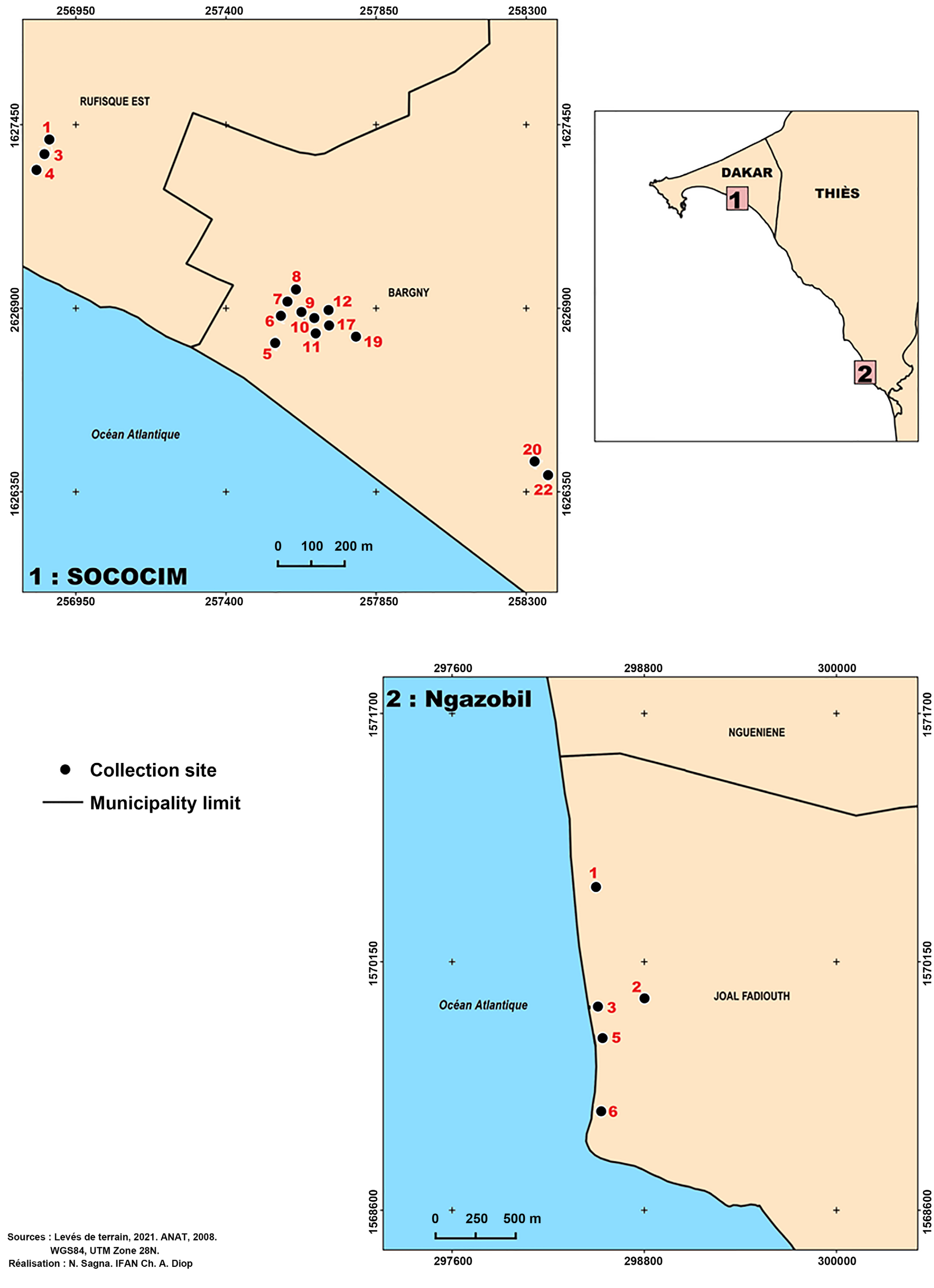

Figure 1. Map of Senegal with the sampling sites indicated (1-sococim, represents the cement plant, 2-Ngazobil is the reference site. The 3rd figure represents the 2 sampling sites in the map of Senegal).

Table 1. Locations of the sampling site.

