Relationship between soil organic matter lability and liming requirement in acid sandy-loam cambisols

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ABSTRACT

It is evident that the presence of organic matters in soil considerably influences by its microbial oxidation to CO_2 the requirement for calcareous compounds as well as the necessary amelioration dose of lime to reduce incurred soil acidity as the impact of balanced buffering CO_2-HCO_3^- system, the more labile the organic matters are. If we take into consideration that the content of soil water per hectare of topsoil is, at the total weight of 6×10^6 kg, approximately, in analyzed sandy-loam soils 1.2×10^6 litre, in the given experiment soil water is just able to use up to 220 kg $CaCO_3$/ha for the fixation of free surplus CO_2 to the value of equilibrium CO_2, at zero elution! From this process, even 300–400 kg water-soluble $Ca(HCO_3)_2$ result. Of course, the ion exchange and the buffering system of the soil have further requirements for Ca compounds. Consequently, an unambiguous conclusion is: doses of calcareous compounds cannot be calculated only with the aim of reducing soil acidity and consumption of Ca nutrient by plants as it is common in the other nutrients. In a practical experiment in watersheds of nine Šumava brooks of the total area of 78.5 km^2 we studied changes in the stability of soil organic matters in the soils of these brooks in relation to variations in calcium carbonate equilibriums in waters from these watersheds in 1986–2004. The loss of the least stable fraction of soil organic matters, and the associated loss of the microbial activity of soils, were found to lead to a decrease in Langelier saturation index I_s in the waters, hence to a reduction in water corrosivity against $CaCO_3$, and so to a smaller need of liming to establish the calcium carbonate equilibrium in soil solutions even though exchange and active acidity of soil increased.

Keywords: liming; soil water; carbonate equilibrium; $CaCO_3$ consumption

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

Total content of calcium in soils most frequently ranges from 0.1 to 1.2% by weight, in three categories as unexchangeable and exchangeable calcium, and calcium in the soil solution. In arable soils with neutral to slightly acid reaction exchangeable calcium accounts for more than 80% of the value of cation exchange capacity, and in forest extremely acid soils for 1–5%, or up to 30% according to some authors (Balík et al. 2005). The weight of exchangeable calcium in the topsoil at CEC = 200 mgekv/kg is 2 t Ca^{2+}/ha.

Calcium in the soil solution that is in equilibrium with exchangeable calcium on organic and mineral soil colloids is in arable soils at concentrations from 40 to 160 mg/l, and in the soil solution of extremely acid forest soils its concentrations range from 0.1 to 5 mg/l. These are however average values, some researchers reported a much wider concentration interval, 20–1520 mg/l with the average 136 mg/l in acid soils and 560 mg/l in alkaline soils (Vaněk et al. 2005).

In the climate of Central Europe 30–350 kg/ha per year of calcium of this category are eluted from arable soils. Calcium in the soil solution comes not only from exchangeable calcium in the sorption complex but also from non-exchangeable calcium, from silicates and calcium carbonates that continually complete the soil solution. Carbonate solubility is closely related to CO_2 production which is determined by biological activity in the

soil, mainly during mineralisation of labile soil organic matters (Kolář et al. 2005b).

A high amount of Ca-compounds is necessary to establish the carbonate equilibrium $[CO_2]_e$ – HCO_3^- in soil water (it markedly increases Ca^{2+} losses by elution) and to create the own buffering system of soil water, which further increases the consumption of Ca-compounds. Rainfalls and corresponding elutions lead to a permanent repetition of these processes. An important role is played by CO_2 concentration in the equilibrium system solid phase of soil – soil water – soil air, which is expressed by its partial pressure.

