

## Some analyses of the CO<sub>2</sub> content of the air in five Polish caves

by

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With 6 figures, 1 photo and 6 tables

**Zusammenfassung.** Analysen, angefertigt im April 1967 auf der schlesischen Hochfläche und in der westlichen Tatra, zeigen häufig sehr geringe CO<sub>2</sub>-Gehalte in den Grotten, teilweise sogar geringer als der mittlere Gehalt der freien Luft; die geringsten Werte scheinen in Kältegebieten aufzutreten.

Die in Schlesien untersuchte Grotte (330 m NN) zeigt während der Schneeschmelze höheren CO<sub>2</sub>-Anteil als die Grotten der Tatra (1000–1200 m NN). Die Ursache dieses Unterschiedes ist zum einen wahrscheinlich abhängig von dem Nachlassen der pflanzlichen Aktivität mit zunehmender Höhe (besonders im Frühlingsanfang), zum anderen aber auch davon, daß bei der Schneeschmelze das Wasser, das in die Hohlräume dringt, keine bemerkenswerten Mengen an CO<sub>2</sub> enthält, im Gegensatz zur allgemeinen Ansicht – und vielleicht auch entgegen dem Normalfall.

Es ist bekannt, daß kälteres Wasser mehr CO<sub>2</sub> aufnehmen kann als wärmeres; aus dieser Relation darf aber nicht allgemein geschlossen werden, daß kaltes Klima oder ein rauher Winter Karst-fördernd sind. Unsere Analysen der Luft in den Grotten der Tatra weisen einen besonders niedrigen CO<sub>2</sub>-Gehalt nach. Das CO<sub>2</sub> war daher zur Zeit der Beobachtungen, selbst bei erhöhten Lösungskoeffizienten, nur in sehr geringer Menge verfügbar.

**Résumé.** Des analyses faites en avril 1967 sur le plateau de Silésie et dans les Tatras occidentales montrent des teneurs en CO<sub>2</sub> fréquemment très faibles dans les grottes, parfois même plus faibles que la teneur moyenne à l'air libre; les chiffres les plus bas semblent en relation avec des milieux froids.

La grotte étudiée en Silésie (alt. 330 m) a des teneurs plus élevées que les grottes étudiées dans les Tatras (alt. 1000 à 1200 m), au moment de la fonte des neiges. La cause de cette différence réside probablement en partie dans la diminution avec l'altitude de l'activité végétale (particulièrement au début du printemps), mais aussi dans le fait que, au moment de la fonte des neiges, les eaux arrivant dans les cavités n'y dégagent pas de quantités notables de CO<sub>2</sub>, contrairement à l'opinion généralement admise – et peut-être contrairement au cas général.

On sait que plus une eau est froide, plus le coefficient de dissolution du CO<sub>2</sub> y est élevé; on ne peut toutefois pas déduire de cette relation qu'un climat très froid ou un hiver rude

favorisent forcément la karstification. Nos analyses ont en effet mis en évidence dans l'air des grottes de Tatra des teneurs en CO<sub>2</sub> particulièrement modestes. Le gaz carbonique, même avec un coefficient de dissolution élevé, n'était donc disponible au moment des observations qu'en quantité très restreinte.

**Streszczenie.** Analizy, wykonane w kwietniu 1967 roku na Wyżynie śląskiej i Tatrach Zachodnich, wykazały, że zawartość CO<sub>2</sub> w powietrzu jaskiń jest często bardzo mała. Czasem jest ona niższa od średniej zawartości CO<sub>2</sub> w wolnym powietrzu. Najniższe wartości zdają się być związane ze środowiskiem zimnym.

Zawartość CO<sub>2</sub> w powietrzu jaskiń na śląsku / wysokość 330 m n.p.m. / jest wyższa od zawartości CO<sub>2</sub> w powietrzu jaskiń tatrzańskich w czasie topnienia śniegu / wysokość 1000–1200 m n.p.m. / . Przyczyną tej różnicy jest prawdopodobnie nie tylko spadek aktywności / szczególnie wczesną wiosną / roślin wraz ze wzrostem wysokości n.p.m., lecz także fakt, że w okresie topnienia śniegu wydzielanie CO<sub>2</sub> z wód dostających się do jaskiń jest nieznaczne. To ostatnie stwierdzenie jest sprzeczne z ogólną opinią na ten temat, i może być niezgodne z najczęściej obserwowanymi przypadkami.

Wiadomo, że im niższa jest temperatura wody, tym wyższy jest współczynnik rozpuszalności CO<sub>2</sub>; nie możemy jednak na podstawie tej zależności wnioskować, że bardzo zimny klimat, lub bardzo mroźna zima musi sprzyjać zjawiskom krasowym. W rzeczy samej nasze analizy wykazały w jaskiniach tatrzańskich niewielkie zawartości CO<sub>2</sub> w powietrzu, co jest niewątpliwie wynikiem słabej aktywności biologicznej roślin, a więc bardzo niskiej produkcji CO<sub>2</sub> przez rośliny. Gaz ten, mimo wysokiego współczynnika rozpuszczalności, w okresie przeprowadzanych badań występował w ograniczonych ilościach.

It is in a cave of the Silesian Upland and in four caves of the Polish Tatra Mts that some forty analyses of CO<sub>2</sub> in air were carried out between the 7 and the 12. 4. 67.

They were worked out by an electrolytic method with a field device contrived by H. KOEPF (1952) and recently described by C. EK, F. DELECOUR and F. WEISSEN (1968).

All the analytical results are listed *in-fine* in the tables A to E and most of them are plotted on the figures 1 to 3.

## I. The caves investigated

### A. Jaskinia Dzwonnicza

1. *The cave* is located at Olsztyn (East of Częstochowa), in the northern part of the Silesian Upland, some 330 m above sea-level. The cave is a narrow and simple gallery, about 70 m long, with few chambers and very few lateral passages; a lot of splendid moonmilk covers the walls. This cave is a branch of the larger Towarnia Cave System which honeycombs one of the residual hills of Upper Jurassic massive limestone.

2. *Meteorological conditions.* During the analyses, the weather was rainy; the air temperature outside was 6° C at 1 m height; at 4 m inside and 30 cm above the floor of the descending entrance gallery, the temperature was only 4.5° C; at 8 m inside, it was, at a height of 30 cm, 5.2° C.