Sample Code	Species/Family	Latitude	Longitude	Distance from cement factory
SOCO01	*Albizia lebbeck*/Fabaceae	N 14˚42'31.8"	WO 17˚15'30.0"	60 m
SOCO03	*Moringa oleifera*/Moringaceae	N 14˚42'33.8"	WO 17˚15'29.3"	60 m
SOCO04	*Calotropis procera*/Apocynaceae	N 14˚42'33.8"	WO 17˚15'29.3"	60 m
SOCO05	*Prosopis chilensis*/Fabaceae	N 14˚42'16.1"	WO 17˚15'07.9"	50 m
SOCO06	*Prosopis chilensis*/Fabaceae	N 14˚42'17.9"	WO 17˚15'05.8"	50 m
SOCO07	*Peltophorum africanum*/Fabaceae	N 14˚42'18.3"	WO 17˚15'05.4"	50 m
SOCO08	*Parkinsonia aculeata* L./Fabaceae	N 14˚42'18.3"	WO 17˚15'05.4"	50 m
SOCO09	*Cordia rothii* Roem. & Schult./Boraginaceae	N 14˚42'16.1"	WO 17˚15'02.8"	30 m
SOCO10	KHAYA SENEGALENSIS/Meliaceae	N 14˚42'16.1"	WO 17˚15'02.8"	50 m
SOCO11	*Leucaena glauca* Benth/Fabaceae	N 14˚42'16.1"	WO 17˚15'02.8"	30 m
SOCO12	*Prosopis chilensis*/Fabaceae	N 14˚42'16.1"	WO 17˚15'02.8"	30 m
SOCO17	poacea/Poacea	N 14˚42'17.4"	WO 17˚15'00.6"	10 m
SOCO19	*Solanum melongena*/Solanaceae	N 14˚42'15.6"	WO 17˚**14**'58.5"	10 m
SOCO20	*Gmelina arborea*/Lamiaceae	N 14˚42'03.0"	WO 17˚**14**'39.5"	10 m
SOCO22	*Bougainvillea spectabilis*/Nyctaginaceae	N 14˚42'03.0"	WO 17˚**14**'39.5"	10 m
Reference sample				
Nga01	*Khaya senegalensis*/Meliaceae	N 14˚47'03.0"	WO 17˚02'44.7"	101.2 km
Nga02	*Ziziphus mucronata*/Rhamnaceae	N 14˚47'39.9"	WO 17˚02'49.8"	101.2 km
Nga03	*Albizia lebbeck*/Fabaceae	N 14˚47'39.9"	WO 17˚02'49.8"	101.2 km
Nga05	*Terminalia capata*/Combretaceae	N 14˚47'32.9"	WO 17˚02'49.8"	101.2 km
Nga06	*Faidherbia albida*/Fabaceae	N 14˚47'32.9"	WO 17˚02'49.8"	101.2 km

2.3. Chemical Treatment

Sample material was purified using an acid-base-acid (ABA) protocol. At first the samples were treated with a 0.5 M HCl solution at 60˚C for about 2 hours. Following a washing step in deionized water, they were introduced into 0.1M NaOH solution at 60˚C for one hour. After washing again, the materials were introduced into a 0.5 M HCl solution at 60˚C for one and a half hour. Finally, the cleaned materials were washed and dried. From the purified materials a subsample containing approximately 1 mg of carbon was taken, packed in an Al capsule, and introduced into the automated combustion and graphitization system AGE [18], where a catalytic reduction on 4 mg of iron powder of the produced CO_2 gas with hydrogen gas took place at 650˚C. Finally, the graphite produced was pressed into Al cathodes which can be introduced into the ion source of the ETHZ AMS instrument.

2.4. Measurements and Calculations

Analysis of samples has been conducted in routine measurements campaigns at the LIPMicadas system at the Laboratory of Ion Beam Physics at ETH Zurich (Swiss Federal Institute of Technology) [19].

Two independent measurements were made for each sample, the first on September 5th, 2021, and the second on October 13th, 2021. For each sample, individual graphite's were prepared using the precleaned material of original sample as described above. The consecutive graphitization of the purified materials enabled preparation of individual cathodes for the AMS analysis. The AMS measurement follows the standard procedure at ETH [20]. SRM 4990C (Oxa II) reference material was used for normalization. Phthalic acid and brown coal samples were used as blank materials. Blank materials were processed in the same way as samples to be analyzed. Thus, eventual contamination during sample preparation can be controlled. During the measurements, the blank materials resulted in less than 0.2% fraction modern which is equivalent to 50,000 yrs BP. In both measurement runs, final uncertainties of less than 3‰ (<24 yrs) could be reached and the results obtained are nice agreement. By combining both data sets, average values are calculated and final uncertainties of 2‰ (16 yrs) can be stated.

