ENVIRA 2017

Environmental ^{14}C and ^{3}H levels in Croatia

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Since 1968 radiocarbon, since 1976 tritium

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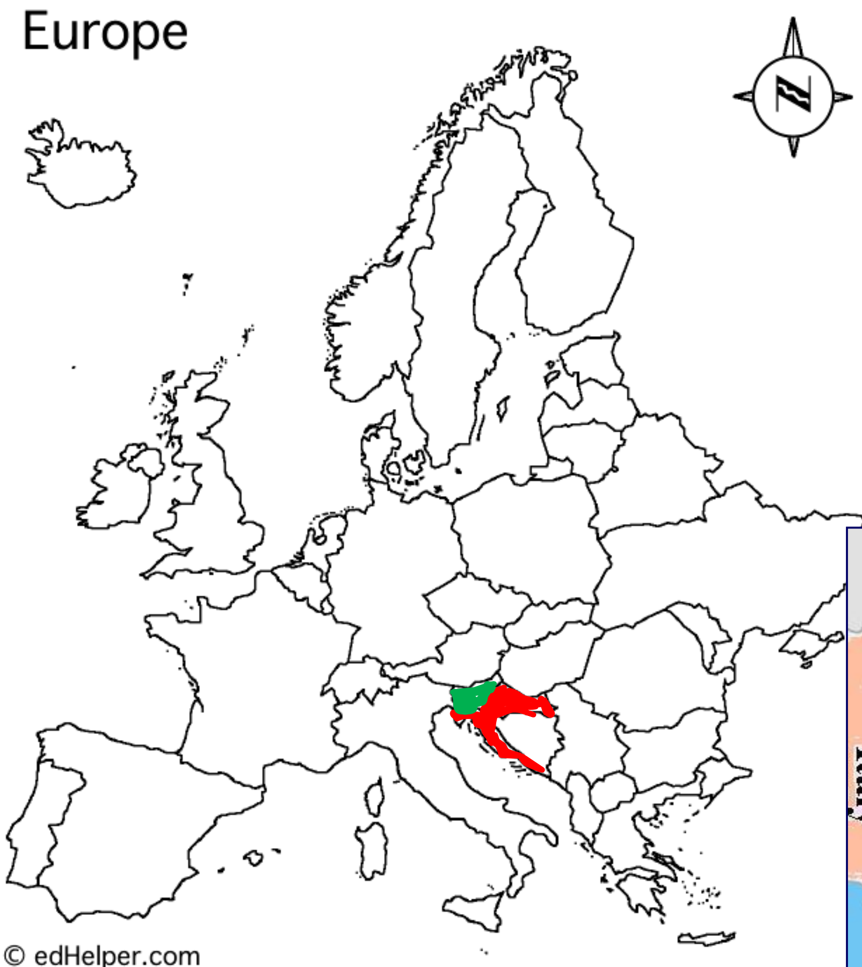
Martina Rožmarić
Matea Krmpotić

Laboratory for low-level radioactivities

- ^{14}C dating of archaeological samples
- Geochronology (secondary carbonates in karst)
- **Monitoring ^{3}H in precipitation and ^{14}C in the atmosphere and biosphere**
- Various applications of isotope methods (^{3}H, ^{14}C, stable isotopes ^{2}H, ^{18}O, ^{13}C)

- Radioactive isotopes ^{3}H and ^{14}C are constituents of H_2O and CO_2 molecules, respectively
- They take part in natural cycles of water and carbon, resp.,
- Their origin is both cosmogenic and anthropogenic
- Natural distributions of both isotopes have been disturbed by human activities in the 20th century
- maximal atmospheric activities observed in 1963-1964 (^{3}H – x1000, ^{14}C – 2x), continuous decrease since then

Regional setting



Methods

Activity concentration of ^{3}**H** was measured by gas proportional counting technique until 2007 and since 2008 by liquid scintillation counting after electrolytic enrichment.

A gas proportional counting technique for ^{14}**C** was replaced by liquid scintillation counting following either benzene synthesis or direct absorption of CO_2

Horvatinčić, N; Barešić, J; Krajcar Bronić, I; Obelić, B. Measurement of Low ^{14}C Activities in Liquid Scintillation Counter in the Zagreb Radiocarbon Laboratory. Radiocarbon 46 (2004) 105-116

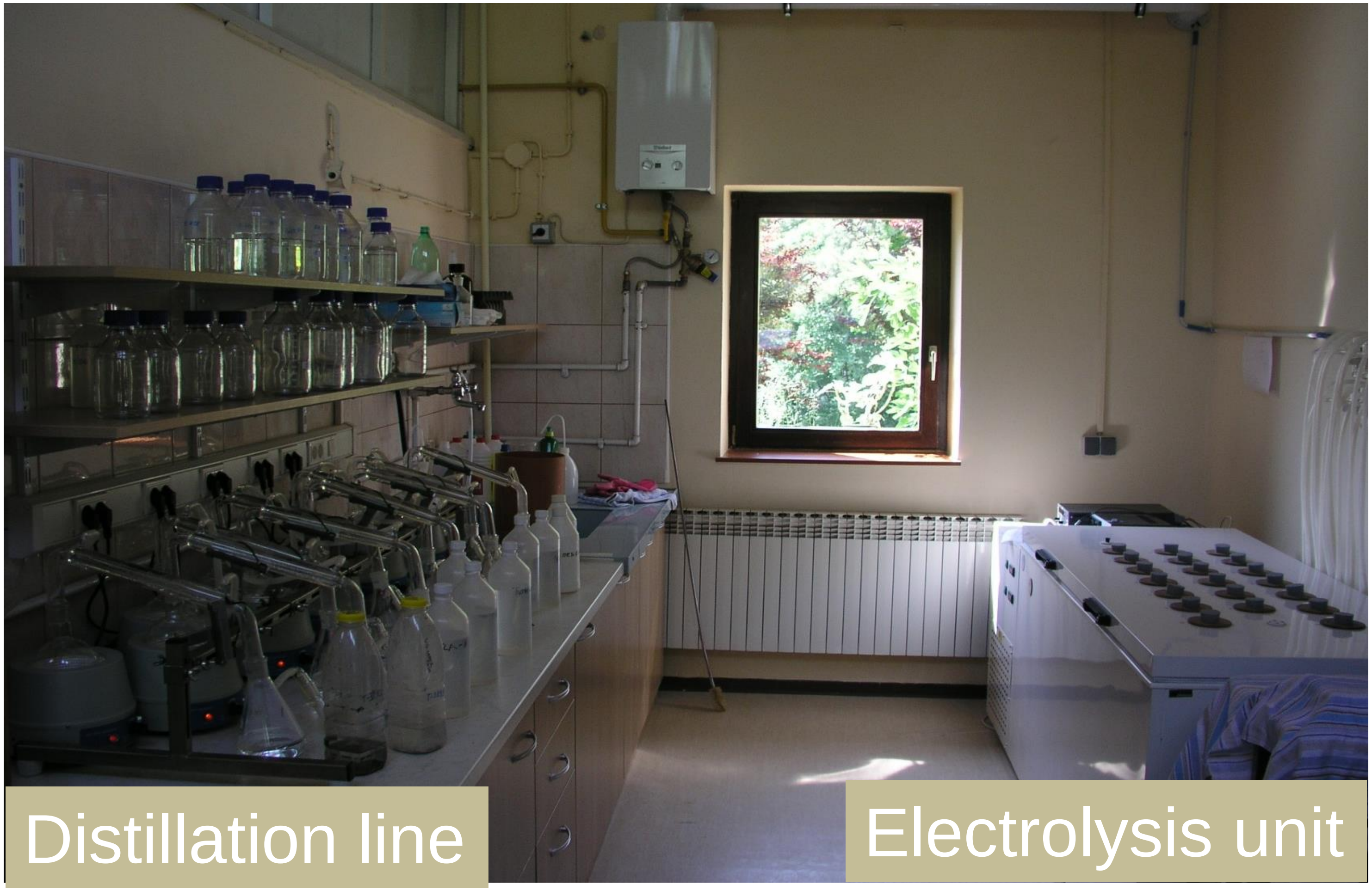
Krajcar Bronić, I; Horvatinčić, N; Barešić, J; Obelić, B. Measurement of ^{14}C activity by liquid scintillation counting. Applied Radiation and Isotopes 67 (2009) 800-804

AMS-^{14}C – graphite target preparation for AMS measurements, since 2008; „feeding laboratory"

Krajcar Bronić, I; Horvatinčić, N; Sironić, A; Obelić, B; Barešić, J; Felja, I. A new graphite preparation line for AMS ^{14}C dating in the Zagreb Radiocarbon Laboratory. Nucl. Instrum. Methods B 268 (2010) 943-946

Sironić, A; Krajcar Bronić, I; Horvatinčić, N; Barešić, J; Obelić, B; Felja, I. Status report on the Zagreb radiocarbon laboratory - AMS and LSC results of VIRI intercomparison samples. Nucl. Instrum. Methods B 294 (2013) 185-188

RBI – Tritium laboratory - Electrolythic enrichment



20 cells, initial volume 500 ml, enrichment factor ≈28;
8 ml + 12 ml UG LLT

RBI – LSC Measurement

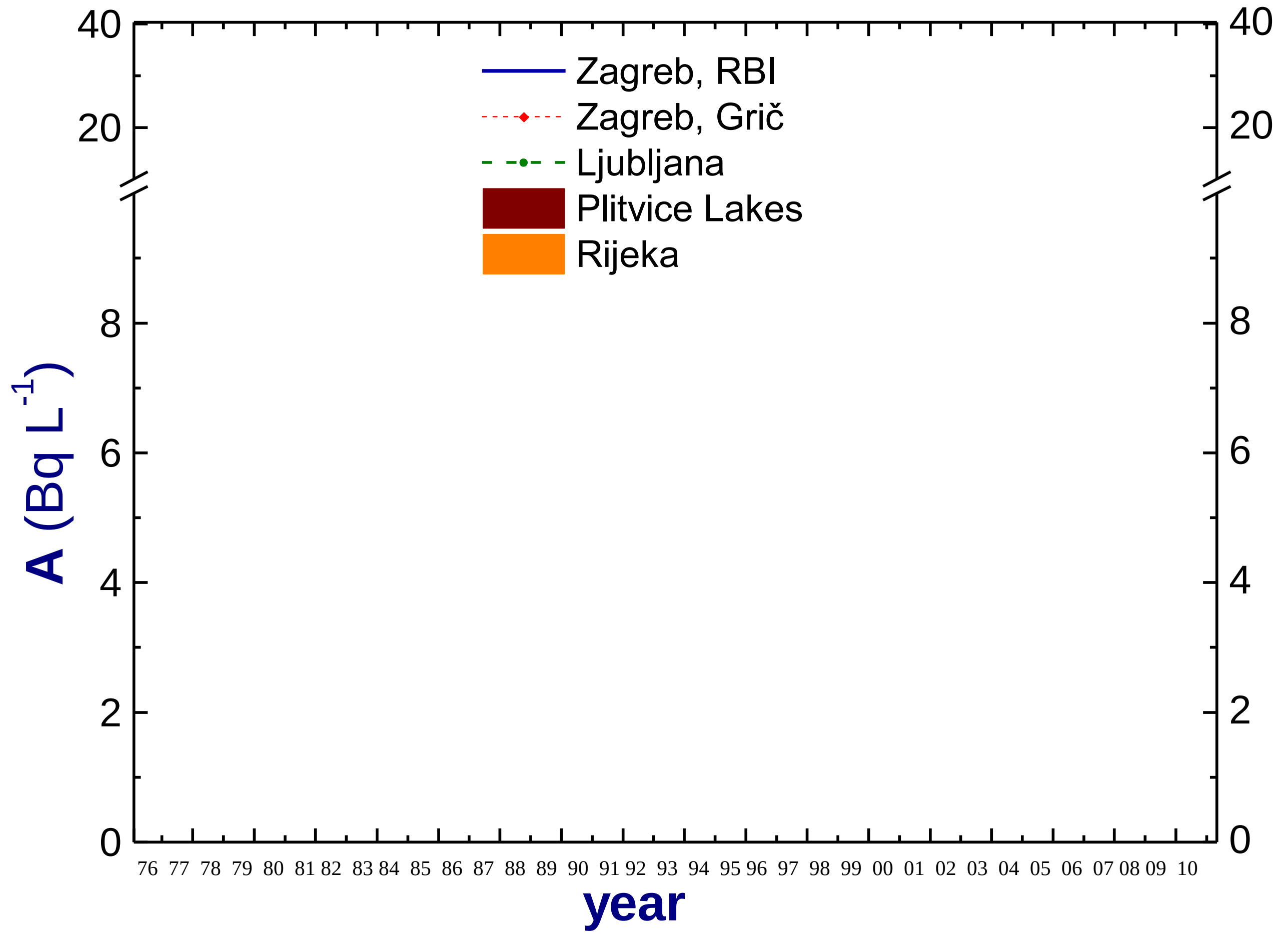
^{3}H – direct measurement
^{3}H – with el. enrichment

LSC-A ^{14}C – absorption of CO_2
LSC-B ^{14}C – benzene synthesis
LSC-F ^{14}C – biogenic fraction

LSC-Quantulus

^{3}H

The long-term data records show seasonal variations superposed on the basic decreasing trend of mean annual values.