Balík et al. (2005) reported 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 (Table 1).
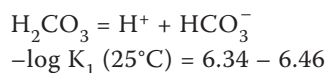
Partial pressure of CO_2, corresponding to the given composition of water, makes it possible to evaluate the degree of water saturation in relation to soil air:

$$\log p_{CO_2} = \log a_{HCO_3^-} - pH - \log K_0 K_1$$

K_0 is the equilibrium constant of the equation:

$$CO_2 + H_2O = H_2CO_3$$
$$-\log K_0 \ (25°C) = 1.47$$
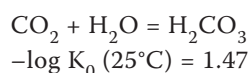
K_1 is the equilibrium constant of the equation:

$$H_2CO_3 = H^+ + HCO_3^-$$
$$-\log K_1 \ (25°C) = 6.34 - 6.46$$

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

$$-\log K_0 = 1.113 + 1.672.10^{-2} \ t - 1.051.10^{-4} \ t^2$$
$$-\log K_1 = 6.576 - 1.250.10^{-2} \ t + 1.405.10^{-4} \ t^2$$

About 99% of CO_2 is dissolved in water in a molecular form, only about 1% reacts with H_2O while H_2CO_3 is formed. Dissolved CO_2 is "free carbon

dioxide" and it is the sum of 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 first dissociation constant K_1 is only an apparent dissociation constant because its numerical value is also related to the mixture of $CO_2(aq)$ and H_2CO_3. In computations the concentration of free CO_2 is substituted into equations. H_2CO_3 is in fact a medium-strong acid with the approximate value of the first dissociation constant $1 \times 10^{-3.5}$.

Ion forms of CO_2 are the ions HCO_3^- and CO_3^{2-}, i.e. "bound" CO_2, which is hydrogen-carbonate and carbonate. The sum of all three forms of CO_2, 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 the combination of equations for distribution coefficients of free CO_2, HCO_3^- and CO_3^{2-} by Henry's law:

$$[H_2CO_3^*] = K_H \times p_{CO_2}$$
$$[HCO_3^-] = K_1/[H^+] \times K_H \times p_{CO_2}$$
$$[CO_3^{2-}] = K_1 K_2/[H^+]^2 \times K_H \times p_{CO_2}$$

where: K_H – Henry's constant
p_{CO_2} – the relative partial pressure of CO_2 in soil air

K_H is equal K_0 in this case. K_2 is the equilibrium constant of the reaction:

$$HCO_3^- = H^+ + CO_3^{2-}$$
$$-\log K_2 \ (25°C) = 10.22 - 10.40$$
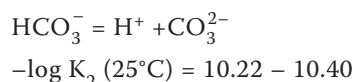
In the atmosphere at 0.03% by vol. CO_2 the pressure p_{CO_2} = 30 Pa, and in these conditions at 10°C about 0.7 mg/l CO_2 is dissolved in water. In the course of degradation of soil organic matters CO_2 content in soil air is up to 100 times higher, depending on the biological activity of soil, on the amount of degradable soil organic matter and especially on its disposition to biochemical oxidation, i.e. on the degree of its stability.

Dissolved free CO_2, i.e. $H_2CO_3^*$, is present in soil water to pH = 8.3. Hydrogen carbonates are dominant, they may be present as simple HCO_3^-, also in ion pairs $[CaHCO_3]^+$, $[MgHCO_3]^+$, and $[MnHCO_3]^+$. In soil water there are normally tens to hundreds of mg/l HCO_3^-, while CO_3^{2-} is hardly provable if recently applied liming does not exert its effect.

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

Table 1. pH in the system soil – water in relation to 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

$$CaCO_3 \rightarrow \leftarrow [CaCO_3 \, (aq)]°$$
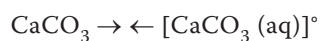
In the presence of dissolved CO_2 in soil water, which is usual, the solubility of $CaCO_3$ is substantially higher thanks to the reaction:

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

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 $[CO_2]_e$. If the amount of CO_2 in soil water is higher than corresponds to $[CO_2]_e$, the water continues to dissolve $CaCO_3$. If it is lower, $CaCO_3$ is precipitated from water on active surfaces. The first paper dealing with calcium-carbonate equilibrium was published at the end of the 19th century by Schlössing and van't Hoff (Lehmann and Reuss 1923). They proved that:

$$[CO_2]_e = const. \, [HCO_3^-]^{2.56}$$

Auerbach corrected this equation:

$$[CO_2]_e = const. \, [HCO_3^-]^3$$

Based on experimental data the same author derived the relation:

$$K_2 = [H^+] \cdot K_s/[Ca^{2+}][HCO_3^-]$$

where: K_s – the product of $CaCO_3$ solubility
K_2 – the second dissociation constant of carbonic acid

If this equation is divided by the term for K_1 (the first dissociation constant of carbonic acid),
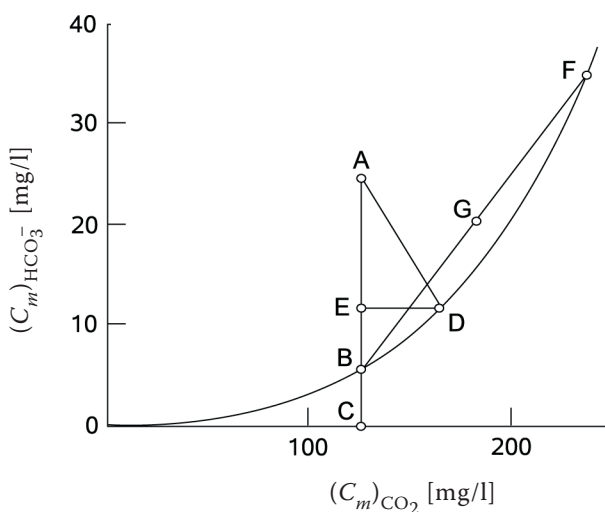

Figure 1. Equilibrium curve of carbonate equilibrium according to Tillmans (1931)

$[H^+]$ is eliminated and the equation is rearranged, then it has this form:

$$[CO_2]_e = K_z/K_1 \times K_s \, [Ca^{2+}] \, [HCO_3^-]^2$$

Graphical representation of Auerbach's relation is a cubic parabola, representing an equilibrium curve of carbonate equilibrium, i.e. of the relation of $[CO_2]_e$ to HCO_3^- concentration in mg/l water (Figure 1, Tillmans 1931).

If the point lies on the curve, soil water is in equilibrium. If it is below the curve, $CaCO_3$ will be precipitated. If it is above the curve, $CaCO_3$ will be dissolved.

According to Tillmans, surplus CO_2, given by the abscissa AB, is CO_2 corrosive against Fe:

$$2\,Fe + 2\,H_2O + 4\,CO_2 = 2\,Fe^{2+} + 4\,HCO_3^-$$

This equation holds good in the absence of oxygen in water. But in normal conditions when soil water contains dissolved oxygen, oxidation of Fe^{2+} to Fe^{3+} takes place with the return of CO_2, which returns to the reaction:

$$4\,Fe^{2+} + 8\,HCO_3^- + 2\,H_2O + O_2 = 4\,Fe(OH)_3 + 8\,CO_2$$
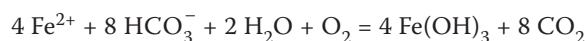
The amount of CO_2, given by the abscissa BC, is equilibrium CO_2 $[CO_2]_e$.

If soil water is in contact with $CaCO_3$, surplus CO_2 reacts according to the equation:

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

From 1 mole of free CO_2 2 moles of HCO_3^- are produced. Soil water is enriched with HCO_3^-, which increases the amount of equilibrium CO_2 in this water. The original composition of soil water given e.g. by point A changes along the abscissa AD in such a way that a decrease in free CO_2 by 10 mg/l causes an increase in HCO_3^- concentration by 27.7 mg/l. The reaction runs as far as point D, when water equilibrium is established. Only a part of surplus CO_2 corresponding to the abscissa AE dissolves $CaCO_3$. Because AB > AE, the corrosivity of CO_2 against $CaCO_3$ is lower than against iron.

