Geological Quarterly, 2008, **52** (2): 115–126

$\delta^{13}C$ of organic atmospheric dust deposited in Wrocław (SW Poland): critical remarks on the passive method

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Górka M. and Jędrysek M.-O. (2008) — $\delta^{13}C$ of organic atmospheric dust deposited in Wrocław (SW Poland): critical remarks on the passive method. Geol. Quart., **52** (2): 115–126. Warszawa.

This paper reports the results of the application of passive collectors to the collection of solid organic atmospheric particles (SOAP) in Wrocław (SW Poland) to carry out stable carbon isotope analyses. $\delta^{13}C$ (SOAP) values collected during the vegetation-free period, from November to March, vary in a narrow range from –24.5 to –27.8‰. We show that $\delta^{13}C$ (SOAP) is able to provide information about atmospheric pollution with respect to different emission sources. $\delta^{13}C$ (SOAP) values collected during the period of vegetation growth, from April to October, show a wide range from –20.5 to –26.9‰. The most probable explanations for the ^{13}C-enriched values in summer are that: (i) the SOAP have been contaminated with fresh and decomposed organic matter in the passive collector and/or (ii) SOAP are derived from outside the city or from outside Poland (C_4 plant particles). Therefore, the $\delta^{13}C$ (SOAP) may not represent a strictly anthropogenic impact. The passive collector method for the (SOAP) collection should be applied only in areas with dry deposition of atmospheric dust where deposited organic matter is not decomposed in the water contained in collectors. We recommend the use of active sampling methods (hi-volume sampler) to collect SOAP useful for carbon isotope analyses.

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Keywords: solid organic atmospheric particles, passive collector method, carbon isotopes.

INTRODUCTION

Atmospheric dust, especially its finest fractions (PM10, PM2,5 and PM1), is very hazardous to human health (lung diseases, allergies, cancers and others; Siegmann *et al*., 1999; Inyang and Bae, 2006). In spite of the modernization of all branches of industry, the dust problem in large urban areas, including Wrocław, remains critical. The agglomeration of Wrocław, with *ca*. 640000 inhabitants and complex old road geometry, results in problems with air quality. Generally, two types of anthropogenic atmospheric pollutants are indicated: (1) low emission (from local heating and traffic pollutants); (2) high emission (from large industrial plants, which are also located in Wrocław).

In this paper we report the results of carbon isotope measurements on solid atmospheric organic particles (SOAP) collected using the passive collector method. The carbon isotope analyses have been made as part of a larger investigation of atmospheric particles (including carbon isotopes from organic particles and oxygen isotopes from mineral particles). The isotopic composition of carbon in SOAP may provide information about its potential sources (soil organic matter, fresh organic matter, organic matter from combusted fossil fuels and others) and indicate areas with stronger anthropogenic impact. Investigations of the air quality in Wrocław, described by other authors, concerned daily fluctuations of CO and NO_x concentration between high buildings (Mikołajczyk *et al*., 1999), SODAR (Sonic Detection And Ranging) methods indicating atmospheric pollutants (Drzeniecka *et al*., 2000), variations of $\delta^{34}S$ (SO_4^{2-}) and $\delta^{18}O$ (SO_4^{2-}) in precipitation and in mineralogical composition of dust (Jędrysek, 2000, 2003; Górka and Jędrysek, 2004*a*, *b*, *c*).

The main goals of our study were: (1) to assess the reliability of the passive collection method for carbon isotope monitoring of atmospheric dust; (2) to determine sources of organic matter in SOAP (anthropogenic or natural); (3) to observe seasonal variations in $\delta^{13}C$ (SOAP); (4) to discriminate potential zonation in atmospheric pollution using isotope analyses combined with meteorological observations.

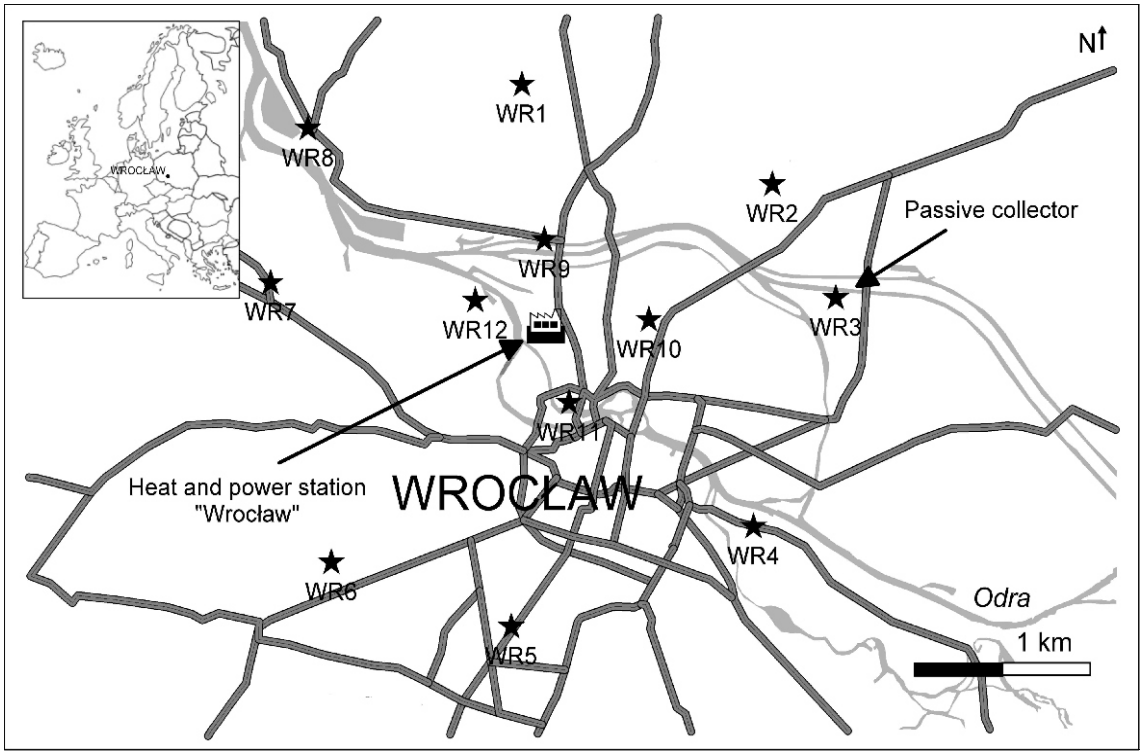

Fig. 1. Location of 12 passive collectors in Wrocław

EXPERIMENTAL PROCEDURES

Nine periods of sampling of atmospheric dust have been carried out in Wrocław (SW Poland). Passive collectors, built of non-reactive materials as described by Jires *et al*. (2002), were located throughout the city. Collectors were located 2.5 m above the ground. The collecting area is 0.0398 m^2 and the volume is *ca*.5 L. To avoid deposition of large non-dust components (leaves, insects) each collector was covered by a plastic grid (mesh size 2 mm).