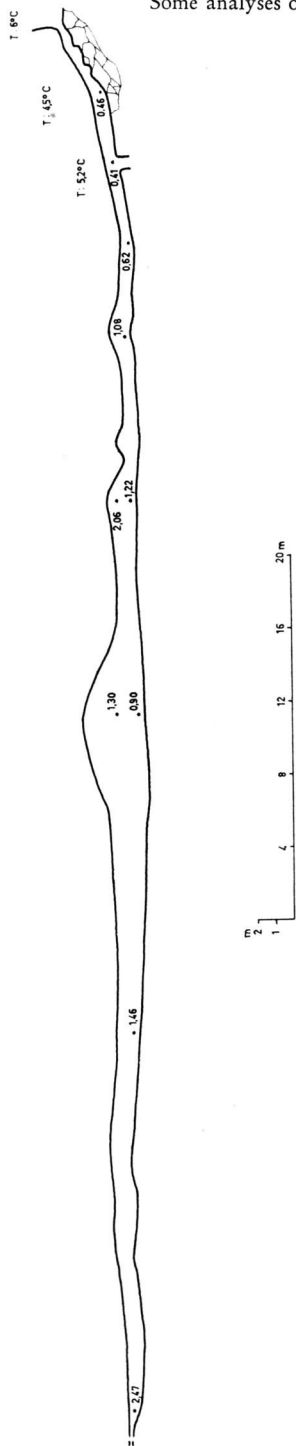


Fig. 1. Jaskinia Dzwonnica. Long section by S. GILEWSKA & C. EK. CO<sub>2</sub> content of the air (mg/l), sampling and analyses by E. GIL, S. GILEWSKA & C. EK. 7. 4. 1967

The temperature at the very end of the cave was measured the 18. 4. 67: 7.3° C. These figures show that cold air was entering along the lower part of the gallery, and cave air was going out along the ceiling (normal winter air circulation in this type of caves: see fig. 1).

3. *The CO<sub>2</sub> gradients.* Fig. 1 clearly shows the horizontal gradient of CO<sub>2</sub>; this gas is more and more abundant toward the end of the cave, ranging from 0.41 to 2.47 mg CO<sub>2</sub>/l air.

In the bulk of the cave, the mean values is between 1 and 2 mg/l.

The values seem to lower in the biggest chamber of the cave. Moreover the values are higher in the upper part of the gallery than nearby the floor. This is due to the winter air circulation, still prevailing in the cave in April 1967: cold air entering below is coming from the free atmosphere, at a moment where the plants activity is very reduced. Air stagnant nearby the ceiling is since a longer time in the cave, and probably enriched in CO<sub>2</sub> by fissures in the cave ceiling, going up to the soil and its confined atmosphere, and by which water is percolating.

Another possible cause of gradient was suggested by Prof. Z. CZEPE: the escape of CO<sub>2</sub> correlative to the formation of moonmilk. This is very likely, but, being unaware of the quantity of moonmilk produced by time unit, we cannot appreciate the importance of the releasing of CO<sub>2</sub> by this means (see A. MASON-WILLIAMS, 1959); particularly, we are ignorant of the respective influences of a physical escape of CO<sub>2</sub> in the atmosphere of the cave by precipitation of the mineral particles, and of a biological releasing due to the activity of microorganisms. Anyway these factors would explain the differences between the CO<sub>2</sub> contents in the narrow gallery and in the rather open space constituted

by the chamber, where the samplings were done farther away from the walls.

The minimum values observed (0.46 and 0.41 mg/l) are a little below the normal values for open air (0.50 to 0.59 mg/l). The accuracy of the device used here is 0.05 mg/l, and it is likely that we really have here, at the end of the winter, two very low values. One will notice that these are between the entrance and a narrow passage to Towarnia Cave.

### *B. Jaskinia Wodna pod Pisaną*

1. *The cave* is located in the talweg of the Kościeliska Valley, in the Polish Western Tatra at some 1000 m above sea-level. Only the region of outlet of the cave is here concerned. It is a labyrinthian system of narrow galleries, generally lowroofed (in many places less than 1.5 m). An underground river flows in the cave and many little tributaries or derivations run over the floors of the passages; also lie there bodies of standing water. No concretions at all are to be seen, but river pebbles, sand and silt.

2. *Meteorological conditions.* All analyses here were done by fine weather, during a period of fast melting of the snow; during the night when analyses 1 and 2 were carried out, a very cold wind was blowing in the valley; the temperature of the water was 3.5° C; the analyses 3 to 8 were done during a sunny day, by lukewarm wind.

The discharge of the Kościeliski River was about 1000 l/sec, while the yield of the underground derivation was some 300 l/sec at the outlet of the cave (see fig. 2).

3. *Low CO<sub>2</sub> content above the water.* Analyses 1 and 2, during the night, at the outlet of the underground river, show a very low CO<sub>2</sub> content. These analyses were done at Zakopane, two hours after sampling, so that an effect of temperature on reaction rate cannot be assumed. The value of 0.43 (twice) is approximate but anyway the true value is of course below normal atmospheric content. At the contrary, analyse 3 made the next day in open air shows during the day a very normal value for free atmosphere: 0.56.

One analysis shows, like it was observed at many other places, a CO<sub>2</sub> content higher in a fissure (3.40) than in the bulk of the air of the cave.

Measures 5 to 9 were all performed just above the water. Sample n° 8, above a pound with putrescent wood floating on standing water, shows a rather high value (2.04). All the other analyses display low values: between 0.67 and 1.11.

One could expect that an important water flow sweeps along, with itself, an air current coming from the most remote parts of the cave and rich in CO<sub>2</sub>; or at least that an important flow coming from remote underground regions carries solved gases which tend to escape when the stream arrives in the open parts of the cave. But *in this case* it is not so: the content of CO<sub>2</sub> above the water is rather low, and, by night, very faint.

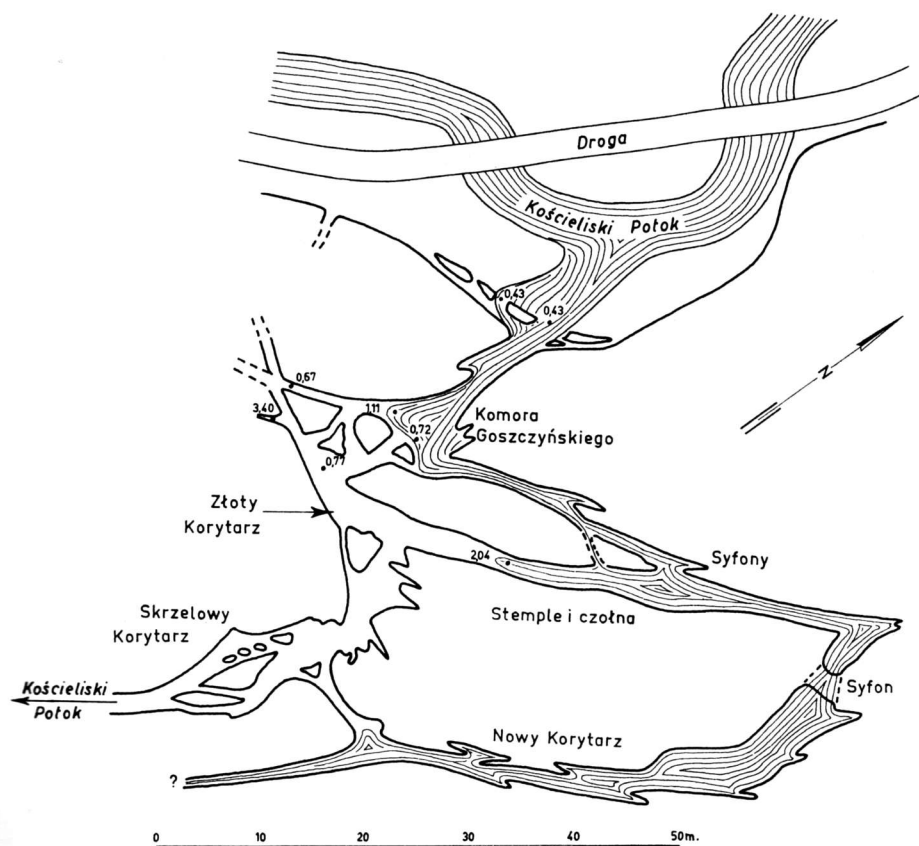


Fig. 2. Fragment of the plan of Jaskinia Wodna pod Pisaną after ST. ZWOLIŃSKI. W podziemiach tatrzańskich, 1961, slightly modified. CO<sub>2</sub> content of the air (mg/l), sampling and analyses by A. KOBYLECKI & C. EK. 11. and 12. 4. 1967

### C. Jaskinia Nad Raptawiczką I

1. *The cave* is at an altitude of some 1200 m, on the west side of Kościeliska Valley.

