Red Clover as a Receptor of CO_2 from the Atmosphere and Some Compounds from Soil

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Abstract

It was found that red clover utilizes from 1.1 to 1.4 kg of CO_2 from the atmosphere to produce 1 kg of dry mattter. This means that 1400 to 1600m^3 of atmospheric air become completely purified from carbon dioxide. Red clover plants usually lose 40.9% of their crop weight during the winter. This results from organic carbon loss equal (in CO_2 units) to 41.8% for physiolopical processes. In the same period however, the ash fraction, larger grows as a simple consequence of actual carbon loss. It is reasonable to assume that the plants do intake mineral compounds from the deeper, not frozen horizons of the soil also during winter.

Keywords: clover, ash, silicium, nitrogen, carbon, carbon dioxide.

Introduction

Human activities, based on utilization of several natural sources of energy (coal, earth oil, earth gas, and others), has been contributing to the growing concentration of CO_2 into the atmosphere. And one of the consequences of the above has been global climate changes (Kyoto Protocol [7]).

According to the Kyoto Protocol [7], Poland is supposed to emit to the atmosphere about 414,930,000 tons of CO_2 per year. This figure means a 3% contribution to global carbon dioxide output. The world's largest CO_2 emitters are the US, with their share equal to as much as 36.1%. Hajduk and Sasimowski report that the yearly amount of CO_2 emitted to the atmosphere in the area of Białystok Province (according to the administrative division of Poland taken from before the recently conducted administration reform) was 863,100 tons CO_2 [4].

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Possible future decrease in CO_2 amounts introduced into the atmosphere may be achieved by means of increased forest area in the continents because forests accumulate large amounts of carbon dioxide, which consists of about 50% carbon. Another solution is increase of biomass production in agriculture, which can also lead to a decrease of CO_2 concentration in the air [2, 3, 8, 9, 11].

Significant amounts of CO_2 are absorbed by waters of seas and oceans. CO_2 becomes bound by Ca and Mg elements present in sea waters and precipitated in the carbonate form - $CaCO_3$ as well as $MgCO_3$. These are relatively hardly soluble compounds. Besides, sea organisms utilizing CO_2 for building their carbonate armors (crustaceans) also contribute to the carbonate-enriched bottom sediments after their death as they deposit in the bottom. In this process bound CO_2 is durably removed from the atmosphere [5, 6]. On the other hand, the CO_2 utilized in the process of photosynthesis by land plants (both wildlife and crop plants) is returned to the atmosphere after plant death and mineralization. Only part of the organic compounds are transformed into relatively long lasting compounds in the soil as humus.

The purpose of the present paper is to follow the dynamics of carbon content in red clover plants during the season of biomass overgrowth, beginning with the harvest of the main crop – summer barley in 1999 till the phase of bloming July10, 2000.

The obtained laboratory data were used for the calculation of demand for CO_2 for producing the final biomass of the plant. Also, content of such elements that had showed correlation with the dynamics of carbon content in red clover plants was studied, including: nitrogen, phosphorus and silica. Considering SiO_2, ash fraction content was also determined in the studied samples of red clover.

Material and Methods

For this study a static fertilization experiment was used, designed according to the so-called Norfolk system (four field rotation). In each treatment equal NPK dosages were applied but in different forms. The fertilization combinations practiced since the year 1955 were the following: mineral NPK, organic –farm manure; the mixed system: 50% of mineral NPK + 50% of farm manure; and the control combination. The fertilizer dosages applied are given in Table 1. The experimental plots were established in Chylice Agricultural Experimental Station; on proper black earths developed from light silty boulder loam.

The soil is classsified in bonitation class IIIa, and to second (good wheat) agricultural complex. The experimental plot's geographical coordinates are: 52°06'N, 20°34' E, and 98m above sea level.

Red clover seeds were sown into the field of summer barley in 1999. The samples were collected several times during growing season, 20 plants were sampled during each growing phase: September 6,1999 (stage of rosette), April 5, 2000 at the stage of rosette, May 30, 2000 stage of stem elongation and bud setting, June 10, 2000 at the beginning of blooming stage, June 15, 2000, at the stage of full florescence and the last sixth growing phases on July 10, 2000 at the stage of blooming conclusion.