It is true that these relations are applicable to soil water for which it approximately holds good that $2\,[Ca^{2+}] = [HCO_3^-]$, i.e. for waters with relatively low salinity. The situation is complicated not only by the ionic strength of soil water, but also by temperature, and also by protonisation and formation of ion pairs of hydrogen carbonates. Langelier (1946) tried to remove these deficiencies and chose $[H^+]$, $[HCO_3^-]$ and $[Ca^{2+}]$ as variables. He got the equation:

$$pH_s = \log K_s/K_2 - \log [Ca^{2+}] - \log [HCO_3^-]$$

pH_s is so called "saturation pH", i.e. the pH value the water would reach if it were in equilibrium with $CaCO_3$ at the given ionic composition (see the Figure 1, point B). If pH_s is compared with the initial pH of soil water, it is possible to determine from the $pH - pH_s$ difference whether there exists water equilibrium or not. It is so called "Langelier saturation index", designated I_s. If its value is negative, the water continues to dissolve $CaCO_3$.

The term $\log K_s/K_2$ in the above equation assumes different values at different temperatures and different contents of solutes in water. It can be found in hydrochemical tables (Fähnrich 1955).

The calculation of CO_2 corrosive against limestone is done according to Unified Methods of Chemical Analyses of Soils (1965).

The pH value of soil water is in the range of 4.5–8.3, and it is mainly given by the equilibrium between free and bound CO_2. It is strongly influenced by humus acids, cations with hydrolysing capacity, presence of phosphates, silicates, hydrogen sulphide, organic acids, and also by biological processes, nitrification and denitrification.

Besides the buffering capacity of soil particles (mineral and especially organic colloids, capable of ion exchange) and chemical buffering effect of $CaCO_3$ in the soil, the buffering capacity of soil water designated as β is very important (Weber 1963).

Buffering capacity of water (β) expresses its capacity to regulate pH changes after the addition of acids and bases. It is defined as the ratio of infinitesimal addition of a strong base (C_b) or strong acid (C_a) in mol/l to the respective change in pH evoked by this addition:

$$\beta = dC_b/dpH = -dC_a/dpH$$

It is an inverse value of the slope of tangent to the titration curve of $pH = f (C_b)$ at the given point. It is given in mol/l and its value is always positive.

Buffering systems in soil water are homogeneous and heterogeneous, the most important homogeneous buffering system is $CO_2 \rightarrow HCO_3^- - CO_3^{2-}$. Maximum buffering capacity is reached in this system at the equality of concentrations $[CO_2]$ = $[HCO_3^-]$, i.e. at pH about 6.34. Heterogeneous buffering systems are ion exchanges, simple ion adsorption, chemisorption, and also precipitation in the soil, respiration of soil microorganisms and many others.

In a humid mountain area the relationship between soil water and surface water of streams is always closer because lighter and incessantly eluted soils in the catchment significantly influence the composition of these waters. In 2002 we compared the quality of surface waters, soils and degree of lability of soil organic matters in 1986 and 2001 (and later in 2004–2005) to determine what changes were caused by a reduction in the intensity of agricultural production in the Šumava area. An experiment was conducted in the catchment of nine Šumava brooks on an area of 78.5 km^2 (Kolář et al. 2002). These results were applied to compute I_s, $H_2CO_3^*$ and $[CO_2]_e$.

If the above statements are summarised, it is not obviously reasonable to consider liming as a mere reduction of soil acidity. Besides the neutralising effect liming must overcome the established buffering systems of soil as well as of soil water. The better the reserve of oxidisable organic matters in soil and the lower the stability of these organic matters (and it is an assumption for a microbially highly active and fertile soil), the higher the consumption of calcareous compounds to establish equilibrium between CO_2 and HCO_3^- and the higher the production of water-soluble $CaHCO_3$. It implies a good reserve of exchangeable calcium in soil on the one hand, but its losses due to elution will be higher on the other hand.

