

## **Chemistry and $\delta^{13}\text{C}$ of Total Dissolved Carbon in Waters of Selected Springs nearby Lublin City**

**Weekly Observations from October 1982 to June 1983**

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The pH,  $\delta^{13}\text{C}$  of total dissolved carbon and  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Ca}^{2+} + \text{Mg}^{2+}$  contents in spring waters were investigated. Changes of these values were recorded for 8 months of 1982 and 1983. The changes were irregular and larger in winter and early spring, than in autumn and late spring. These changes and a long-term trend observed in October and November are discussed in terms of models of Deines *et al.* (1974) and the theory of mixing of waters (Wigley and Plummer 1976).

### **Introduction**

The pH,  $\delta^{13}\text{C}$  value and concentrations of the following species:  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+} + \text{Mg}^{2+}$  in waters from 3 springs located a few km north of Lublin City were investigated weekly for 8 months in 1982 and 1983.

Similar investigations had been performed from January to May 1977, where samples were taken from 24 springs and wells from SW Lublin Upland. Results were presented in Halas *et al.* (1982, 1983), and Staniaszek and Halas (1986). Those investigations revealed strong seasonal variations in chemistry and isotopic composition of dissolved carbonate. The variations were discussed in terms of the dissolution of carbonate rocks. The models of carbonate dissolution of Deines *et al.* (1974) were extended by considering mixing effects (Wigley and Plummer 1976; Staniaszek and Halas 1985). These effects, caused mainly by the redistribution of dissolved carbon-bearing species, are significantly nonlinear and asymmetrical with respect to the fraction of the second solution in a binary mixture.

The main purpose of this study was to observe the chemical and isotope compositions *more frequently* than previously (Staniaszek and Halas 1986) for a better understanding of the reasons of their temporal variations. Therefore the number of springs investigated was limited to three of the most productive ones in the vicinity of our laboratory, from which the water samples were taken out weekly. Inasmuch as  $\delta^{13}\text{C}$  value of total carbonate species dissolved in water ( $\delta^{13}\text{CT}$ ) is a very sensitive parameter, we anticipated from its observation, to draw conclusions about inflows of “new” waters to the aquifer in winter and spring.

### Description of Study Area

The study area is a portion of NW Lublin Upland, near Lublin City. The sampling points are marked on the map in Fig. 1. The springs are located in the middle and lower part of the drainage basin of the Ciemięga river, the total area of which is about 150 km<sup>2</sup>. The ground waters in this area, like in other parts of Lublin Upland, have complicated circulation patterns owing to the complex geological structure of the bedrock and its cover.

The geological profile of the study area may be briefly described as follows. A thick layer (up to 800 m) of Cretaceous limestones (in some places overlain by thin and irregular strata of Paleocene limestones) is covered by Pleistocene loess which has a thickness ranging up to twenty metres. Both kinds of limestones may play the role of the aquifer rock, however in our particular case Cretaceous limestones are more important.

A major part of the ground water is retained in fractures, vugs, and tectonic cracks of the limestones. The role of pores in water accumulation and circulation is minor. The infiltrating waters are retained by irregularly developed layers of clay-

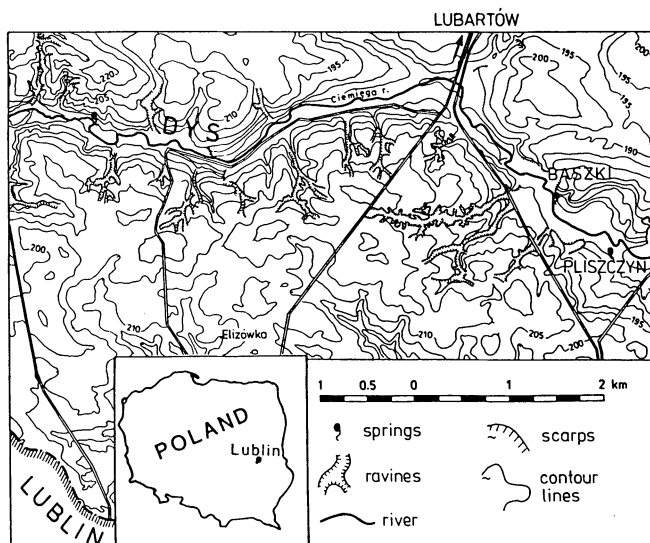


Fig. 1. Sketch map of the study area.