The plants sampled were subjected to cleaning, then were dried at 60 – 70°C, ground and subjected to determination of:

1.Carbon with the Tiurin method;

2.Total nitrogen with the Kielhfos method.

The ash fraction was determined by burning the plant material at 520°C. The ash was dissolved in 1% HCl and in the solution were determined :

1.Phosphorus – with use of the colorimetric method;

2.Silicon dioxide (silica) – with use of the weight method, after precipitation and leaching by 1% HCl and then the sample was burnt at 900°C.

Each analysis was repeated twice from each field, and the experiment was carried out in four replications following the design of randomized blocks. As a result, all the data included in the tables of the present paper, are mean values calculated on the basis of 8 repetitions each.

Results

Carbon in organic compounds is one of the most stable elements of plant biomass. Its amount does not, practically, depend on the applied forms of fertilizers. Red clover plants harvested from the stubble field contained the highest carbon contents of organic compounds in the control without fertilization; considering the NPK fertilization treatments, the plants have significantly lower amounts of organic carbon compounds; but the lowest concentration was at the other fertilization treatment (Table 2). With time, the actual differences in carbon contents become less significant and finally vanish between fertilization treatments and control.

Significant loss in carbon content was observed during the wintertime period. This should be related to the weight loss of the crop: the actual weight loss was equal to 40.9% on average and was nearly identical with the observed loss of carbon content (41.8%). The loss of carbon in the plant biomass results in increased amounts of $H_2PO_4^-$ (36.2% on average), nitrogen (12.8%) and ash constituents (as much as by 57%) as compared with the autumn period). It is reasonable to assume that the loss of carbon content from the organic compounds is compensated by the higher

Table 1. Fertilization routine within a rotation cycle**).

Crop rotation	Fertilizer treatments								
	Mineral			Manure [t/ha]	Mineral+organic			Manure [t/ha]	Control
	N	P	K		N	P	K		
	[kg/ha]				[kg/ha]				
Root crop	110	27.5	191	40	55	13.7	95.5	20	0
Spring barley + clover	70	27.5	66.4	20	35	13.7	33.2	10	0
Clover	0	27.5	66.4	0	0	13.7	33.2	0	0
Winter wheat	70	27.5	66.4	20	35	13.7	33.2	10	0
In rotation cycle	250	110	390.2	80	125	54.8	195.1	40	0

**) Untill 1961 mineral fertilization volume was 50% lower and manure was only applied for the root crop.

content of phosphorus and nitrogen: the two latter elements' increase almost equal the observed loss of organic mass of red clover plants.

It is clearly visible from the calculations that the crop loss of red clover during the wintertime nearly equals the carbon loss in the same period as expressed in CO_2 (yield: 40.9% and 41.8% CO_2). The associated with the above phenomena increase of nitrogen and phosphates contents suggests that the plant mainly utilizes carbonates for the respiration processes during wintertime. Its protein resources are maintained intact. As a consequence, the growth of nitrogen and phosphate content is more or less fullfilled by the actual loss of carbon in the form of CO_2 (Table 2).

As soon as the growing period starts in the spring, red clover gradually regain the carbon lost during the winter. Consequently, the contents of N and $H_2PO_4^-$ gradually decrease (Table 2).

No organ related differentiation in the concentration of organic matter carbon content was found; all organs (stems, leaves, and flover) have similar amounts of carbon in their tissues, like to that in the whole of the plant (Table 2). It is possible to calculate the desired amount of CO_2 to produce a unit of biomass in the process of photosynthesis - based on the actual content of carbon in plant mass. On average, the plants use 1100 - 1400g CO_2 to produce 1kg of dry matter. Assuming that the atmospheric air contains in normal circumstances 0.04% CO_2 concentration, one may come to the conclusion that there are 0.4l carbon dioxide in 1m^3 of air. Then, given one liter of CO_2 equal 1.96g, it is $0.4 \cdot 1.96 = 0.784$g of carbon dioxide in 1m^3 of the atmosphere. If so, the production of 1kg of dry biomass of red clover is accompanied by 1400 to 1600m^3 of atmospheric air CO_2 free.

And this result is very important from the point of view of climate protection. The applied fertilizer forms do not impact significantly on the amount of carbon in red clover plants (Table 2). As a result, the averaged values of carbon content as given in Table 2 do not differ much from the amounts in particular fertilizer treatments.