It is a small cave, some 24 m long: a short gallery leads to a rather spacious chamber, which in turn is continued by another passage, rather narrow. In fact, the entrance leads not only to the mapped cave but also to another part of the cave, opposite (see fig. 3, the schematic plan, up right). Considering that the two regions of the cave are connected by an entrance widely open to outside conditions, we have only studied one part. The floor of the cave is mainly formed by

rock debris. A small snow patch, blown by the wind, remained in the entrance passage and some ice stalagmites were observed in the same passage.

**2. Meteorological conditions.** The weather was fine during analyses and the snow was melting fast. But, after sunset, the wind was very cold. Temperature outside varied from  $10^{\circ}\text{C}$  (analyse 1) down to  $5^{\circ}\text{C}$  (analyse 16).

In the cave itself, water was dropping from the roof in rather important quantity; this was very probably related to snow melt, as was also the thick fog clouding the very end of the cave. The air was blowing outside, what is normal in winter regime in this cave, which is at the upper part of a complex system: the air is warmer in the cave than outside and escapes thus upside from the cave;

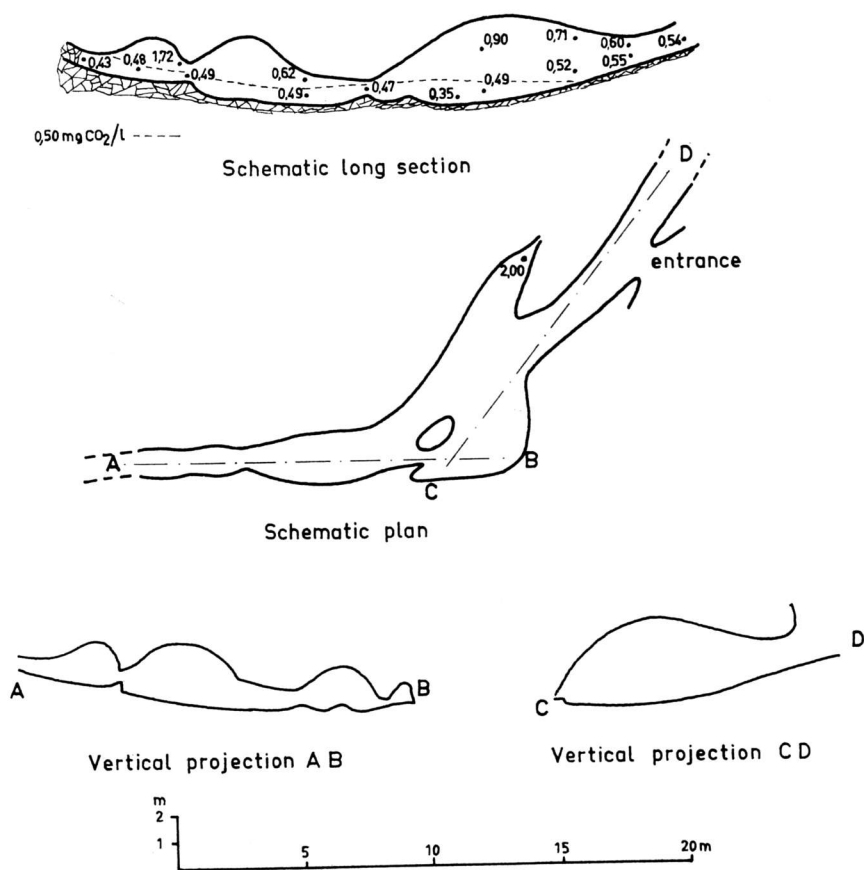


Fig. 3. Fragment of Jaskinia nad Raptawicką I by A. KOBYLECKI. CO<sub>2</sub> content of the air (mg/l). Sampling and analyses by L. KASZOWSKI, A. KOBYLECKI, A. KOTARBA & C. EK. 11. 4. 1967

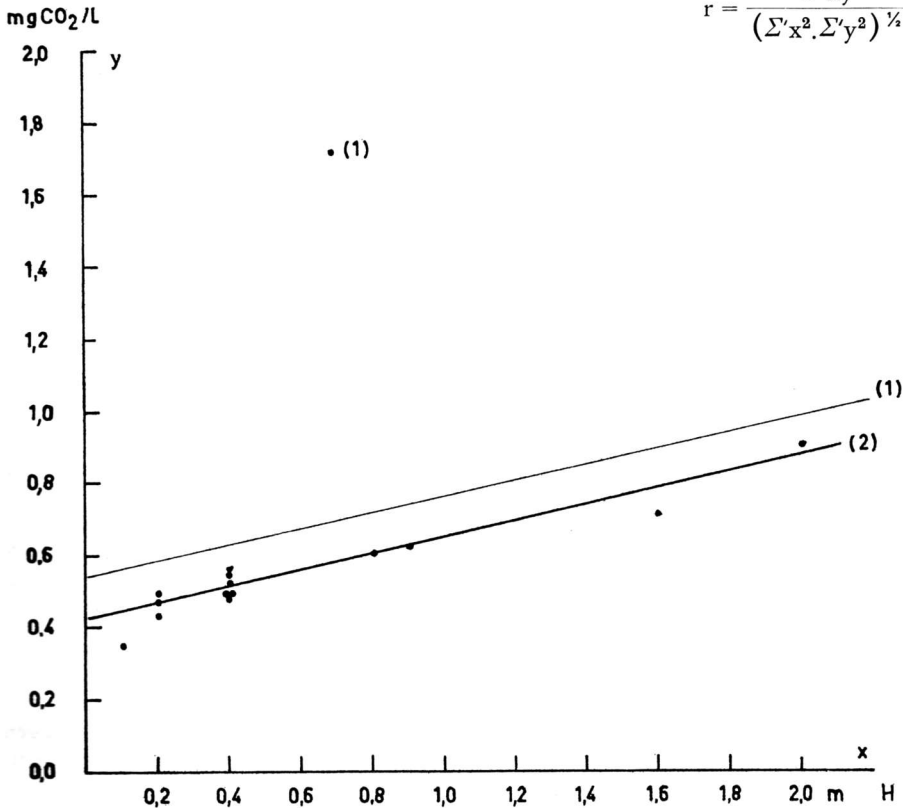
being cooled in the open part of the cave, the air becomes then supersaturated with water, and fog appears.