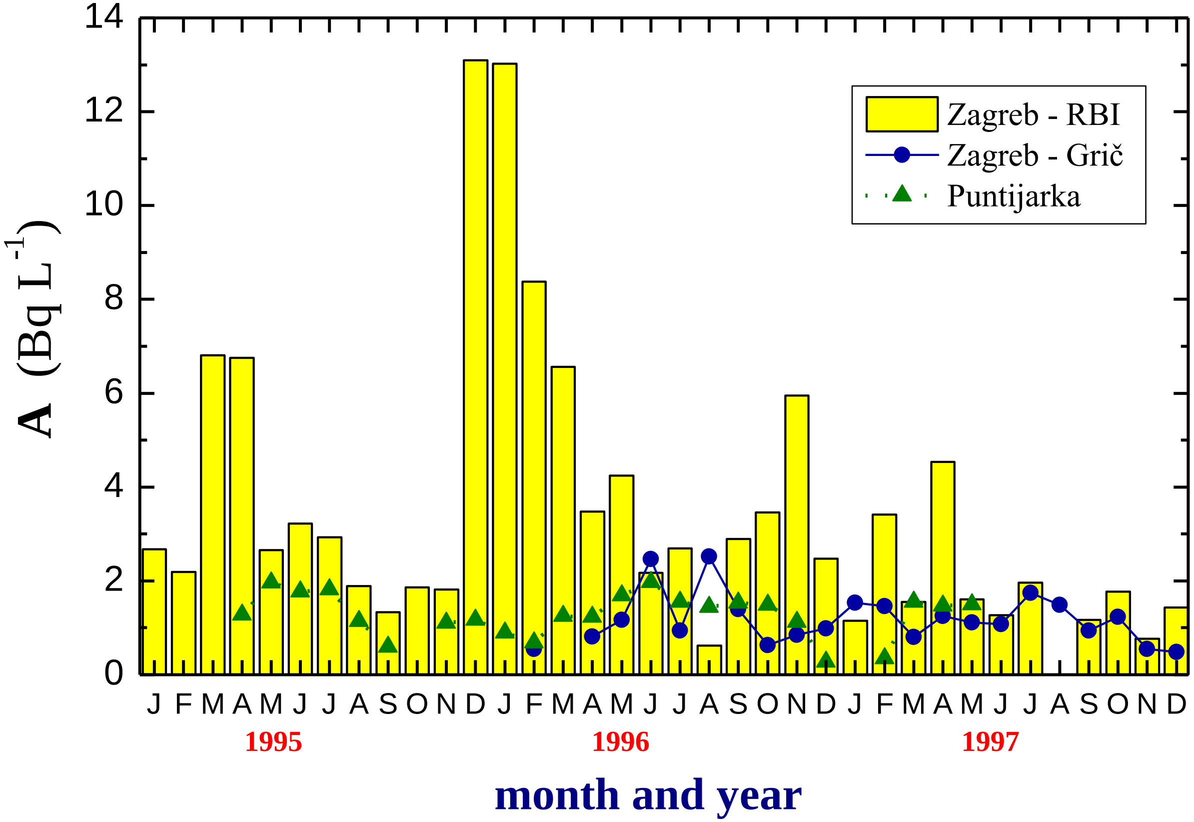
Long-term data on ^{3}H activity concentration in monthly precipitation in Zagreb and Ljubljana (Slovenia) exist for the period since 1976 and 1981, respectively (Krajcar Bronić et al., Radiocarbon 40 (1998) 399; Vreča et al., Geologija 57 (2014) 217)

For shorter periods of time the data exist for several stations along the Adriatic coast and for the continental station Plitvice Lakes (Croatia).
(Krajcar Bronić et al., Arhiv za higijenu rada i toksikologiju 57 (2006) 23,
Vreča et al., J. Hydrology 330 (2006) 457)

^3H

TRITIUM IN PRECIPITATION

Zagreb area, 1995 - 1997

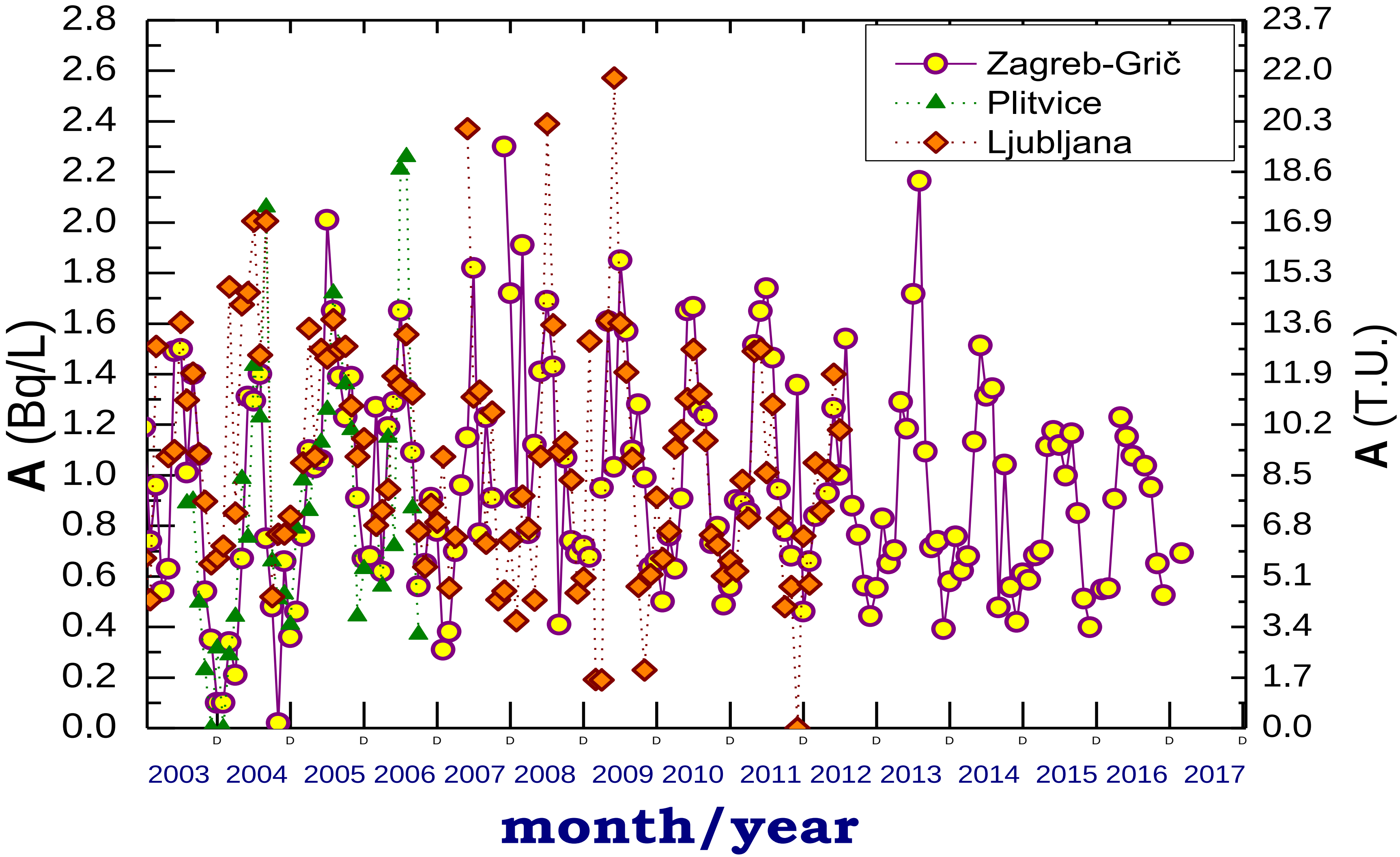


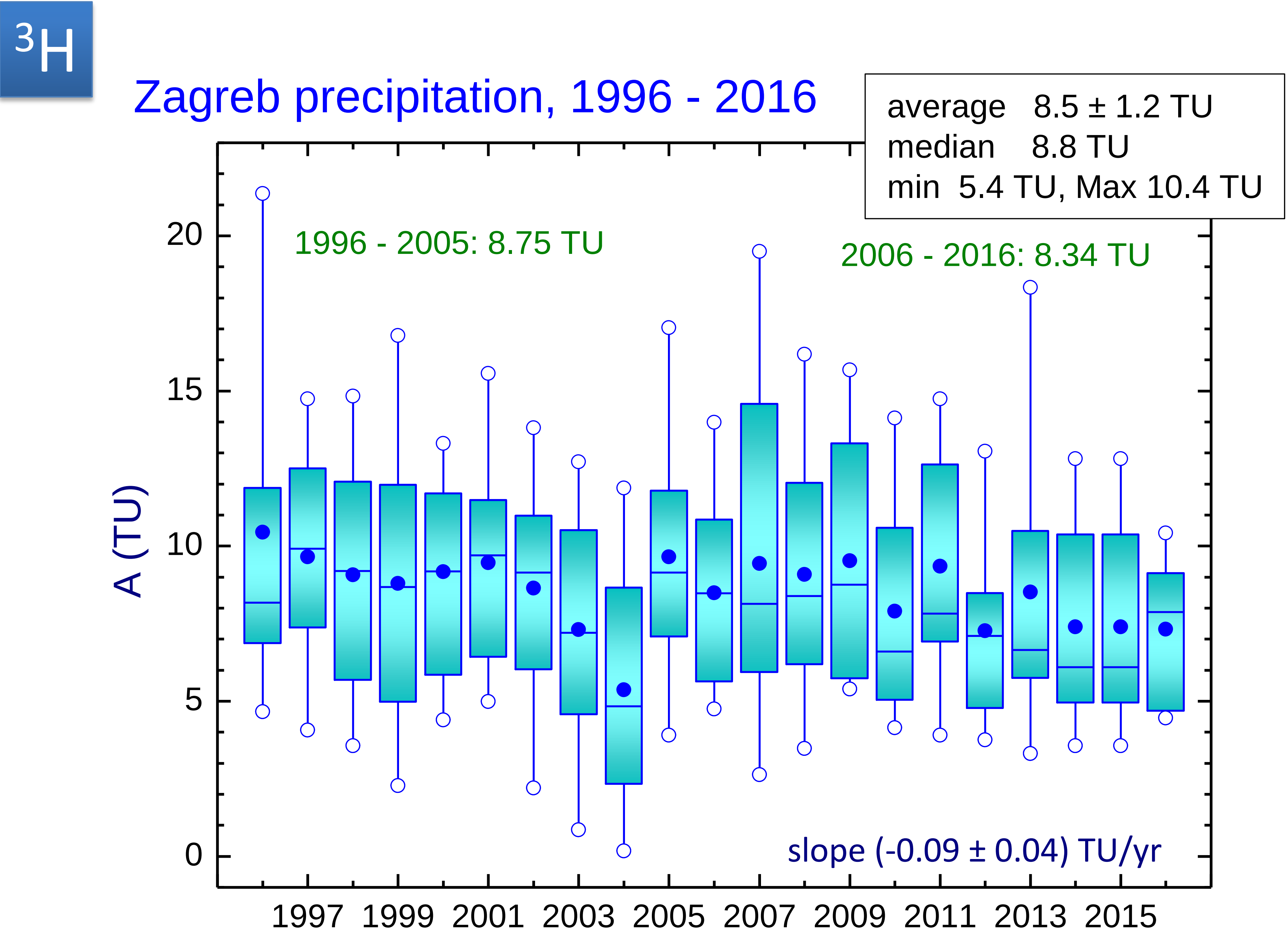
Local contamination at site Zagreb – RBI → sampling location changed to Zagreb – Grič