Table 1 – Hydrological characteristics of investigated springs

Location of Spring	Average productivity (l/sec)	Absolute height (m)	Aquifers Limestone
Dys	5	181.7	Paleocene and Cretaceous
Baszki	20	172.0	Cretaceous
Pliszczyn	50	170.5	Cretaceous

rich limestones, which occur in different horizons (Michalczyk *et al.* 1983). A further complication in the geological structure of the bed-rock is the vertical and lateral variability of limestones. Some layers are developed as soft marl and/or chalk whereas in others are hard rock. The depth of the water table in this area is 20 to 40 m, depending on the topology.

The selected springs are located in the river valley near the villages of Dys, Baszki and Pliszczyn (Fig. 1), and will be referred to by the name of appropriate village. Essential hydrogeological characteristics of these springs are summarized in Table 1. For a more detailed description of the investigated area the reader is referred to: Butrym *et al.* (1982), Harasimiuk (1980), Harasimiuk and Henkiel (1982), Michalczyk *et al.* (1983).

### Analytical Procedures

One-litre glass bottles were filled with water samples for measuring pH,  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  content. These bottles were immediately transported to the laboratory and measurements were performed within several hours after sampling. By transporting a bottle of tap water into the field and back to the laboratory, it was shown that pH of water samples remains almost constant during the first three hours after sampling. The  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{Ca}^{2+} + \text{Mg}^{2+}$  contents were measured by titration methods.

Total dissolved carbon was precipitated as  $\text{BaCO}_3$  in the field using one-litre glass bottles filled with 75 ml of saturated  $\text{BaCl}_2\text{-NH}_4\text{OH}$  solution. The precipitate was rinsed with boiled doubly distilled water, centrifuged, and dried. The  $\text{CO}_2$  was subsequently derived for isotope analysis from  $\text{BaCO}_3$  by treatment with 100%  $\text{H}_3\text{PO}_4$  in a vacuum line (McCrea 1950). The isotope ratio determinations were carried out by means of a Nier-type mass spectrometer with an improved inlet system (Halas 1980) and on-line data processing (Halas and Skorzynski 1980, 1981).

The following standards: NBS-20, NBS-22 and KH-2 were used for the calibration of the working standard. Precisions of 0.05 permil were obtained in  $\delta^{13}\text{C}$  (and  $\delta^{18}\text{O}$ ) measurements, 0.02 in pH, and 0.05 mVal/l for  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Ca}^{2+} + \text{Mg}^{2+}$  determinations. The  $\delta^{18}\text{O}$  values were determined occasionally in order to obtain the correction factor for  $\delta^{13}\text{C}$  (Craig 1957).

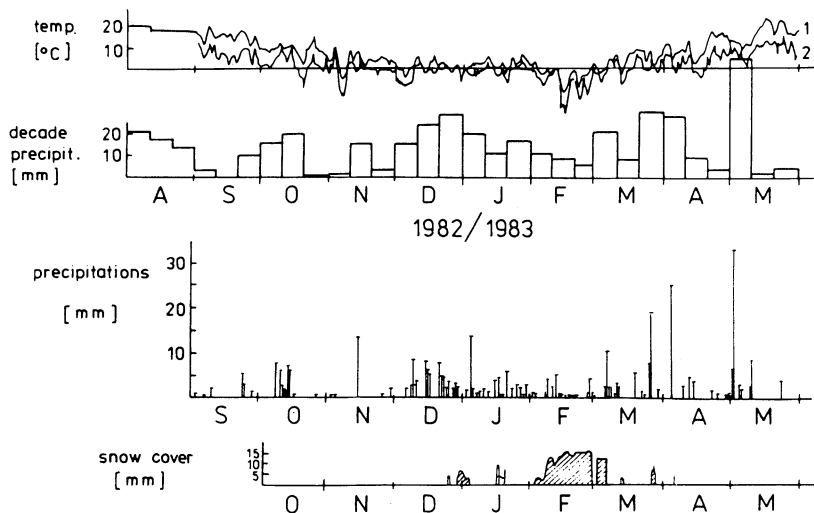


Fig. 2. Meteorological data versus time over which springs were sampled.

## Results

The results of the investigation are shown in Table 2 and in Figs. 3, 4, 5, 6. Preliminary results were reported at the 10th All-Union Symposium on Stable Isotopes in Geochemistry in Moscow (Staniaszek and Halas 1984). Meteorological data taken from the Radawiec meteorological station located 17 km from Dys are given in Fig. 2 and the temporal variations of all the measured parameters of the spring waters are given in Fig. 3.