MATERIAL AND METHODS

A demonstration experiment was conducted to prove these considerations.

Topsoil samples were taken from acid sandy-loam Cambisols in the locality České Budějovice (A), Ktiš (B) and Kubova Huť (C). In these samples we determined exchange pH, liming need according to Schachtschabel from a potentiometric titration curve, cation exchange capacity and degree of sorption saturation V. C_{ox} and stability of organic matters were determined by means of the rate constant of their biochemical oxidation according to the method we published some time ago (Kolář et al. 2005a, b).

Soil water was extracted from topsoil samples cooled to 4°C with degasified distilled water with moist lentils of NaOH of the same temperature under the cap of an absorber. Unfortunately, we could not use any common methods to extract soil water because it would not be possible to determine free CO_2.

In the extracts we measured solutes, acid neutralising capacity $ANC_{4.5}$, free CO_2, bound CO_2, Ca^{2+},

HCO$_3^-$ and pH. From these values we calculated pH$_s$ according to the above-mentioned formula using the tabular value log K$_s$/K$_2$ for the detected amount of solutes and temperature of 10°C. Langelier saturation index I$_s$ was computed from this data. Measured values of pH were compared with pH 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.

In the second part of this study soil samples were enriched with a dose of 5 g of dry matter of organic matters/500 g of soil sample because according to some authors the fertile soil can transform up to several tens of tons of organic matters DM per year. Sources of organic matters were dried ground farmyard manure (originally 14.3% organic matters) (variants X), dried clover meal (variants Y) and glucose (variant Z). In these samples the above-mentioned soil characteristics were determined immediately after sample treatment and after 180-day incubation of samples wetted to 50% of their water retention capacity in a thermostat at 25°C while evaporated water was continually added.

In the third part of this study, based on the results of the cited paper Kolář et al. (2002), from the values of [Ca^{2+}] and [HCO$_3^-$] and the value of K$_s$:K$_2$ for the given content of solutes and temperature 10°C 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 surface waters Langelier saturation index I$_s$. Comparing the pH value of waters with theoretical

Table 2. Analyses of soil samples (ABC) on the first and 180th day after incubation start at 25°C with 1% addition of organic matter in the form of dried ground farmyard manure (X), clover meal (Y) and glucose (Z)

	Day	A	B	C	AX	AY	AZ	BX	BY	BZ	CX	CY	CZ
pH/KCl	1	6.25	5.91	5.60	6.30	6.20	6.25	6.00	5.92	5.90	5.80	5.68	5.60
	180	6.19	6.03	5.60	6.18	6.05	6.05	5.82	5.71	5.63	5.75	5.50	5.38
Liming need (acetate method – Schachtschabel) [0.1 CaO t/ha]	1	11	15	35	11	11	11	15	16	15	35	35	34
	180	11	16	35	14	16	17	19	21	21	38	41	41
Liming need (potentiometric titration curve) [0.1 CaO t/ha]	1	16	16	30	16	16	16	16	16	16	29	30	29
	180	16	16	31	21	23	24	22	24	24	34	37	37
CEC (Mehlich) [mval.chem. eqv./kg]	1	219	175	134	219	219	219	175	176	175	132	133	133
	180	225	180	136	231	229	219	185	183	175	138	135	132
Degree of sorption saturation V [%]	1	83	68	53	81	82	80	65	65	67	55	54	55
	180	82	69	55	82	84	82	66	68	67	52	53	55
C$_{ox}$ (ISO 14235) [%]	1	1.12	1.50	1.84	2.03	1.99	2.13	2.47	2.42	2.50	2.90	2.81	2.84
	180	1.01	1.31	1.76	1.47	1.43	1.00	1.99	2.00	1.32	2.55	223	1.65
Rate constant of biochemical oxidation of C-compounds K [24 hours]	1	0.02	0.03	0.05	0.25	0.31	0.81	0.26	0.33	0.81	0.28	0.35	0.83
	180	0.02	0.03	0.03	0.14	0.11	0.02	0.10	0.10	0.03	0.15	0.15	0.03

