Carbon isotope composition (^{14}C and ^{13}C) of the atmospheric CO_2 at several locations in Croatia

Ines Krajcar Bronić[1], Damir Borković[1], Emma Hess[2], Tjaša Kanduč[3], Jadranka Barešić[1], Andreja Sironić[1]

[1]Department of Experimental Physics, Ruđer Bošković Institute, Zagreb, Croatia
[2]Department of Physics (student), University of Rijeka, Rijeka, Croatia
[3]Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia

krajcar@irb.hr

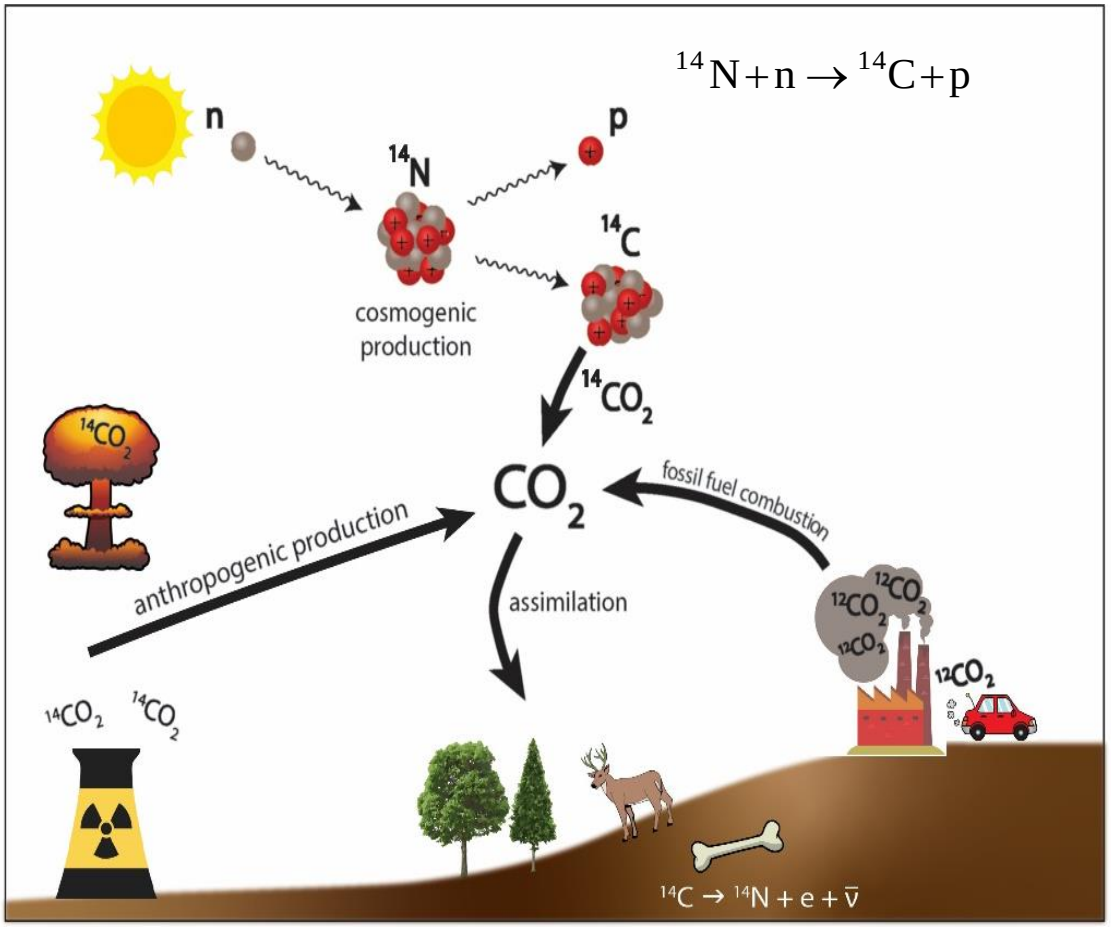
15th INTERNATIONAL SYMPOSIUM ON RADIATION PHYSICS (ISRP-15)
Kuala Lumpur – Malaysia, 6 – 10 December 2021

^{14}C

Radiocarbon is of both cosmogenic and anthropogenic origin.

