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Influence of the Degree of Soil Organic Matter Lability on the Calcium Carbonate Equilibrium of Soil Water

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Abstract: In average samples of three sandy-loamy acid Cambisols from a South Bohemian area labile organic matters were determined by the permangate method modified by the dichromate method, and the rate constant of their biochemical oxidation was determined in hot water extracts of the samples. The need of liming was determined by means of 2 methods. In soil solutions of these samples, all values necessary to evaluate their calcium carbonate equilibriums were determined. The soil samples were enriched with 3% of dry matter of two organic materials, farmyard manure and meadow clover meal, and were incubated at 25°C for 180 days under wetting above 50% of their retention water capacity, and after this procedure all analyses were repeated. Both methods were found to increase the need of liming in all three soils: the more labile the organic matter in 3% addition, the higher the need. The meadow clover matter was more labile than the farmyard manure matter. All three methods for the study of soil carbon lability yielded similar results while the potassium permanganate method was more sensitive than the dichromate one. Increases were observed in equilibrium $[\mathrm{Cr}(\mathrm{H_2CO_3^*})]$ and in Langelier saturation index I_s. This means that soil liming cannot be considered only as an adjustment to the soil acidity and supply of calcium to plants to meet their requirements, but also as a replacement of the spontaneous adjustment to calcium carbonate equilibrium of soil water, for which through mineralisation of labile organic matters in conditions of our experiment about 220 kg $CaCO_3$ per hectare of land were consumed on condition that it was not necessary to re-establish it. The process of Ca-compound consumption to establish the calcium carbonate equilibrium is controlled exclusively by the degree of mineralising organic matters lability while the influence of soil properties is only marginal. The same results were provided by the comparison of calcium carbonate equilibriums in nine Šumava brooks of the total watershed area 78 564 km^2 with the degree of lability of organic matters in their sediments in 1986, 2001 and 2004. A reduction in the intensity of agricultural production in 1986–2004 resulted in an increase in the stability of organic matters in the sediments, in a decrease in I_s, and in a lower corrosivity of brooks water towards $CaCO_3$. However, the quality of soils and their potential soil fertility decreased due to the loss of labile organic matters.

Keywords: calcium carbonate equilibrium; degree of lability; liming need; soil organic matter; soil water

The soil liming and doses of lime fertilisers are mostly considered only as measures taken to adjust soil acidity and to meet calcium requirements of plants.

In the climate of Central Europe, 30–350 kg/ha of calcium per year are eluted from arable soils. $CaCO_3$ solubility is related to CO_2 production that is determined by the biological activity in soil, mainly in the course of mineralisation of labile soil organic matters.

A considerable amount of Ca-compounds is necessary to establish the carbonate equilibrium

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Table 1. pH values in the system soil – water in relation to the partial pressure of CO_2 in equilibrium air

	Partial pressure of CO_2 (kPa)			
	0.03	0.1	1.0	10
Soil with 9% $CaCO_3$	8.3	8.0	7.4	6.7
Soil without $CaCO_3$	6.9	6.7	6.4	6.0
Distilled water	5.7	5.4	4.9	4.4

$[Cr(H_2CO_3^*)] – C(HCO_3^-)$ in the soil water and also to create the proper buffering system of the soil water. Rainfalls and the respective elutions lead to an incessant repetition of these processes.

Table 1 (Balík *et al.* 2005) shows the pH values in the system soil – water in relation to the partial pressure of CO_2 in the air, which is in equilibrium with this system.

The partial pressure of CO_2, corresponding to the given composition of water, makes it possible to evaluate the degree of water saturation compared to soil air:

$$\log p_{CO_2} = \log a_{HCO_3^-} - pH - \log K_0K_1$$

K_0 is the equilibrium constant of the equation:

$$CO_2 + H_2O = H_2CO_3$$

$$-\log K_0\ (25°C) = 1.47$$

K_1 is the equilibrium constant of the equation:

$$H_2CO_3 = H^+ + HCO_3^-$$

$$-\log C_1\ (25°C) = 6.34 - 6.46$$

The values of both constants depend on temperature according to the relations:

$$-\log K_0 = 1.113 + 1.672 \times 10^{-2}\, t - 1.051 \times 10^{-4}\, t^2$$

$$-\log K_1 = 6.576 - 1.250 \times 10^{-2}\, t + 1.405 \times 10^{-4}\, t^2$$

About 99% of CO_2 is dissolved in water in the molecular form, only about 1% reacts with H_2O while H_2CO_3 is produced. The dissolved CO_2 is free carbon dioxide and is the sum of the concentrations of freely hydrated carbon dioxide $[CO_2(aq)]$ and H_2CO_3. In literature, it is often designated by the symbol $H_2CO_3^*$ (Pitter 1981).