The conventional radiocarbon age is expressed by the formula above according to [21]:

$$\mathrm{Age}(\mathrm{BP}) = 8033 \times \ln\left(\frac{1}{1+\frac{\Delta^{14}\mathrm{C}}{1000}}\right). \tag{1}$$

From this equation $\Delta^{14}C$ values can be deduced

$$\Delta^{14}\mathrm{C}\ (‰) = 1000 \times \left(\exp\left(-\frac{\mathrm{Age}}{8033}\right) - 1\right) \tag{2}$$

The $\delta^{13}C$ values as given in **Table 2** are the result of the AMS measurements. They are representative for fractionation effects which may occur during sample preparation and measurement procedure and are used to extrapolate these fractionation effects on the measured $\Delta^{14}C$ (‰) (calculated from Equation (2)) and are the basis of the applied fractionation correction. They cannot be used to assess the $\delta^{13}C$ of the original sample material.

2.5. Estimation of Fossil Fuel Component

To estimate the local Suess effect in the studied area, the fraction F(%) of fossil-fuel derived CO_2 that was incorporated by the plant material can be calculated according to Equation (3).

$$F = \frac{\left(\Delta^{14}\mathrm{C}_{\mathrm{ref}} - \Delta^{14}\mathrm{C}_{\mathrm{meas}}\right)}{\left(\Delta^{14}\mathrm{C}_{\mathrm{ref}} - \Delta^{14}\mathrm{C}_{\mathrm{foss}}\right)} \tag{3}$$

A value of F = 10‰ indicates that 1% of the carbon plant material originates from the CO_2 emission of the cement factory. We use $\Delta^{14}C_{foss}$ = −1000‰, as fossil fuel CO_2 is totally depleted of ^{14}C ([22]), $\Delta^{14}C_{ref}$ is the average radiocarbon content observed at the reference site.

Table 2. $\delta^{13}C$ (‰) and $\Delta^{14}C$ (‰) values for different types of tree leave samples.

Sample Number	Sample Code	Species/Family	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)
01	SOCO1	*Albizia lebbeck*/Fabaceae	−26.85 ± 0.05	12.0 ± 2.0
03	SOCO3	*Moringa oleifera*/Moringaceae	−30.13 ± 0.05	15.3 ± 2.0
04	SOCO4	*Calotropis procera*/Apocynaceae	−29.37 ± 0.05	11.9 ± 2.0
05	SOCO5	*Prosopis chilensis*/Fabaceae	−25.18 ± 0.05	1.6 ± 2.0
06	SOCO6	*Prosopis chilensis*/Fabaceae	−23.03 ± 0.05	12.1 ± 2.0
07	SOCO7	*Peltophorum africanum*/Fabaceae	−20.76 ± 0.05	13.4 ± 2.0
08	SOCO8	*Parkinsonia aculeata* L./Fabaceae	−23.59 ± 0.05	12.7 ± 2.0
09	SOCO09	*Cordia rothii* Roem. & Schult./Boraginaceae	−22.81 ± 0.05	9.9 ± 2.0
10	SOCO10	Khaya Senegalensis/Meliaceae	−27.24 ± 0.05	12.5 ± 2.0
11	SOCO11	*Leucaena glauca* Benth/Fabaceae	−23.98 ± 0.05	8.9 ± 2.0
12	SOCO12	*Prosopis chilensis*/Fabaceae	−24.09 ± 0.05	8.0 ± 2.0
17	SOCO17	poacea/Poacea	−23.76 ± 0.05	12.6 ± 2.0
19	SOCO19	*Solanum melongena*/Solanaceae	−27.00 ± 0.05	12.2 ± 2.0
20	SOCO20	*Gmelina arborea*/Lamiaceae	−24.21 ± 0.05	6,0 ± 2.0
22	SOCO22	*Bougainvillea spectabilis*/Nyctaginaceae	−24.39 ± 0.05	5.0 ± 2.0
Reference Samples				
01	Nga01	*Khaya senegalensis*/Meliaceae	−26.08 ± 0.05	15.0 ± 2.0
02	Nga02	*Ziziphus mucronata*/Rhamnaceae	−26.46 ± 0.05	16.7 ± 2.0
03	Nga03	*Albizia lebbeck*/Fabaceae	−23.62 ± 0.05	14.1 ± 2.0
05	Nga05	*Terminalia capata*/Combretaceae	−21.79 ± 0.05	17.9 ± 2.0
06	Nga06	*Faidherbia albida*/Fabaceae	−25.79 ± 0.04	15.4 ± 2.0