Plots of  $\text{HCO}_3^-$  versus pH,  $\text{Ca}^{2+} + \text{Mg}^{2+}$  versus pH, and  $\delta^{13}\text{C}_T$  versus pH are given in Figs. 4, 5, 6, respectively. In order to present the results conveniently, the period of observation has been divided into three parts.

*The first*, from October, 7th to December 14th (points 1 to 10 in Figs. 4, 5 and 6), was rather dry and hot. Whereas most parameters remained stable, the pH and  $\delta^{13}\text{C}$  of total dissolved carbonate species ( $\delta^{13}\text{C}_T$ ) increased. This is particularly evident in Figs. 4a, 5a and 6a. The increase in  $\delta^{13}\text{C}$  may reflect loss of  $^{13}\text{C}$  depleted  $\text{CO}_2$ , a reduced input of soil  $\text{CO}_2$  and/or changes in the  $\delta^{13}\text{C}$  value of soil  $\text{CO}_2$ . This is consistent with the fact that the aquifer has a weak contact with the soil reservoir of  $\text{CO}_2$ , through the network of small cracks in the bedrock. Therefore changes of  $\delta^{13}\text{C}$  in the soil reservoir should influence the isotopic compositions of the springs. After heavy rains in the second half of November, the  $\delta^{13}\text{C}_T$  value decreased. However changes in pH values over this time were small.

*The second period*, from December 14th to March 2nd (points 10 to 20), was wet with numerous inflow events. All the parameters varied frequently and irregularly

## Chemistry of Springs

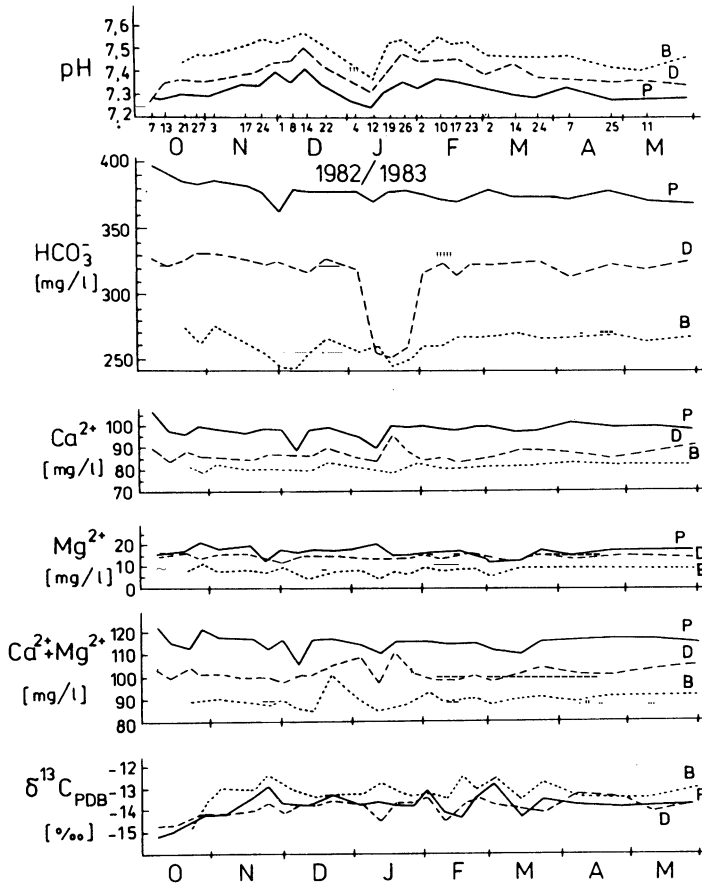


Fig. 3. Parameters of spring waters versus time. In all plots: B = Baszki (dotted lines), D = Dys (dashed lines), P = Pliszczyn (bold lines). Numbers 1 to 24 correspond to the sampling dates in Table 2.

(Figs. 3, 4b, 5b and especially Fig. 6b). For example in Fig. 2, a decrease of pH was observed from December 14th to January 12th, then it increased and remained higher from February onwards. Strong variations in  $\text{Ca}^{2+} + \text{Mg}^{2+}$  content may be noted in December and January. The  $\delta^{13}\text{CT}$  values measured in that time were the most sensitive indicators of inflows. From December to March the  $\delta^{13}\text{CT}$  varied strongly and chaotically (Fig. 6b).

*The third period* from March 2nd to May 30th (points 20 to 26) was also wet, but the temperature was higher. Therefore the rain water either evaporated or was taken up by plants, especially in April and May. Most of the measured parameters became almost stable (Figs. 4c, 5c, 6c).