Krajcar Bronić et al., Radiocarbon 40 (1998) 399

^3H

The data recorded during last 2 decades, show almost constant mean annual ^3H activity concentration of about 9 TU for the continental stations





^3H
Zagreb precipitation, 1996 - 2016
average 8.5 ± 1.2 TU
median 8.8 TU
min 5.4 TU, Max 10.4 TU
1996 - 2005: 8.75 TU
2006 - 2016: 8.34 TU
slope (-0.09 ± 0.04) TU/yr
A (TU)
0
5
10
15
20
1997
1999
2001
2003
2005
2007
2009
2011
2013
2015

^3H

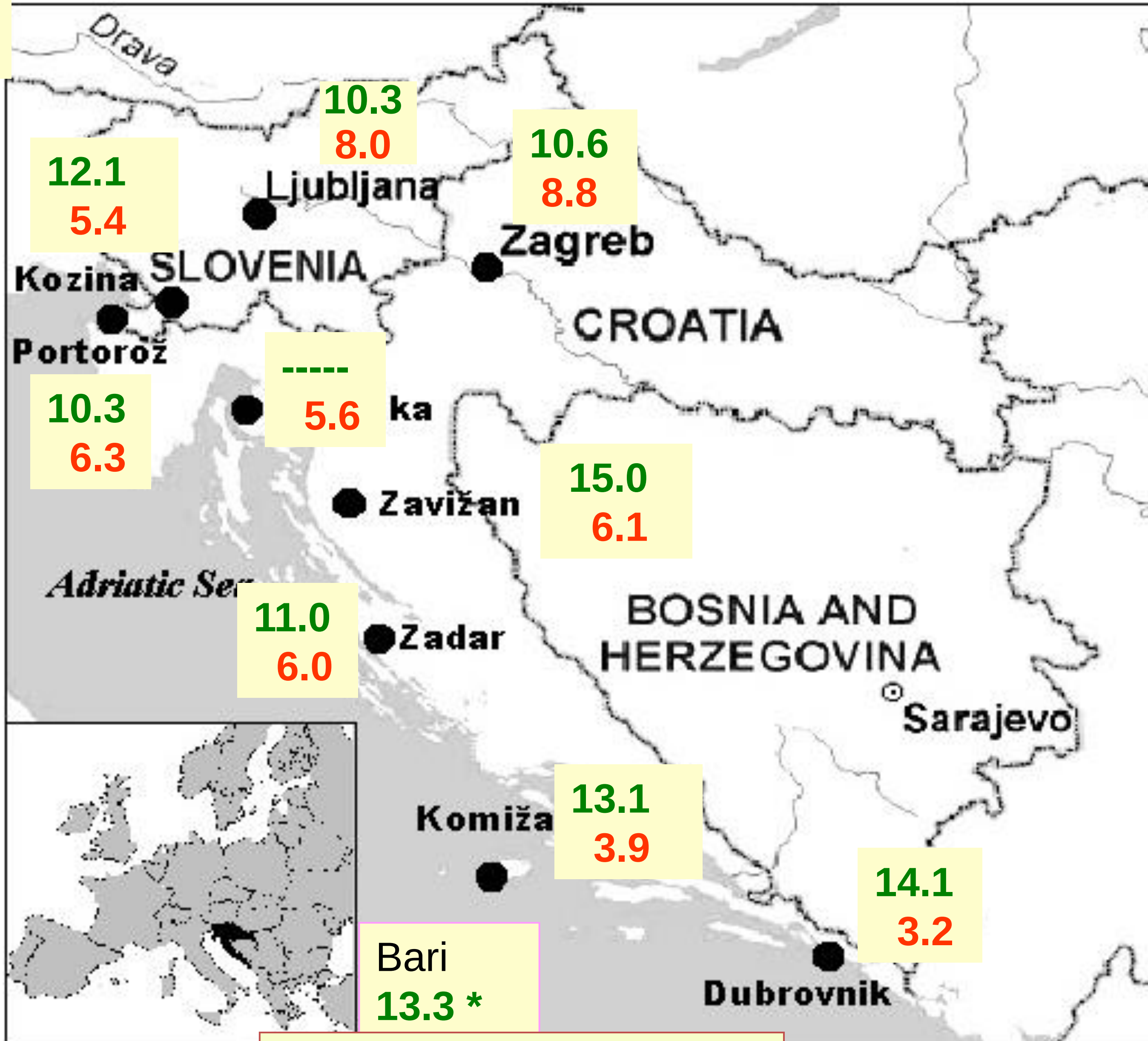
Comparison of continental and maritime stations

Vreča et al., J. Hydrology 330 (2006) 457

d-excess (‰)
A ^{3}H (TU)

Basovizza
11.1 *

Trieste
10.2 *



* Longinelli and Selmo, 2003

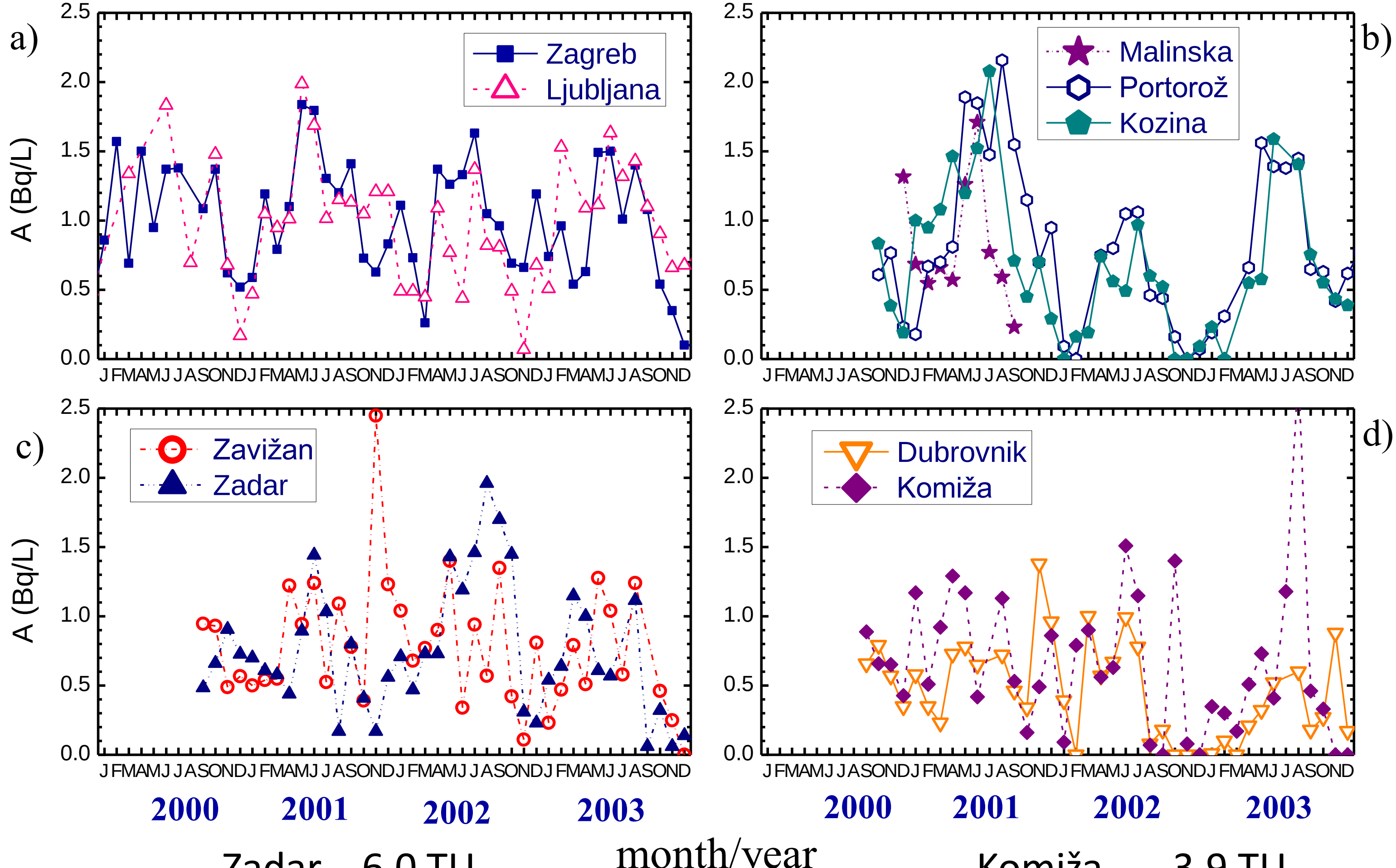
Influence of Mediterranean air masses, d > 10 ‰

higher d values in autumn-winter precipitation (mean monthly d-excess higher than 10 ‰ at all stations)

^{3}H

Zagreb 8.8 TU
Ljubljana 8.0 TU

Portorož 6.3 TU
Kozina 5.4 TU



Zadar 6.0 TU
Zavižan 6.1 TU

Komiža 3.9 TU
Dubrovnik 3.2 TU

^{3}H

Comparison: continental, maritime and high-altitude stations

	Sampling site	2001 – 2003 mean A (TU)	correlation with Zagreb	Deuterium excess (‰)	Maritime air masses
continental	Zagreb	8.8		10.6	0 %
	Ljubljana	8.0	0.60	10.3	15 – 25 %
North and mid-adriatic (higher altitude stations)	Portorož	6.3	0.55	10.3	26 – 62 %
	Kozina	5.4	0.55	12.1	
	Malinska	5.6			
	Zadar	6.0	0.34	11.0	
	Zavižan	6.1	0.40	15.0	
South Adriatic	Komiža	3.9	0.31	13.1	84 – 87 %
	Dubrovnik	3.2	0.20	14.1	100 %

^{14}C

^{14}C activity in the atmospheric CO_2

Zagreb: period (1985) - 1993 – 2016

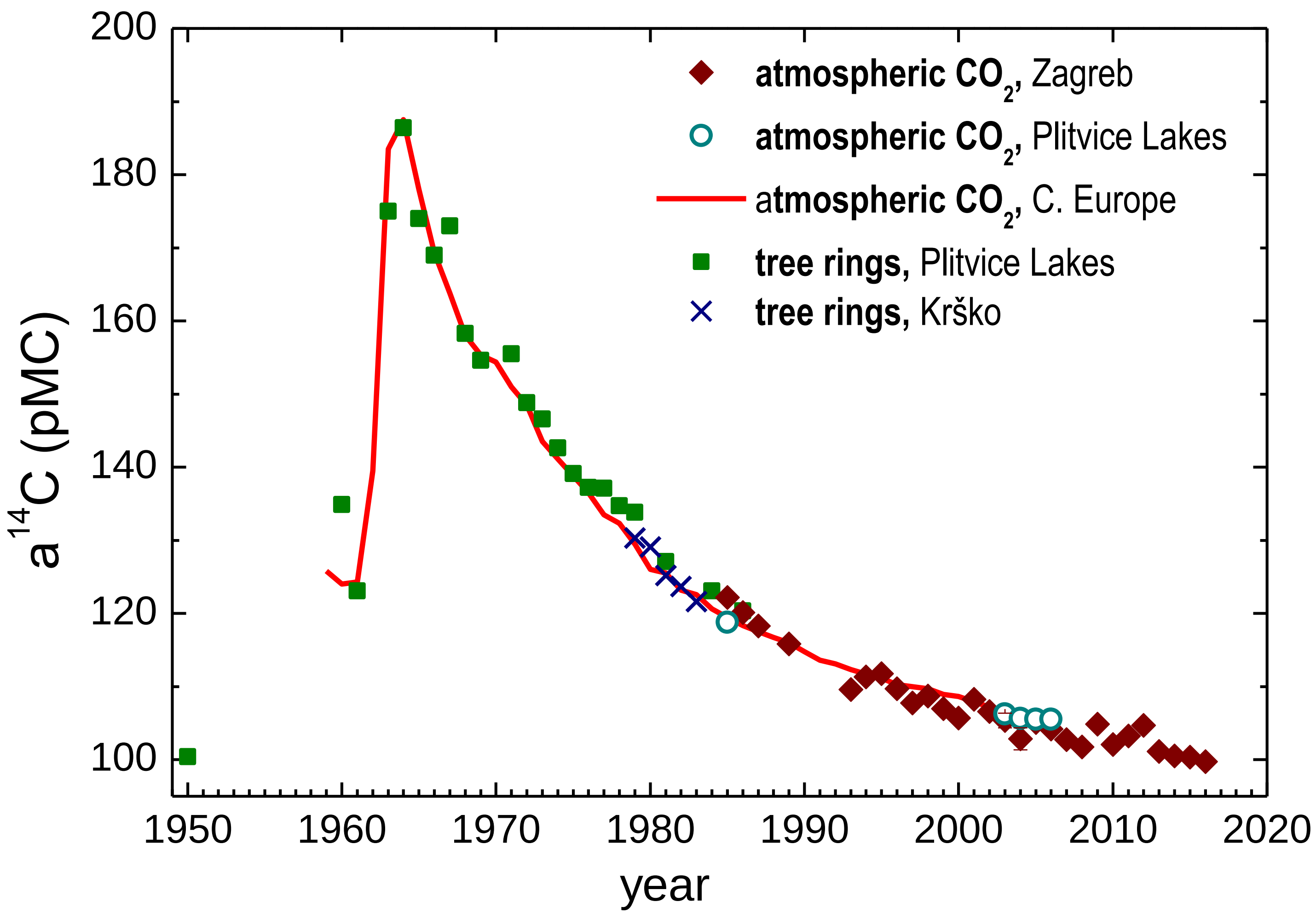
Krajcar Bronić et al., Radiocarbon 1998,
Krajcar Bronić et al., Nucl. Instrum. Meth. 2010