Table 3. Analyses of soil solutions (ABC) on the first and 180th day after incubation start at 25°C with 1% addition of organic dry matter in the form of dried ground farmyard manure (X), clover meal (Y) a glucose (Z)

	Day	A	B	C	AX	AY	AZ	BX	BY	BZ	CX	CY	CZ
Solutes [mg/l]	1	280	160	118	294	287	618	175	167	501	126	122	460
	180	282	155	119	315	307	284	199	186	184	148	131	130
Free CO_2 [mg/l]	1	20.4	40.6	60.5	20.4	40.6	60.5	20.4	40.6	60.5	20.4	40.6	60.5
	180	24.3	43.1	61.7	57.4	88.3	126.3	52.5	85.6	120.1	61.3	82.1	128.1
Bound CO_2 (mg/l)	1	41.8	31.6	22.0	45.2	42.7	42.5	31.0	32.2	32.8	22.1	22.5	21.8
	180	48.4	47.5	34.5	75.4	61.5	80.6	65.4	55.4	90.1	47.7	42.1	85.9
Equilibrium CO_2 [mg/l]	1	2.0	1.1	0.6	2.4	2.1	2.1	1.0	1.1	1.1	0.6	0.6	0.6
	180	2.8	2.6	1.3	9.7	5.2	11.7	6.1	4.0	17.4	2.7	2.1	14.7
HCO_3^- [mg/l]	1	115.9	87.2	61.0	125.0	117.9	116.4	85.4	89.7	91.0	61.5	63.9	60.0
	180	134.2	132.5	94.0	209.3	170.8	223.0	182.1	151.2	250.0	132.5	118.0	238.1
pH/H_2O	1	6.80	6.20	5.80	6.82	6.80	6.79	6.95	6.62	6.20	6.90	6.58	5.80
	180	6.72	6.13	5.60	6.62	6.72	6.60	6.84	6.50	6.00	6.72	6.53	5.50
pH (Nachtigall)	1	7.14	6.71	6.38	7.17	6.84	6.66	7.01	6.71	6.54	6.86	6.55	6.36
	180	7.12	6.87	6.57	6.93	6.65	6.62	6.90	6.63	6.70	6.62	6.52	6.64
Difference pH/H_2O – pH (Nachtigall)	1	−0.3	−0.5	−0.7	−0.4	0.0	+0.2	−0.1	−0.1	−0.3	+0.1	0.0	−0.6
	180	−0.4	−0.7	−0.1	−0.3	+0.1	0.0	−0.1	−0.1	−0.7	+0.1	0.0	−1.1

pH 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 in relation to the other buffering systems because the difference in 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 (1954).

These results were compared with the average value of the degree of stability of soil organic matters in the soil samples 0–20 cm of the particular watersheds that were taken in a square grid of the side 1 km (16 samples from 9 km^2) by means of

Table 4. Analyses of soil solutions (ABC) on the first and 180th day after incubation start at 25°C with 1% addition of dry matter in the form of dried ground farmyard manure (X), clover meal (Y) and glucose (Z)

	Day	A	B	C	AX	AY	AZ	BX	BY	BZ	CX	CY	CZ
Acid neutralising capacity* $ANC_{4.5}$ (total alkalinity) [mmol/l]	1	1.9	1.4	1.0	2.0	1.9	1.9	1.4	1.5	1.5	1.0	1.0	1.0
	180	2.2	2.1	1.5	3.4	2.8	3.7	3.0	2.5	2.1	2.2	1.9	3.9
Saturation pH_s	1	–	–	–	–	7.0	7.0	7.0	6.7	–	6.9	6.7	–
	180	–	–	–	–	7.1	7.2	7.1	6.9	–	7.0	6.9	–
Langelier saturation index I_s (pH – pH_s)	1	–	–	–	–	−0.2	−0.2	0.0	−0.1	–	0.0	−0.1	–
	180	–	–	–	–	−0.4	−0.4	−0.3	−0.4	–	−0.3	−0.4	–

