GEOCHRONOMETRIA Vol. 24, pp 59-61, 2005 – *Journal on Methods and Applications of Absolute Chronology*

THE CONCENTRATION AND δ^{13}C OF CO_2 IN THE URBAN ATMOSPHERE OF TEL-AVIV

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Key words:
URBAN POLLUTION,
ATMOSPHERIC CO_2, ^{13}C
IN URBAN AREA

Abstract: Carbon dioxide was extracted from the ambient air at a main intersection in down town Tel-Aviv during the course of one winter day. The volume and stable carbon isotopic composition of the urban atmosphere is temporally quite variable (rising to as much as 590 ppm) and strongly affected by automobile emissions which are depleted in ^{13}C.

1. INTRODUCTION

The impact of the "Suess Effect" (Suess, 1955) on the global atmosphere has increased dramatically in the 20th century. Measurements carried out at Maona Loa, Hawaii have monitored a rise in atmospheric CO_2 from 316 ppm in 1959 to 373 ppm in 2002 (Keeling and Whorf, 2004), with a concomitant depletion of δ^{13}C. The δ^{13}C of the atmospheric CO_2 has presently decreased to approximately -8‰ from the pre-industrial value of approximately -6‰ (Wang *et al.*, 1998). The rise of the concentration in the atmosphere closely parallels the emissions history of fossil fuels, which are depleted in carbon isotopes - the "Suess Effect" (Suess, 1955), and land use changes (Schimel *et al.*, 1994). The monitoring of the atmospheric concentration and isotopic composition of CO_2 thus resembles studies of air pollution radiocarbon concentration in recent wood (e.g. Rakowski *et al.*, 2004), which is very important for the global warming controversy. One obvious source for the increase in CO_2 is urban contributions. Studies of the land-atmosphere exchange in cities are now being conducted (Pataki *et al.*, in press). Clark-Thorne and Yapp (2003) have related low δ^{13}C values coupled with elevated concentration of CO_2 (between 369 and 415 ppm in a relatively open area and 392 to 475 ppm near a heavy traffic highway) in urban Dallas as largely due to fuel emissions.

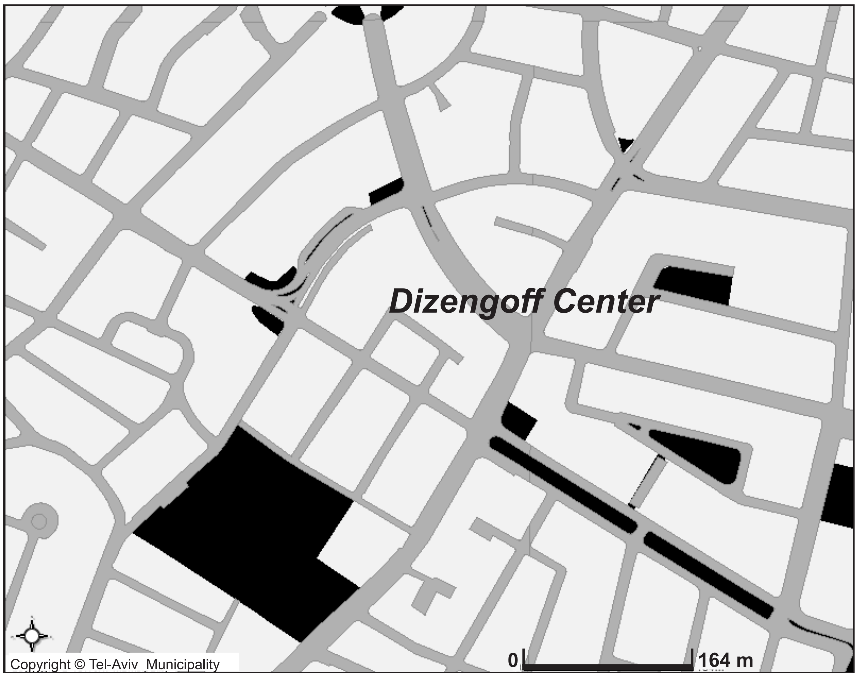

***Fig 1.** The collection site in Tel-Aviv.*

We present the results of monitoring of the air during the course of a typical working day in metropolitan Tel-Aviv situated on the coastal plain near the Mediterranean Sea. The sampling was carried out in the commercial downtown area at the junction of the Dizengoff Center mall (**Fig. 1**). There we sampled air when the road lights changed from red to green and noted the number of vehicles that crossed the junction.