- **Cosmogenic** or natural radiocarbon is formed in the atmosphere in nuclear reactions
- **Anthropogenic** carbon is produced in (1) various nuclear facilities and (2) during atmospheric nuclear and thermonuclear bomb testing.
- Anthropogenic source of carbon (^{14}C-free) – use of fossil fuels for energy production

Naturally produced CO_2 and that formed by fossil fuel combustion are characterized by different content of the stable isotope ^{13}C ($\delta^{13}C$ values) in addition to their different ^{14}C content.



Krajcar Bronić, I. et al. (2020) Properties, behavior and potential health effects of 14C..

Aim

- The carbon isotope composition (^{13}C and ^{14}C) of the atmospheric CO_2 can indicate sources of CO_2 at each location, if it is far from nuclear facilities.

- ^{14}C activity in the atmospheric CO_2 in Zagreb, Croatia, has been monitored since 1985.

- Recently we have started monitoring carbon isotope composition at several other locations in Croatia (city of Rijeka and rural areas around Zagreb and Rijeka)

Aim: to determine influence of fossil fuel combustion on atmospheric ^{14}C activity and $\delta^{13}C$ values at different locations

Hypothesis: urban sites are affected by fossil fuel uses, which is reflected in the carbon isotope composition of atmospheric CO_2

Sampling sites

Monitoring of ^{14}C activity concentration in monthly atmospheric samples of CO_2 at **Zagreb (Croatia)** has been performed since 1985, regularly since 1994 .

Characteristic of sampling locations

location	type	Lat.	Long.	Alt. m a.s.l.	T annual mean (°C)	P (mm)
Zagreb-RBI	urban	45° 49´	15° 58´	165	1986-1995 11.2 ± 0.7* 1996-2006 12.1 ± 0.8 2012-2018 13.5 ± 0.4	880
Cvetković	Rural / clean	45° 39´	15° 39´	90		
Rijeka	Urban	45° 20´	14° 26´	85	13.8	1530
Gornje Jelenje	Rural + road	45° 23´	14° 28´	300	12	1700
Parg	Rural / clean	45° 35´	14° 37´	840	7.2	1840

* Krajcar Bronić et al., *Water*-12-00226

Three sampling methods

a) **Static** absorption of atmospheric CO_2 on NaOH
b) **Dynamic** absorption of atmospheric CO_2, pumping air thought NaOH solution. Constant temperature and air flow maintained.
c) **Spot** atmospheric CO_2 sampling; air collected in „bags”

integral sample - represents average value over the period and place at which the sample is taken;

spot sample - a discrete sample representative at the time and place at which the sample is taken;

Two measurement techniques:

LSC-B – Liquid Scintillation Counting, benzene synthesis

AMS – Accelerator Mass Spectrometry

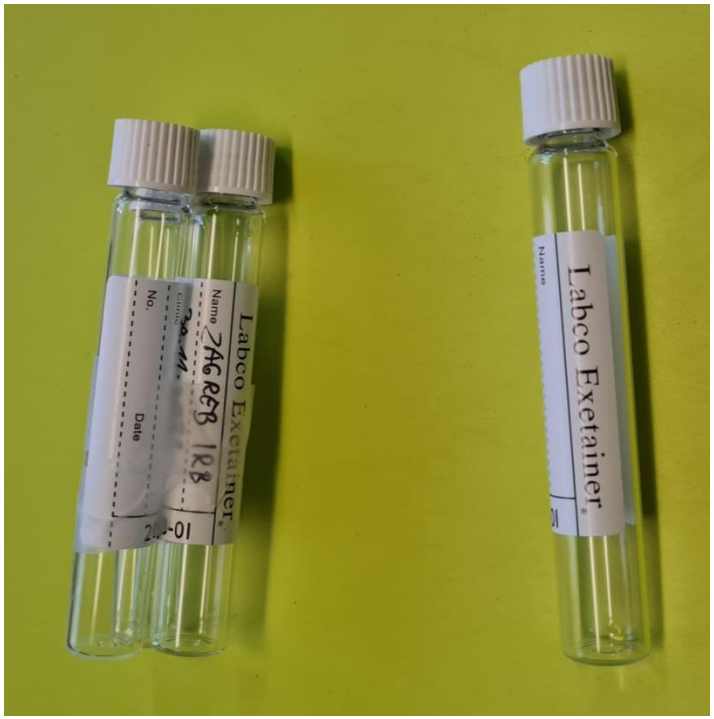
LSC Quantulus 1220

AMS at CAIS, Univ. Georgia, Athens, GA, USA

Comparison of methods

Sampling method	Period	Measurement method	$\delta^{13}C$	Comment
Static	Integral	LSC & AMS	No	Simple, can be performed at remote sites
Dynamic	Integral	LSC & AMS	Yes	Adjustable flow rate and temperature
Spot	Discrete	AMS	Yes	discrete sample