*$ANC_{4.5}$ is the acid neutralising capacity, it is the neutralising acid-base capacity that is an integral of buffering capacity in a chosen range of pH; the sample is titrated with acid to pH = 4.5; in titration with base to pH = 8.3 we will determine the base capacity (formerly called "total acidity") $BNC_{8.3}$; in waters in the interval of pH = (4.5 <—> 8.3) it holds good that the concentration of total CO_2, designated C_T, is $ANC_{4.5}$ + $BNC_{8.3}$ [mmol/l]

Table 5. Basic characteristics of the watersheds under study

Sample	Stream	Area (km²)	Forest percentage (%)	Altitude above sea level (m)	Specific outflow (1/s/km²)
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

GPS with a GARMIN e TREEX device, expressed by the rate constant of their biochemical oxidation (Kolář et al. 2003, 2005a).

The calculations from analytical data from 1986 and 2001 were complemented by the calculations from data acquired in 2004–2005.

The results were processed by mathematical and statistical methods for several-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 of the demonstration trial; the results of its hydrochemical analyses and calculations are given in Tables 3 and 4.

The distribution of CO_2 forms in water can be calculated from acid-base neutralising capacities if the carbonate buffering system is dominant in relation to the other buffering systems. It is shown by a comparison of the measured pH value of water with the value calculated from the concentrations of $H_2CO_3^*$, HCO_3^- and CO_3^{2-}. It is conditioned by correspondence of 0.1 pH. Only variants AY, AZ, BX, BY, CX and CY satisfied this condition, i.e. all variants with clover meal and two variants with farmyard manure. Only these variants provided reliable data for the final calculations of Ca-compound consumption to establish the carbonate equilibrium of soil water. Langelier saturation index was computed in these variants only. Its value was negative in all cases; mineralisation of farmyard manure and clover meal increased wa-ter corrosivity against $CaCO_3$ twice to four times in all soil samples, and it is interesting that this increase was higher than that caused by glucose (twofold increase), which acidified the variants after incubation more than farmyard manure and clover meal. The incubation had a slight effect on CEC in all soil samples while the effect of manure was the most marked among the organic additives. The need of liming according to the potentiometric titration curve was mostly higher than when calculated according to Schachtschabel. After incubation the highest decrease in C_{ox} was measured in glucose whereas it was the lowest after manure addition and in more acid soil C. The values of rate constants correspond to this pattern: they were the most stable in variants with manure addition – obviously due to the influence of the content of bedding straw and to the presence of a higher amount of stabilised components.

After mineralisation the extracts of soil water had a higher content of solutes – except the variants with glucose, which was fully mineralised to CO_2. The highest amount of aggressive CO_2 was not measured in variants with glucose but in variants with clover meal, and a lower amount was determined in variants with manure, which is logical considering the value of the stability of its organic matters.

If we take into account only the difference between free and equilibrium CO_2, in variants with manure it is 40–60 mg/l CO_2 and in variants with clover meal about 80 mg/l CO_2, and if topsoils of these soils contain on average $1.2.10^6$ l water/ha, stechiometry indicates that after the breakdown of added organic matters water in the soil on an area of 1 ha to a depth of 40 cm requires to establish

a new carbonate equilibrium 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 soil permeability. It is to note that in spite of the ideal conditions of long-term incubation only 40–50% of added organic matters was mineralised as shown by 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 a reduction in acidity of the solid phase of soil which after mineralisation of organic matters amounts to 2.1–3.7 t/ha CaO for soils ABC, i.e. 4–7 t $CaCO_3$/ha, in the form of an ameliorating dose, as indicated by the potentiometric titration curve.