3. Results and Discussion

Sampling was done at two sites. The first is the reference site or clean air site which is a village called Ngazobil (N 14˚47'39.9"; Wo 17˚02'49.8"). Ngazobil is located at the Atlantic Ocean coastline, surrounded by sea waters that often cause winds, and the local air conditions are mostly dominated by seabreeze. The only main activity is fishing, so no industrial complexes and traffic could be responsible for any increase in local fossil CO_2 release. Thus, we can regard Ngazobil as free of urban pollution. The $\Delta^{14}C$ values of the 5 samples (Nga01, Nga03, Nga05, and Nga06) are very consistent and scatter within a 3.8‰ range, only. This justifies calculating the average value of $\Delta^{14}C_{ref}$ = 15.89 ± 0.65‰ and using it as reference to calculate the F value of urban pollution at the Rufisque site. It is lower than the value for atmospheric $\Delta^{14}CO_2$ (51‰) of 2012 as published by [23]. By extrapolating the trend in the Hua data to 2017, a global atmospheric $\Delta^{14}CO_2$ value would result in the range of ~20‰. This is still higher than the Ngazobil average value. However, more recent $\Delta^{14}CO_2$ data from Switzerland observed from tree leaves collected between 2012 and 2016, would suggest a $\Delta^{14}CO_2$ value of ~15‰, based on the 2016 result and an average annual decline of 4.4‰ (Synal pers. communication). This is in nice agreement with our reference value.

All $\Delta^{14}CO_2$ data at the Rufisque site are lower than the Ngazobil average value (**Figure 2**). We observe $\Delta^{14}CO_2$ values between 1.6‰ and 15.3‰. This clearly indicates the impact of the local cement production and the lower the $\Delta^{14}CO_2$ is, the higher is the impact of fossil CO_2 releases. In the district of Colobane located 60 m from the cement factory we observe $\Delta^{14}C$ values of 11.96‰, 15.31‰, and 11.88‰, respectively. Even if these relatively high values remain lower than those obtained at the reference site. The lowest $\Delta^{14}C$ (1.57‰) value was observed at a location within a approx. 50 m range from the leaves of a prosopis chilensis tree. In a salad field at the same distance to the factory, samples SOCO06, SOCO07, SOCO08 and SOCO10 gave the $\Delta^{14}C$ values of 12.00‰, 13.38‰, 12.65‰, 9.86‰ and 12.46‰ respectively. Although these ^{14}C concentrations are relatively close to the reference value, the impact of the fossil CO_2 is significant. On the other hand, four samples (SOCO17, SOCO19, SOCO20 and SOCO22) were taken at a distance of 10m from the factory. They fall into two distinct groups, giving values of $\Delta^{14}C$ 12.63‰, 12.19‰ and 5.99‰, 5.02‰, respectively. The first group shows a week, the second a rather strong impact from the CO_2 emissions. By using Equation (3), these results are converted into fraction fossil fuels F(%.) as shown in **Table 3** demonstrating the degree of the Suess effect for each location