**3. Stratification of CO<sub>2</sub>.** CO<sub>2</sub> content corresponds, nearby the entrance, to normal open air values. Farther on, nearby the roof, values are slightly higher. At the contrary, near the floor, and particularly in the lowest points, the air is very unusually poor in CO<sub>2</sub>.

Nearby the roof, CO<sub>2</sub> is more and more abundant when one goes from the entrance to the extremity. On the floor, this gradient does not clearly appear.

Sixteen measurements were carried out in the cave, one of them being in a fissure and fifteen in the bulk of the main passage. This number of analyses made it possible to calculate the correlation ( $r$ ) between the height ( $x$ ) above the floor and the CO<sub>2</sub> content ( $y$ ) of the air following the formula:

$$r = \frac{\sum' xy}{(\sum' x^2 \cdot \sum' y^2)^{1/2}}$$



(1) considering 15 points;  $y = 0.469 + 0.256 x$

(2) considering 14 points;  $y = 0.409 + 0.229 x$

Fig. 4

The result,  $r = 0.419$ , means that the probability of a correlation between  $x$  and  $y$  is somewhat less than 90% (see fig. 4, line n<sup>o</sup> 1). It is easy to see that the point whose  $y$  is equal to 1.72 is quite abnormal. We don't know if the cause of this is an error or another factor than the height acting here. However, if we reject this point,  $r$  becomes equal to 0.959, and the non-existence of the correlation becomes practically impossible (see fig. 4, line n<sup>o</sup> 2).

The CO<sub>2</sub> content higher near the roof than near the ground shows that there is no static density equilibrium (CO<sub>2</sub> is denser than air). The observed distribution of values can be related either with temperature, or with air blow, or with humidity.

*Temperature:* the values below 0.50 mg are observed only in a possibly stagnant, cold air mass lying on the floor, in the bottom of this U-shaped hole. Warmer air coming from inside parts of the cavernous system would bring near the ceiling an air richer in CO<sub>2</sub>.

*Wind:* a draught blows in the narrow passages of the cave. It confirms that the cave is blowing air outside (hence higher values near the roof).

*Humidity, water:* when the water drops from the ceiling, it is warmer than the lower air layer of the cave; the splash on the floor divides these "warmer" drops into a great number of small droplets, forming a mist; the droplets having a very small diameter, the escape of the air and its CO<sub>2</sub> from the water is much easier than from big drops; being warmer than the air layer near the floor, the air rich in CO<sub>2</sub> escaping in the splash zone rises toward the ceiling. This thermic explanation of the CO<sub>2</sub> bedding in the cave was proposed by T. NIEDŹWIEDŹ.

This hypothesis supposes that a difference of probably 4 to 6° C is sufficient to induce a rapid rise of the gas escaping toward the ceiling. If this rising is not rapid, the gas will become colder and will stay below. Moreover, the high density of CO<sub>2</sub> leads us to suppose that it is escaping with—and within—the air previously solved in the splashing drops: CO<sub>2</sub> considered alone is normally too heavy to rise above an air even 4 to 6° C colder than CO<sub>2</sub>.

But one of us (A. K.) proposes to assume that the turbulence of the atmosphere in the splash zone, because of the abundant dropping of water, *expels* the air rich in CO<sub>2</sub> escaping from the water: the splash itself pushes air masses above; this assumption would probably help to admit the proposal of T. NIEDŹWIEDŹ. The ideas here presented are qualitatively concordant with the results of B. DIXON & A. RUSSEL (1950), B. DIXON & G. HANDS (1957) and also with experiments by H. ROQUES (1964).

#### D. *Jaskinia Raptawicka*

1. *The cave* is at 1170 m, on the west side of the Kościeliska Valley. It is an *avenue* of some 10 m depth, widely open, and continued at its bottom by some spacious chambers.

2. *Meteorological conditions.* Concerning meteorological conditions, see *Jaskinia nad Raptawicką I*; the air temperature outside during analyses was 5° C.



3. *CO<sub>2</sub> in the bottom of the aven.* Three samples were taken at man's height in three points of the cave. The observed gradient is concordant with the relative altitude of the three points; just under the aven: 0.37; in a chamber nearby, a little higher: 0.47; at the extremity of another passage nearby, a little below: 0.32.

This aven probably collects cold atmospheric air only, exclusive of any soil air, at the places here sampled; it is widely open, and the samples were not taken in confined places. The values here obtained are the smallest ever found by us and it is worthy to note that the lowest layers are here also the poorest in CO<sub>2</sub>, contrarily to a gradient of gravity of CO<sub>2</sub> which is denser than air.

#### *E. Jaskinia Oblazkowa*

1. *The cave* is lying on the western side of the Kościeliska Valley at an altitude of about 1120 m. This cave is mostly horizontal, rather complex, but the two samples were taken nearby the spacious entrance, where some ice stalagmites and ice floors were slowly melting.

2. *Meteorological conditions.* About the weather, see Jaskinia nad Raptawicką I; the air temperature was, outside, about 9° C.

3. *CO<sub>2</sub> in air just nearby melting ice.* 0.94 mg CO<sub>2</sub>/l air were found at 20 cm above an ice patch on the soil in the entrance chamber, but 0.46 mg/l only in a natural niche in an ice stalagmite. The electrolytic cell having displayed the last result, rather low, was immediately tested in the outer atmosphere and provided there a result of 0.49 mg/l, which is very normal at this altitude.

However the measurements are much too few on this subject, we can assume that the slow melt of the ice stalagmite did not furnish any measurable CO<sub>2</sub> to the confined atmosphere of the niche.

## II. Comments on the results

### 1. *Problems related to altitude and to atmospheric pressure*

Atmospheric pressure decreases when altitude increases so that at 1000 to 1200 m it is equal to some 9/10 of the pressure at sea level. So, if partial pressure of CO<sub>2</sub> is constant, the weight of CO<sub>2</sub> by liter of air normally decreases from 0.59 mg/l (760 mm Hg, 0° C) or 0.55 mg/l (760 mm Hg, 20° C) to 0.53 mg/l (680 mm Hg, 0° C) or 0.55 mg/l (680 mm Hg, 20° C). Moreover the field device employed can suffer an error of  $\pm 0.05$  mg/l.

One can see that the influence of the decreasing pressure cannot explain by itself the lowest values here mentioned.

The decrease of CO<sub>2</sub> partial pressure in atmosphere at increasing altitudes, following P. N. TWIERSKOJ (1962) is here negligible (0.029 % vol. at 21 Km alt., against 0.033 % vol. at sea level).

One could assess that we should reduce our figures from mg/l to corresponding partial pressure. But this is contrary to the general purpose of this research,

which is concerned with the action of  $\text{CO}_2$  on limestone; to dissolve a given volume of limestone we need a definite *weight* of  $\text{CO}_2$ .