The ions HCO_3^- and CO_3^{2-} are ion forms of CO_2, i.e. bound CO_2, which is of hydrogen-carbonate and carbonate types. The sum of all three forms of CO_2, i.e. the free and both forms of bound CO_2, is designated as total CO_2.

The open carbonate system with constant partial pressure of CO_2 can be described by means of the combination of the equations for Henry's law distribution coefficients of free CO_2, HCO_3^-, and CO_3^{2-}:

$$[H_2CO_3^*] = K_H \times p_{CO_2}$$

$$[HCO_3^-] = K_1/[H^+] \times K_H \times p_{CO_2}$$

$$[CO_3^{2-}] = K_1K_2/[H^+]^2 \times K_H \times p_{CO_2}$$

where:

K_H – Henry's constant

p_{CO2} – relative partial pressure of CO_2 in soil air

K_H – equal K_0 in this case; C_2 is the equilibrium constant of the reaction:

$$HCO_3^- = H^+ + CO_3^{2-}$$

$$-\log C_2\ (25°C) = 10.22 - 10.40$$

In the atmosphere of 0.03% of CO_2 by vol. p_{CO2} = 30 Pa, and under these conditions about 0.7 mg/l CO_2 is dissolved in water at 10°C. In the course of degradation of soil organic matters, CO_2 content in soil air is up to 100 times higher, depending on the biological activity of soil, on the amount of degradable soil organic matter and, especially, on its liability to biochemical oxidation, i.e. on the degree of its stability.

The dissolved free CO_2, i.e. $H_2CO_3^*$ is present in soil water until pH = 8.3 is reached.

If water does not contain any dissolved CO_2, the solubility of $CaCO_3$ at 20°C is about 15 mg/l, as reported by Pitter (1981):

$$CaCO_3 \rightarrow \leftarrow [CaCO_3\ (aq)]°$$

In the presence of dissolved CO_2 in soil water, which is usual, the solubility of $CaCO_3$ is substantially higher due to the reaction:

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2\ HCO_3^-$$

The equilibrium between HCO_3^-, free CO_2 and Ca^{2+} is established. The corresponding CO_2 from the equation is equilibrium CO_2, designated as $[CO_2]_e$, and its concentration as $[Cr(H_2CO_3^*)]$. If the amount of free CO_2 in soil water is higher than that corresponding to $Cr(H_2CO_3^*)$, water continues to dissolve $CaCO_3$. If it is lower, $CaCO_3$ is precipitated from water on active surfaces.

The calcium carbonate equilibrium may be influenced by six components: $H_2CO_3^+$, HCO_3^-, CO_3^{2-}, Ca^{2+}, H^+, OH^-. Therefore, six equations independent of, one another are necessary for its solution (Pitter 1999):

(a) Two equations for the dissociation constants of carbonic acid K_1 and K_2

(b) Equation for the solubility product of $CaCO_3$ (s) K_s

(c) Equation for the ionic product of water K_w

(d) Electroneutrality equation
$c(H^+) + 2\,c(Ca^{2+}) = c(HCO_3^-) + 2\,c(CO_3^{2-}) + c(OH^-)$

(e) Equation of analytical concentrations
$c(CO_2)_T = c(H_2CO_3^*) + c(HCO_3^-) + c(CO_3^{2-})$

It is also influenced by the water temperature and ionic strength (s). The calcium carbonate equilibrium can be described by two equations composed of combined Eqs (a), (b), and (c):

$$CaCO_3\,(s) + H_2CO_3^* = Ca^{2+} + 2\,HCO_3^- \qquad (1)$$
$$K_A = K_1 \times K_s \times K_2^{-1} = 10^{-4.345};\ (T = 25°C)$$

$$CaCO_3\,(s) + H^+ = Ca^{2+} + HCO_3^- \qquad (2)$$
$$K_B = K_s \times K_2^{-1} = 10^{2.01};\ (T = 25°C)$$

Eq. (1) shows that $CaCO_3$ is neither dissolved nor precipitated when a certain concentration of free carbon dioxide is reached. This free CO_2, which is in equilibrium with the concentration of Ca^{2+} and HCO_3^- ions, is called equilibrium carbon dioxide [$Cr(H_2CO_3^*)$]. If the concentration of free CO_2 is lower than the concentration of equilibrium CO_2, water will tend to precipitate $CaCO_3$, if it is higher than the latter one, water will dissolve it.