12 passive collectors were place in areas of predominantly old-compact settlement, high traffic pollution, and distributed 1–3 km around the hard coal-fueled heat and power station "Wrocław" (potentially the largest single emitter in Wrocław; Fig. 1). All the collectors were installed in November 2003 and the samples were gathered every two months over nine collection-periods.

Before the carbon isotope analyses, the dust material from the collectors was dried, weighed and washed with a 0.3M HCl solution (1 hour) in order to remove inorganic carbon phases (mainly carbonates and hydroxides; Connin *et al*.,1997; Collins *et al*.,1999). The dust samples were then divided in half, and dried for 24 hours at 50°C. One part was washed with perhydrol (30% H_2O_2) in order to remove organic matter (SOAP), as described by Jackson (1985). The contribution of the SOAP fraction to the total dust was determined by the weight loss and the total dust, the inorganic mineral fraction and the organic fraction were calculated and expressed in $mg/m^2/day$. The other fraction of total dust particles containing SOAP was combusted with copper oxide (CuO) wire, under vacuum at 900°C using the sealed quartz tube method (Boutton, 1991; Skrzypek and Jędrysek, 2005). The CO_2 obtained was cryogenically purified and collected in glass ampoules. Carbon isotope ratios were analyzed using mass spectrometer *MI-1305* (produced at the Sumach factory, USRR) (Department of Mass Spectrometry at UMCS, Lublin, Poland) and a *Finnigan MAT Delta E* mass spectrometer (Laboratory of Isotope Geology and Geoecology at University of Wrocław, Poland). The error of the $\delta^{13}C$ determination was below 0.1‰, for both the types of mass spectrometer used. The carbon stable isotope standards used were IAEA NBS-22 and NBS-19.

We also measured the carbon isotope composition of other potential sources of carbon in dust particles (soil, grass, leaf, insect, building plaster, coal, furnace black, and soot from diesel and gasoline car engines). Leaves, grass, and insects were incubated in rain water for one month to simulate the decomposition processes of SOAP in the water stored in the passive collectors.

Meteorological data were obtained from the Meteorological Observatory of Wrocław (University of Wrocław). Complete meteorological data were collected 60 times per hour. Predominant wind directions and wind velocities were calculated as a sum of frequency in the individual angle interval. Maps of the spatial distribution of SOAP deposition and $\delta^{13}C$ values were made using the *Golden Software Surfer 8.0* (choosing the interpolation kriging method). Graphs and correlations were obtained using *Golden Software Grapher 5.0* software.

RESULTS

The geochemical and isotope data were obtained over nine collection periods from 20.11.2003 to 25.05.2005. The mass of the particles collected using the passive collectors has been calculated as total and SOAP dust deposition [mg/m^2/day] and reported in Tables 1 and 2, respectively. Deposition of the total dust varied from 4.53 to 195.76 mg/m^2/day with a minimum value on January 2004 and a maximum value on July 2004; the average value for each sampling period varied from 18.56 to 86.85 mg/m^2/day. The deposition of the SOAP varied from 0.62 to 114.34 mg/m^2/day with a minimum value on January 2005 and a maximum value on July 2004; the average for each sampling period varied from 3.62 to 31.86 mg/m^2/day. The standard deviations of total dust and SOAP deposition for winter periods are less than 14 and 5 respectively.

Table 3 reports the percentage contribution of organic matter to total dust deposition. The organic matter contribution varied from 1.88 to 74.56% with a minimum value on January 2005 and a maximum value on July 2004; the average for each sampling period varied from 12.12 to 50.00%. In Table 4 and Figure 2 we report the carbon isotope composition of SOAP. The standard deviation of $\delta^{13}C$ (SOAP) values varied around 0.5. The $\delta^{13}C_{PDB}$ value of SOAP varied from –27.8 to –20.5‰ with a minimum value on March 2004, and a maximum value on July 2004; the average for each sampling period varied between –26.8 and –23.4‰. The spatial distribution of the SOAP deposition in Wrocław during the nine periods is reported graphically in Figure 3. The spatial distribution of the $\delta^{13}C$ values of SOAP in Wrocław during the nine periods investigated is shown in Figure 4. The correlation between the amount of deposited SOAP [mg/m^2/day] and its $\delta^{13}C$ [‰] values is rather low, $R^2 = 0.28$ (Fig. 5).

The $\delta^{13}C$ values of soil organic matter sampled on 24.03.2005 at each dust sampling station varied from –26.8 to –24.0‰, the average being –25.7‰ (Table 5). The concentration of the organic matter in the soil varied from 0.88 to 4.09% with an average of 2.38% (Table 5). Although in general there is no correlation between the system $\delta^{13}C$ (SOAP) and the corresponding $\delta^{13}C$ (soil), there are two periods of remarkable correlation between soil and SOAP carbon isotope composition (Table 4): $R^2 = 0.28$ (period from 17.05.2004 to 22.07.2004) and $R^2 = 0.35$ (period from 21.09.2004 to 24.11.2004).

The $\delta^{13}C$ values obtained for other organic matter sampled randomly in Wrocław (Wrocław organic matter — WOM) and being a potential

Table 1

Total dust deposition [mg/m^2/day] in Wrocław (20.11.2003–25.05.2005)

Passive collector	Total (organic and inorganic) solid atmospheric particles deposition [mg/m^2/day]											
	Period											
	20.11.2003–13.01.2004	05.01.2004–15.03.2004	11.03.2004–19.05.2004	17.05.2004–22.07.2004	20.07.2004–23.09.2004	21.09.2004–24.11.2004	22.11.2004–26.01.2005	24.01.2005–24.03.2005	23.03.2005–25.05.2005	Min.	Max.	Stand. dev.	Average
WR1	20.72	34.19	96.19	50.34	75.37	84.21	32.97	8.11	71.63	8.11	96.19	30.63	52.64
WR2	34.10	44.31	13.67	104.43	112.30	62.00	45.98	51.32	102.86	13.67	112.30	34.96	63.44
WR3	4.53	n.a.	36.56	28.71	20.12	39.73	16.10	17.44	34.25	4.53	39.73	12.12	24.68
WR4	6.28	26.7	67.60	60.72	51.42	99.99	30.96	24.37	62.78	6.28	99.99	28.55	47.87
WR5	21.44	42.83	94.77	77.92	n.a.	72.22	30.88	17.14	149.34	17.14	149.34	44.78	63.32
WR6	11.15	39.63	92.63	61.69	155.50	53.92	22.65	21.23	73.41	11.15	155.50	44.86	59.09
WR7	18.47	36.98	147.42	102.59	92.76	75.43	33.80	42.37	137.15	18.47	147.42	46.87	76.33
WR8	20.16	29.16	105.81	89.99	31.42	n.a.	n.a.	33.31	52.13	20.16	105.81	33.28	51.71
WR9	13.64	59.34	32.32	25.16	124.31	13.22	26.23	28.25	67.78	13.22	124.31	35.66	43.36
WR10	35.68	46.7	129.44	78.77	138.34	158.54	52.57	35.35	126.54	35.35	158.54	49.06	89.10
WR11	28.49	50.21	132.14	195.76	72.25	37.04	20.53	41.26	31.38	20.53	195.76	58.74	67.67
WR12	8.06	8.21	59.27	93.47	81.59	12.62	12.32	10.46	60.98	8.06	93.47	35.00	38.55
Min.	4.53	8.21	13.67	25.16	20.12	12.62	12.32	8.11	31.38				
Max.	35.68	59.34	147.42	195.76	155.50	158.54	52.57	51.32	149.34				
Stand. dev.	10.38	13.62	42.61	44.73	43.13	41.81	12.05	13.48	39.21				
Average	18.56	38.02	83.99	80.80	86.85	64.45	29.54	27.55	80.85				