## 2. Problems related to temperature and to vegetation

The observed values were sometimes (A 1 and 2, B 1 and 2, C 9 and 15, D 7 and 3) lower than atmospheric normal values. We had never seen such cases in Belgium. Of course, measurements in Poland were made at a moment where vegetation is still very little active. This does not explain at all values below atmospheric values known.

After these analyses, and considering 1° that temperature variations are neutralized in the electric circuit of the device by a diode, and 2° that temperature influence in the cells was anyway impossible for measures B 1 and 2, made *in a house* in Zakopane, it seems that  $\text{CO}_2$  partial pressure in the atmosphere is much lower in the mountainous area investigated than generally admitted.

This idea seems us to be contrary to S. W. TROMP's assumption (1963): "The great constancy of  $\text{CO}_2$  content of the atmosphere was demonstrated by CARPENTIER in 1937" and to the general opinion.

The values below normal open-atmosphere value have been observed:

- a) in the cold (5° C) descending narrow gallery of the entrance of Dzwonnicza;
- b) at the outlet of Wodna pod Pisaną river, during the night only;
- c) just at the floor level of the lowest point of Nad Raptawicką I, probably in the coldest place of this cave, and at the very end of the same cave, in the fog;
- d) in the wide spaces of Raptawicka, which seems to be a trap for cold mountainous air.

The only common point that is conspicuous to these places seems to be low temperature.

The fog at the very end of Nad Raptawicką I shows another danger for the sampling: absorption of  $\text{H}_2\text{O}$  in the cell (remark of A. K.). However, at + 5° C, the weight of water in air at 100 % humidity is some 7 mg/l. This content seems to be quite negligible as a cause of error in the electrolysis. But this problem is to be kept in mind.

One will notice that in Raptawicka the gradient of  $\text{CO}_2$  is not related to its density. But as very probably there is a density gradient of air masses there, the coldest masses being below, it is possible that the observed gradient in  $\text{CO}_2$  is simply showing that the colder is the air, the less there is  $\text{CO}_2$  in it; for such an unbalanced state to stay,  $\text{CO}_2$  must there display almost no diffusion at all.

The highest values (2 mg/l and more) were observed:

- once nearby the ceiling and once at the extremity of Dzwonnicza (A 6 and 10);
- in a narrow fissure at Wodna pod Pisaną (B 4) and above a body of standing water with putrescent matters (B 8);
- in a fissure in Nad Raptawicką I (C 16).

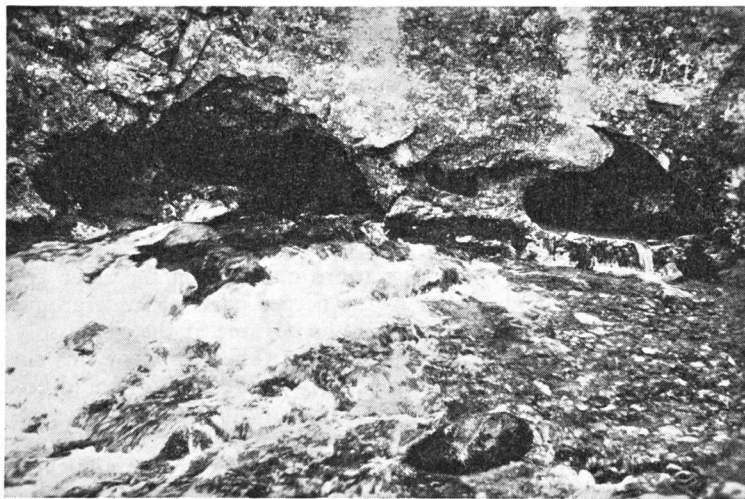
The fissures seem richer in  $\text{CO}_2$ ; considering the measures done in Belgium, this is probably here also related with arrival of biogenic (pedologic)  $\text{CO}_2$  from the vegetal soil.

The content of CO<sub>2</sub> nearby the ceiling is probably related with the fact that in winter-time the air of the cave, richer in CO<sub>2</sub>, is warmer than the outside air which is thus denser.

### 3. Comparison of the CO<sub>2</sub> contents of air and water

Some analyses of the CO<sub>2</sub> content of the streams were carried out by two of us (K. O. and B. O.) during our stay in Tatra Mts.

Five of the analyses concern waters of the Kościeliski Basin: a spring near Hala Pisana displayed 4.0 mg CO<sub>2</sub>/l water and a tributary, the Kraków Stream, contained 6.2 mg CO<sub>2</sub>/l; the Kościeliski River itself, as well underground as on the surface just upward and downward of the Cave Wodna pod Pisana, showed 3.1 mg CO<sub>2</sub>/l.



The twin-tube outlet of Jaskinia Wodna pod Pisana

Since the three last measurements gave equal results, it is likely that the underground course is not long enough to change the CO<sub>2</sub> content of the stream—at least in April 1967.

However, the value of the CO<sub>2</sub> contents in the air which would be in equilibrium with the determined quantity of CO<sub>2</sub> in the water of Kościeliski Stream, should be some 2 mg CO<sub>2</sub>/l on the base of calculations. This closely corresponds to the CO<sub>2</sub> content that we found just nearby the surface of stagnant water with decaying vegetal matter (B 8: 2.04 mg/l); one can also notice that this value is just intermediate between a measurement in a fissure of the cave (B 4: 3.40 mg/l) and another measurement in the cave, above the subterranean stream (B 7: 0.72 mg/l).

In the Table I the empirical data for  $\text{CO}_2$  and  $\text{Ca}^{++}$  concentrations are compared to these theoretically calculated for assumed equilibria.

Table 1 Comparison of the contents of  $\text{CO}_2$  and  $\text{Ca}^{++}$  measured and calculated

1	$\text{CO}_2$ measured in air of Cave Wodna Pod Pisaną	3.40— 0.67	Range of contents, mg/l.
2	$\text{CO}_2$ in water, calculated for equilibrium with (1)	5.1 — 1.05	
3	$\text{CO}_2$ determined in water from sampled places	6.2 — 3.1	
4	$\text{Ca}^{++}$ concentration in water calculated for equilibrium with (1)	11.6 — 2.12	
5	$\text{Ca}^{++}$ concentration determined in waters	38.2 — 15.0	
6	free $\text{CO}_2$ concentration in water calculated for equilibrium with (5)	17.0 — 8.76	

On the base of Table 1 (1, 2, 3) it may be seen that the contents of  $\text{CO}_2$  determined in water are in general slightly higher than those calculated for equilibrium with the  $\text{P}_{\text{CO}_2}$  measured in the cave air. Thus, it seems plausible that the values of  $\text{CO}_2$  concentrations observed in the river are the residues of  $\text{CO}_2$  dissolved at higher  $\text{P}_{\text{CO}_2}$  in the deeper parts of underground karst ways in contact with the river bed. It would be possible, if the gas dissolved there had no time to equilibrate with  $\text{P}_{\text{CO}_2}$  in free air. The reason of this slow equilibration could be the formation of hydrates  $\text{CO}_2 \cdot n\text{H}_2\text{O}$  which could be kind of "traps" for the molecules of  $\text{CO}_2$ .