The equation of the equilibrium curve is derived from Eq. (1):

$$Cr(H_2CO_3^*) = (K_A)_c^{-1} \times c(Ca^{2+}) \times c^2(HCO_3^-) \qquad (3)$$

where:

$(K_A)_c$ – concentration value of the equilibrium constant

Each type of water does not have its own equilibrium curve according to its composition.

On condition that the simplified electroneutrality equation: $2\,c(Ca^{2+}) \cong c(HCO_3^-)$ holds good and HCO_3^- and Ca^{2+} are dominant in water, Eq. (3) changes its form to:

$$c(H_2CO^*) = \frac{1}{2\,(K_A)_c} \times c^2(HCO_3^-) \qquad (4)$$

In the Central Europe, the simplified Eq. (4) has been used to determine the corrosive aggressivity of water for several decades but it provides only a rough estimate, being based on very simplifying assumptions, and also because the determination of free CO_2 from $BNC_{8..3}$ (base neutralising capacity) is not quite precise.

In 1936 Langelier defined the so called saturation index I_s:

$$I_s = pH - pH_s \qquad (5)$$

where pH is the measured value of the water sample and pH_s is the calculated pH value of water that is reached if it is in equilibrium with $CaCO_3$ (s) at a given composition:

$$pH'_s = \log K_B - \log c(Ca^{2+}) - \log c(HCO_3^-) \qquad (6)$$

However, the calculated value pH'_s is only fictitious because the dissolution or precipitation of $CaCO_3$ is connected with the changes in Ca^{2+} and HCO_3^- concentrations including the changes in ionic strength. We should not substitute the original concentrations of Ca^{2+} and HCO_3^- in Eq. (6) but the equilibrium concentrations of C_e, however, these are not known in advance.

If $I_s < 0$, Eq. (2) proceeds from the left to the right, i.e. water dissolves $CaCO_3$ (s). If $I_s = 0$, water is in calcium carbonate equilibrium. If $I_s > 0$, $CaCO_3$ (s) is precipitated from water.

The above-mentioned lack of exactness and the formation of ion associates and other complexes of Ca^{2+}, e.g. those with organic matters cause that fictitious pH'_s is always higher than the actual pH_s, and therefore the water aggressivity is always higher than in reality.

If the above statements are summarised, obviously, a great simplification is to consider liming as a mere attenuation of soil acidity. Besides the neutralising effect, liming must overcome the established buffering systems not only in soil but also in soil water. The better the reserve of oxidable organic matters in soil and the lower the stability of these organic matters (and this is an assumption for microbially highly active and fertile soils), the higher the consumption of Ca-compounds to establish equilibrium between CO_2 and HCO_3^- and the higher the production of water-soluble $CaHCO_3$.

This implies a good reserve of exchangeable calcium in soil on one hand but, on the other hand, its losses due to elution will be higher.

MATERIAL AND METHODS

Topsoil samples were taken from acid sandy-loamy Cambisols in the localities České Budějovice (A), Ktiš (B), and Kubova Huť (C), which differ from one another by very diverse lability of the soil organic matters. This lability was determined on the basis of oxidability by neutral 333mM $KMNO_4$ according to Blair *et al.* (1995), we also used the original Walkley-Black method (Walkley & Black 1934) as modified by Walkley (1947): oxidation with 0.167M $K_2Cr_2O_7$ in the mediums of 12N, 18N and 24N H_2SO_4 (Chan *et al.* 2001).

The study of organic matters lability in the soil samples was completed by determining the rate constant of their biochemical oxidation in the water-soluble fraction that may be extracted with boiling water under a reflux condenser within 1 h (Kolář *et al.* 2003, 2005).

In the soil samples, the need for liming was also determined from the ratio of H^+ in the sorption complex of soil according to Adams and Evans (1990) and from the potentiometric titration curve in 1M KCl at titration up to pH = 7.0, and further the cation exchange capacity CEC according to Gillman (1979) and the degree of sorption saturation *V*.

Soil water was obtained from the topsoil samples cooled to 4°C using the extraction with degassed distilled water under the cap of an absorber with moist lenses of NaOH of the same temperature. Unfortunately, we could not use any common method to extract soil water (pressure one and ethanol extraction with subsequent distillation) because of the impossibility to determine free CO_2.