n.a. — not analyzed

Table 2

SOAP dust deposition [mg/m^2/day] in Wrocław (20.11.2003–25.05.2005)

Passive collector	Solid organic atmospheric particles (SOAP) deposition [mg/m^2/day]												
	Period												
	20.11.2003–13.01.2004	05.01.2004–15.03.2004	11.03.2004–19.05.2004	17.05.2004–22.07.2004	20.07.2004–23.09.2004	21.09.2004–24.11.2004	22.11.2004–26.01.2005	24.01.2005–24.03.2005	23.03.2005–25.05.2005	Min.	Max.	Stand. dev.	Average
WR1	7.20	3.25	10.44	16.49	28.34	19.17	0.62	n.a.	10.03	0.62	28.34	9.06	11.94
WR2	13.19	7.18	6.12	52.09	66.67	15.39	7.35	7.36	47.59	6.12	66.67	23.74	24.77
WR3	3.33	n.a.	13.49	11.02	3.06	15.37	n.a.	n.a.	12.71	3.06	15.37	5.33	9.83
WR4	3.50	6.62	35.12	35.30	6.94	14.49	2.73	1.70	33.75	1.70	35.30	14.84	15.57
WR5	6.62	8.54	23.67	29.89	n.a.	27.20	1.43	n.a.	30.82	1.43	30.82	12.35	18.31
WR6	3.86	6.53	11.52	13.22	20.42	18.39	1.30	n.a.	10.35	1.30	20.42	6.69	10.70
WR7	10.28	13.22	64.19	59.18	38.88	40.45	4.50	6.91	85.31	4.50	85.31	29.18	35.88
WR8	15.03	17.64	61.60	27.97	14.61	n.a.	n.a.	17.06	18.57	14.61	61.60	16.90	24.64
WR9	8.78	22.90	20.01	5.56	67.43	3.02	7.76	0.95	32.17	0.95	67.43	21.00	18.73
WR10	10.25	6.97	38.13	35.07	43.42	100.03	6.11	3.41	47.43	3.41	100.03	30.88	32.31
WR11	11.82	11.05	41.07	114.34	31.61	16.34	1.79	7.92	7.18	1.79	114.34	35.07	27.01
WR12	5.40	2.79	11.73	35.57	29.11	n.a.	2.57	n.a.	18.77	2.57	35.57	13.18	15.13
Min.	3.33	2.79	6.12	5.56	3.06	3.02	0.62	0.95	7.18				
Max.	15.03	22.90	64.19	114.34	67.43	100.03	7.76	17.06	85.31				
Stand. dev.	3.92	6.13	19.95	29.37	21.35	27.42	2.63	5.44	22.46				
Average	8.27	9.70	28.09	36.31	31.86	26.99	3.62	6.47	29.56				

Explanations as in Table 1

Table 3

Contribution of SOAP in Wrocław (20.11.2003–25.05.2005)

Passive collector	Contribution of organic matter in dust [%]												
	Period												
	20.11.2003–13.01.2004	05.01.2004–15.03.2004	11.03.2004–19.05.2004	17.05.2004–22.07.2004	20.07.2004–23.09.2004	21.09.2004–24.11.2004	22.11.2004–26.01.2005	24.01.2005–24.03.2005	23.03.2005–25.05.2005	Min.	Max.	Stand. dev.	Average
WR1	34.73	9.50	10.85	32.77	37.60	22.77	1.88	n.a.	14.00	1.88	37.60	13.38	20.51
WR2	38.68	16.21	44.81	49.88	59.37	24.82	15.97	14.34	46.27	14.34	59.37	16.94	34.48
WR3	73.50	n.a.	36.92	38.37	15.19	38.68	n.a.	n.a.	37.09	15.19	73.50	18.76	39.96
WR4	55.75	24.79	51.95	58.14	13.50	14.49	8.83	6.98	53.77	6.98	58.14	22.31	32.02
WR5	30.87	19.94	24.97	38.35	n.a.	37.66	4.62	n.a.	20.64	4.62	38.35	11.78	25.29
WR6	34.63	16.46	12.43	21.43	13.13	34.11	5.75	n.a.	14.10	5.75	34.63	10.43	19.01
WR7	55.65	35.76	43.55	57.68	41.91	53.62	13.31	16.3	62.21	13.31	62.21	17.68	42.22
WR8	74.56	60.49	58.22	31.08	46.50	n.a.	n.a.	51.22	35.63	31.08	74.56	15.00	51.10
WR9	64.36	38.6	61.92	22.11	54.24	22.83	29.58	3.35	47.47	3.35	64.36	20.54	38.27
WR10	28.72	14.94	29.46	44.52	31.38	63.09	11.62	9.65	37.48	9.65	63.09	17.12	30.10
WR11	41.48	22.00	31.08	58.41	43.75	44.10	8.74	19.19	22.88	8.74	58.41	15.65	32.40
WR12	67.07	34.00	19.79	38.06	35.68	n.a.	20.86	n.a.	30.78	19.79	67.07	15.75	35.18
Min.	28.72	9.50	10.85	21.43	13.13	14.49	1.88	3.35	14.00				
Max.	74.56	60.49	61.92	58.41	59.37	63.09	29.58	51.22	62.21				
Stand. dev.	17.07	14.63	17.03	13.12	16.03	15.12	8.31	15.93	15.48				
Average	50.00	26.61	35.50	40.90	35.66	35.62	12.12	17.29	35.19				

Explanations as in Table 1

Table 4

^{13}C of SOAP in Wrocław (20.11.2003–25.05.2005)