In addition, we cannot exclude the possibility that the factor of solubility of  $\text{CO}_2$  in a dynamic system (flowing water) may be a little higher than that used commonly for a static system.

The five samples of water analysed in the Kościeliski Basin were—like most of the waters studied in neighbouring valleys—oversaturated with calcium bicarbonate with regard to  $\text{P}_{\text{CO}_2}$  measured in air.

The oversaturation may be explained in two ways:

a)  $\text{Ca}^{++}$  ions dissolved in waters being equilibrated with higher  $\text{P}_{\text{CO}_2}$  in the deeper parts of karst ways. The  $\text{Ca}^{++}$  concentration in water equilibrated there does not decrease (or not too much) in spite of small  $\text{P}_{\text{CO}_2}$  in the sampled places. It is possible because of the very complicated and slow equilibrium process of the system:  $\text{CaCO}_3 - \text{CO}_2 - \text{H}_2\text{O}$ . This process probably includes many stages.

It is probable that in this unequilibrium state the process of precipitation of  $\text{CaCO}_3$  goes slower than that of "trapping" of  $\text{CO}_2$  molecules into hydrates, formation of  $\text{HCO}_3^-$  and dissolution of  $\text{CaCO}_3$ .

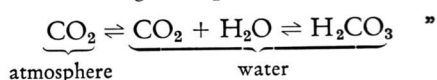
If the above explanation were true we could have some information about P<sub>CO<sub>2</sub></sub> in the unexplored parts of the cave-system (mainly fissures). P<sub>CO<sub>2</sub></sub> could be calculated from the measured Ca<sup>++</sup> concentration.

b) The P<sub>CO<sub>2</sub></sub> over the sampled water was never as high as calculated on the base of formula:  $\log P_{CO_2} = A + \log Ca^{++} - pH$ , where Ca<sup>++</sup> and pH are measured analytically. The big quantity of Ca<sup>++</sup> could be, in the case, dissolved by flowing water because of continuous collecting of CO<sub>2</sub> from the cave and outside air, or from the soil and organic matter being in contact with the bed of the river. Of course, the slow equilibration process and unequilibrium state mentioned in (a), plays the same role in the case.

This explanation is in agreement with ALEKIN's statement (1956): "Waters containing more than 16–22 mg Ca<sup>++</sup> per liter should be unstable as P<sub>CO<sub>2</sub></sub> in atmosphere is too low, but the river waters in natural conditions are practically stable containing 60–80 mg Ca<sup>++</sup> per liter.

It is possible because of:

1) continuous providing of CO<sub>2</sub> by decaying organic matter and 2) slowness of the equilibration process including absorption and hydration:



The decision which of the mechanisms is more true: (a) or (b), requires many new observations and measurements.

Concerning the formula:  $P_{CO_2} = A + \log Ca^{++} - pH$ , we must admit that it is true for waters containing only Ca<sup>++</sup> and HCO<sub>3</sub><sup>-</sup> ions, while in Tatra noticeable quantities of Mg<sup>++</sup> and SO<sub>4</sub><sup>--</sup> ions are found (see OLEKSYNOWA & KOMORNICKI, 1965 e.g.).

The conclusions of this comparison of some air analyses and water analyses are:

- 1°) that the concentration range of CO<sub>2</sub> determined in water of the Kościeliski Stream is in approximate agreement with the quantities measured in the air of Cave Wodna pod Pisaną;
- 2°) that the waters are oversaturated with Ca(HCO<sub>3</sub>)<sub>2</sub> either because of higher partial pressure of CO<sub>2</sub> in deeper parts of karst ways or of a cave system, or because of continuous contact and gradual collecting of CO<sub>2</sub>, used farther for dissolving CaCO<sub>3</sub> by flowing, unequilibrated (in the static sense of the word) water.

#### 4. Comparative results in Belgium

Fig. 6 shows an example of a Belgian cave of a type similar to caves Dzwonnica and Nad Raptawicką I: a subhorizontal cave, with one practicable entrance and a slightly U-shaped profile allowing gas accumulation near the bottom. The profile is here accompanied by the relative temperature survey.

A former paper (C. EK, F. DELECOUR & F. WEISSEN, 1968) has shown that the values observed in Belgium, during the months of May to July, were 2 to

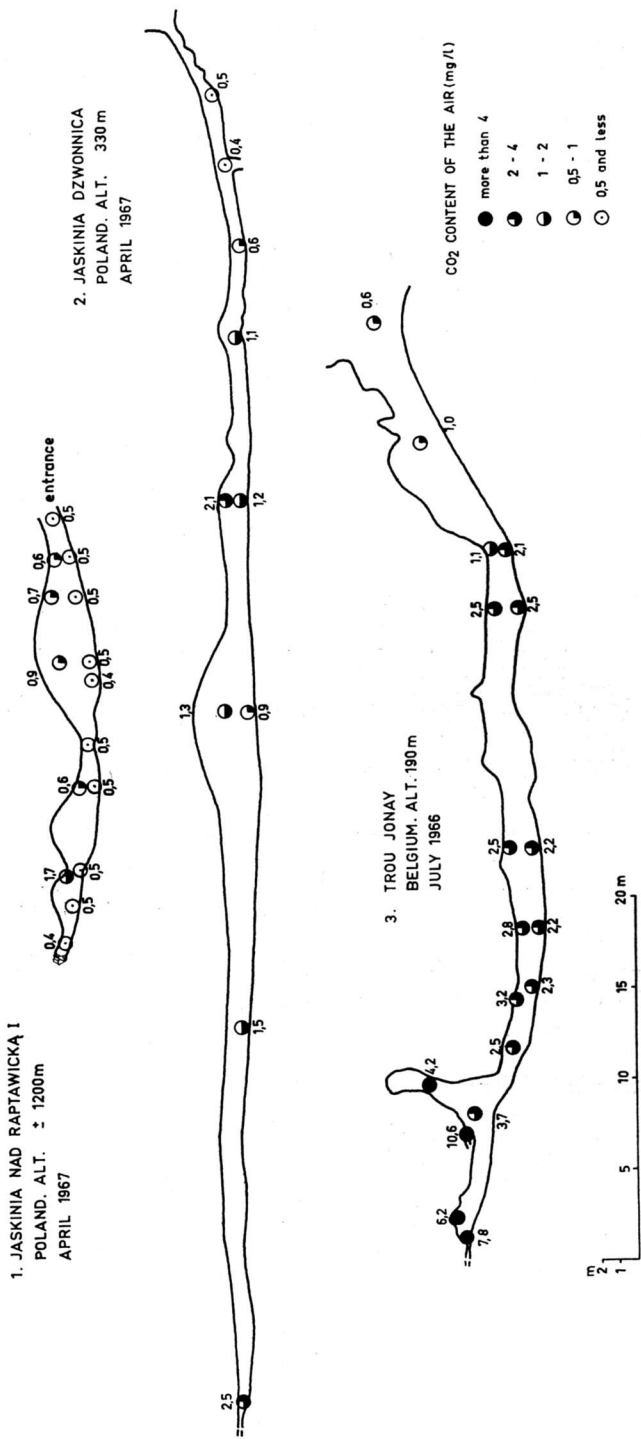


Fig. 5. Comparison of three caves, long sections

4 times higher than the corresponding values (center of a chamber; narrow fissure . . .) in Poland.