Calcium carbonate equilibriums were determined by classical analytical methods of hydrochemistry taking into account their lack of exactness that was mentioned in the introductory part. This study, however, being aimed at comparative measurements, we are convinced that the results are at least comparable even though they are not precise enough.

In the extracts, we measured the solutes, acid neutralising capacity $ANC_{4.5}$, free CO_2, bound CO_2, Ca^{2+}, HCO_3^-, and pH. Using these values, we calculated pH_s according to the above-mentioned formula using the tabular value log K_p/K_2 for the detected amount of solutes and temperature of 10°C. Langelier saturation index I_s was computed from these data. The measured values of pH were compared with those calculated according to Nachtigall from free and bound CO_2 (Lhotský 1954). Equilibrium CO_2 was determined on the basis of $ANC_{4.5}$ from Lhotský's tables.

The soil samples were enriched with a dose of 15 g of dry matter of organic matters/500 g of soil sample. Dried ground farmyard manure (originally 14.3% organic matters) (treatments X) and dried clover meal (treatments Y) were the sources of organic matters. In these samples, the above-mentioned soil characteristics were determined immediately after the sample treatment and again after 180-day incubation of the samples wetted to 50% of their water retention capacity in a thermostat at 25°C while the evaporated water was continually added (Tables 2–5).

In the next part of this study, in the waters coming from 9 Šumava brooks (Table 6), based on the results of the cited paper by Kolář *et al.* (2002), and from the values of (Ca^{2+}) and (HCO_3^-) and the value of $K_p:K_2$ for the given content of solutes and the temperature of 10°C as well as from the table reported by Pitter (1981), we calculated the value of saturation pH_s according to Langelier and from the difference $pH-pH_s$ of the surface waters the Langelier saturation index I_s. Comparing the pH value of the waters with theoretical pH values calculated according to Nachtigall from free and bound CO_2 (Lhotský 1954), we found out that in the waters of all 9 Šumava brooks the carbonate buffering system was dominant over other buffering systems because the differences between both values did not exceed 0.1 pH.

The values of equilibrium CO_2 were derived from acid neutralising capacity $ANC_{4.5}$ while the values of free CO_2 were computed from base neutralising capacity $BNC_{8.3}$ according to Lhotský's tables (Lhotský 1954).

These results were compared with the average values of carbon content determined by the method C_{pm} (Blair *et al.* 1995) and with the rate constants of biochemical oxidation of labile organic matters determined by the same method as used in the incubation experiment with average samples of sediments of these brooks.

The calculations from the analytical data obtained between 1986 and 2001 were complemented by

Table 2. The analyses of soil samples (ABC) on the first and 180th day after the start of incubation at 25°C with an addition of organic dry matter in the form of dried ground farmyard manure (X) and clover meal (Y)

	Day	A	B	C	AX	AY	BX	BY	CX	CY	$lsd_{0.05}$
pH/KCl	1	6.25	5.91	5.60	6.30	6.20	6.00	5.92	5.80	5.68	0.26
	180	6.19	6.03	5.60	6.18	6.05	5.82	5.71	5.75	5.50	0.19
Liming need (Adams & Evans 1990) (0.1 CaO t/ha)	1	11	15	35	11	11	15	16	35	35	2.10
	180	11	16	35	14	16	19	21	38	41	2.89
Liming need (potentiometric titration curve) (0.1 CaO t/ha)	1	16	16	30	16	16	16	16	29	30	1.82
	180	16	16	31	21	23	22	24	34	37	1.95
Cation exchange capacity (Gillman 1979) (mmol.chem.eq./kg)	1	219	175	134	219	219	175	176	132	133	18.30
	180	225	180	136	231	229	185	183	138	135	24.15
Degree of sorption saturation *V* (%)	1	83	68	53	81	82	65	65	55	54	16.40
	180	82	69	55	82	84	66	68	52	53	22.18

Table 3. Total organic carbon TOC (%) (ISO 10694), oxidable carbon determined by 333mM $KMnO_4$ C_{pm} (%) (Blair *et al.* 1995), oxidable carbon determined according to Walkley-Black C_{WB} (%) (Walkley & Black 1934), and the rate constant k_1 (24 h) of biochemical oxidation of labile organic matters extracted with hot water (Kolář *et al.* 2003, 2005); soil samples ABC with 3% additions of organic dry matter of manure (X) and clover meal (Y)