Passive collector	$\delta^{13}C_{PDB}$ [‰] (SOAP)												
	Period												
	20.11.2003 –13.01.2004	05.01.2004– 15.03.2004	11.03.2004– 19.05.2004	17.05.2004– 22.07.2004	20.07.2004– 23.09.2004	21.09.2004– 24.11.2004	22.11.2004– 26.01.2005	24.01.2005– 24.03.2005	23.03.2005– 25.05.2005	Min.	Max.	Stand. dev.	Average
WR1	–25.9	–26.8	–25.9	–24.4	–21.8	–21.5	–26.6	–26.7	–26.7	–26.8	–21.5	2.11	–25.1
WR2	–24.5	–26.7	–25.7	–24.6	–22.4	–25.6	–26.1	–26.5	–22.9	–26.7	–22.4	1.52	–25.0
WR3	n.a.	n.a.	–25.6	–24.8	–26.0	–25.4	–25.8	–26.1	–26.1	–26.1	–24.8	0.48	–25.7
WR4	n.a.	–27.8	–26.9	–23.7	–24.7	–20.9	–27.0	–27.3	–24.4	–27.8	–20.9	2.34	–25.3
WR5	–26.0	–27.1	–24.1	–20.6	n.a.	–22.8	–26.7	–26.1	–25.8	–27.1	–20.6	2.25	–24.9
WR6	n.a.	–26.8	–25.5	–24.3	–22.6	–21.7	–26.3	–26.3	–26.2	–26.8	–21.7	1.93	–25.0
WR7	–25.9	–27.0	–24.5	–20.5	–23.1	–25.0	–26.5	–26.9	–24.5	–27.0	–20.5	2.09	–24.9
WR8	–26.0	–26.9	–24.2	–25.3	–22.8	n.a.	n.a.	–27.3	–24.4	–27.3	–22.8	1.61	–25.3
WR9	n.a.	–26.2	–24.6	–25.5	–26.9	–23.8	–25.6	–26.2	–26.2	–26.9	–23.8	0.99	–25.6
WR10	–25.5	–26.5	–24.5	–21.5	–21.7	–21.7	–25.8	–26.3	–21.4	–26.5	–21.4	2.25	–23.9
WR11	–25.0	–25.9	–23.3	–23.0	–23.0	–25.8	–26.8	–26.6	–25.9	–26.8	–23.0	1.55	–25.0
WR12	n.a.	n.a.	–25.7	–22.2	–24.0	–24.9	–26.7	–27.2	–26.0	–27.2	–22.2	1.74	–25.3
Min.	–26.0	–27.8	–26.9	–25.5	–26.9	–25.8	–27.0	–27.3	–26.7				
Max.	–24.5	–25.9	–23.3	–20.5	–21.7	–20.9	–25.6	–26.1	–21.4				
Stand. dev.	0.56	0.52	1.01	1.78	1.70	1.88	0.47	0.47	1.59				
Average	–25.6	–26.8	–25.1	–23.4	–23.5	–23.6	–26.4	–26.6	–25.0				
R^2 $\delta^{13}C$ (SOAP) to $\delta^{13}C$ (soil)	0.01	0.11	0	0.28	0.03	0.35	0.12	0.03	0.08				

Explanations as in Table 1

Table 5

Contribution and the ^{13}C value of organic matter from soil sampled on 24.03.2005

Sample station	Organic matter from soil	
	$\delta^{13}C_{PDB}$[‰]	Organic matter [%]
WR 1	–26.3	2.33
WR 2	–26.2	1.47
WR 3	–26.8	3.61
WR 4	–24.5	4.09
WR 5	–24.0	0.88
WR 6	–25.6	0.91
WR 7	–26.2	2.24
WR 8	–26.6	3.22
WR 9	–25.9	2.09
WR 10	–24.7	2.53
WR 11	–25.7	3.22
WR 12	–26.1	1.95
Min.	–26.8	0.88
Max.	–24.0	4.09
Average	–25.7	2.38

Table 6

$^{13}C_{PDB}$ [‰] value of the Wrocław organic matter collected for the experiment

Sample name	Wrocław organic matter (WOM)	
	$^{13}C_{PDB}$[‰] before incubation	$^{13}C_{PDB}$[‰] after 1 month of incubation
grass	–30.5	–30.7
algae[1]	n.a.	–30.7
leaf	–27.3	–28.4
algae[2]	n.a	–28.8
insect	–30.0	–30.3
coal[3]	–24.2	n.a.
coal[4]	–25.7	n.a.
furnace black[5]	–24.5	n.a.
diesel soot	–28.3	n.a.
gasoline soot	–26.8	n.a.
Min.	–30.5	–30.7
Max.	–24.2	–28.8
Average	–27.2	–29.8

[1]algae formed in the beaker during incubation of grass (see Introduction); [2]algae formed in the beaker during incubation of leaf (see Introduction); [3]low-quality black coal used in heating and power station "Czechnica" in Siechnice — high emission; [4]high-quality black coal used in local hearts — low emission; [5]furnace black obtained from the chimney where high-quality black coal (low emission) has been burned; n.a. — not analyzed

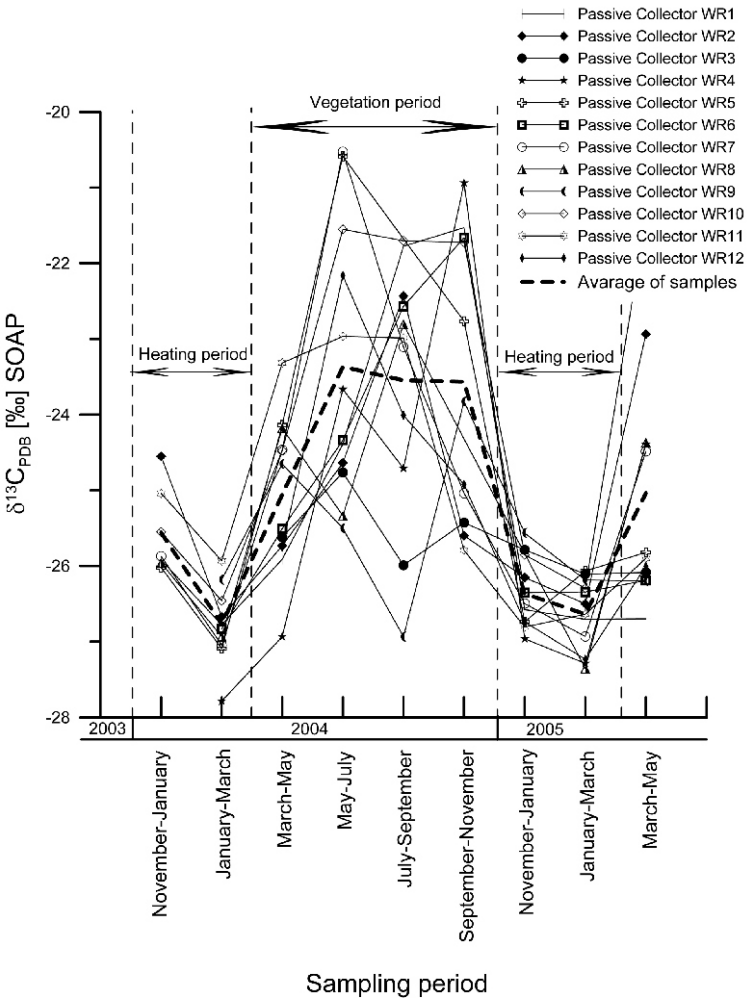

Fig. 2. Seasonal variations in the $\delta^{13}C$ value of the solid organic atmospheric particles (SOAP) in Wrocław

source of SOAP are shown in Table 6. The $\delta^{13}C$ (WOM) values vary from –24.2 to –30.5‰. The $\delta^{13}C$ value of organic matter samples incubated in rainwater varied from –28.4 to –30.7‰. Beside SOAP and WOM, we also measured the $\delta^{13}C$ value of carbonates from that plaster that covers buildings (–15.0‰; n = 6).