Sampling atmospheric CO_2 for $\delta^{13}C$ determination



Measurement
IRMS Europa Scientific 20-20
Continuous flow IRMS ANCA-TG preparation module
J. Stefan Institute, Ljubljana, Slovenia
(Tjaša Kanduč)

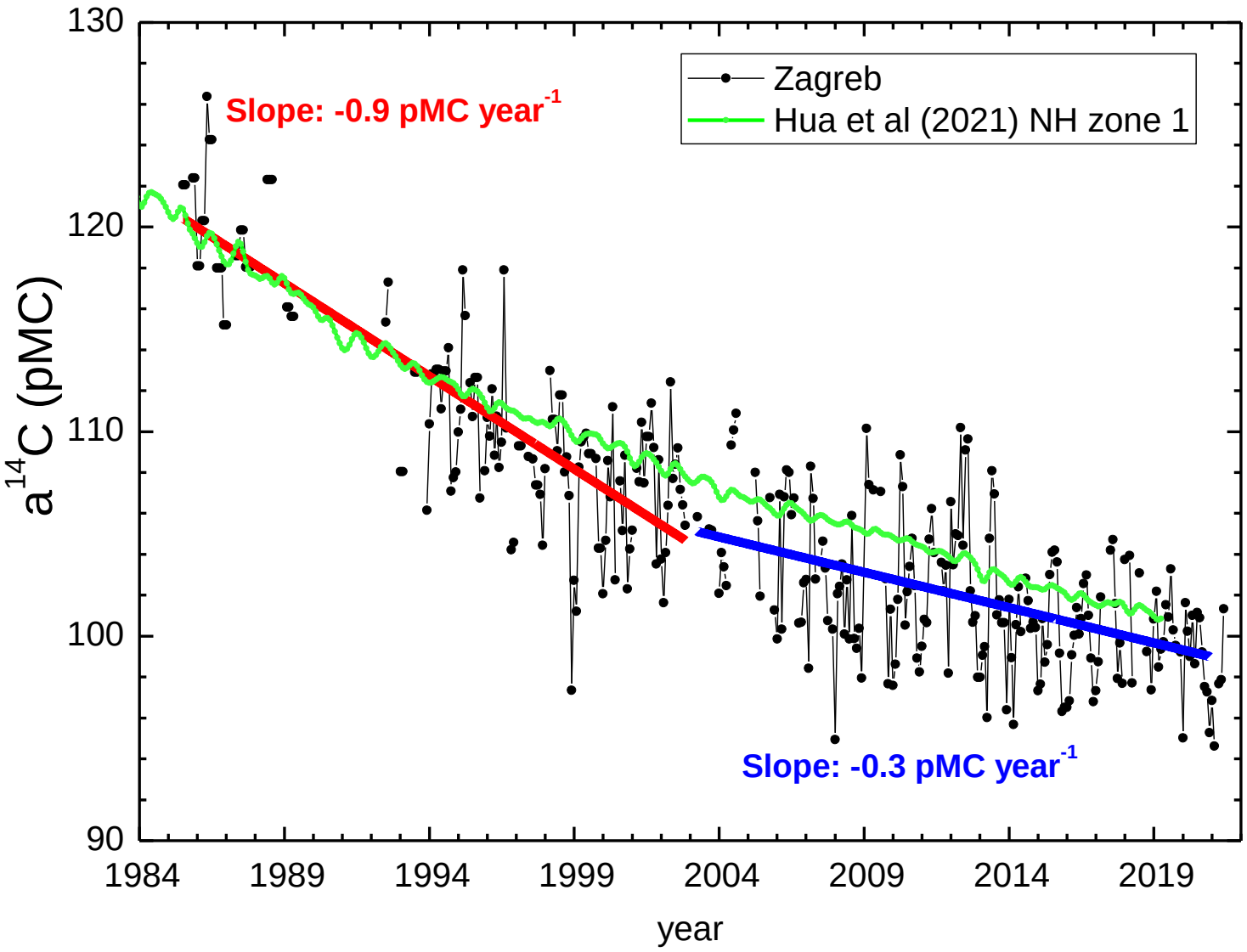
Comparison of measurement techniques

Location	Period	Sampling method	$a^{14}C$ (pMC) LSC-B	$a^{14}C$ (pMC) AMS	$\delta^{13}C$ (‰)
Zagreb	3/2020	Static	100.23 ± 0.69	100.15 ± 0.27	-28.06
	8/2020	Static	100.90 ± 0.58	100.57 ± 0.28	-24.46
	10/2020	Static	97.52 ± 0.61	98.67 ± 0.27	-24.48
Cvetković	2/2020	Static	100.03 ± 0.70	101.01 ± 0.27	-29.36
	8/2020	Static	101.25 ± 0.60	101.10 ± 0.28	-23.41
	10/2020	Static	100.37 ± 0.82	100.20 ± 0.27	-25.84
	11/2020	Static	99.79 ± 0.48	99.59 ± 0.29	-25.44
Rijeka	2/2021	Static	97.48 ± 0.82	98.09 ± 0.27	-25.05
Parg	2/2021	Static	100.92 ± 0.71	100.30 ± 0.27	-26.25
G. Jelenje	2/2021	Static	100.17 ± 0.68	100.28 ± 0.27	-26.32

Comparison of sampling techniques

static		$a^{14}C$ (pMC)	spot	$a^{14}C$ (pMC)	dynamic	$a^{14}C$ (pMC)
5/2020	Zagreb	101.02 ± 0.65	26.5.2020.	101.19 ± 0.27		
10/2020		97.52 ± 0.61	13.10.2020.	99.48 ± 0.28		
1/2021		96.85 ± 0.61			4.1.-1.2.	97.70 ± 0.26
					4.1.-15.1	97.97 ± 0.26
					15.1.-1.2.	96.97 ± 0.27
3/2021			4.3.2021.	99.91 ± 0.27		
4/2021		97.66 ± 0.61	2.4.2021.	99.24 ± 0.27	1.4.-30.4.	98.99 ± 0.27
					1.4.-15.4.	98.96 ± 0.28
					15.4.-30.4.	99.12 ± 0.27
5/2021		97.86 ± 0.43	3.5.2021.	99.66 ± 0.27		
12/2020	Cvetković	99.13 ± 0.71	31.12.2020.	99.05 ± 0.27		
4/2021 C		98.47 ± 0.64	2.4.2021.	98.18 ± 0.30		
5/2021 C		99.21 ± 0.79	3.5.2021.	99.71 ± 0.27		