## Chemistry of Springs

13	12/01/83	7.37	4.26	3.96	0.44	4.40	-12.74	7.31	4.20	4.20	1.10	5.30	-14.54	7.25	6.10	4.50	1.68	6.18	-13.66
		260	79.4	5.3	84.7				256	84.2	13.4	97.6			372	90.2	20.4	110.6	
14	19/01/83	7.52	4.00	3.92	0.64	4.56	-13.16	7.40	4.10	4.32	1.14	5.46	-13.65	7.32	6.20	5.03	1.29	6.32	-13.77
		244	78.6	7.8	86.4				250	96.6	13.9	110.5			378	100.8	15.7	116.5	
15	26/01/83	7.54	4.08	4.08	0.58	4.66	-13.35	7.48	4.23	4.38	1.14	5.52	-13.69	7.36	6.05	4.99	1.30	6.29	-13.72
		249	81.8	7.1	88.9				258	87.8	13.9	101.7			369	100.0	15.8	115.8	
16	2/02/83	7.49	4.24	4.16	0.80	4.97	-13.24	7.45	5.20	4.24	1.24	5.48	-13.40	7.33	6.16	5.00	1.34	6.34	-13.17
		259	83.4	9.7	93.1				317	85.0	15.1	100.1			376	100.2	16.3	116.5	
17	10/02/83	7.56	4.27	4.02	0.70	4.72	-13.44	7.45	5.33	4.27	1.13	5.40	-14.58	7.37	6.12	4.94	1.37	6.31	-14.23
		260	80.6	8.5	89.1				325	85.6	13.7	99.3			373	99.0	16.7	115.7	
18	17/02/83	7.52	4.37	4.04	0.79	4.83	-12.47	7.46	5.17	4.18	1.29	5.47	-13.88	7.36	6.07	4.89	1.43	6.32	-14.37
		267	81.0	9.6	90.6				315	83.8	15.7	99.5			370	98.0	17.4	115.4	
19	23/02/83	7.53	4.38	4.06	0.78	4.84	-13.08	7.44	5.27	4.22	1.29	5.51	-13.45	7.35	6.12	4.98	1.28	6.26	-13.44
		267	81.4	9.5	90.9				321	84.6	15.7	98.7			373	99.8	15.6	115.4	
20	2/03/83	7.48	4.39	4.08	0.50	4.58	-12.62	7.39	5.29	4.25	1.11	5.36	-13.76	7.33	6.21	5.00	1.00	6.00	-12.83
		268	81.8	6.1	87.9				323	85.2	13.5	98.7			379	100.2	12.2	112.4	
21	14/03/83	7.47	4.42	4.06	0.77	4.83	-13.48	7.44	5.32	4.42	1.09	5.51	-13.94	7.30	6.13	4.89	1.06	5.95	-14.36
		270	81.4	9.4	90.8				325	88.6	13.2	101.8			374	98.0	12.9	110.9	
22	24/03/83	7.47	4.38	4.07	0.80	4.87	-12.74	7.38	5.38	4.44	1.27	5.71	-14.08	7.29	6.13	4.89	1.50	6.39	-13.52
		267	81.6	9.7	91.3				328	89.0	15.4	104.4			374	98.0	18.2	116.2	
23	7/04/83	7.48	4.37	4.15	0.50	4.87	-13.31	7.50*	5.13	4.38	1.12	5.50	-13.29	7.33	6.10	5.07	1.23	6.30	-13.75
		267	83.2	6.1	89.3				313	87.8	13.6	101.4			372	101.6	15.0	116.6	
24	25/04/83	7.43	4.42	4.07	0.80	4.87	-13.50	7.36	5.31	4.25	1.26	5.51	-13.49	7.28	6.18	4.98	1.43	6.41	-13.88
		270	81.6	9.7	91.3				324	85.2	15.3	100.5			377	99.8	17.4	117.2	
25	11/05/83	7.41	4.32	4.09	0.77	4.86	-13.40	7.36	5.24	4.37	1.25	5.62	-14.03	7.28	6.08	4.98	1.44	6.42	-13.77
		264	82.0	9.4	91.4				320	87.6	15.2	102.8			371	99.8	17.5	117.3	
26	30/05/83	7.47	4.37	4.07	0.80	4.87	-12.95	7.34	5.32	4.52	1.20	5.72	-13.68	7.28	6.04	4.90	1.46	6.36	-13.66
		267	81.6	9.7	91.3				325	90.6	14.6	105.2			368	98.2	17.7	115.9	

\* This value was treated as outlier, because the level of water in the stream was high and the stream water was mixed with the spring water.

Fig. 4.