Plitvice Lakes - not continuous atmospheric CO_2 record
tree rings used for reconstruction of the bomb peak

Nuclear Power Plant Krško (SLO) – since 2006 continuous data record - atmospheric CO_2 and biological samples

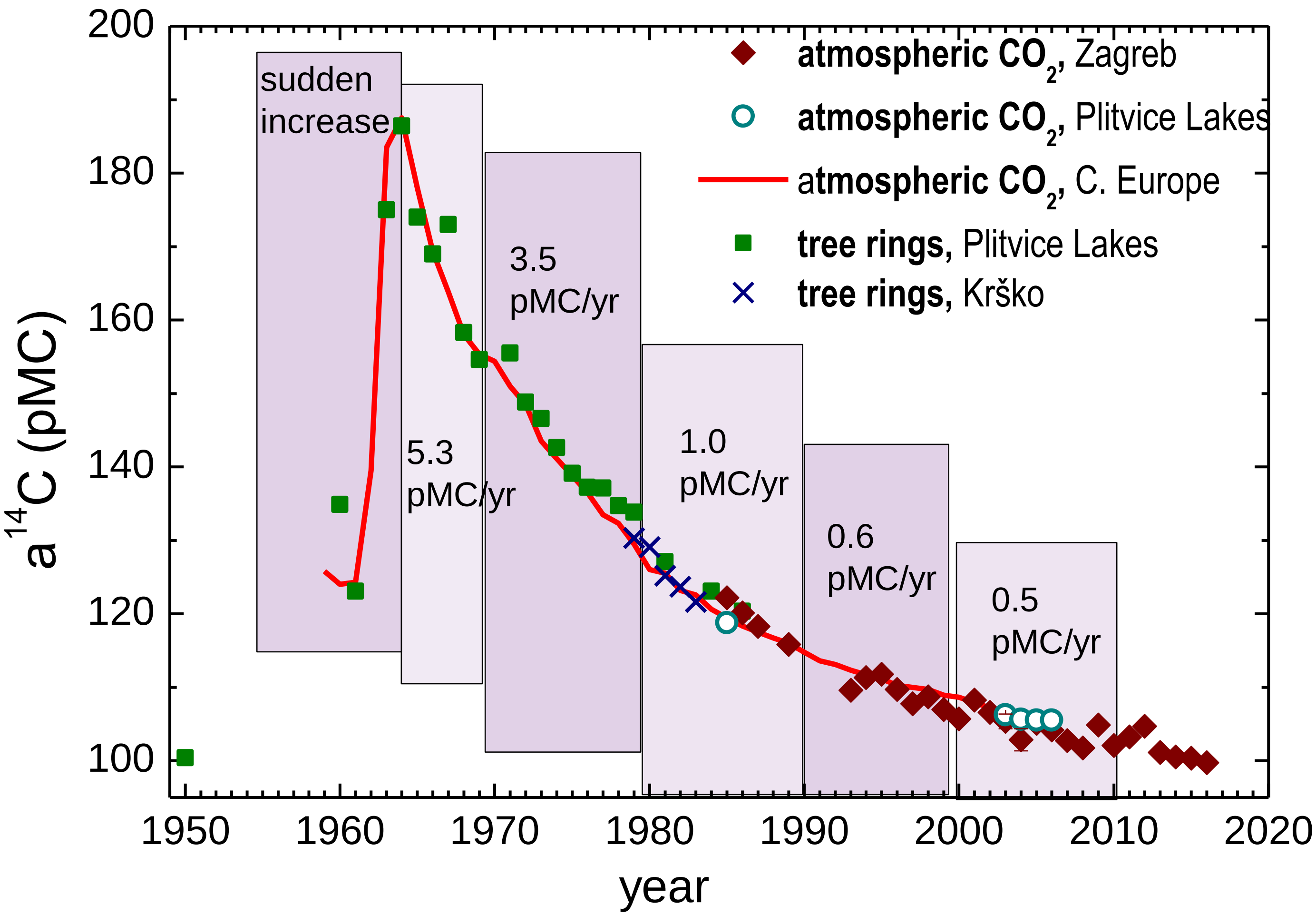
^{14}C

$a^{14}C$ in atmospheric CO_2 and tree rings
anthropogenic disturbance of natural radioactivity



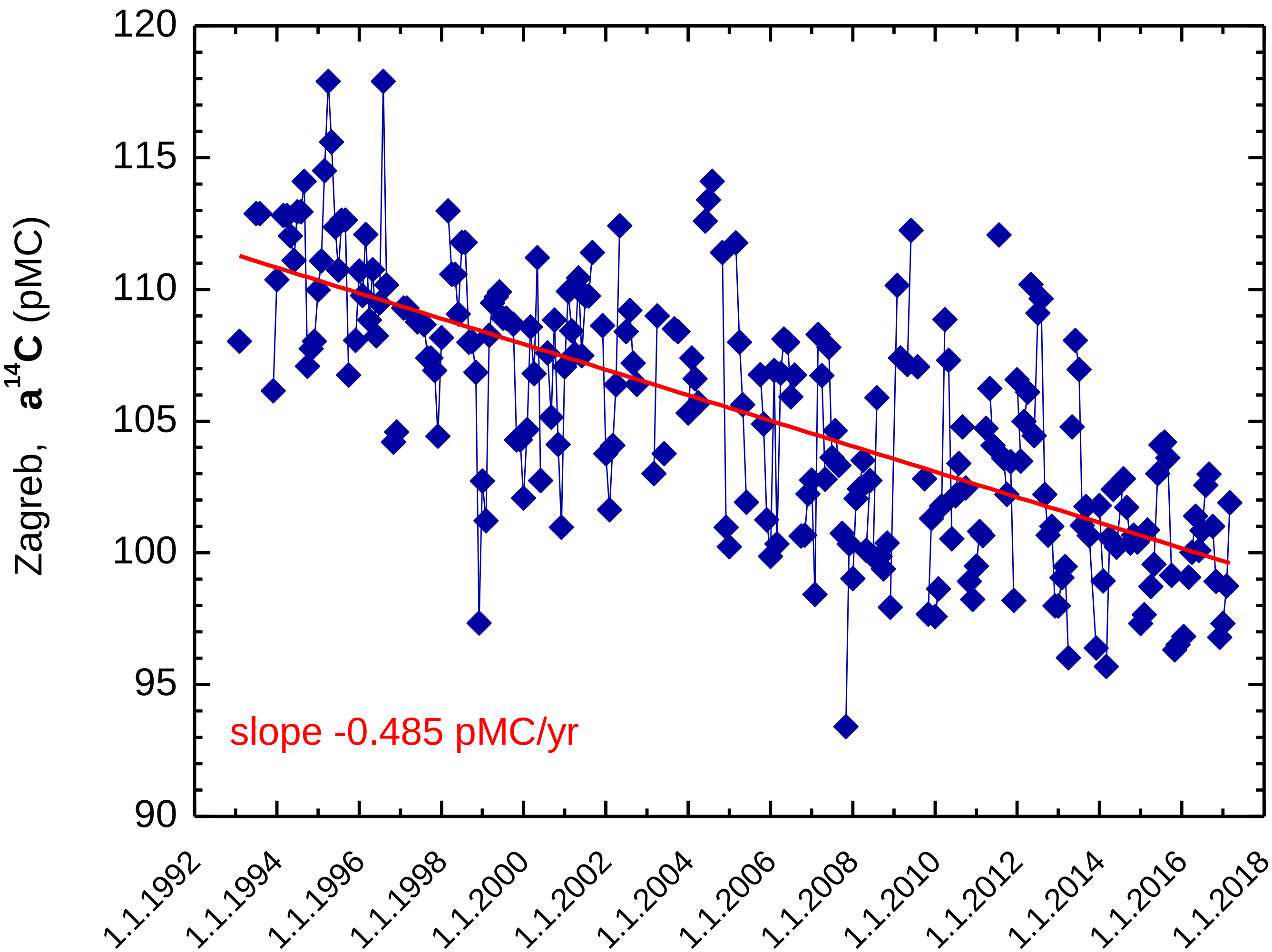
^{14}C

a^{14}C decreasing rate (Schauinsland data)