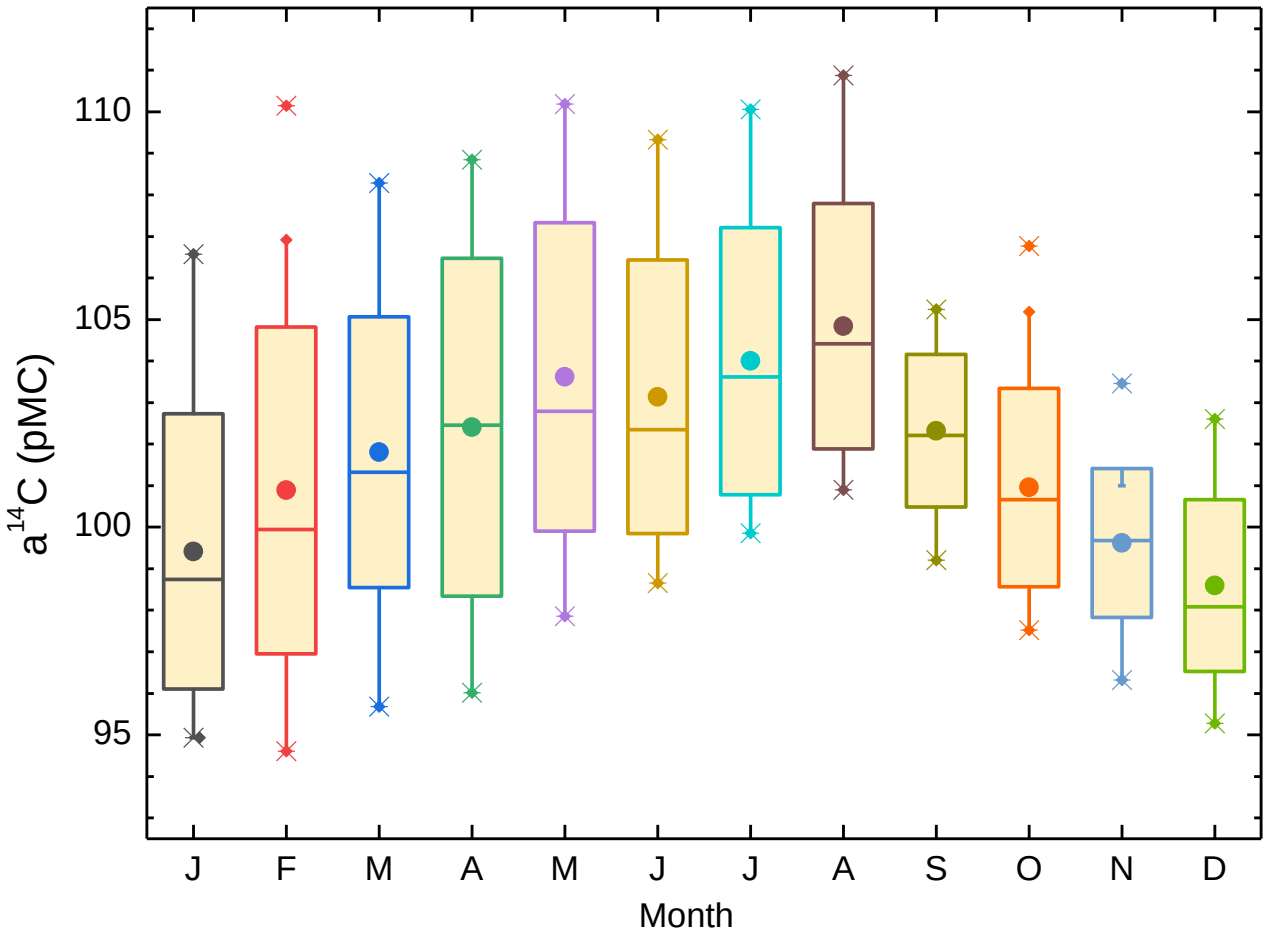
Zagreb – long term ^{14}C data