	Day	A	B	C	AX	AY	BX	BY	CX	CY	$lsd_{0.05}$
TOC (%)	1	1.12	1.50	1.84	2.03	1.99	2.47	2.42	2.90	2.81	0.20
	180	1.01	1.31	1.76	1.47	1.43	1.99	2.00	2.55	2.23	0.25
k_1 (24 h)	1	0.02	0.03	0.05	0.25	0.31	0.26	0.33	0.28	0.35	0.01
	180	0.02	0.02	0.03	0.14	0.11	0.10	0.10	0.15	0.15	0.01
C_{pm} (%)	1	0.16	0.25	0.39	0.57	0.70	0.49	0.80	0.76	0.90	0.12
	180	0.14	0.22	0.37	0.26	0.26	0.38	0.39	0.46	0.40	0.05
C_{WB} (%)	1	0.82	1.17	1.31	1.70	1.77	1.98	2.13	2.41	2.53	0.23
	180	0.75	1.02	1.25	1.23	1.27	1.59	1.76	2.10	2.10	0.19

the calculations coming from the data acquired in 2004–2005 (Gergel 2006).

The results were processed by mathematical and statistical methods for few-element sets at a significance level α = 0.05 and 95% reliability interval from the range of results according to Dean and Dixon (Eckschlager *et al.* 1980).

RESULTS AND DISCUSSION

Table 2 shows the results of soil analyses obtained in the incubation experiment changes of carbon forms (Tables 3 and 4); the respective results of its hydrochemical analyses and calculations are given in Table 5.

The distribution of CO_2 forms in water can be calculated from acid-base neutralising capacities if the carbonate buffering system in it is dominant over the other buffering systems. It may be proved from a comparison of the pH value of water measured with that calculated from the concentrations of $H_2CO_3^*$, HCO_3^- and CO_3^{2-}. The condition is the coincidence at 0.1 pH. Out of all treatments, only the treatments AY, BX, BY, CX, and CY satisfied this condition, i.e. all treatments with clover meal and two treatments with farmyard manure. Only these treatments provided reliable data for the final calculations of Ca-compounds consumption to establish the carbonate equilibrium of soil water. Langelier saturation index was computed in these treatments only. Its value was negative in all cases; mineralisation of farmyard manure and clover meal increased the water corrosivity toward $CaCO_3$ twice to four times in all soil samples. Incubation slightly influenced the CEC in all soil samples while among the organic additives only the effect of manure was marked. The need for liming according to the potentiometric titration curve was mostly higher than that calculated according to Adams and Evans (1990). After incubation, the smallest decrease in C_{ox} was measured after the manure addition, and it was the smallest in more acid soil C. The values of the degree of organic matter lability are fully consistent with this situation: they were the most stable in the treatments with manure addition – obviously due to the influence of the content of bedding straw and the presence of a higher amount of stabilised components.

After mineralisation, the extracts of soil water had a higher contents of solutes. The highest amount

Table 4. Fractionation of organic carbon C_{WB} (%) by the modified Walkley-Black method (Chan *et al.* 2001) at various concentrations of H_2SO_4; percentage of total soil carbon in the dry matter of sample is given in brackets; soil samples ABC with 3% additions of organic matter of manure (X) and clover meal (Y)

Day	Fraction	A	B	C	AX	AY	BX	BY	CX	CY	$lsd_{0.05}$
1	1	0.29 (35)	0.43 (37)	0.46 (35)	0.68 (40)	0.73 (41)	0.83 (42)	1.09 (51)	0.92 (38)	1.14 (45)	0.06
	2	0.20 (25)	0.32 (27)	0.35 (27)	0.51 (30)	0.71 (40)	0.73 (37)	0.68 (32)	0.96 (40)	0.96 (38)	0.03
	3	0.16 (19)	0.18 (15)	0.21 (16)	0.31 (18)	0.23 (13)	0.24 (12)	0.21 (10)	0.34 (14)	0.25 (10)	ns
	4	0.17 (21)	0.24 (21)	0.29 (22)	0.20 (12)	0.11 (6)	0.18 (9)	0.15 (7)	0.19 (8)	0.18 (7)	0.04
180	1	0.24 (32)	0.33 (32)	0.37 (30)	0.43 (35)	0.46 (36)	0.54 (34)	0.69 (39)	0.69 (33)	0.80 (38)	0.13
	2	0.18 (24)	0.25 (25)	0.30 (24)	0.38 (31)	0.41 (32)	0.54 (34)	0.60 (34)	0.76 (36)	0.71 (34)	0.15
	3	0.18 (24)	0.24 (24)	0.35 (28)	0.18 (15)	0.15 (12)	0.22 (14)	0.18 (10)	0.23 (11)	0.19 (9)	ns
	4	0.15 (20)	0.19 (19)	0.22 (18)	0.23 (19)	0.25 (20)	0.29 (18)	0.30 (17)	0.42 (20)	0.40 (19)	0.09