2. METHODS

The samples were collected on the site on January 20, 2004 between 6:00 and 18:30, during the green light phases. The details of the sampling and the number of vehicles that passed through the junction during the sampling are given in **Table 1**. Sample 3 is from an enclosed overpass, approximately 10m above the road.

To measure the concentration of CO_2 in the air (in ppm) we used highly evacuated calibrated glass vessels equipped with valves. We collected the air by opening the valve of the vessel at a height of about a meter and a half above the sidewalk and between one and two meters from the curb. After waiting a short time for equilibration with the atmosphere the vessel was resealed. In the lab we connected each vessel to a vacuum system, which was then evacuated up to its valve. We then opened the valve and slowly pumped the air out of the vessel. We first froze the humidity with dry ice ethanol mixture and then the CO_2 with liquid N_2. We measured the volume of the CO_2 in a calibrated volume in the vacuum system. The ^{13}C was measured by mass spectrometer on the collected CO_2. The laboratory work was done in the Department of Environmental Sciences and Energy Research and in the Kimmel Center for Archaeological Sciences – both in the Weizmann Institute of Science.

3. RESULTS

Table 1 shows the results of our sampling on January 20, 2004. The ppm was calculated simply as the ratio of the volume of CO_2 that we collected to the calibrated volume of the vessel. The CO_2 concentration ranged from 386 ppm to 590 ppm. The associated $\delta^{13}C$ values ranged from -10.2 to -14.5‰. With the exception of the Sample 2 (**Table 1**), which exhibited the lowest concentration, all of these values exceed the concentrations and are considerably depleted compared to the control values obtained for clean modern air of 385 ppm of CO_2 and $\delta^{13}C$ = -8.5‰. Yet, as the Sample 2 was associated with a considerably depleted $\delta^{13}C$ value of -11.3‰, there was concern that this represented an incomplete volumetric extraction. Thus, a second sampling was carried out on February 17, 2004, with the same sampling vessel at the same time of the day when the same number of vehicles passed by. This time a concentration of 452 ppm of CO_2 was measured. It is of interest to note that Sample 3 was collected in an enclosed space considerably above the road and presumably sealed off from the outside air. Though the concentration here is less than the ambient outside air, it is obvious that it is closer to that of the outside air than what can be taken to be typical "clean air".

4. DISCUSSION

All of the air samples taken throughout the day contain carbon dioxide concentrations that are much greater than representative of clean air. Likewise the carbon isotopic composition is considerably depleted compared to the clean air values at the time of sampling. There is a coefficient of correlation of 0.62 between the concentration of CO_2 in the air and the number of vehicles that passed the junction at the time of sampling. This suggests that car emissions are responsible for the increase in the carbon dioxide of the urban atmosphere. This correlation is considerably strengthened considering that the $\delta^{13}C$ values of automobile fuels (-18‰ to -34‰; Clark-Thorne and Yapp, 2003) are considerably depleted compared to the value of atmospheric CO_2. The values found here are in the lower range of the isotopic composition of air sampled near a forest floor (-9 to -14‰; Farquahar *et al.*, 1989). Obviously, this explanation can be disregarded for our study site where the number of trees is very low.

There is a clear indication that urban transportation is the source of significant CO_2 additions that greatly alter the carbon isotopic composition of CO_2 of urban air. In urban Dallas the CO_2 was found to range between 392 and 475 ppmV (Clark-Thorne and Yapp, 2003). The values in Tel-Aviv exceed the maximum values measured there. The concentrations of CO_2 appear to remain above "normal" background values throughout the day. The concentrations of other, unmeasured, potential contaminants derived from automobile exhaust such as CO, particulates, etc. should also be investigated for elevated concentrations in urban areas.

***Table 1**. Results of the sampling and measurements of urban air in Tel-Aviv.*

Sample No.	Time	Vehicles	Air volume (ml)	CO_2 (ml)	CO_2 (ppm)	$\delta^{13}C$(‰)
1	6:00	2	994.0	0.45	448.7	-11.1
2	10:00	13	2072.6	0.80	386.0	-11.3
3	10:00		2246.4	0.94	417.3	-10.2
4	13:30	39	2051.5	1.21	589.8	-14.5
5	15:30	51	2252.4	1.07	475.0	-12.4
6	18:30	60	1054.5	0.54	508.3	-11.5

In column 3 "Vehicles" mean the number of vehicles that passed the junction during the green light phase.

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