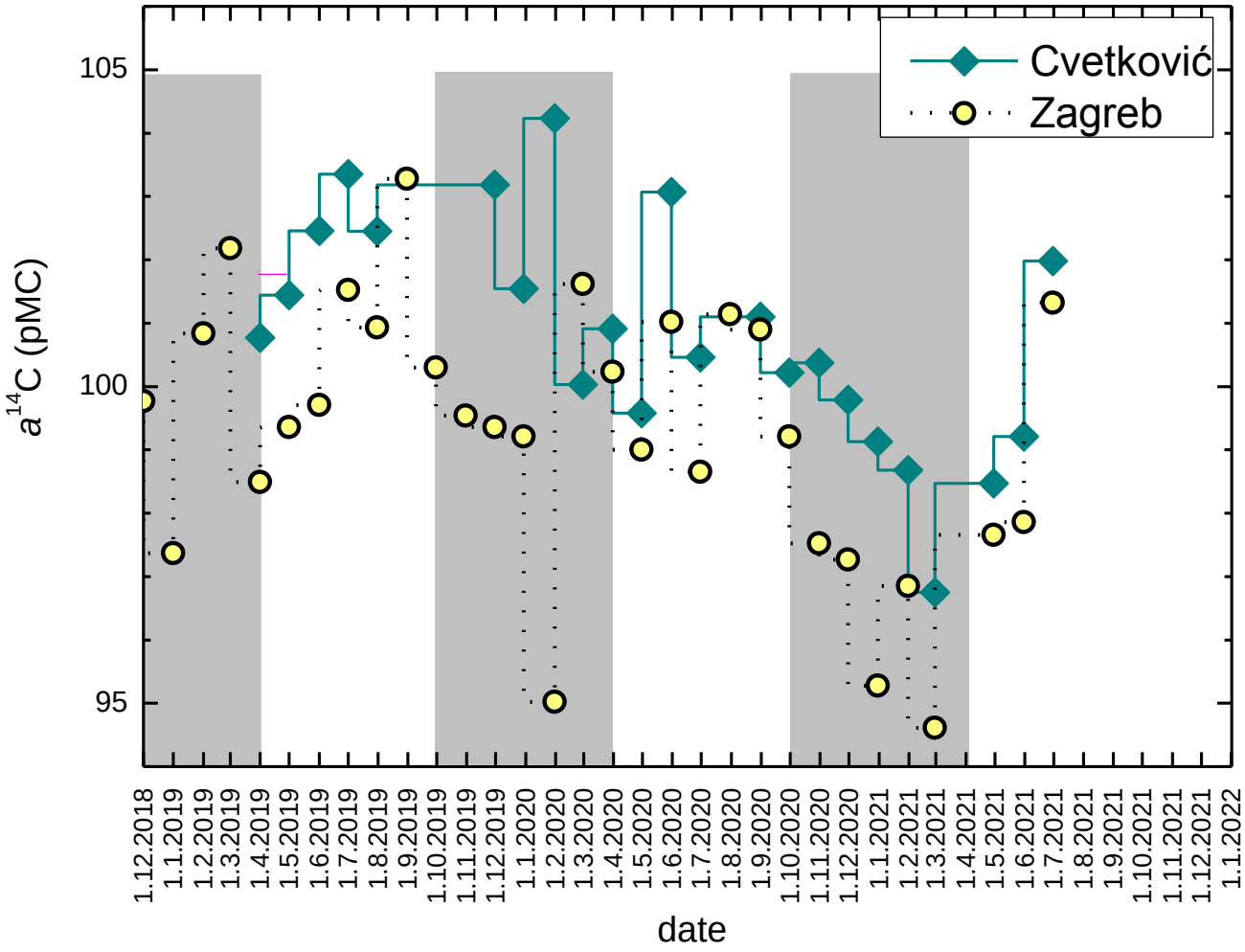
^{14}C activity decreases: **-0.9 pMC per year** 1985 – 2003