Fractions: 1 = 12N H_2SO_4; 2 = 18–12N H_2SO_4; 3 = 24–18 N H_2SO_4; 4 = TOC–24N H_2SO_4

Table 5. The analyses of soil solutions (ABC) on the first and 180th day after the start of incubation at 25°C with 3% addition of organic matter in the form of dried ground farmyard manure (X), clover meal (Y)

	Day	A	B	C	AX	AY	BX	BY	CX	CY
Solutes (mg/l)	1	280	160	118	294	287	175	167	126	122
	180	282	155	119	315	307	199	186	148	131
Free CO_2 (mg/l)	1	20.4	40.6	60.5	20.4	40.6	20.4	40.6	20.4	40.6
	180	24.3	43.1	61.7	57.4	88.3	52.5	85.6	61.3	82.1
Bound CO_2 (mg/l)	1	41.8	31.6	22.0	45.2	42.7	31.0	32.2	22.1	22.5
	180	48.4	47.5	34.5	75.4	61.5	65.4	55.4	47.7	42.1
Equilibrium CO_2 (mg/l)	1	2.0	1.1	0.6	2.4	2.1	1.0	1.1	0.6	0.6
	180	2.8	2.6	1.3	9.7	5.2	6.1	4.0	2.7	2.1
HCO_3^- (mg/l)	1	115.9	87.2	61.0	125.0	117.9	85.4	89.7	61.5	63.9
	180	134.2	132.5	94.0	209.3	170.8	182.1	151.2	132.5	118.0
pH/H_2O	1	6.80	6.20	5.80	6.82	6.80	6.95	6.62	6.90	6.58
	180	6.72	6.13	5.60	6.62	6.72	6.84	6.50	6.72	6.53
pH (Nachtigall)	1	7.14	6.71	6.38	7.17	6.84	7.01	6.71	6.86	6.55
	180	7.12	6.87	6.57	6.93	6.65	6.90	6.63	6.62	6.52
Difference of pH/H_2O – pH (Nachtigall)	1	–0.3	–0.5	–0.7	–0.4	0.0	–0.1	–0.1	+0.1	0.0
	180	–0.4	–0.7	–0.1	–0.3	+0.1	–0.1	–0.1	+0.1	0.0
Acid neutralising capacity* $ANC_{4.5}$ ($KNK_{4,5}$) (total alkalinity) (mmol/l)	1	1.9	1.4	1.0	2.0	1.9	1.4	1.5	1.0	1.0
	180	2.2	2.1	1.5	3.4	2.8	3.0	2.5	2.2	1.9
Saturation pH_s	1	–	–	–	–	7.0	7.0	6.7	6.9	6.7
	180	–	–	–	–	7.1	7.1	6.9	7.0	6.9
Langelier saturation index I_s ($pH - pH_s$)	1	–	–	–	–	–0.2	0.0	–0.1	0.0	–0.1
	180	–	–	–	–	–0.4	–0.3	–0.4	–0.3	–0.4

*$ANC_{4.5}$ is acid capacity, i.e the neutralising acid-base capacity that is an integral of buffering capacity in the selected interval of pH; the sample is titrated with an acid to pH = 4.5; in lye titration to pH = 8.3, the base capacity (previously called “total acidity”) is determined by means of $ZNK_{8.3}$; in waters in the interval of pH = (4.5 <—> 8.3) it holds good that the concentration of CO_2, designated as C_T, equals $KNK_{4.5} + ZNK_{8.3}$ (mmol/l)

of aggressive CO_2 was found with the treatments with clover meal, while a lower amount was detected in the treatments with manure, which is logical considering the value of organic matters stability.