In Belgium were observed some vertical gradients of CO<sub>2</sub> content. It seems that in the sampled places in Poland, there is sometimes a gradient, and sometimes no gradient of CO<sub>2</sub> (at the scale of sampling), but in fact, *different air layers* which do not mix; therefore, a more detailed survey would probably show a repartition of *air masses* without –or with very thin– transitions. This observation is also probably related with the low temperature during measurements.

However few are the analyses, they unquestionably provide an interesting statement: CO<sub>2</sub> was in April 1967 in the investigated area much less than in summer 1966 in Belgian caves, and also less than in a Belgian cave at the end of March 1967 (these last results yet unpublished).

Since these caves differ by their altitudes, and the analyses by the season when they were carried out, the differences in CO<sub>2</sub> content seem strongly correlative with the differences of vegetation; see fig. 5.

SCHOELLER (1950) noticed in spring *waters* a gradient of CO<sub>2</sub> very similar to the one we notice in caves *air*: a general decrease of CO<sub>2</sub> when altitude increases and temperature lowers; he thought the lessening of biological activity to be responsible for this.

### *Temporary Conclusions*

1. Our 41 analyses have of course no statistical significance for the areas investigated. They were only intended to provide a comparison of some caves of the Tatra Mts during the period of snow melting with a cave of the Silesian Upland at the same moment, and also with some former analyses in Belgian caves.

But the measurements also displayed some general results interesting by themselves.

While two measurements were done outside of the caves for checking the device (0.49 and 0.56 mg CO<sub>2</sub>/l air), 36 analyses were carried out in underground galleries and chambers, giving results ranging from 0.32 to 2.06 mg/l; 3 titrations in fissures displayed 2.00 to 3.40 mg/l.

2. It will be kept in mind, in all following statements, that this small number of analyses prevents us from general conclusions and allows only particular conclusions and general assumptions. If more CO<sub>2</sub> titrations are necessary, in various types of weather particularly, we also noticed during our analyses the necessity of detailed thermic, barometric and hygrometric data: a complete meteorological survey of the caves studied would provide useful informations.

3. Among our local conclusions, we can state that we found very small amounts of CO<sub>2</sub> in the caves investigated, and sometimes less than in a normal free atmosphere.

The lowest figures were obtained in the bottom of the aven Raptawicka, while a very low CO<sub>2</sub> content was also found in the lowest (and also very probably coldest) place of Jaskinia nad Raptawicką I. Wodna pod Pisaną displayed minimum values during the night. CO<sub>2</sub> was surprisingly not abundant above the underground river of this cave. At Oblazkowa, the air in the immediate

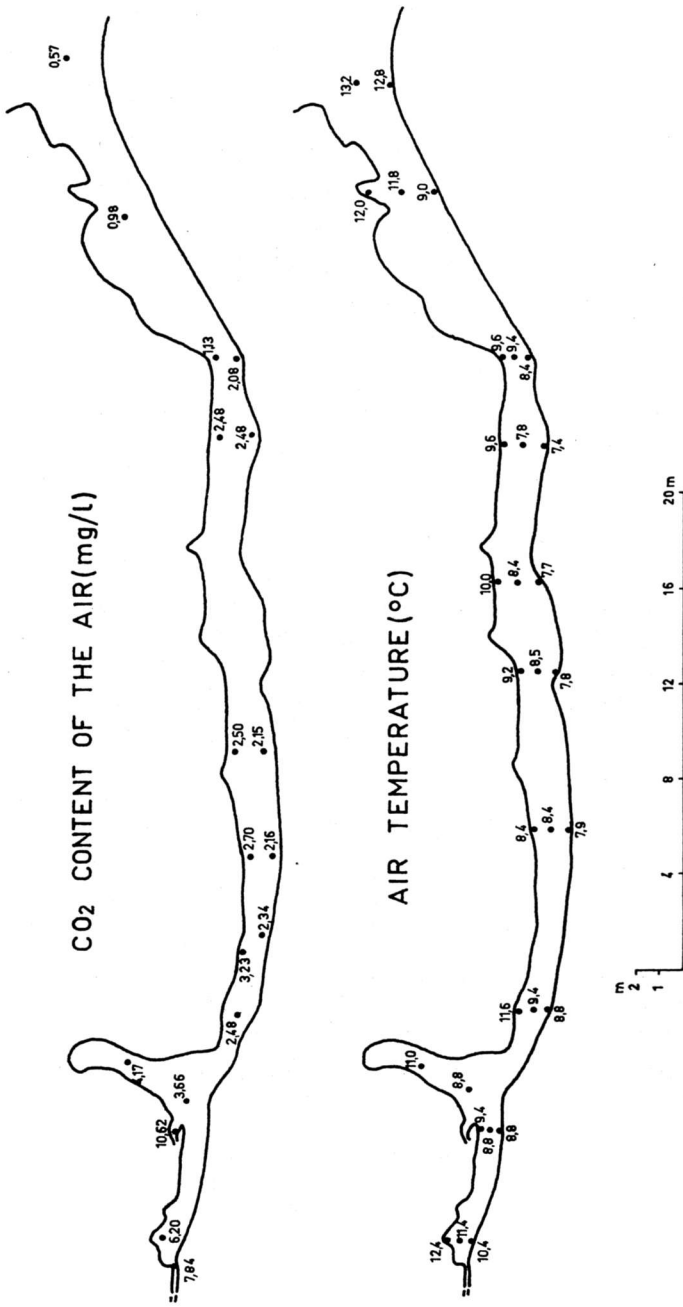


Fig. 6. Le Trou Ionay, long section by C. Ek. Sampling and analyses by F. DELECOUR, C. Ek & F. WEISSEN. 14. 7. 1966



vicinity of ice formations displayed once a moderate and once a very faint CO<sub>2</sub> content.

4. Jaskinia Dzwonnica, in the Silesian Upland, was rather rich in CO<sub>2</sub>, if compared to the caves investigated in Tatra Mts. In the Tatra, Wodna pod Pisana, in the *thalweg* of the Kościeliski River, displays contents higher than the caves located at higher levels on the side of the Valley.

5. As a whole, the figures obtained in April in some Polish caves were lower than the results of investigations in Belgian caves (fig. 6). Most of the measures in Belgium were carried out from May to July 1966; but some titrations made in March 1967 furnished also figures higher than Polish ones.

Belgian caves concerned are lying at 100 to 250 m above sea-level; Dzwonnica in the Silesian Upland is situated at some 330 m, while the Tatra caves investigated are at altitudes ranging from 1000 to 1200 m.

Belgian caves are under woods (coniferous and deciduous) and pastures; Dzwonnica is lying under poor pastures; Tatra caves here concerned are in coniferous forests, in great part under melting snow at the moment of investigation.