-0.3 pMC per year 2003 – 2020

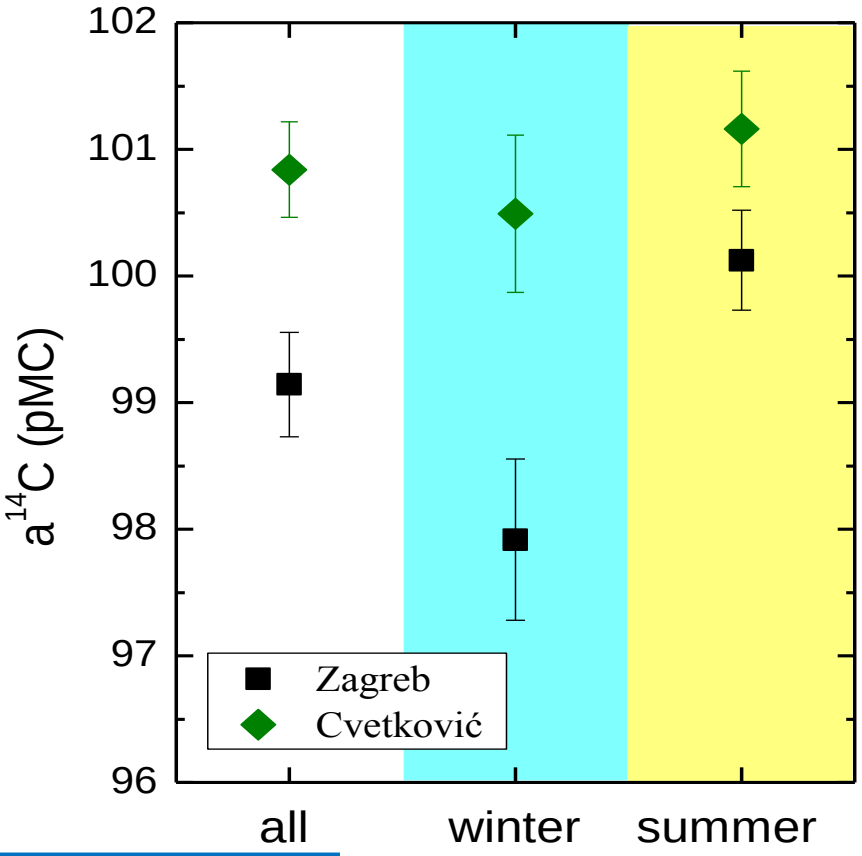
Seasonal fluctuations, 2003 – 2020, Zagreb