Meteorological data indicate that predominant wind directions in Wrocław are south-west and north-east, and additionally south-east (except in summer). Winds in Wrocław are classified as of low speed, the two month-period average velocity being lower than 3 m/s. The major wind velocities are well correlated with the major wind directions (SW), but the strongest wind episodes correspond mainly to a NNW wind direction. Although it is not possible to compare, spatially, geochemical data (SOAP deposition and $\delta^{13}C$ (SOAP)) to single-point meteorological data, meteorological data indicate the potential directions of air pollutant transport (SW–NE).

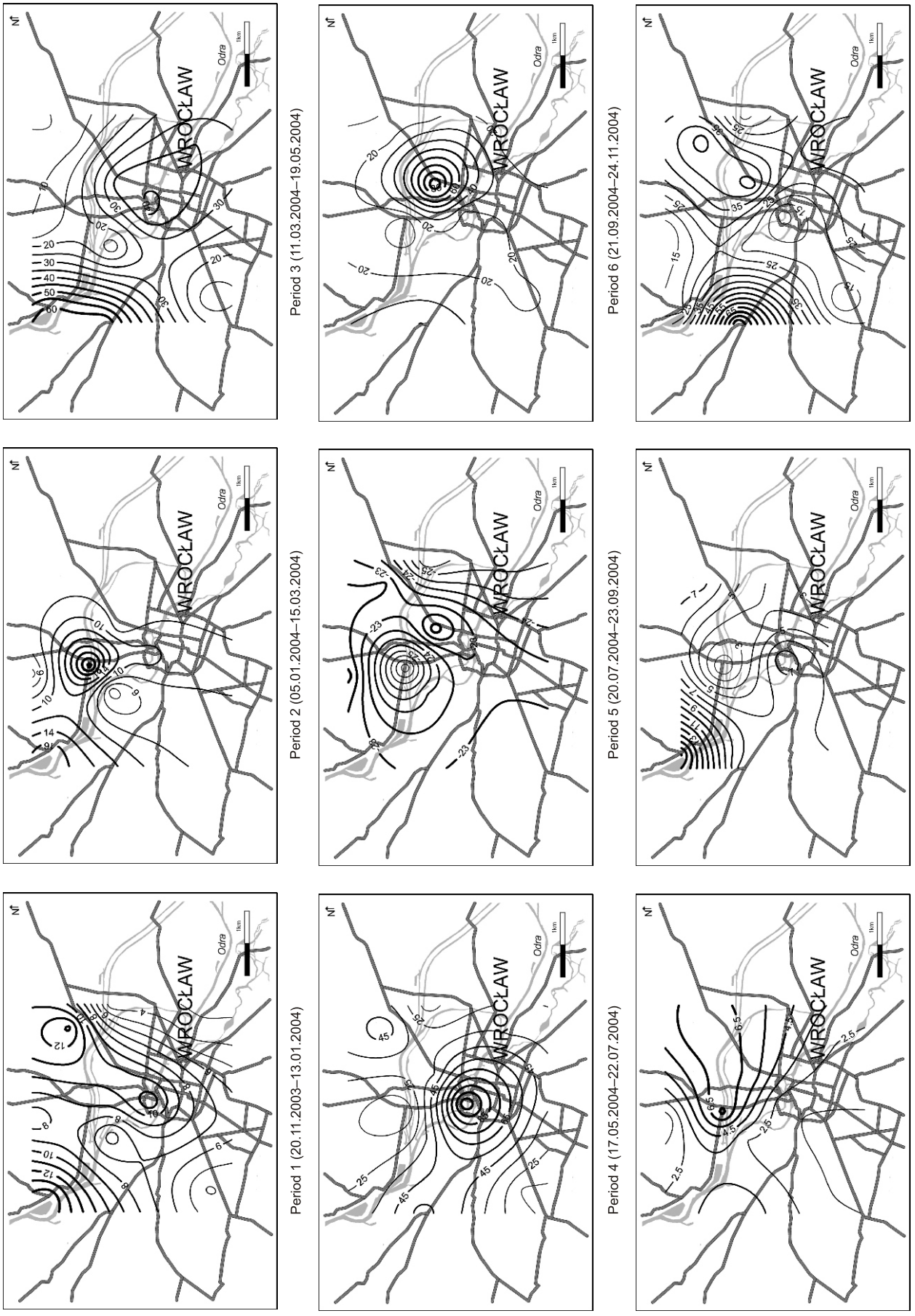

Fig. 3. Spatial distribution of solid organic atmospheric particle fall [mg/m^2/day] in Wroclaw