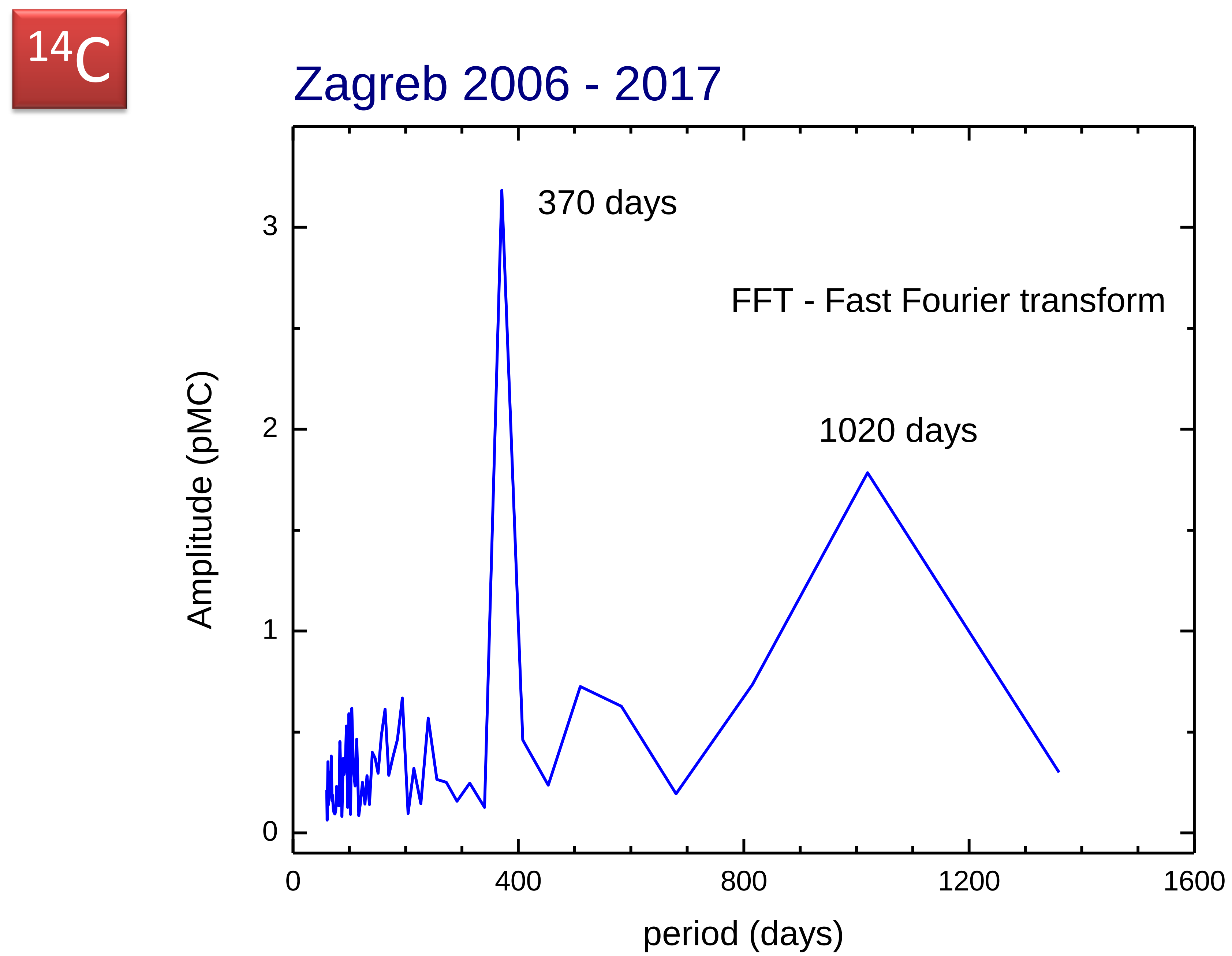


^{14}C

Zagreb, 1993 - 2016



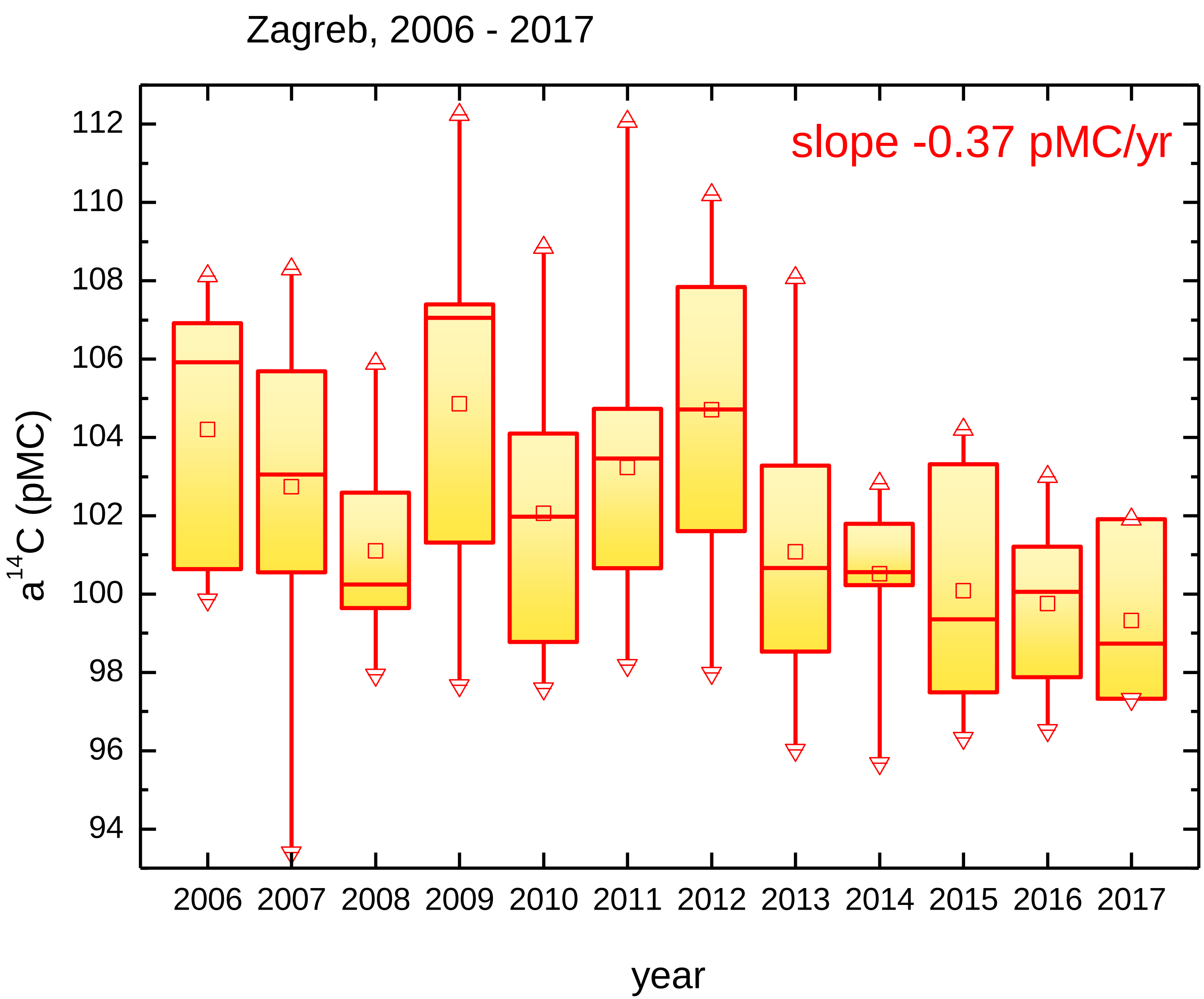
decreasing trend of -0.46 ± 0.04 pMC/yr (mean annual values) or -0.485 pMC/yr (monthly data) with seasonal variations superposed on the trend



^{14}C
Zagreb 2006 - 2017
370 days
FFT - Fast Fourier transform
1020 days
Amplitude (pMC)
period (days)
0
1
2
3
0
400
800
1200
1600

^{14}C

Zagreb, 2006 - 2017



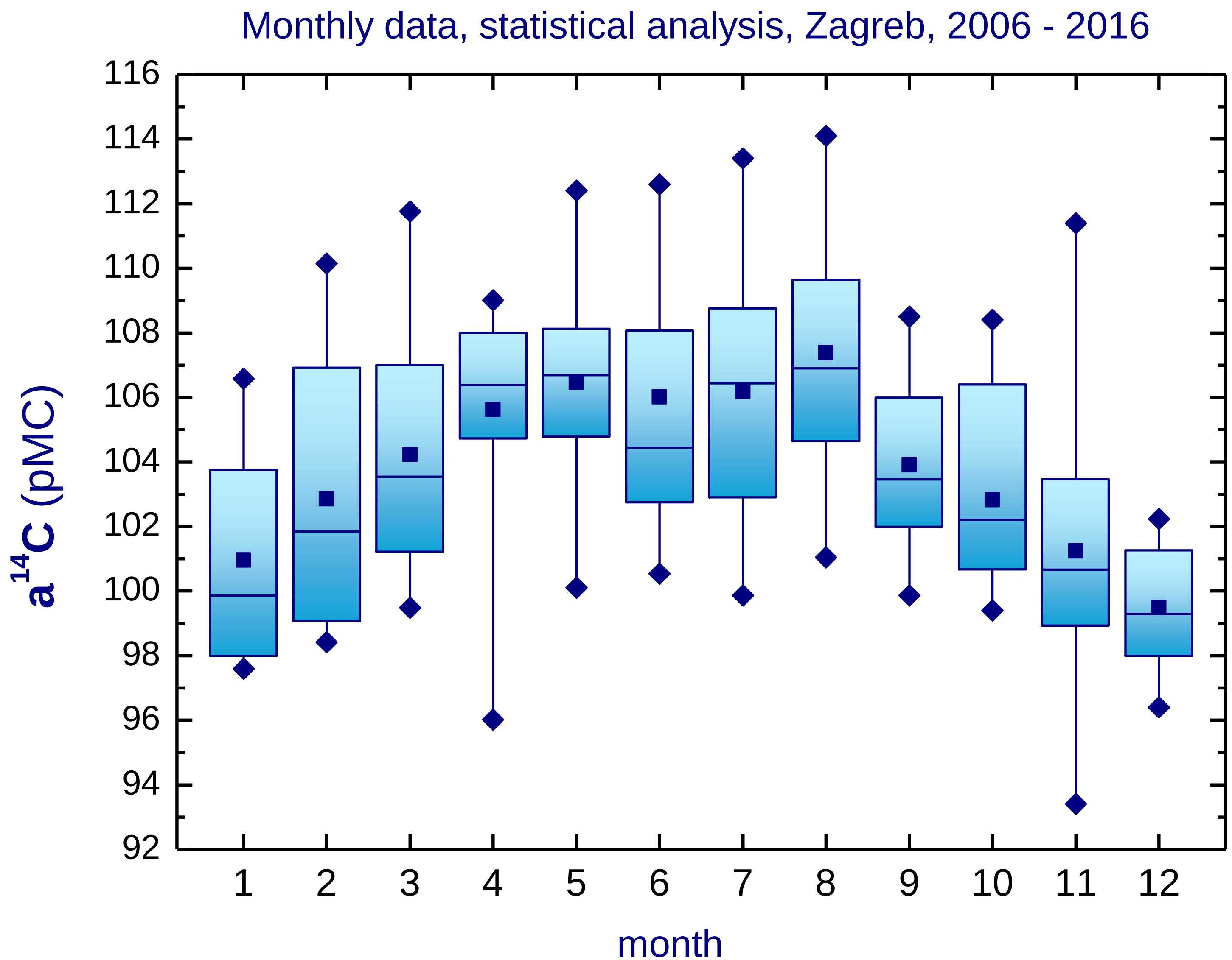
^{14}C

$a^{14}C$ decreasing rates, pMC/yr

period	Global data (Schaunsland)	Zagreb data	
1964 - 1969	5.3		
1970 - 1979	3.5		
1980 - 1989	1.0		
1984 - 1989		1.3	Not systematic data
1990 - 1999	0.6		
1993 - 2005		0.58	
2000 - 2003	0.5		
2005 - 2017		0.37 0.40	Monthly data mean annual

^{14}C

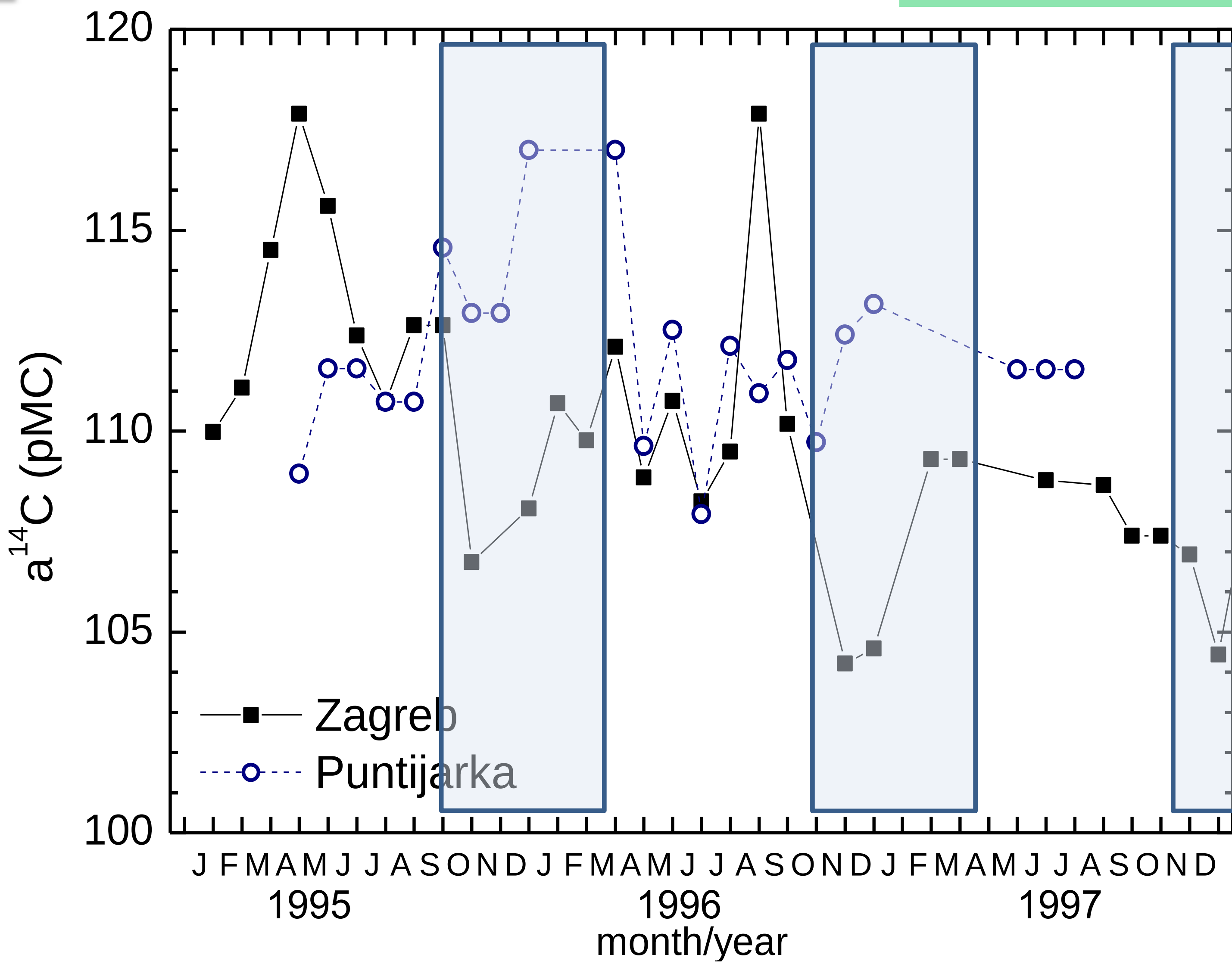
Seasonal variations
Zagreb, 2006 - 2016



14C

^{14}C in an urban centre and the clean-air site (1)