Zagreb and Cvetković, 2019-2021

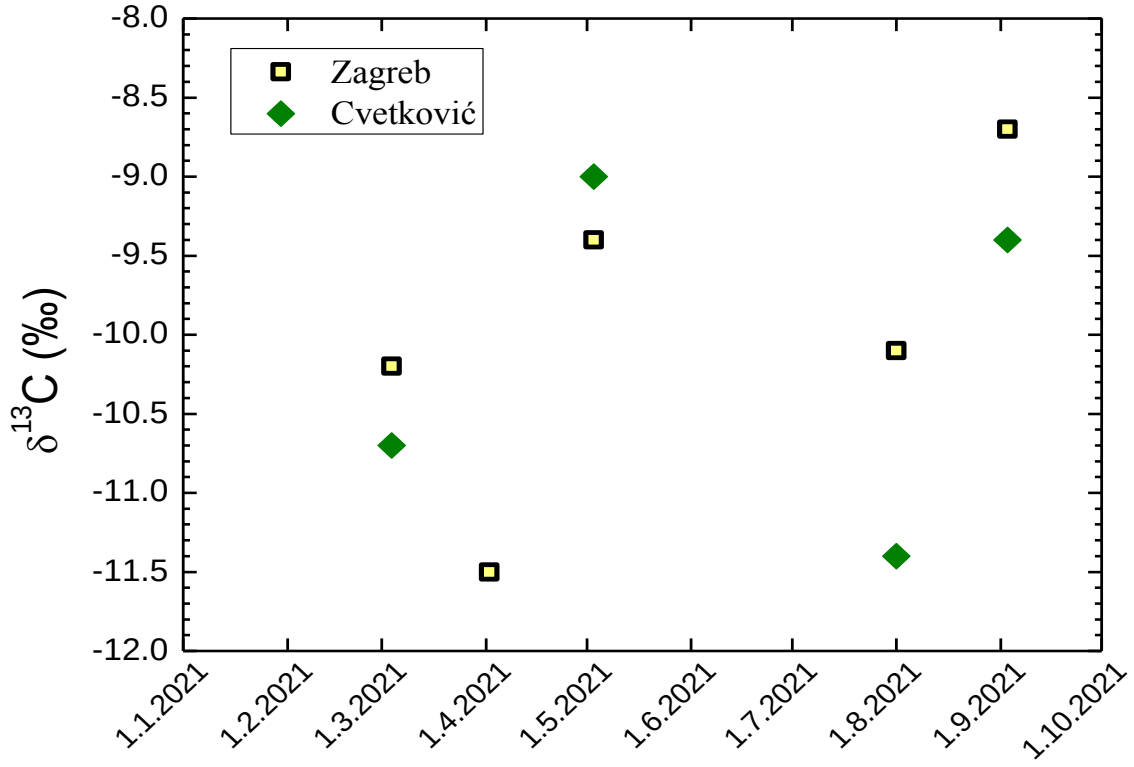


- lower $a^{14}C$ values in Zagreb than at the clear site (Δ 1.69 pMC, p = 0.051)
- larger difference in winter (Δ 2.54 pMC, p = 0.013) than in summer (Δ 1.03 pMC, p = 0.059)