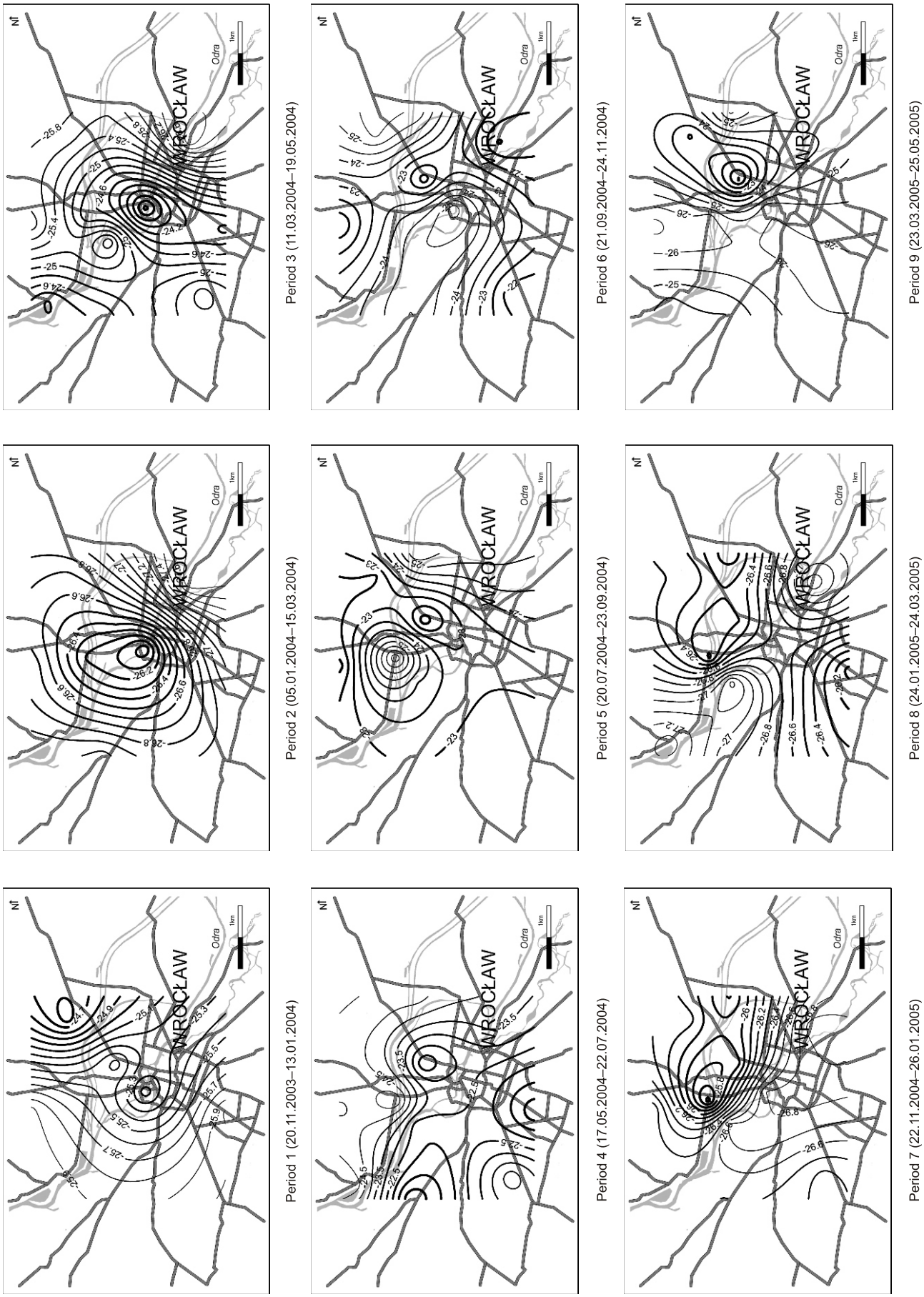

Fig. 4. The spatial distribution of the $\delta^{13}C_{PDB}$ [‰] value of solid organic atmospheric particles in Wroclaw

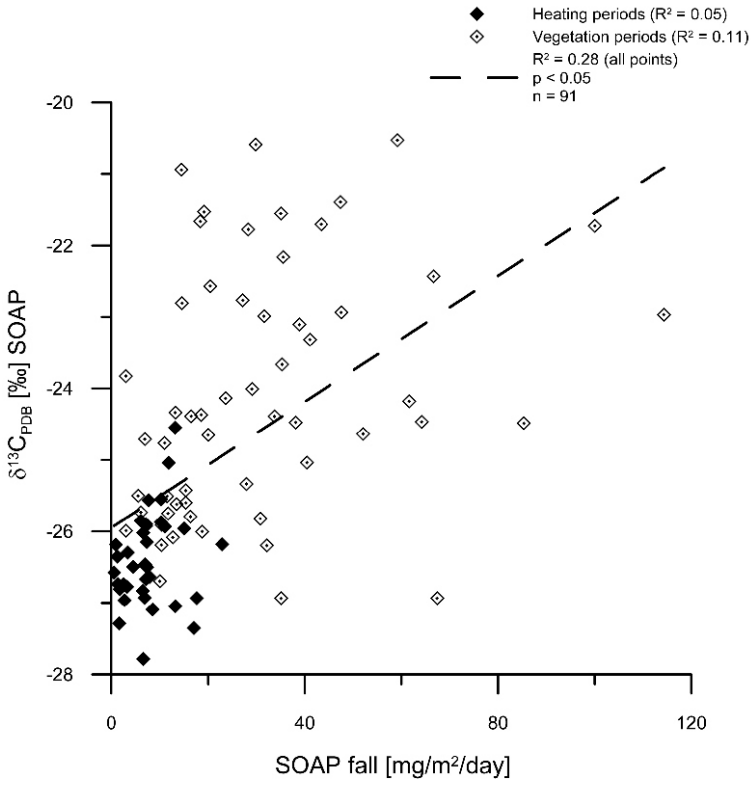

Fig. 5. Relations between the $\delta^{13}C$ (SOAP) and SOAP fall in Wrocław

DISCUSSION

Firstly, we have observed seasonal variations in SOAP concentrations as well as in their $\delta^{13}C$ values (Figs. 2 and 5). During the heating period (from late autumn to early spring), SOAP fall and the $\delta^{13}C$ varies within relatively narrow ranges (Figs. 2 and 5). When vegetation grows (from late spring to early autumn), SOAP fall and the $\delta^{13}C$ varies within wide ranges (Figs. 2 and 5). The spring to autumn deposition of total (organic and inorganic) dust in Wrocław is higher (Table 1 and 2) than in the winter period. A similar pattern has been observed at Karlsruhe, Germany (Norra and Stüben, 2004). We suggest that this is due to higher concentrations of organic matter in the atmosphere during the growing period (pollen, fragments of plants, insects, *etc.*) as well as to stronger deflation (particles from soil that is unfrozen and not covered by snow are easily deflated). Also, the growth of algae, fungi and bacteria in collectors contaminating the SOAP concentrations is possible.

The explanation of the $\delta^{13}C$ (SOAP) variations is problematic. Moreover, the expected SOAP $\delta^{13}C$ values during the heating period should vary between –24‰ (when the combustion of coal dominates) and –27‰ (when the combustion of diesel and oil dominates). Our expectations are supported by observations relating to liquid fuels reported by Widory *et al.* (2004), e.g. regular and unleaded fuel combustion generates particles showing $\delta^{13}C$ values –24.2 ±0.6‰, whereas diesel fuel particles have $\delta^{13}C$ values of –26.5 ±0.5‰. Through investigations on the carbon isotope composition of Polish coal carried out by Kotarba and Clayton (2003) indicated values of about –23.8 ±0.4‰ for Lower Silesia. The SOAP $\delta^{13}C$ value during the vegetation period was expected to vary between –28 and –30‰ due to the $\delta^{13}C$ of local C_3 plants, which can be the main source of SOAP during the growing season.