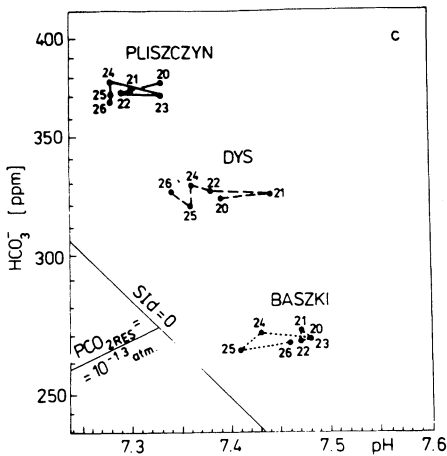
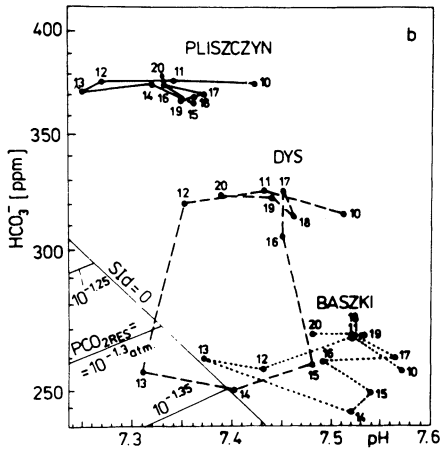
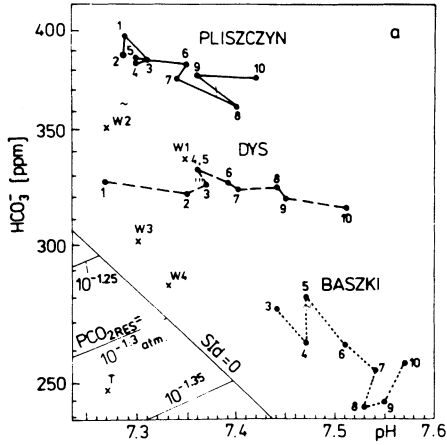
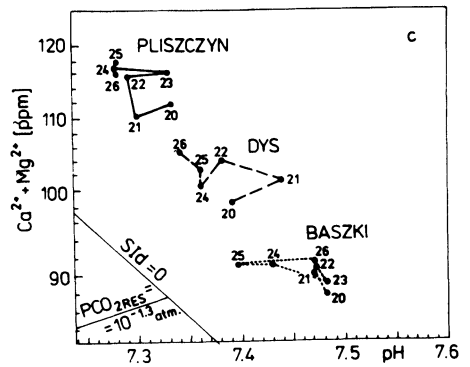
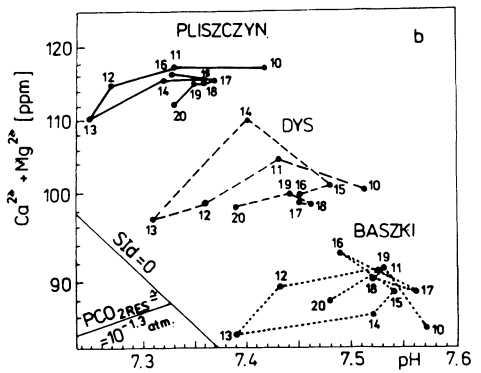
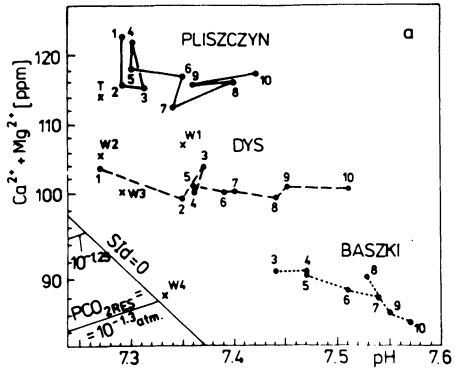


Fig. 5.





## Discussion

The period of observation was very suitable for investigating variable infiltration rates. The summer of 1982 was very long, dry, and hot. The thick strata of loess in large parts of the study area moderated the inflows of new water to the aquifer. Since the aquifer is large in comparison to the inflows, the changes of all the parameters characterizing the water chemistry were very small. However, the methods used here were sensitive enough to detect those changes.

The permeabilities of different soils (sands, loesses etc.) and bedrock limestones (clay-rich, soft marl, chalk etc.) result in water flowing to the aquifer with different velocities dependent upon the flowpath. Therefore descending waters acquire different chemical and isotopic compositions which are in turn different from those of the aquifer. Mixing of waters throughout the aquifer is not immediate because of its large areal extent. Consequently, the aquifer water is isotopically and chemically inhomogeneous and one inflow event results in gradual changes of the parameters in water sampled at the spring outlet.