6. While the range of values is larger in Belgium (up to 4.1 mg/l in galleries, up to 10 in fissures), the gradients seem to be more moderate in Belgian caves; the changes of content are observed on so small distances in some Polish caves that it would probably be more accurate to speak about different air layers which do not mix; a detailed survey would probably show a repartition of air masses without—or with very thin—transitions. This is very likely to be related with the low temperature during the Polish investigations; we assume that cold weather strongly restrains the diffusion.

7. It seems worthy to note that at low temperature, in the mountain, at the end of the winter, we have undoubtedly found contents of CO<sub>2</sub> lower than the 3/10000 admitted to be a world mean value. This is fully contradictory to the opinion of W. TROMP (1963) and, probably, to the very general opinion that CO<sub>2</sub> nearby the surface of the earth has a rather constant minimum value, in natural environment, all the exceptions known being higher (very dense forest, putrescent aggregates . . .).

8. Snow is very generally considered as a rich reservoir of CO<sub>2</sub>. The measurements done during a very typical period of snow melt show that the escape of CO<sub>2</sub> from the snow is in this case, in a regional scope, not the source of a high CO<sub>2</sub> content in the air of the caves of the area where snow is melting.

9. Anyway, it is well known that it is *unjustifiable* to deduce *a priori* from this law that a low temperature favours karstification, because the amount of CO<sub>2</sub> solved in water depends upon the partial pressure of CO<sub>2</sub> in the air and in the present case, this pressure (*also* if one considers the influence of the altitude) is very low in the Polish caves investigated by cold weather.

We suppose that the main cause of this is the very poor vegetal activity, but the problem is probably more complex and seems to us to be correlated also with the presence of snow or ice, and involves influences of different meteorological factors.

*Aknowledgements*

This work was realized thanks to a cultural accord between the Jagiellonian University of Kraków and the University of Liège.

The Jagiellonian University provided a total support to the working team, generously offering field vehicle and lodging, and completely supporting with a great and hearty hospitality the stay in Poland of the Belgian member of the team. All authors are indebted to Rector Magnificus M. KLIMASZEWSKI who kindly and generously encouraged the work and offered opportunities of discussions with Cracovian professors and searchers.

In the field work took an active part, beside the authors, E. GIL and A. KOTARBA, who provided particularly helpful discussion.

The authors are also greatly indebted to Prof. P. MACAR, to Prof. Z. CZEPPE and to Mr. T. NIEDŹWIEDŹ, who read the manuscript and offered useful criticism, and to many searchers of the Jagiellonian University and the Polish Academy of Sciences who showed a very sympathetic interest in this work and worthily discussed the method and the results.

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Table A Jaskinia Dzwonnica

Silesian Upland		Alt.: 330 m; Analyses: 7. 4. 1967, 9. a. m. — 1 p. m.
N <sup>o</sup> of the analysis, location of the sample, CO <sub>2</sub> content (h = height of sampling above the floor of the cave or above the ground).		
N <sup>o</sup>	Location	mg CO <sub>2</sub> /l
1	Entrance, rock debris, h : 30 cm	0.46
2	Main gallery, facing a small lateral gallery, h : 30 cm	0.41
3	Main gallery, h : 30 cm	0.62
4	Main gallery, h : 30 cm	1.08
5	Main gallery, h : 30 cm	1.22
6	Main gallery, same site as 5, h : 110 cm	2.06
7	A chamber in the main gallery, h : 30 cm	0.90
8	Same site as 7, h : 170 cm	1.30
9	Main gallery, h : 30 cm	1.46
10	Extremity of the cave, h : 20 cm	2.47

Table B Jaskinia Wodna pod Pisaną

Tatra Alt.: some 1000 m  
 An. n<sup>o</sup> 1 and 2: 11. 4. 1967, at 10 p. m. An. n<sup>o</sup> 3 to 9: 12. 4. 1967, 11 a. m. — 4 p. m.

N<sup>o</sup> of the analysis, location of the sample, CO<sub>2</sub> content (h = height of sampling above the floor of the cave or above the ground).

No	Location	mg CO <sub>2</sub> /l
1	Main outlet of the resurgent flow, h: 25 cm (10 p. m.)	0.43
2	Minor outlet of the resurgent flow, h: 25 cm (10 p. m.)	0.43
3	Free atmosphere, nearby the cave, h: 160 cm	0.56
4	Extremity of a dry fissure in the cave, h: 100 cm	3.40
5	Above a low derivation of the underground river, h: 30 cm	0.67
6	Above almost standing water in a creek, h: 30 cm	1.11
7	Above the main stream, h: 30 cm	0.72
8	Above a body of deep, standing water, with putrescent wood, h: 30 cm	2.04
9	Above shallow, almost standing water, h: 30 cm	0.77

Table C Jaskinia nad Raptawicką I

Tatra Alt.: some 1200 m Analyses: 11. 4. 1967, 1—9 p. m.

N<sup>o</sup> of the analysis, location of the sample, CO<sub>2</sub> content (h = height of sampling above the floor of the cave or above the ground).

No	Location	mg CO <sub>2</sub> /l
1	Entrance, h: 40 cm	0.54
2	Main gallery, h: 40 cm	0.55
3	Main gallery, same location as 2, h: 80 cm	0.60
4	Main gallery, entrance of the main chamber, h: 40 cm	0.52
5	Main gallery, same location as 4, h: 160 cm	0.71
6	Main chamber, h: 40 cm	0.49
7	Main chamber, same location as 6, h: 200 cm	0.90
8	Main chamber, h: 10 cm	0.35
9	Main gallery, h: 20 cm	0.47
10	Main gallery, h: 40 cm	0.49
11	Main gallery, same location as 10, h: 90 cm	0.62
12	Main gallery, h: 20 cm	0.49
13	Main gallery, h: 70 cm	1.72
14	Main gallery, h: 40 cm	0.48
15	Main gallery, extremity, h: 20 cm	0.43
16	In a fissure of the main chamber, h: 130 cm	2.00

Table D Jaskinia Raptawicka

Tatra Alt.: some 1170 m		Analyses: 11. 4. 1967, 8—9 p. m.
N <sup>o</sup> of the analysis, location of the sample, CO <sub>2</sub> content (h = height of sampling above the floor of the cave or above the ground).		
N <sup>o</sup>	Location	mg CO <sub>2</sub> /l
1	Bottom of the aven, just under the entrance pit, h: 160 cm	0.47
2	Idem, a little below 1, on a rock-debris slope, h: 160 cm	0.37
3	Farther in the cave, lower than 1 and 2, h: 160 cm	0.32

Table E Jaskinia Oblazkowa

Tatra Alt.: some 1120 m		Analyses: 11. 4. 1967, 2—4 p. m.
N <sup>o</sup> of the analysis, location of the sample, CO <sub>2</sub> content (h = height of sampling above the floor of the cave or above the ground).		
N <sup>o</sup>	Location	mg CO <sub>2</sub> /l
1	Entrance chamber, just above an ice patch on the floor, h: 20 cm	0.94
2	Main gallery, at some 15 m of the entrance, in a niche (hollow) in an ice stalagmite, h: 20 cm	0.46
3	Free atmosphere nearby the entrance of the cave	0.49

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