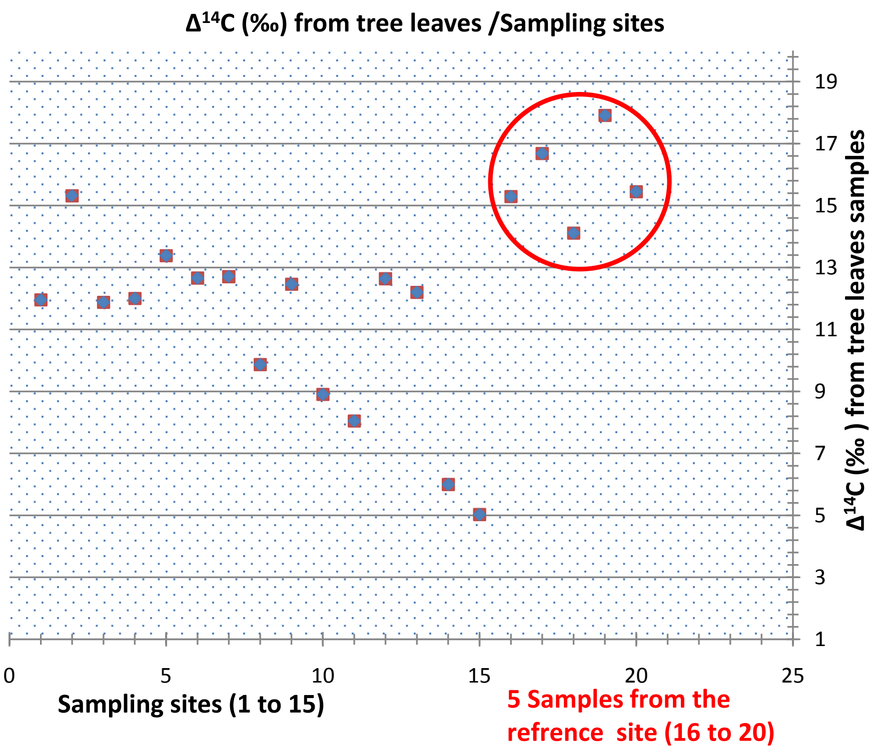

Figure 2. Radiocarbon content $\Delta^{14}C$ in different types of tree leaves, collected in 2017 from 15 locations of the cement factory compared with 05 samples from the reference area.

Table 3. Fossil fuel fractions *F*(%) in the studied areas derived from ^{14}C content in tree leaves.

Sample Code	Species	*F*(‰)
SOCO1	*Albizia lebbeck*/Fabaceae	3.9
SOCO3	*Moringa oleifera*/Moringaceae	0.6
SOCO4	*Calotropis procera*/Apocynaceae	4.0
SOCO5	*Prosopis chilensis*/Fabaceae	14.1
SOCO6	*Prosopis chilensis*/Fabaceae	3.8
SOCO7	*Peltophorum africanum*/Fabaceae	2.5
SOCO8	*Parkinsonia aculeata* L./Fabaceae	3.2
SOCO09	*Cordia rothii* Roem. & Schult./Boraginaceae	5.9
SOCO10	KHAYA SENEGALENSIS/Meliaceae	3.4
SOCO11	*Leucaena glauca* Benth/Fabaceae	6.9
SOCO12	*Prosopis chilensis*/Fabaceae	7.7
SOCO17	poacea/Poacea	3.2
SOCO19	*Solanum melongena*/Solanaceae	3.6
SOCO20	*Gmelina arborea*/Lamiaceae	9.7
SOCO22	*Bougainvillea spectabilis*/Nyctaginaceae	10.7

due to anthropogenic $^{14}CO_2$ emissions from the cement factory. In general, there is no clear trend between distance from the factory and the observed ^{14}C depletion a week tendency indicating higher impact at lower distances to the factory may be suggested by the data set. However, very local effect as observed at sampling points SOCO20/22 and SOCO05 may overrule a general tendency. It is remarkable that for these samples between 1% - 1.5% of the organic carbon has originated from the fossil fuel emissions of the cement factory.

So far, sampling was carried out on a single season (2017). Confirmation of the values over a longer time period would be helpful to draw more solid conclusions. For an assessment of the Suess effect, these values should be compared with those obtained at points around the alleged source of pollution.

4. Conclusion

This study falls within the general framework of the determination of air pollution due to fossil CO_2 by the various cement factory installed in Senegal. The SOCOCIM cement factory, which is the oldest in Senegal, was the subject of a collection of samples to determine the excess CO_2 due to the anthropogenic effect. A dilution of the ^{14}C concentration was determined following the contribution of the fossil CO_2 component emitted by the cement factory. The depletion of ^{14}C in the studied areas can reach an F-value of up to 1.5% of fossil carbon in the biomass of samples under investigation. This could be attributed to the emissions of cement factory that releases large amounts of CO_2, which could reach the selected sampling sites with the south-east - north-west direction wind that prevails most of the year. Future studies and measurements will be carried out in the Department of Rufisque to determine the effect of Suess in other nearby villages and observe any change in the atmosphere of the concentration of ^{14}C over time.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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