Zagreb (110.0 + 3.4) pMC
Puntijarka (111.0 + 2.2) pMC

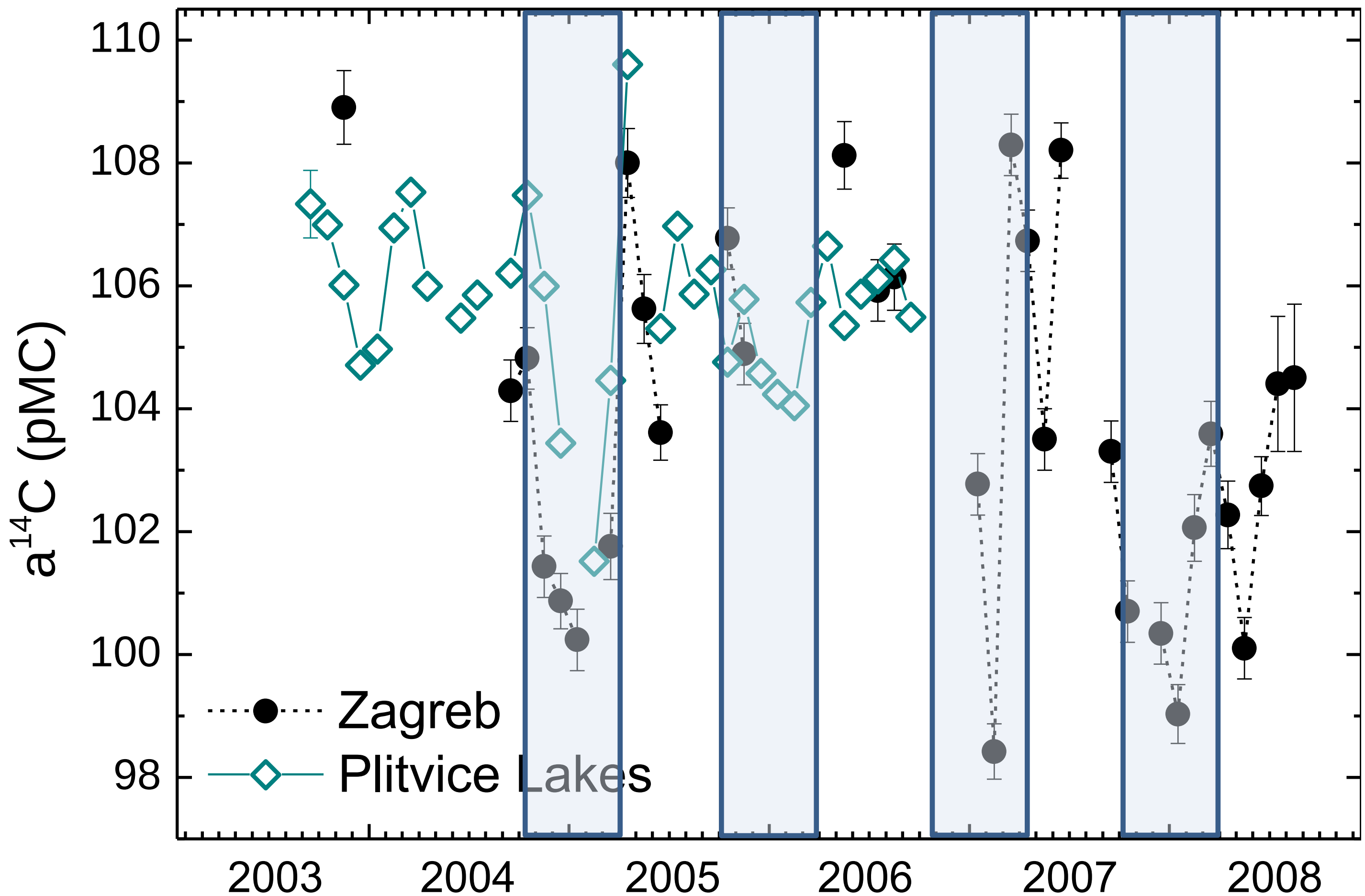


Krajcar Bronić et al. Radiocarbon application in environmental science and archaeology in Croatia. Nucl. Instrum. Methods A 619 (2010) 491–496. doi:10.1016/j.nima.2009.11.032

^{14}C

^{14}C in an urban centre and the clean-air site (2)

Zagreb (104.1 + 2.9) pMC
Plitvice Lakes (105.7 + 1.5) pMC

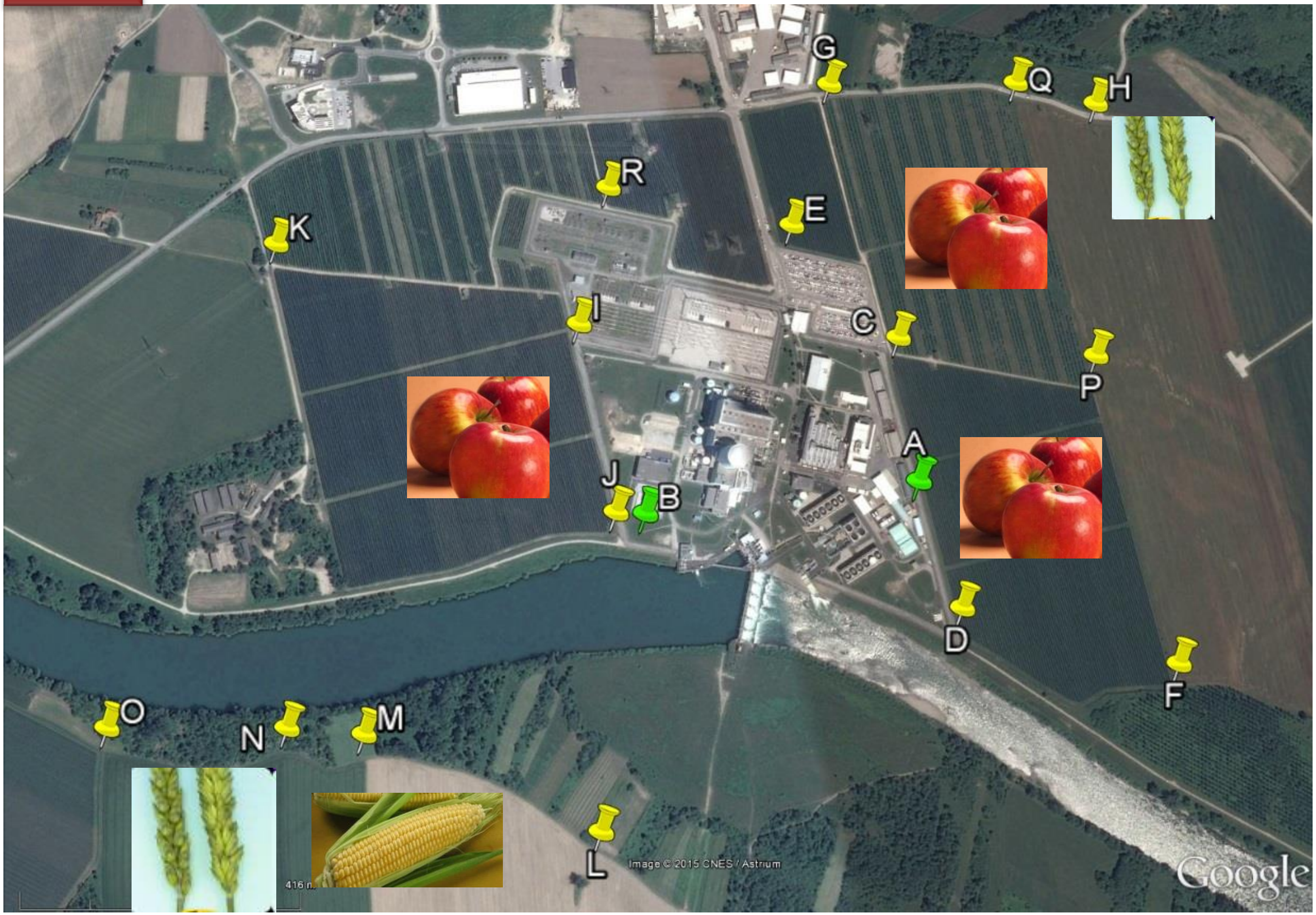


The winter minima in atmospheric $^{14}CO_2$ activity are systematically lower than 100 pMC, probably due to the contribution of fossil fuel combustion in the city area.

Krajcar Bronić et al. Radiocarbon application in environmental science and archaeology in Croatia. Nucl. Instrum. Methods A 619 (2010) 491–496. doi:10.1016/j.nima.2009.11.032

NEK

Sampling locations



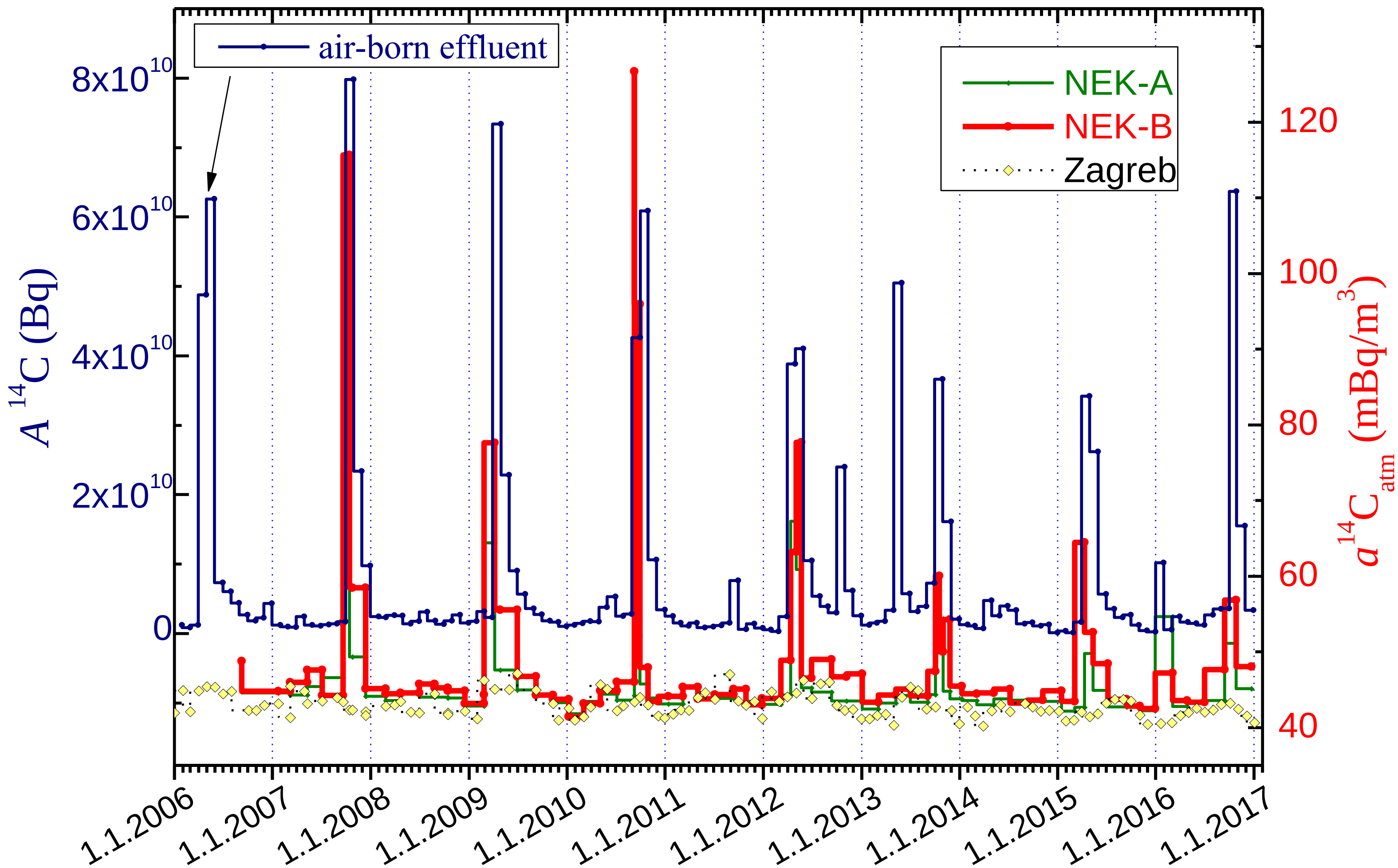
Systematic and continuous monitoring ^{14}C activity in atmospheric CO_2 and biological samples (apples, vegetable, cereals, corn) in the vicinity of the Nuclear Power Plant Krško (NEK) in Slovenia has been performed since 2006.