As in our previous papers, (Staniaszek and Halas 1985, 1986) the closed system conditions (CSC) curves of the model developed by Deines *et al.* (1974) are drawn with the experimental data in Figs. 4, 5, 6. The open and closed system models for the dissolution of carbonate rocks were discussed by Holland *et al.* (1964), Thrailkill (1968), and Langmuir (1971).

Although the waters investigated were oversaturated, the parameters of the soil CO<sub>2</sub> reservoir (PCO<sub>2RES</sub> and  $\delta^{12}\text{C}_{\text{RES}}$ ) were estimated by extrapolation of the model curves in Figs. 4, 5, and 6. The PCO<sub>2RES</sub> values estimated from Figs. 4 and 5 were below 10<sup>-1.3</sup> atm. for Baszki (10<sup>-1.4</sup> – 10<sup>-1.3</sup> atm.), above this value for Dys, and higher than 10<sup>-1.3</sup> atm. for Baszki (10<sup>-1.4</sup> – 10<sup>-1.3</sup> atm.), above this value for Dys, and higher than 10<sup>-1.2</sup> atm. for Pliszczyn spring. The temporal variations of PCO<sub>2RES</sub> were small in these springs. The work by Staniaszek and Halas (1985) showed that when mixing occurs, the parameters PCO<sub>2RES</sub> and  $\delta^{13}\text{C}_{\text{RES}}$  do not indicate the real, average values of PCO<sub>2</sub> and  $\delta^{13}\text{C}$  of CO<sub>2</sub> in the soil, but some modified values. However when their changes are small, these values are close to the real ones.

For  $\delta^{13}\text{C}_{\text{RES}}$ , the situation was more complicated. From Fig. 6 it is clear that changes in this value were much higher,  $\delta^{13}\text{C}_{\text{RES}}$  varied from -26 to -22 permil. In

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Fig. 4. Temporal variations in HCO<sub>3</sub><sup>-</sup> and pH along the evolution lines of CSC. Point T refers to the spring located near Turka village (see Fig. 1), points W1 to W4 refer to the springs of Wierzchowiska village in SW Lublin Upland. Numbers 1 to 24 correspond to dates in Table II.

Fig. 5. Temporal variations in Ca<sup>2+</sup> + Mg<sup>2+</sup> and pH along the evolution lines of CSC. Points T and W and numbers 1-24 are explained in Figs. 3 and 4.