Nitrogen is the second most important element of organic matter in plants. Nitrogen content in the plants of red clover is relatively lower after the main crop (spring barley) harvest; it reaches its peak at the start of the vegetation period in the spring. In the subsequent stages of biomass growth nitrogen content in red clover becomes stable till the moment bloming is completed, when it diminishes slightly (Table 2). Considering particular plant organs (stems, leaves and flowers), it must be concluded that during the earliest stages of bloming the highest content of nitrogen occurs in leaves. On the other hand during the blossom finish period, the highest nitrogen content was found in flowers. Stems have relatively lowest content of nitrogen and, consequently, that of crude proteins (Table 2).

Out of the total content of nitrogen in stems, leaves, and flowers at the initial stage of florescence, 19.6% is that nitrogen contained in stems, 41.4% N in leaves, and the remaining 39.0% N in inflorescence. On the other hand, at the period of florescence end, stems accumulate 15.9% N on average, leaves 39.4% N, and inflorescence - 44.7% of the plant's total nitrogen. The seasonal change has been the result of the preparatory processes leading to seed setting by the plant that force nitrogen to be removed first of all from the stems, and to a lower degree from the leaves to the inflorescence.

The fertilizer forms practiced do not cause significant variation of nitrogen content in the plant, nor in any of its organs. What is clearly influential in the actual nitrogen content in red clover is temperature and the plant develop-

Table 2. Concentration of some elements and compounds in different development stages of red clover.

Treatment	Determined value	Whole plant						Parts of plants					
		Sampling time						Stems	Leaves	Blossom	Stems	Leaves	Blossom
		1 2)	2 2)	3 2)	4 2)	5 2)	6 2)	4 2)	4 2)	4 2)	6 2)	6 2)	6 2)
Fertilized 1)	Carbon[%]	34.3	23.7	27.2	29.9	31.7	31.8	29.6	30.0	31.8	32.1	30.9	32.0
Control	Carbon [%]	37.9	24.0	27.5	29.2	32.0	32.0	29.3	29.0	30.7	31.8	32.2	32.4
Fertilized 1)	Nitrogen[%]	3.17	3.33	2.53	2.47	2.53	2.26	1.64	3.47	3.25	1.27	3.32	3.77
Control	Nitrogen [%]	2.70	3.77	2.66	2.48	2.57	3.32	1.57	3.32	3.23	1.41	3.04	3.46
Fertilized 1)	C/N	10.8	7.1	10.8	12.0	12.5	14.1	18.0	8.7	9.5	25.3	9.4	8.5
Control	C/N	14.0	6.4	10.3	11.8	12.5	9.6	18.7	8.7	9.5	22.6	10.6	9.4
Fertilized 1)	$H_2PO_4^-$ [%]	0.95	1.24	0.70	0.65	0.56	0.56	0.48	0.79	0.99	0.38	0.69	1.01
Control		0.82	1.15	0.64	0.62	0.54	0.54	0.43	0.78	0.93	0.38	0.55	0.97
Fertilized 1)	SiO_2 [%]	2.44	21.4	2.82	0.51	0.54	0.38	0.31	0.80	0.46	0.57	1.80	0.73
Control		1.96	11.6	3.38	0.58	0.80	1.28	0.46	0.74	0.62	0.91	2.09	0.84
Fertilized 1)	Ash [%]	13.0	30.3	10.4	8.6	8.4	8.3	7.2	11.2	7.0	6.6	11.3	7.5
Control	Ash [%]	9.0	20.8	12.2	8.0	8.9	8.3	6.1	10.2	7.1	6.2	11.0	7.6

1) Average from three fertilizers combinations (Tab. 1)

2) Sampling time: 1 = 1999-09-06; 2 = 2000-04-05; 3 = 2000-05-30; 4 = 2000-06-10; 5 = 2000-06-15; 6 = 2000-07-10

mental stage.

The carbon-to-nitrogen (C/N) ratio is relatively low in red clover. It reaches its seasonal minimum ranging from 4.0 to 7.1 in the winter; after that it continuously increases untill the stage of blossom shedding and it reaches the range 9.6 - 14.1. The low value of the ratio is maintained regardless of the actual form of nitrogen fertilizer; this is mainly the consequence of the rather high nitrogen content in the papilionaceous plants. Its minimum level, which is reached just after the winter, is a consequence of the utilization of carbohydrates in the winter period for the energetic physiological processes, a trend that leads to increased protein content in the plant.