NEK

Control site

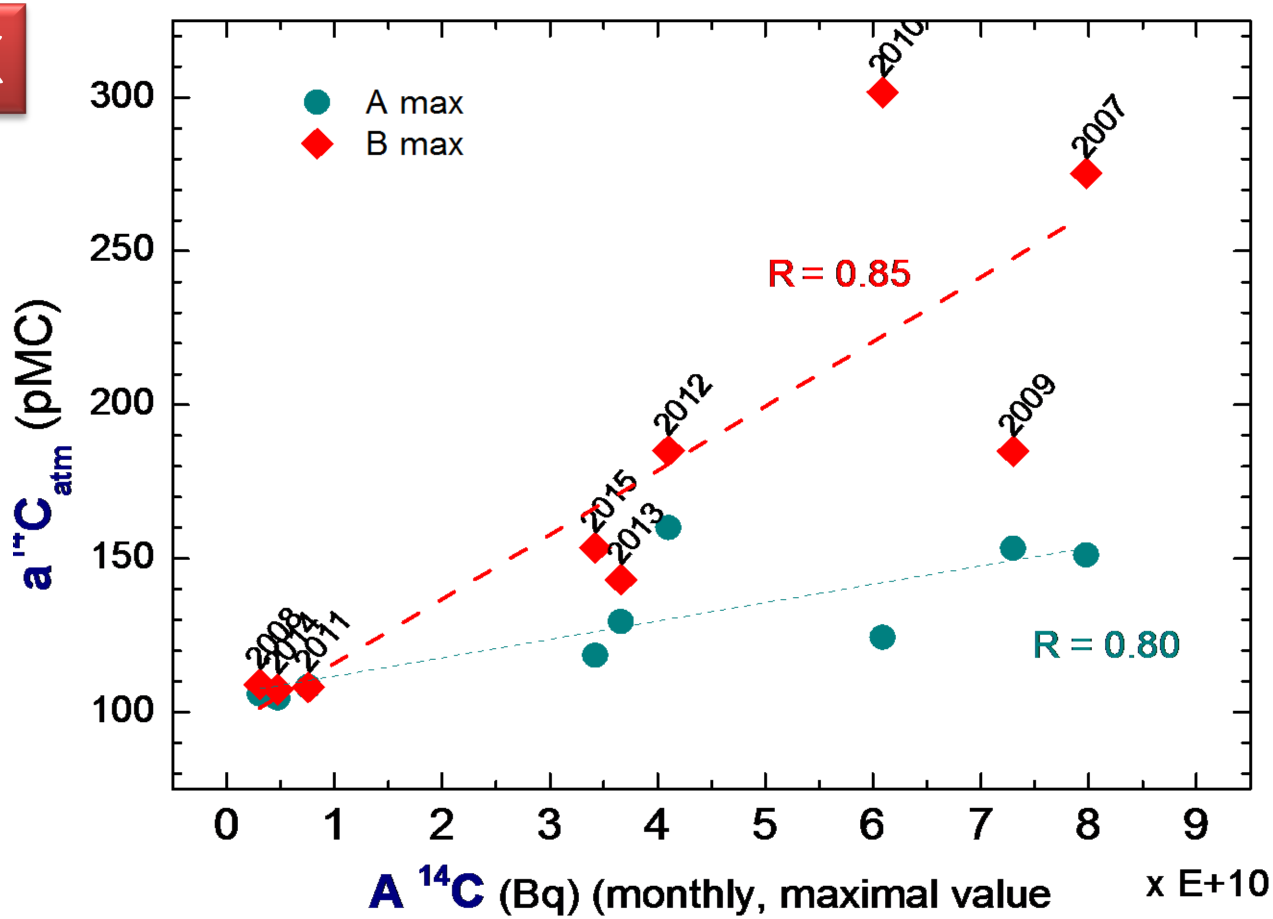
NEK

Atmospheric CO_2



* Measured at the Jožef Stefan Institute, Ljubljana, Slovenia

NEK

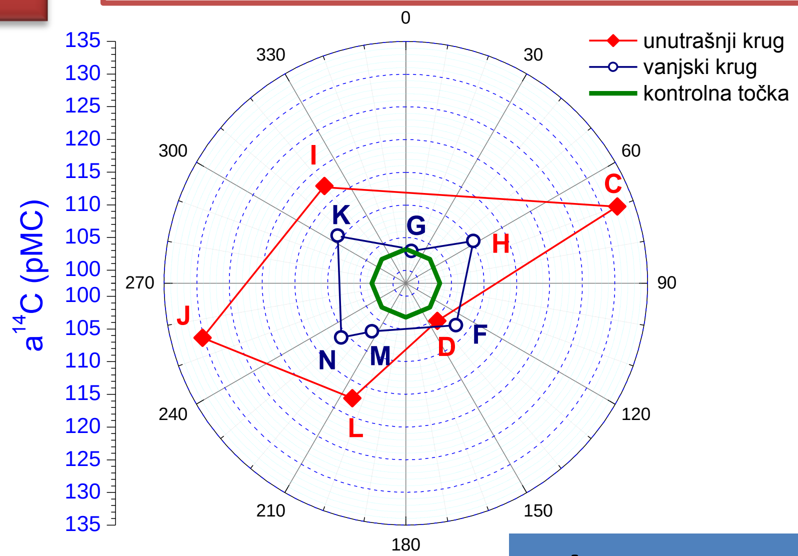


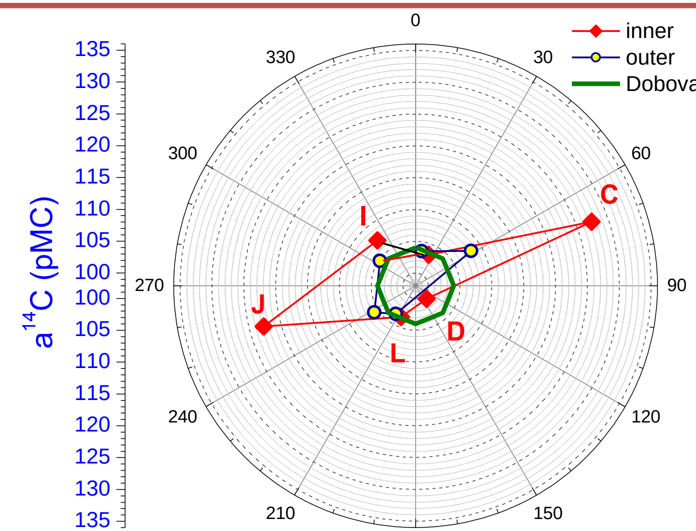
^{14}C activity in atmospheric CO_2 at locations **A** and **B** (maximal values), correlated with the highest ^{14}C activity in monthly gaseous effluents released during the outage periods. Atmospheric ^{14}C activity at the location **B** is always slightly higher than that at the location **A**.

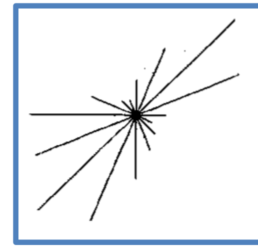
The higher the ^{14}C activity of gaseous effluent, the higher the atmospheric ^{14}C activity.

NEK

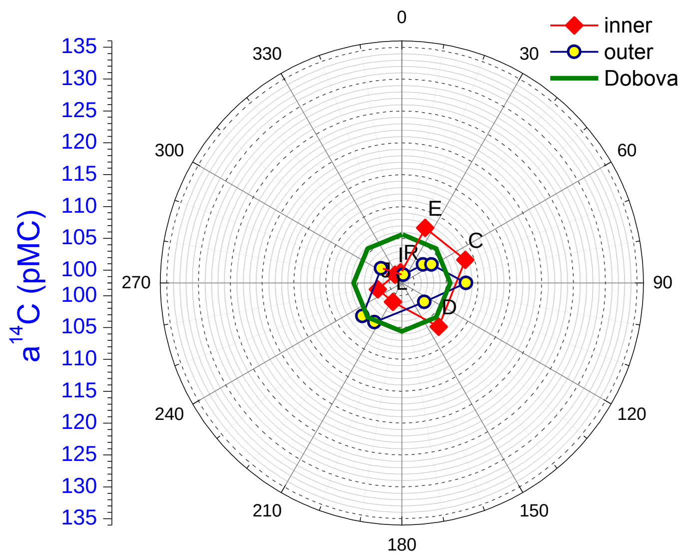
^{14}C in biological samples, spatial distribution