The data obtained during the heating season are close to the expected values (Table 4), but only in those areas of Wrocław where old settlements with low emissions dominated (Fig. 4). However, surprisingly, the SOAP $\delta^{13}C$ during the growing period varied within a wide range from –20.5 to –27.8‰ (Table 4 and Fig. 2). The higher carbon isotope ratio during the growing season cannot be explained by the presence of soil particles in the total dust fall. This is because the $\delta^{13}C$ value of the soil organic matter collected close to the passive collectors varied between –24.0 and –26.8‰ (Table 5). Weak positive correlations between the $\delta^{13}C$ (soil) and $\delta^{13}C$ (SOAP) values were observed only during the late spring (17.05.2004 to 22.07.2004; $R^2 = 0.28$) and early autumn (21.09.2004 to 24.11.2004; $R^2 = 0.35$). This implies increased deposition of wind-borne soil organic matter in the collectors, and meteorological data indicate that wind directions and velocity were similar during these two periods. The higher $\delta^{13}C$ of the C_3 soil organic matter observed by previous authors reported $\delta^{13}C$ values ranging between –23 and –20‰ (Staddon, 2004) is not applicable in our case, because Wrocław $\delta^{13}C$ values are lower (Table 5). Therefore, organic matter of soil origin cannot explain the highest $\delta^{13}C$ values (close to –21‰) obtained in passive collectors (Table 4 and Fig. 2).

We have to consider whether it is possible that SOAP were potentially partially altered or decomposed *in situ* in the wet conditions inside the rainwater-filled plastic collectors during the growing period. The isotope ratios of the SOAP in the collectors could perhaps be influenced by atmospheric CO_2 dissolved in rainwater with the consequent abundant growth of algae, fungi and bacteria contaminating the SOAP isotopic values. The $\delta^{13}C$ value of the atmospheric CO_2 in the city downtown varies between –8 and –13‰ (Szaran, 1990; Kuc, 1991; Staddon, 2004; Szaran *et al.*, 2005) — this results in higher $\delta^{13}C$ of the organic matter grown in the collectors if dissolved CO_2 can be used for the production of this organic matter. It follows that, both the amount of collected organic matter and its carbon isotope ratios may not be representative of pristine SOAP.

A weak positive correlation between SOAP [mg/m^2/day] and its $\delta^{13}C_{PDB}$ [‰] ($R^2 = 0.28$) was found (Fig. 5), but this is not evidence that the $\delta^{13}C$ of SOAP is controlled by the origin of the accumulated SOAP. For further evidence, a simple experiment was carried out. Local organic matter soaked for one month in rainfall water had $\delta^{13}C$ values that were slightly lower than those obtained from fresh organic matter before incubation (Table 6). Although a one-month incubation is a short time compared to the two-month sampling periods, the slight negative change in $\delta^{13}C$ values goes in the opposite direction compared to the expected strong positive change. A similar ^{13}C isotope depletion resulting from decomposition of organic matter in the soil has been no-

ticed by other authors (Deines, 1980; Benner *et al*., 1987; Lichtfouse *et al*., 1995). Plant lipids and lignin are ^{13}C-depleted relative to bulk tissue, whereas amino acids, cellulose and hemicellulose are usually ^{13}C-enriched (Lichtfouse *et al*., 1995). Since lipids and lignin are more resistant to biodegradation relative to other plant constituents, and because the major part of plant carbon is rapidly recycled to the atmosphere, the accumulation of plant matter into soil (or other decomposed matter) by selective preservation of plant lipids, or lignin, *vs*. polysaccharides should have led to a notable shift of the isotope compositions of soil organic components towards ^{13}C-depleted values (Lichtfouse *et al*., 1995). This may be a plausible explanation for our experimental results, but does not explain the relatively high $\delta^{13}C$ values obtained during the growing period (Table 4 and Fig. 2). According to these results, we conclude that the passive collector method cannot be applied in regions with predominantly wet deposition, especially in summer.

The cause of the high-$\delta^{13}C$ values also cannot result from the contribution of plaster from the building surface ($\delta^{13}C = -15.0‰$) because carbonates were removed from each SOAP sample (XRD confirmed) before the isotope analyses and because high-$\delta^{13}C$ values obtained during summer were not observed during the winter period when a considerably more active physical weathering of building plaster is expected.

We hypothetically suggest (not confirmed by palynological investigations) that the organic dust is delivered from outside of the city or even outside of Poland (particles, especially pollen, delivered from C_4 plants have a distinctly higher $\delta^{13}C$ value, close to –13‰ (Staddon, 2004)).

At this stage we are unable to explain the high $\delta^{13}C$ (SOAP) values collected during the growing period (Table 4 and Fig. 2). A plausible mechanism could be the formation and accumulation of microbiological organic matter within or/and on the surface of SOAP and mineral particles. This newly formed organic matter should be expected to show high $\delta^{13}C$ values resulting from the assimilation of ^{13}C-enriched dissolved inorganic carbon (DIC) being close to isotopic equilibrium with atmospheric CO_2. Also, sequential degradation would enrich the carbon pool, as the light CO_2 leaves the system.

Alternatively, we can hypothetically suggest that the dust collected in Wrocław may be transported from outside the city or even from outside of Poland. High $\delta^{13}C$ values are characteristic of C_4 plants which are typical of warmer climates. The main C_4 plant cultivated in Poland is maize, but its amount in agricultural crops is still of negligible importance.

No relatively significant correlation has been observed between meteorological data (wind roses) and geochemical data as spatial distribution of SOAP deposition (Table 2) and spatial distribution of $\delta^{13}C$ (SOAP) (Table 4).

Regardless of the previous considerations, the passive method of collection of solid organic atmospheric particles during the growing period to carry out carbon isotope analyses is problematic and perhaps not applicable in rainy areas. Consequently, SOAP carbon isotopic analyses should be preferentially collected by means of high-flow analyzers (pumps) with quartz filters, particularly during summer.

CONCLUSIONS

1. The passive method for the collection of solid organic atmospheric particles for carbon isotope analyses is not applicable in rainy areas during the growing period.

2. The use the active sampling methods (hi-volume sampler) for the collection of SOAP for carbon isotope analyses should always be preferred.

3. During the winter (heating period) the deposition of SOAP and its $\delta^{13}C$ (SOAP) values indicate the fossil fuel-burning origin of SOAP in Wrocław.

4. During the summer (growing period) the deposition of SOAP and its $\delta^{13}C$ (SOAP) values may not be representative of pristine SOAP or indicate the C_4 SOAP origin from outside the city or from outside Poland.

5. Meteorological data do not indicate unequivocal directions of transport of air atmospheric pollutants in the agglomeration of Wrocław.

Acknowledgements. Meteorological data were obtained from the Meteorological Observatory of Wrocław (Section for Meteorology and Climatology, University of Wrocław). We would like to acknowledge A. Kałużny for his substantial help in fieldwork, G. Skrzypek, D. Lewicka and A. Trojanowska for their critical remarks. We thank C. Turich for language correction and scientific consultancy.