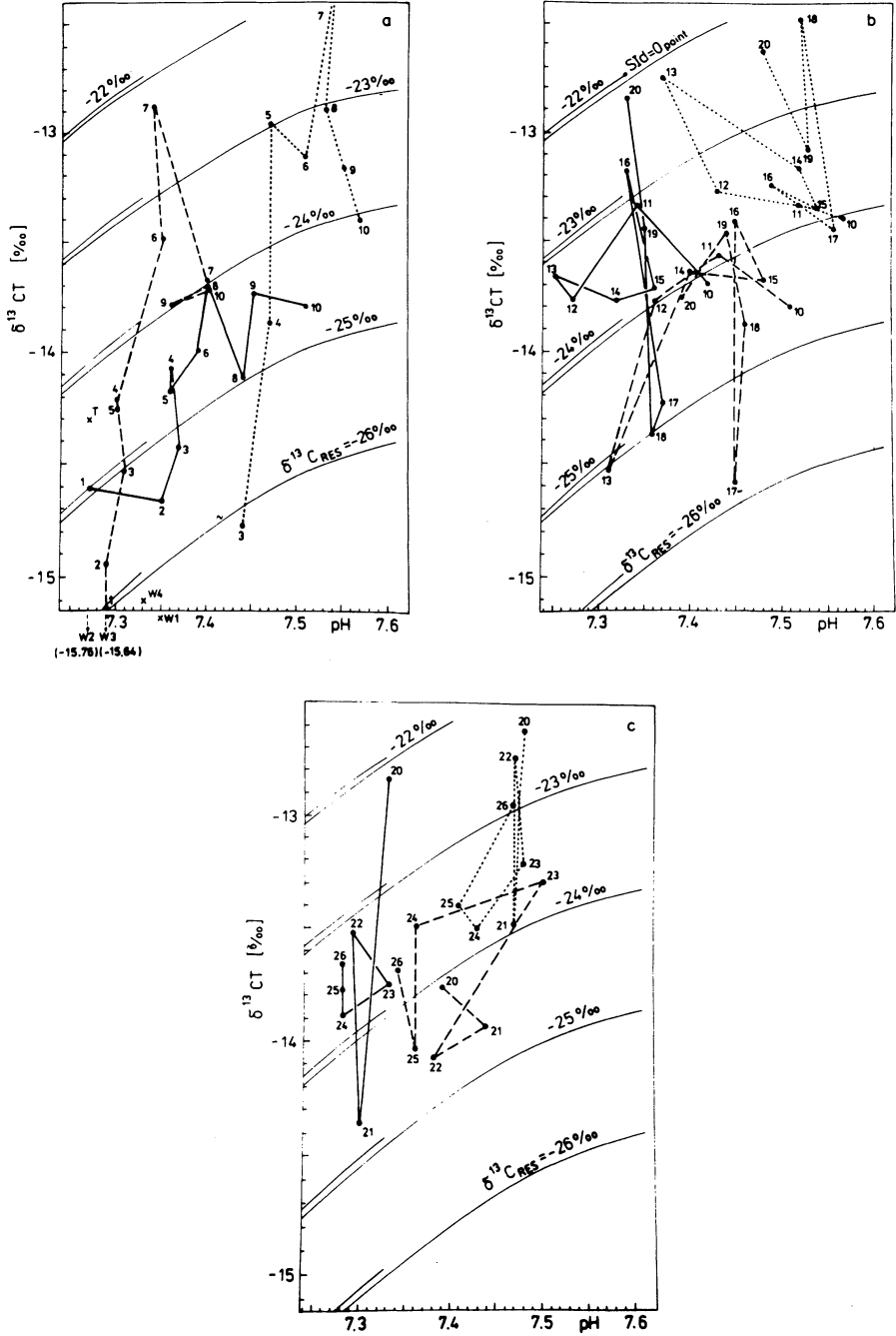


Fig. 6. Temporal variation in  $\delta^{13}\text{CT}$  and pH along the evolution lines of CSC. Points T and W and numbers 1-24 are explained in Figs. 3 and 4.

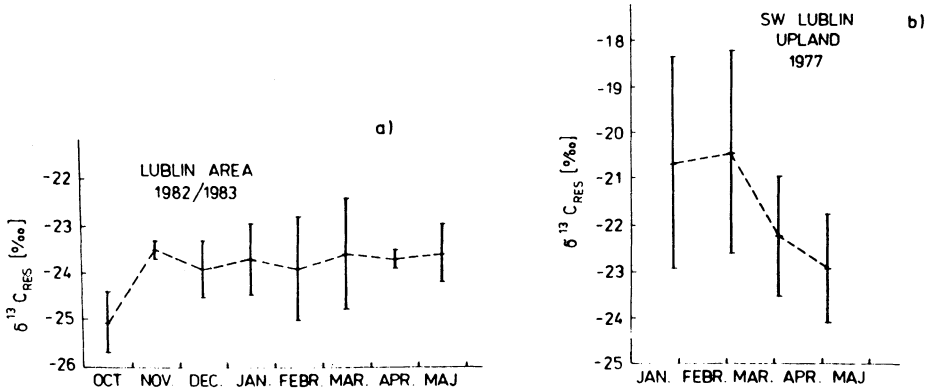


Fig. 7. The results of evaluation of 95% confidence interval for  $\delta^{13}C_{RES}$ . a) In Lublin area  $\delta^{13}C_{RES}$  was calculated for 3 springs with samples taken from 2 to 4 times per month. b) In SW Lublin Upland the  $\delta^{13}C_{RES}$  parameter was calculated for 24 springs and wells sampled once a month.

such a case  $\delta^{13}C_{RES}$  does not indicate the real average values for  $CO_2$  generated in the soil. The mixing effects and loss of  $CO_2$  may extend the range of  $\delta^{13}C_{RES}$  considerably. This parameter may be considered to be a sensitive indicator of inflows only. In order to compare monthly variations in  $\delta^{13}C_{RES}$  during the investigation period the 95% confidence interval ( $\delta - S$ ,  $\delta + S$ ) were evaluated using Student's *t*-distribution, where  $\delta$  is the average value, and

$$S = \frac{1}{2} t_{0.05} \sqrt{\frac{\sum_{i=1}^n (\delta_i - \bar{\delta})^2}{n-1}}$$

*n* is a number of results obtained during one month for all three springs.