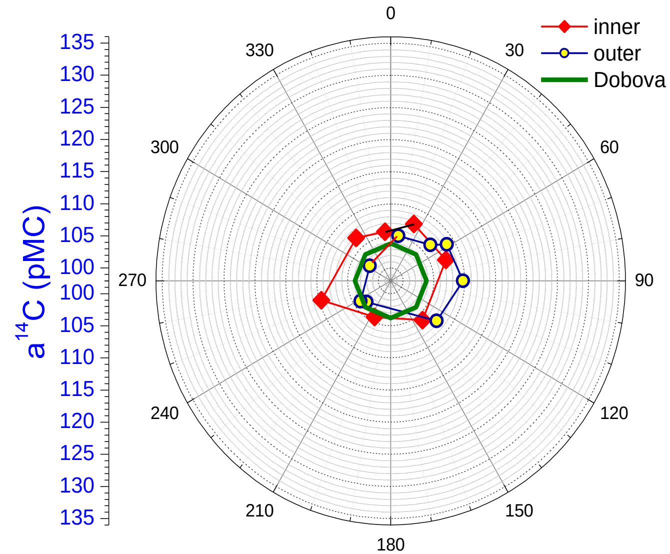






7/2006 refuelling **10/2006**





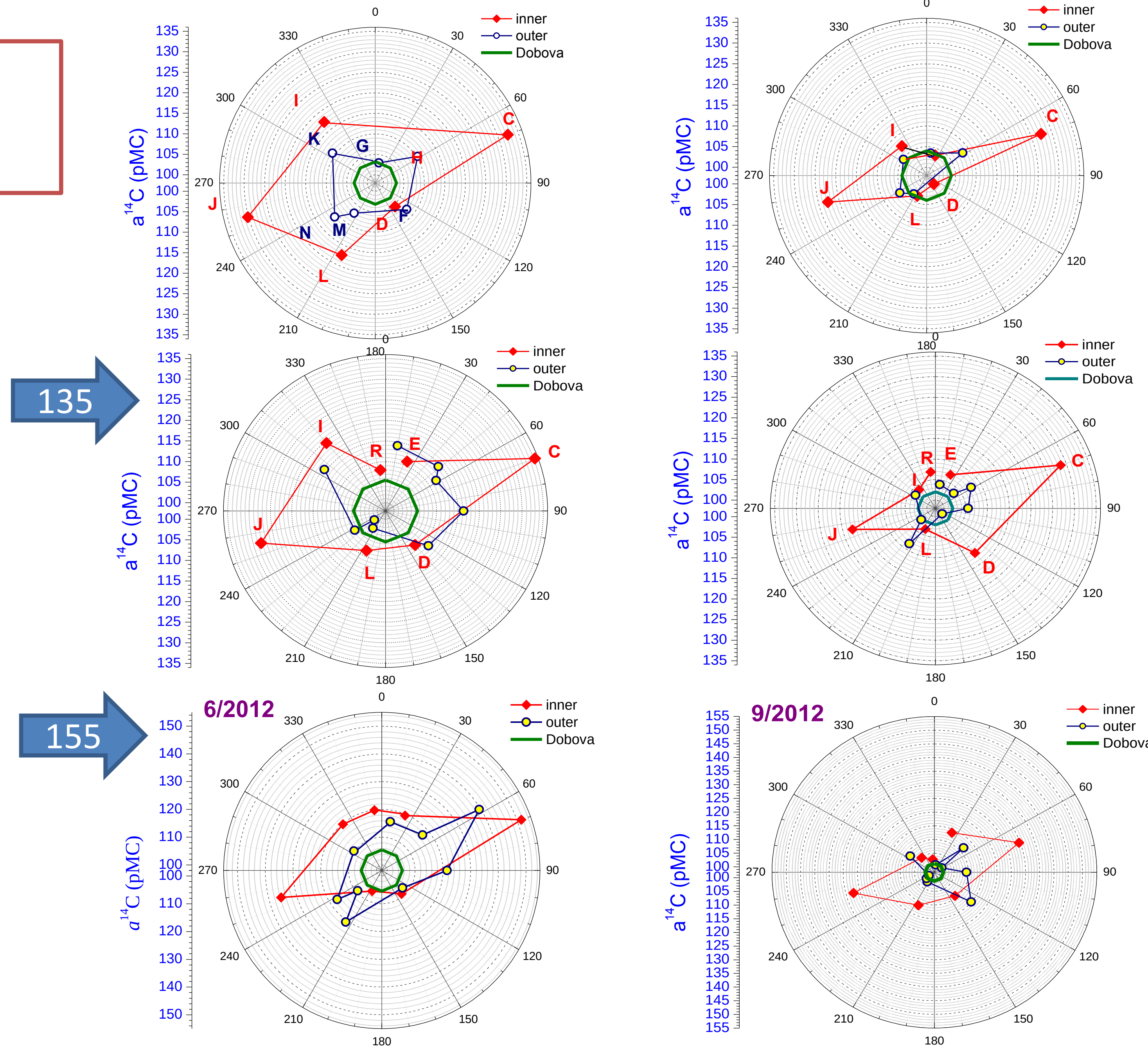
7/2007 **9/2007**

Sampling after spring (April) refuelling

2006

2009

2012



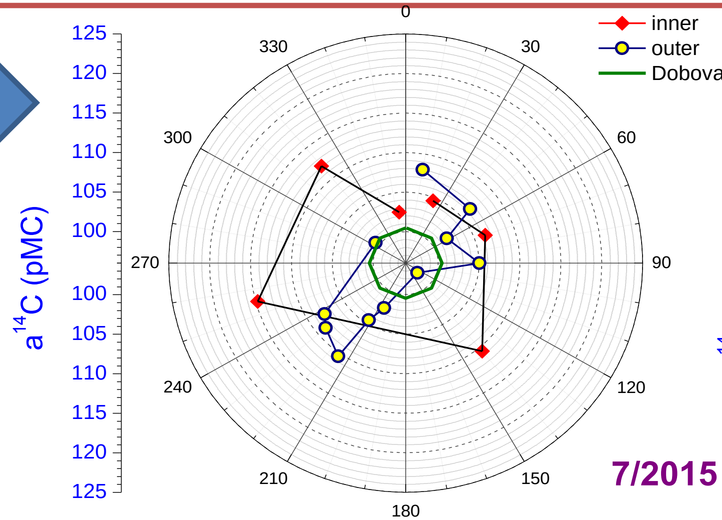
NEK

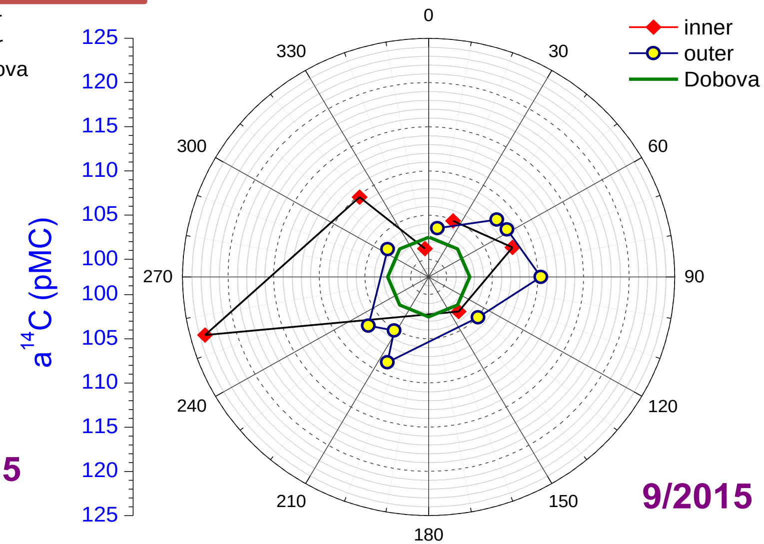
NEK

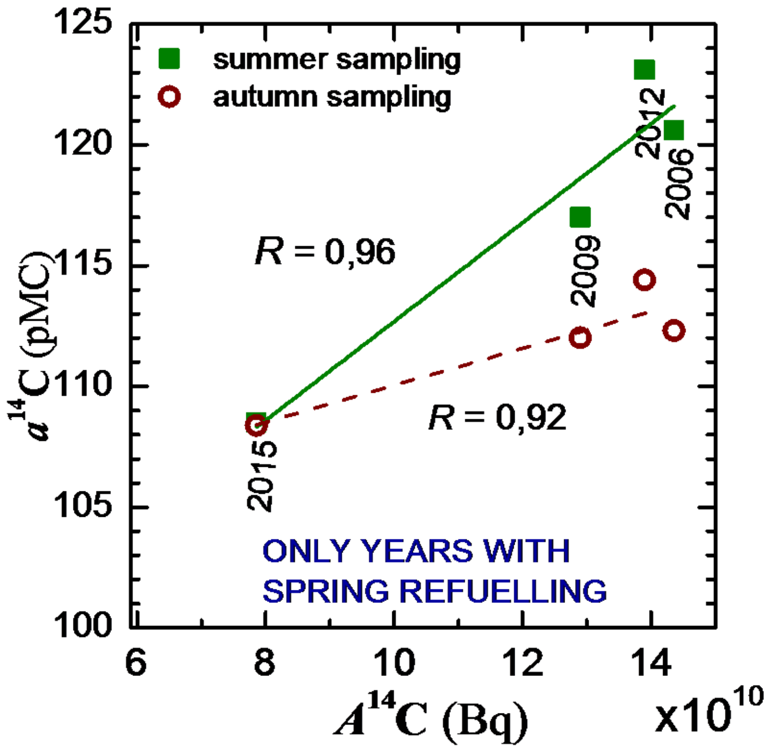
Spring refuelling - 2015

115

2015







- good correlation between the released $A^{14}C$ and the mean $a^{14}C$ of the inner locations

- higher $a^{14}C$ in samples taken in summer than in the autumn samples, because during spring plants use CO_2 from the atmosphere immediately after the refuelling

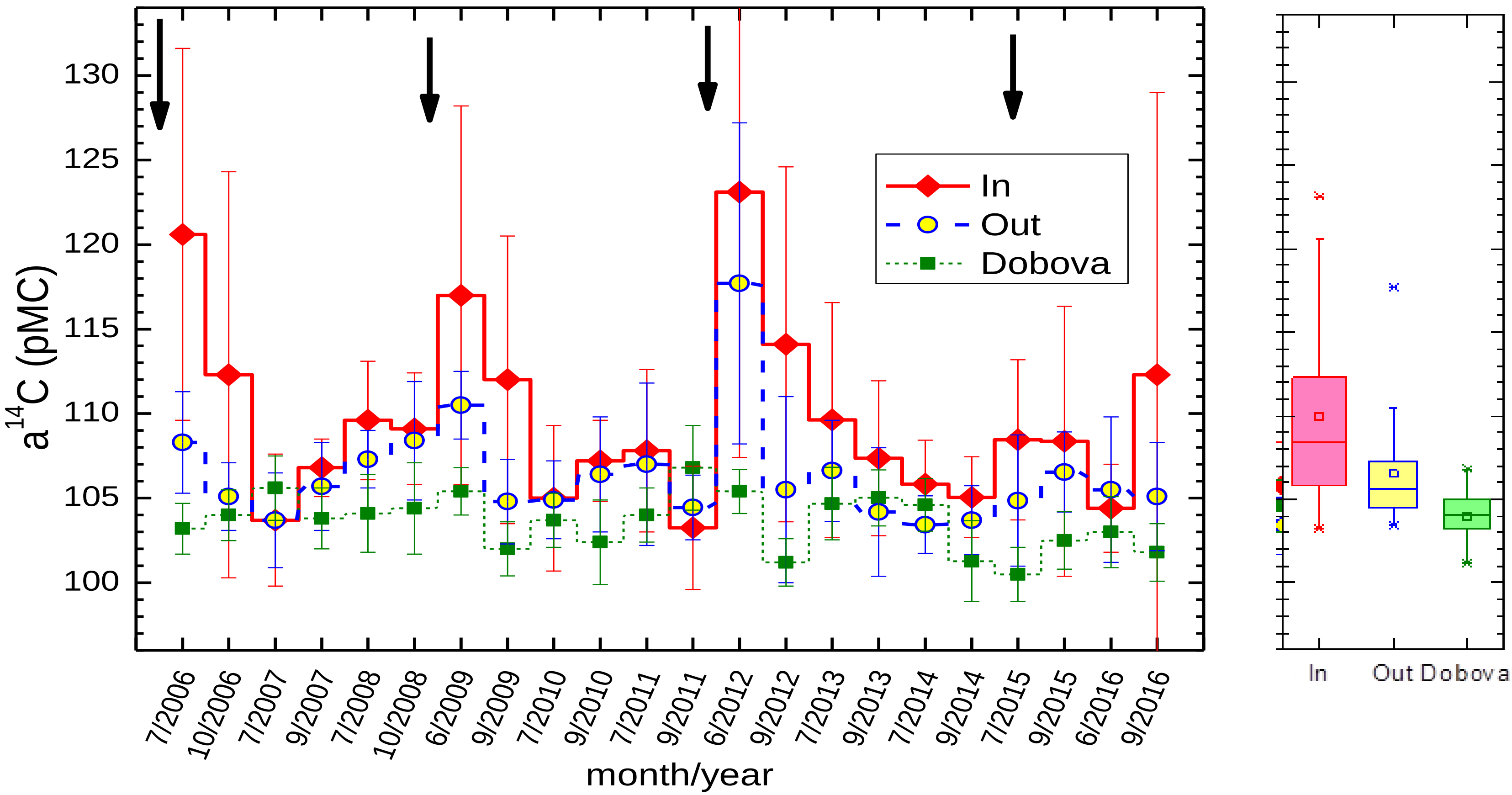
NEK

Seasonal average values

↓ Spring refuelling – before the vegetation period – significantly affects distribution of ^{14}C activitis in plants in summer sampling, somewhat less in autumn sampling.

Autumn refuelling – after the vegetation period – does not influence plant ^{14}C activity in the next year.

In years without a refuelling – $a^{14}C$ in the outer circle of NEK similar to the $a^{14}C$ at the control location Dobova, in the inner circle higher $a^{14}C$ values



NEK

Comparison of the average plants a^{14}C values in the inner circle (C, D, E, I, J, R), in the outer circle (F, G, H, K, L, M, N, O, P, Q) around NEK, at the control location Dobova, and the atmospheric a^{14}C in Zagreb

	Average a^{14}C (pMC) 2006 – 2016
Inner circle	**109.7 ± 4.1**
Outer circle	**106.4 ± 1.9**
Control location - Dobova	**103.6 ± 1.0**
Zagreb (atm. CO_2)	**102.3 ± 1.2**

Concluding remarks 1/2

- Environmental levels of ^{3}H and ^{14}C were presented
- Both isotopes are of cosmogenic origin
- Natural distributions of both isotopes have been disturbed by human activities in the 20th century
  continuous decrease since then with variable decrease rates
- Seasonal fluctuations superposed to the decreasing trends
- During last 10-20 years very slow decrease rates
- These „anthropogenically modified natural distributions" present now „new natural global" environmental levels
- Global environmental levels further modified by local effects

Concluding remarks 2/2

3 types of environmental sites

1. „clean-air" sites – influenced by the global effects only
2. Local effects that increase the „new natural" levels
   (sources of ^{3}H and ^{14}C - nuclear power plants, industry, medical facilities…)
3. Local effects that lower the „new natural" levels
   (^{3}H-free and ^{14}C-free sources – fossil fuels in industrial and urban areas, sea-water…)

Thank you