If we take into account only the difference between free and equilibrium CO_2, it represents 40–60 mg/l CO_2 in the treatments with manure and about 80 mg/l CO_2 in those with clover meal if topsoils of these soils contain on average 1.2 $\times 10^6$ l water/ha, stechiometry indicates that, after the breakdown of the added organic matters, the water in soil on an area of 1 ha to a depth of 40 cm requires to establish a new carbonate equilibrium of 0.22 t $CaCO_3$ at zero elution! At the existing elution, Ca^{2+} consumption is covered from its soil reserve. The elution always takes place to a larger or smaller extent in relation to the soil permeability. It is to note that in spite of the ideal conditions of long-term incubation only 40–50% of the added organic matters was mineralised as shown by changes in C_{ox}. To the above-mentioned consumption of $CaCO_3$ for the establishment of a new carbonate equilibrium of soil water, it is necessary to add the main consumption for the attenuation of acidity of the solid phase of soil which, after the mineralisation of organic matters, amounted to 2.1–3.7 t/ha CaO for soils ABC, i.e. 4–7 t $CaCO_3$/ha, as indicated by the potentiometric titration curve.

When evaluating these results, we must not forget the fact that calcium carbonate equilibriums in soil water are complicated by the formation of ion associates and other calcium complexes, e.g. those with organic matters. The concentration of simple Ca^{2+} ions is decreased in this way and the calculated pH_s value is then higher. Thus the water corrosivity is higher than it corresponds to the calculation omitting associates and other complexes (Snoeying & Jenkins 1980; Pitter 1999).

Several aspects concerning the relationship between soil liming and soil organic matter have been described in literature: microbial activity of acid soils increases, which increases the mineralisation of soil organic matter (Curtin *et al.* 1998; Chapin *et al.* 2003; Lalande *et al.* 2009); de-acidification reduces the noxious effect of aluminium with the same resultant effect (Fageria & Baligar 2008); fractionation of soil organic matter and the proportion of water-soluble, i.e. labile, carbon are changed (Manna *et al.* 2007; Bishop *et al.* 2008; de Oliveira *et al.* 2008); water stability of soil aggregates is increased (Grieve *et al.* 2005); the consumption of Ca-compounds increases in relation to the degree of soil organic matter lability (Kolář *et al.* 2007); nitrification increases (Dorland *et al.* 2004); and few papers deal also with the problem of the relation between the labile soil organic matter and soil water (Kolář *et al.* 2002). We are very sorry not to have found any paper solving the relation between the labile soil organic matter and its corresponding calcium carbonate equilibrium in soil water. The reason may be that only since 2005 (Haynes 2005) the degree of soil organic matter lability has been considered as an important factor of the potential soil productivity.

Table 6. Basic characteristics of the watersheds under study

Sample	Stream	Area (km^2)	Forest percentage (%)	Altitude a.s.l. (m)	Specific outflow ($1/s/km^2$)
101	Malý Strážný	6.035	20	630–750	8.59
102	Sušský	13.323	30	600–830	8.59
103	Práčovský	8.153	30	510–650	10.59
104	Močeradský	7.308	30	630–800	7.82
105	Zdíkovský	16.963	40	570–770	7.40
106	Zvíkovský	6.992	30	480–610	9.61
107	Buďský	7.111	30	490–690	9.61
108	Popelicko-Dluhošťský	7.779	60	580–770	11.34
109	Kondračský	4.900	20	490–630	6.18

Table 7. Differences of free CO_2 ($H_2CO_3^*$) and equilibrium CO_2 ($[CO_2]_e$), saturation pH_s according to Langelier, saturation index I_s in the waters of the Šumava brooks, and labile carbon C_{pm} and the rate constant k_1 of biochemical oxidation of organic matters in the brooks sediments in 1986, 2001 and 2004 (the reliability interval of the mean was calculated for the significance level $P = 0.05$)