The range of the C/N ratio is typical for red clover stems and it shows the growing trend till the period of blossom shedding. The ratio is equal to 18.3 at the beginning of florescence and it becomes 24.0 at the time of blossom shedding (Table 2). The ratio is practically identical for leaves and inflorescence, ranging within 8.5 to 10.6.

Such low ratio C/N in red clover plants contributes to increased mineralization of crop organic residuals and may also contribute to the humification process and humus formation in the soil. It must be concluded that carbon dioxide bound by red clover may be returned to the atmosphere within a short time following the processes of mineralization and humification. This opinion is confirmed by the study of Roszak [11].

The carbon/phosphorus (C/P) ratio is wide in red clover. It gradually increases from the start of biomass growth onset till the end of the growing season. Its lowest value is observed in early spring: 61 on average. After the harvest of main crop, that is during the period of free growth of red clover, the C/P ratio is 121 on average; and in the moment of blooming shed it grows to 177. Considering particular organs of the plant, the relatively lowest C/P ratio is characteristic of flowers and is equal to about 100. Those most variable ratios in the stems of red clover plants ranged from about 200 to 266. The ratio for leaves is moderate, between that of blossom and stems.

The C/P ratio may be an indicator of the share of complex proteins in plant biomass, similar to the ratio C/N expresses as the total share of proteins in the plant.

Phosphorus (H_2PO_4) content shows similar trends to that of nitrogen. Its highest content occurs after the winter and further decreases very slowly till the stage of blossom shed. This trend has been most likely due to carbohydrate loss as observed along the winter time (with maintained integrity content of nucleic acids). The stems contain relatively low amounts of phosphates, richer are leaves, and inflorescence are the richest (Table 2).

On average, stems contain 19.8% of total phosphorus in the plant, leaves - 33.8%, and inflorescence - 46.4%.

Ash content decreases with growing amounts of carbon compounds in the plant. Ash share is high in the studied plants during the period of spring season vegetation. It ranges depending on applied fertilizer form, from 20.8% in the control treatment to 33.8% in the organic-mineral treatment.

Ash content becomes stable and not dependent on the fertilizer form at the moment of blossom set till the end stage of blossom shed and it varies within 8.3 - 8.9%.

Ash content is similar in stems and inflorescence and it is significantly higher in leaves. Total amount of ash substances equal 100%, stem accumulate on average 25.8 to 27.5%, leaves 44.0%, and inflorescence 29.0%.

The ratio ***ash/nitrogen*** is maintained at a stable level during the period of red clover plant biomass accumulation (leaving aside the wintertime changes in the balance). The plant utilizes soil nitrogen and ash substances in the proportion 1.0 to 3.3 - 3.9. Stems accumulate the relatively largest quantity of ash substances per nitrogen unit, varying from 4.2 to 5.0%, and florescence accumulates relatively low amounts of ash: merely from 2.0 to 2.2%. Similarly stable is the ratio ***organic carbon/ash substances***. This ranges from 2.9 to 3.8 with one exception only: early spring. Stems and inflorescence show a similar ratio: from 4.3 to 4.9; while the value in leaves varies from 2.7 to 2.8% on average.

Noteworthy, while determining the ash fraction after dissolution in HCl, the potential presence of quartz grains was also detected, enabling us to exclude the possibility of pollution on the surface of plants. The very high ash share in red clover plants after the period of winter suggested the possibility of occurrence of mineral grains on the surface of leaves. Such a phenomenon was reported for potato stems [1]. No mineral grains were found in the case of red clover plants. The presence of colloidal silica - SiO_2 - was detected by snow-like color during the majority of periods of biomass growth. But instead, observed after winter period of red clover, growth and ash content equal 20.8 to 30.3% on average) silica has a pinkish color. Attempts to wash it out using different concentrations of HCl did not succeed. No compounds of Fe and Mn were found in SiO_2 material. It is difficult, therefore, to determine the actual cause of the pinkish color of the silica present in the tissues of red clover in wintertime.