The results  $\delta \pm S$  are shown in Fig. 7a. For comparison, the results  $\delta \pm S$  for 25 springs and wells, investigated in 1977, are shown in Fig. 7b (Staniaszek and Halas 1986). It has been noted that in winter and early spring the *S*-values are larger than in late spring or in autumn, for those waters. A similar feature has been seen in the current investigation.

From Fig. 7, another interesting conclusion may be drawn. In October 1982, the springs in the Lublin area had the lowest  $\delta^{13}C_{RES}$  values. For SW Lublin Upland there were also lower  $\delta^{13}C_{RES}$  values in April and May than in January 1977. This may result from a decrease of  $\delta^{13}C$  value for  $CO_2$  generated in soil during summer, and may indicate that all springs investigated in 1982 and 1983 have rather weak contact with the  $CO_2$  reservoir. Thus the changes in  $\delta^{13}C$  of  $CO_2$  in the soil may be the most probable explanation of changes in the  $\delta^{13}CT$  value in October and November 1982.

Despite the above complication the  $\delta^{13}C_{RES}$  values obtained are consistent with

data for soil CO<sub>2</sub>. The δ<sup>13</sup>C of CO<sub>2</sub> in the soil reservoir depends on the kind of vegetation. For example, if the organic matter in agricultural soils is made up mainly of decaying corn stalks, the CO<sub>2</sub> generated should have a δ<sup>13</sup>C value close to -13 permil (Bender 1968; Smith and Epstein 1971). Measurements by Smith (1971) have shown that CO<sub>2</sub> respired by corn have similar <sup>13</sup>C contents. CO<sub>2</sub> in Russian agricultural and forest soils has δ<sup>13</sup>C values from -18 to -28 permil (Galimov 1966).

The results of analysis of δ<sup>13</sup>CT and chemistry of waters sampled from other springs also point to very low values of δ<sup>13</sup>C for CO<sub>2</sub> in the soil in October 1982. The values for the Turka spring (Lublin area) and the Wierzchowiska springs (SW Lublin Upland) are shown in Figs. 4a, 5a and 6a (points T, W1, W2 and W3 respectively). For example, the Wierzchowiska 3 (W3) spring was investigated from January to May 1977 (Staniaszek and Halas 1986) and the results were as follows (Table 3):

Table 3 - Summary of δ<sup>13</sup>CT determinations for Wierzchowiska 3 spring

Date	pH	δ <sup>13</sup> CT (permil)
January 20th, 1977	7.10	-13.14
March 3rd, 1977	6.30	-14.00
April 1st, 1977	6.80	-14.08
May 5th, 1977	7.45	-13.42
October 12th, 1982	7.30	-15.64

The above data convince us that, aside from frequent variations in winter and early spring, parameters of spring waters undergo long-term changes. When water remains in the aquifer for a long time without any inflows e.g. Lublin area in 1982, the long-term changes must be explained by mechanisms other than inflow (weak contact with soil CO<sub>2</sub>, or loss of CO<sub>2</sub> from the water).

From January 4th to February 2nd, a significant decrease in HCO<sub>3</sub><sup>-</sup> content was recorded in the Dys spring. Surprisingly the Ca<sup>2+</sup> + Mg<sup>2+</sup> contents in this spring did not follow large changes in HCO<sub>3</sub><sup>-</sup> content.

## Conclusion

This work supplements and recapitulates the papers by Halas *et al.* (1982, 1983) and by Staniaszek and Halas (1984, 1986), on seasonal changes of <sup>13</sup>C/<sup>12</sup>C ratios and chemistry of ground waters. These papers describe the changes in the parameters of spring waters and explain them in terms of inflows of new water into the aquifer during the wet and cold months of winter and early spring. It has been noted that this process proceeds continuously since waters from different areas, differing in their parameters, flow into the aquifer with different velocities. When

new waters are mixed with the aquifer water, changes of its parameters are anticipated. These changes are small but detectable, because the aquifer content is large in comparison to the amount of new water. Sometimes, non-linearities in the mixing effects magnify these changes. Since the aquifer is not homogeneous, the changes of parameters of water taken from the springs are multidirectional and irregular.

Besides frequent changes caused by inflows of new water, long-term trends have been recorded. The trends were noted especially in the case of the most accurately determined parameter  $\delta^{13}\text{CT}$ . In October 1982 all the investigated springs had unusually low  $\delta^{13}\text{CT}$  values, which should reflect low  $\delta^{13}\text{C}_{\text{RES}}$ . These changes in the  $\delta^{13}\text{C}_{\text{RES}}$  parameters may be a result of a weak contact with the soil  $\text{CO}_2$ .

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