Sample	1986					2001					2004				
	$H_2CO_3^*$–$[CO_2]_e$ (mg/l)	pH_s	I_s	k_1 (24 h)	C_{pm} (g/kg)	$H_2CO_3^*$–$[CO_2]_e$ (mg/l)	pH_s	I_s	k_1 (24 h)	C_{pm} (g/kg)	$H_2CO_3^*$–$[CO_2]_e$ (mg/l)	pH_s	I_s	k_1 (24 h)	C_{pm} (g/kg)
101	240 ± 38	6.82	–0.28	0.035 ± 0.004	2.85 ± 0.23	62 ± 14	6.50	–0.03	0.009 ± 0.001	0.94 ± 0.14	53 ± 7	6.52	–0.01	0.009 ± 0.000	1.10 ± 0.13
102	132 ± 26	6.99	–0.18	0.028 ± 0.002	2.50 ± 0.25	48 ± 9	6.60	–0.01	0.008 ± 0.000	0.90 ± 0.18	40 ± 2	6.60	–0.01	0.007 ± 0.001	0.95 ± 0.12
103	286 ± 41	7.00	–0.41	0.019 ± 0.001	1.40 ± 0.20	53 ± 7	6.64	0.00	0.015 ± 0.002	1.10 ± 0.15	54 ± 8	6.57	–0.00	0.009 ± 0.000	1.10 ± 0.10
104	154 ± 38	6.74	–0.23	0.026 ± 0.001	3.04 ± 0.34	44 ± 6	6.51	–0.01	0.010 ± 0.004	0.90 ± 0.12	36 ± 9	6.60	–0.02	0.009 ± 0.001	1.10 ± 0.14
105	198 ± 40	6.92	–0.14	0.012 ± 0.000	1.27 ± 0.18	61 ± 9	6.78	–0.02	0.007 ± 0.000	0.98 ± 0.15	55 ± 12	6.72	–0.01	0.007 ± 0.000	1.00 ± 0.12
106	352 ± 69	7.12	–0.52	0.048 ± 0.002	4.01 ± 0.51	57 ± 12	6.59	–0.03	0.010 ± 0.001	0.99 ± 0.10	50 ± 9	6.45	–0.01	0.009 ± 0.000	0.98 ± 0.10
107	132 ± 24	7.05	–0.18	0.017 ± 0.001	0.98 ± 0.13	48 ± 10	6.81	–0.04	0.010 ± 0.000	1.06 ± 0.15	47 ± 8	6.47	–0.02	0.010 ± 0.002	0.95 ± 0.12
108	176 ± 27	6.94	–0.25	0.019 ± 0.001	1.15 ± 0.14	70 ± 8	6.74	–0.10	0.004 ± 0.000	0.92 ± 0.14	65 ± 10	6.64	–0.01	0.006 ± 0.001	0.91 ± 0.10
109	220 ± 44	6.79	–0.33	0.030 ± 0.002	2,47 ± 0.19	44 ± 6	6.42	–0.02	0.006 ± 0.000	0.95 ± 0.11	40 ± 6	6.33	–0.01	0.006 ± 0.000	0.90 ± 0.12

Table 6 shows the characteristics of the catchments of nine Šumava brooks where practical surveys were done. Detailed analyses of waters of these brooks in 1986, 2001, and 2004 and the analyses of soils of these watersheds including the evaluation of the degree of stability of their organic matters and fractionation of their carbon were described by Kolář *et al.* (2002) and Gergel (2006). These analyses documented that a reduction in the farming intensity in the area concerned resulted in a decrease in the content of $N\text{-}NO_3^-$ in the brook waters to 66% of that value when the landscape was used for intensive agricultural production, and the content of $N\text{-}NH_4^+$ decreased even to 7% of the original value. In the soils of brook watersheds, the content of total C_{org} did not actually change, and active soil carbon C_{hws} decreased. It is to conclude that the reduction in the agricultural production in the Šumava area in 1986–2004 slightly increased the elution of degradable organic matters from the watershed soils but these matters increased their stability in soils in the given period. In this way, the soils are deprived of the most valuable fraction of soil organic matters providing an available source of energy for their microbial populations. It is naturally reflected in calcium carbonate equilibriums of waters from the soils of the watersheds of Šumava brooks, in a difference in the means of free and equilibrium CO_2, saturation pH_s according to Langelier, and saturation index I_s in the brook waters. Table 7 shows the differences in these analytical computed data on the brook waters from 1986, 2001, and 2004 as compared to the differences in C_{pm} and K that indicate the degrees of lability of soil organic matters in the sediments of these brooks. Obviously, in 1986–2004 as a result of the reduction in the intensity of agricultural production, a strong increase occurred in the stability of soil organic matter in the soils of the watersheds of brooks in whose waters the difference between free and equilibrium CO_2 considerably diminished, which also decreased Langelier saturation index. Paradoxically, from the aspect of calcium carbonate equilibriums in soil water, the soils in the Šumava area currently need less $CaCO_3$ than at the time of intensive farming although they undergo significant acidification. We cannot confirm the ecological ideas suggesting that the soil at rest recovers its potential productivity and produces a higher amount of labile organic matters as a source of energy for soil microorganisms. The process in the Šumava area is contradictory.

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