The ash contains first of all silica SiO_2, in the period from autumn till the end of May, but in period from blossoming till inflorescence shed its content are low. Silica is probably similar to N, K, P, Ca and other elements, a biogenic compound. It occurs in relatively high amounts in the leaves of red clover, and in least amounts in the stems; inflorescence contains moderate amounts of the SiO_2.

Out of the total silica amount in red clover,stems accumulate it from 20.0 to 23.0%; leaves 48.0 to 57.0%, and inflorescence - from 23.0 do 49.0% of total SiO_2.

One cannot determine clearly the effect of different fertilizer forms for the accumulation of silica and ash substances in the studied plants. It seems, however, that one of the substantial factors is undoubtedly the thermal conditions under which the plants develop.

Discussion

The development of plans is mainly dependent on CO_2 available in the atmosphere, and water and mineral nutrient resources in the soil. Mineral nutrient uptake from the soil are quite low: they contribute 5-10% to the dry weight of the majority of plants.

The simplified scheme of chemical reactions as taking part in the plant during the processes of photosynthesis and absorption of CO_2 is as follows:

$$6\ CO_2 + 6\ H_2O + E = C_6H_{12}O_6 + 6\ O_2$$

or, when quantified:

$$264g\ CO_2 + 108g\ H_2O + 2817kJ = 180g\ \text{carbohydrates} + 192g\ \text{oxygen}.$$

To produce 1 g of glucose in the process of photosynthesis, 1.07g of oxygen are released to the atmosphere and stored 15.65kJ of solar energy. This is the energy all living creatures, from the most primitive to man himself, utilize. Therefore, the harvest residuals in a stubble field, or the fallen leaves and nidles in forest ecosystems, are utilized by soil micro- and mezofauna as well as by microbes. Following the organisms' metabolism leading to mineralization of decayed plant parts, significant amounts of CO_2 are again released to the atmosphere. It is commonly accepted that the soils of agrosystems excrete from 20 to 50kg CO_2 per day per ha, on average; and forest soils supply to the atmosphere four-to-five times greater amounts of CO_2. On the other hand, an average agricultural crop utilizes about 120kg CO_2/ha per day. If so, the sources and sinks of CO_2 are not in balance. The soil supplies only a third part of required CO_2, and the rest comes from the adjacent atmosphere [9]. During wintertime, however, vegetation mainly releases CO_2 to the atmosphere and this, one may conclude, associated with rainfall precipitation gives the carbonic acid which, when reaches soils, contributes to their increased acidification.

It should be emphasized that the CO_2 cycle in nature is to a large degree complicated and a difficult task to balance fully.

Among other things, we do not know what is the actual CO_2 per cent that becomes transformed into H_2CO_3 during precipitation events, and comes back to the soil. The soils of Poland store at present from 4 to 5 billion tons of carbon in humus, peat and other compounds. Assuming the mineralization of all humus accumulated in Poland's soils has taken place, as much as from 14 to 18 billion CO_2 tons would be released to the atmosphere. The release of surplus amounts of CO_2 and other gases to the atmosphere as a result of human activities may significantly alter the natural climatic trends on a global scale [3, 4, 5, 6, 8, 9, 10].

The study of red clover as presented in this paper suggests that the plant binds from the atmosphere significant amounts of CO_2,but smaller however than those bound by the cereal crops. To produce 1 ton of red clover dry matter from 1.1 to 1.4 ton of CO_2 is needed, and if so the plant giving two harvests per year enables the fixation of several tons of atmospheric CO_2 per year.

Conclusion

The following general statements may be proposed as a result of our study of red clover and the possibilities to use carbon from atmospheric CO_2 in the process of photosynthesis:

1. Red clover plants take up from 1.1 to 1.4 kg of atmospheric CO_2 to produce 1 kg of dry mass. This is equivalent of 1400 to 1600m^3 of atmospheric air cleaned from carbon dioxide.
2. The studied plants use mainly carbohydrates during winter for their physiological processes (respiratory processes). This is concluded from the evidently enlarge content of nitrogen and phosphorus in the plants.
3. The applied forms of fertilizers (mineral, organic and mixed: organic-mineral) do not produce any clear differences in the content of nitrogen, phosphorus, and silica in the plants of red clover.
4. The observed weight loss of red clover plants during the winter period of growth are caused by CO_2 release during respiration and CO_2 released amounts are equal to weight loss of plant mass.

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