Table 5 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 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). These analyses documented that a reduction in farming intensity in the area concerned decreased the content of $N\text{-}CO_3^-$ in the brook waters to 66% of the value under the intensive agricultural use of landscape 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 change in fact, and active soil carbon C_{hws} decreased. It is interesting that the values of COD_{Mn} (chemical oxygen demand determined by a permangate method) in waters showing the proportion of easily degradable organic matters increased. This apparent paradox is explained by the fact that the rate constant of biochemical oxidation of soil organic matters decreased, or the stability of easily degradable soil matters is higher. Lower values of C_{hws} and markedly lower values of nitrification test, basal respiration carbon, microbial biomass carbon and Hendrix index of biological activity of soil correspond with the above finding. It is to conclude that the reduction in agricultural production in the Šumava area in 1986–2004 slightly increased the elution of degradable organic matters from 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 the calcium carbonate equilibriums of waters from the soils of watersheds of Šumava brooks,

Table 6. Differences in 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 Šumava brooks and rate constant k_1 of biochemical oxidation of organic matters in the soils of watersheds of these brooks in 1986, 2001 and 2004

Sample	1986				2001				2004			
	$H_2CO_3^*\text{-}(CO_2)_e$ (mg/l)	pH_s	I_s	k_1 (24 hours)	$H_2CO_3^*\text{-}(CO_2)_e$ (mg/l)	pH_s	I_s	k_1 (24 hours)	$H_2CO_3^*\text{-}(CO_2)_e$ (mg/l)	pH_s	I_s	k_1 (24 hours)
101	240 ± 38	6.82	–0.28	0.035 ± 0.004	62 ± 14	6.50	–0.03	0.009 ± 0.001	53 ± 7	6.52	–0.01	0.009 ± 0.000
102	132 ± 26	6.99	–0.18	0.028 ± 0.002	48 ± 9	6.60	–0.01	0.008 ± 0.000	40 ± 2	6.60	–0.01	0.007 ± 0.001
103	286 ± 41	7.00	–0.41	0.0190 ± 0.001	53 ± 7	6.64	0.00	0.015 ± 0.002	54 ± 8	6.57	0.00	0.009 ± 0.000
104	154 ± 38	6.74	–0.23	0.026 ± 0.001	44 ± 6	6.51	–0.01	0.010 ± 0.004	36 ± 9	6.60	–0.02	0.009 ± 0.001
105	198 ± 40	6.92	–0.14	0.012 ± 0.000	61 ± 9	6.78	–0.02	0.007 ± 0.000	55 ± 12	6.72	–0.01	0.007 ± 0.000
106	352 ± 69	7.12	–0.52	0.048 ± 0.002	57 ± 12	6.59	–0.03	0.010 ± 0.001	50 ± 9	6.45	–0.01	0.009 ± 0.000
107	132 ± 24	7.05	–0.18	0.017 ± 0.001	48 ± 10	6.81	–0.04	0.010 ± 0.000	47 ± 8	6.47	–0.02	0.010 ± 0.002
108	176 ± 27	6.94	–0.25	0.019 ± 0.001	70 ± 8	6.74	–0.10	0.004 ± 0.000	65 ± 10	6.64	–0.01	0.006 ± 0.001
109	220 ± 44	6.79	–0.33	0.030 ± 0.002	44 ± 6	6.42	–0.02	0.006 ± 0.000	40 ± 6	6.33	–0.01	0.006 ± 0.000

in the difference in means of free and equilibrium CO_2, saturation pH_s according to Langelier and saturation index I_s in brook waters. Table 6 shows differences in these analytical computed data on brook waters from 1986, 2001 and 2004 compared to differences in the degree of stability of soil organic matters in soils of these watersheds in the values of the rate constant of their biochemical oxidation. Obviously, in 1986–2004 as a result of reduction in the intensity of agricultural production there was a strong increase in the stability of soil organic matters in the soils of watersheds of brooks in the waters of which a 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 certain ecological ideas that the soil at rest recovers in terms of potential productivity and produces a higher amount of labile organic matters as a source of energy for soil microorganisms. In the Šumava area it is contrariwise.

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