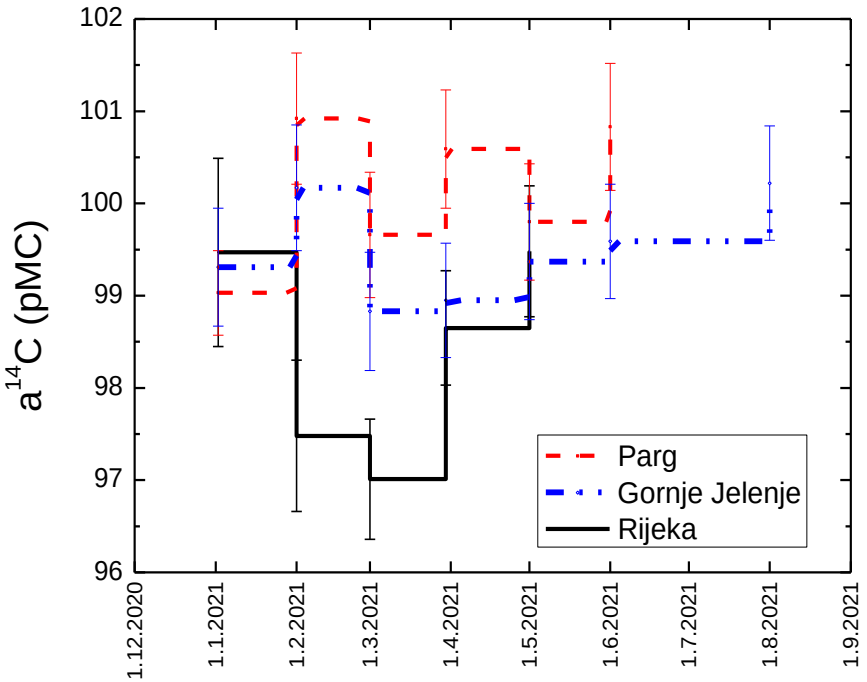
		Cvetković		Zagreb	
	N	mean	SE	mean	SE
All data	23/27	100.83	0.38	99.14	0.41
Summer Apr-Sept	12	101.15	0.46	100.12	0.39
Winter Oct-March	10	100.46	0.69	97.92	0.64

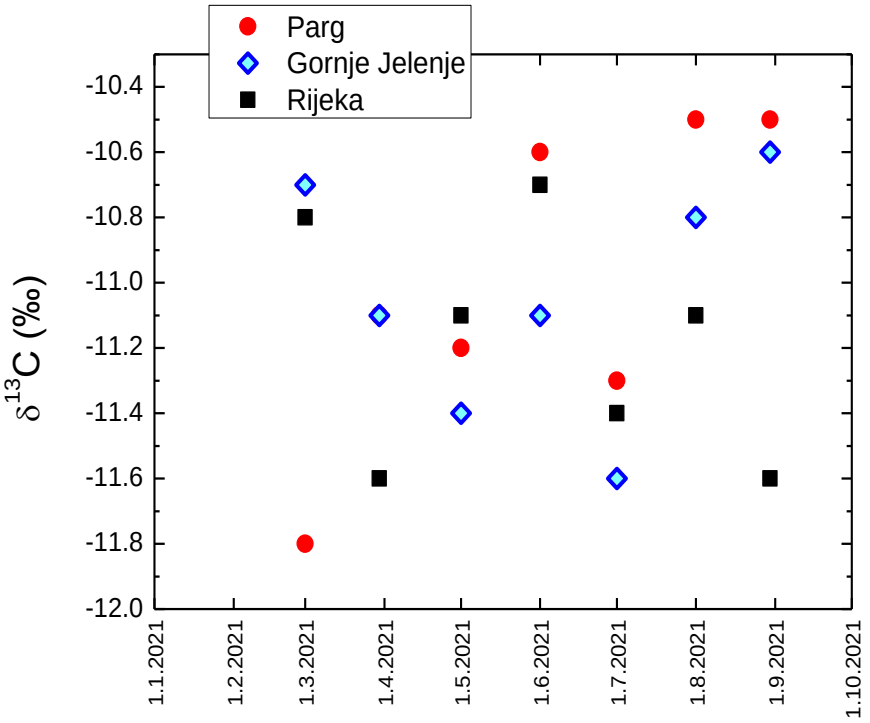
Zagreb and Cvetković, 2021



		Cvetković		Zagreb	
	N	mean	SE	mean	SE
All data	4/5	-10.11	0.56	-9.98	0.47

Rijeka and surroundings, 2021





	a^{14}C (pMC)	δ^{13}C (‰)
Parg	100.1 ± 0.7	-11.00 ± 0.49
Gornje Jelenje	99.5 ± 0.5	-11.04 ± 0.37
Rijeka	98.4 ± 1.1	-11.18 ± 0.36

Concluding remarks

- Sampling techniques have been validated, and their dis/advantages determined
- Measurement techniques validated, depend on the mass of the collected carbon, results are comparable
- Rural locations show higher ^{14}C activities
- The difference is larger during winter due to more intense fossil fuel combustion in the cities

Damir Borković – Ph.D. Thesis (Zagreb and Cvetković, and tree rings during last century)
Emma Hess – master thesis (Rijeka and surroundings)

Thank you