This study was supported by the Ministry of Education and Science of Poland: grant No. 3 T09D 086 28 and Wrocław University grants No. 1017/S/ING/05-IX. 2022/W/ING/05-49. 2022/W/ING/05-12.

Authors are very grateful to A. Longinelli and M. Zimnoch for their critical remarks of the manuscript and for their valuable suggestions.

REFERENCES

BENNER R., FOGEL M. L., SPRAGUE E. K. and HODSON R. E. (1987) — Depletion of ^{13}C in lignin and its implications for stable isotope studies. Nature, **329**: 708–710.

BOUTTON T. W. (1991) — Stable carbon isotope ratios of natural materials: I. Sample preparation and mass spectrometric analysis. In: Carbon Isotope Techniques (eds. D. C. Coleman and B. Fry). Acad. Press Inc., Harcourt Brace, Publishers, San Diego.

COLLINS H. P., BLEVINS R. L., BOUNDY L. G., CHRISTENSEN D. R., DICK W. A., HUGGINS D. R. and PAUL E. A. (1999) — Soil carbon dynamics in corn-based agroecosystems: Results from carbon-13 natural abundance. Soil Sci. Soc. Am. J., **63**: 584–591.

CONNIN S. L., VIRGINIA R. A. and CHAMBERLAIN C. P. (1997) — Carbon isotopes reveal soil organic matter dynamics following arid land shrub expansion. Oecologia, **110**: 374–386.

DEINES P. (1980) — The isotopic composition of reduced organic carbon. In: Handbook of Environmental Isotope Geochemistry (eds. P. Fritz and J. Ch. Fontes): 329–406. Elsevier, Amsterdam.

DRZENIECKA A., PEREYMA J., PYKA J. L. and SZCZUREK A. (2000) — The influence of meteorological conditions on atmospheric pollutions in centre of Wrocław (in Polish with English summary). Ecol. Chem. Engin., **7** (8–9): 865–882.

GÓRKA M. and JĘDRYSEK M.-O. (2004*a*) — C and S isotope variations in solid atmospheric particles and sulfate in precipitations in Wrocław (SW Poland). Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz. Bd., **8**: 41–45. Isot. Works Vol. Graz .

GÓRKA M. and JĘDRYSEK M.-O. (2004*b*) — Solid atmospheric particles and wet precipitations in Wrocław (SW Poland): mineralogical and isotopic preliminary studies. Pr. Spec. Pol. Tow. Miner., **24** : 179–182.

GÓRKA M. and JĘDRYSEK M.-O. (2004*c*) — Isotopic analyses of solid atmospheric particles and sulphates from precipitation as an indicator quantitative assess of anthropogenic impact in downtown Wrocław (in Polish with English summary). In: Ochrona powietrza w teorii i praktyce (eds. J. Konieczyński and R. Zarzycki): 141–152. Inst. Podst. Inż. Środ. PAN, Zabrze.

INYANG H. I. and BAE S. (2006) — Impacts of dust on environmental systems and human health. J. Hazardous Mater., **132**: v–vi.

JACKSON M. L. (1985) — Soil chemical analysis — Advanced Course, 2nd ed., 11th printing, published by the author. Madison, WIS 53705 (revised from 1956 edition).

JĘDRYSEK M.-O. (2000) — Oxygen and sulphur isotope dynamics in the SO_4^{2-} of an urban precipitation. Water, Air and Soil Pollut., **117**: 15–25.

JĘDRYSEK M.-O. (2003) — New data on $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values in precipitation: potential indicator of the origin of surficial and groundwater recharge (in Polish with English summary). In: Współczesne problemy hydrogeologii (eds. H. Piekarek-Jankowska and B. Jaworska-Szulc), **11** (2): 157–164. Wyd. Politech. Gdańskiej.

JIRES A., EL-HASAN T. and MANASRAH W. (2002) — Qualitative evaluation of the mineralogical and chemical composition of dry deposition in the central and southern highlands of Jordan. Chemosphere, **48**: 933–938.

KOTARBA M. J. and CLAYTON J. L. (2003) — A stable carbon isotope and biological marker study of Polish bituminous coals and carbonaceous shales. Inter. J. Coal Geol., **55** (2–4): 73–94.

KUC T. (1991) — Concentration and carbon isotopic composition of atmospheric CO_2 in southern Poland. Tellus, **43B**: 373–378.

LICHTFOUSE E., DOU S., GIRARDIN C., GRABLY M., BALESDENT J., BEHAR F. and VANDENBROUCKE M. (1995) — Unexpected ^{13}C-enrichment of organic components from wheat crop soils: evidence for the *in situ* origin of soil organic matter. Org. Geochem., **23** (9): 865–868.

MIKOŁAJCZYK A., PEREYMA J. and SZCZUREK A. (1999) — Ocena wpływu warunków meteorologicznych na jakość powietrza w Śródmieściu Wrocławia. POL-IMIS '99 III Sympozjum Ocena Wielkości Imisji Zanieczyszczeń Powietrza. Wyd. PZITS, **764**: 71–80.

NORRA S. and STÜBEN D. (2004) — Trace element patterns and seasonal variability of dust precipitation in a low polluted city — the example of Karslruhe/Germany. Environ. Monit. Assess., **93**: 203–228.

SIEGMANN K., SHERRER L. and SIEGMAN H. C. (1999) — Physical and chemical properties of airborne nanoscale particles and how to measure the impact on human health. J. Molecular Structure (Theochem), **458**: 191–201.

SKRZYPEK G. and JĘDRYSEK M.-O. (2005) — $^{13}C/^{12}C$ ratio in peat cores: Record of past climates. Environ. Chemistry— Green Chemistry and Pollutants in Ecosystems, (ed. E. Lichtfouse, J. Schwarzbauer and D. Robert).

STADDON P. L. (2004) — Carbon isotopes in functional soil ecology. TRENDS in Ecology and Evolution, **19** (3).

SZARAN J. (1990) — The $\delta^{13}C$ and CO_2 concentration in the air. In: Course-book of Isotope Geology, (ed. M.-O. Jdęrysek). Third School on Physics of Minerals, part **1** — Isotopes: 160–168., Wrocław Univ. and Comm. Mineral. Sci.

SZARAN J., DUDZIAK A., TREMBACZOWSKI A., NIEZGODA H. and HAŁAS S. (2005) — Diurnal variations and vertical distribution of $\delta^{13}C$, and concentration of atmospheric and soil CO_2 in a meadow site, SE Poland. Geol. Quart., **49** (2): 135–144.

WIDORY D., ROY S., MOULLEC Y. L. GOUPIL G., COCHERIE A. and GUERROT C. (2004) — The origin of atmospheric particles in Paris: a view through carbon and lead isotopes. Atmosph. Environ., **38**; 953–961.