A method to determine mineralization kinetics of a decomposable part of soil organic matter in the soil

L. Kolář, F. Klimeš, R. Ledvina, S. Kužel

Faculty of Agriculture, University of South Bohemia in České Budějovice, Czech Republic

ABSTRACT

A new method was proposed that complements the value of active carbon in the soil expressed as hot-water soluble carbon C_{hws}. The method is based on vacuum measurements of biochemical oxygen demand (BOD) of soil suspensions using an Oxi Top Control system manufactured by the WTW Merck Company that is destined for hydrochemical analyses of organically contaminated waters. Measurements will provide BOD values for particular days of incubation; total limit BOD_t can be determined from these values, and it is possible to calculate the rate constant k_1 of mineralization of a decomposable part of soil organic matter. It is typical of soil organic matter (SOM) of a given soil sample and comparable with the BOD_5:COD (chemical oxygen demand) ratio that is used to evaluate degradability of water organic contamination in hydrochemical analytics.

Keywords: soil organic matter (SOM); decomposable part of SOM; mineralization kinetics; analytical method

Soil organic matter (SOM) undergoes short- and long-term transformations in the soil. Long-term transformations last for tens of years and establish a new dynamic equilibrium. The amount of long-time unchangeable inert soil organic matter can be determined from unfertilized parcels of long-term trials. There exists a relation between the content of fine particles in soil (below 6.3 µm) and the amount of carbon in inert soil organic matter (Körschens 1980). A difference between total content of C_{org} in farmed soils and the calculated content of inert carbon is considered as carbon of decomposable organic matters C_{dec}. Under a dynamic equilibrium a portion of SOM is mineralized during one growing season, and the same portion is newly formed. This portion of soil organic matter is considered as active and its carbon is active organic carbon. To determine the active carbon the easiest and most suitable method is determination of so called hot water extractable C_{hws} (Körschens et al. 1990, Schulz 1990, Weigel et al. 1998). Carbon C_{dec} of decomposable organic matters was studied by Kubát and Vrzáková (1984), Kubát and Veselý (1986). Schulz (1997) expressed the relation between decomposable C_{dec} and C_{hws} by the equation $C_{dec} = 15C_{hws}$.

C_{dec} and/or C_{hws} are important as energy substrates for soil microorganisms and material for mineralization, therefore they belong to the main traits of soil productivity. Optimum value of C_{hws} in basic types and textures of soils is 0.3–0.6 g/kg, i.e. 0.03–0.06%.

Through their enzymes soil microorganisms are able to mineralize less soluble carbon sources while the rate of this process is different. In the present paper we tried to determine C_{dec} of decomposable organic matters more exactly employing reaction kinetics of their mineralization. For this purpose we used biochemical oxygen demand (BOD), a current method of hydrochemical analytics for determination of organic contamination; it is regularly carried out as five-day incubation (Czech designation is BSK and BSK_5) or as BOD_t (BSK_c) – i.e. the limit value of total biochemical oxygen demand (Horáková et al. 1989).

The rate of biochemical oxidation of organic matters as a first-order reaction is proportionate to the residual concentration of the matters that have not undergone oxidization yet:

$$\frac{dy}{dt} = K_1(L - y) = K_1 L_2$$

where: L = total BOD
y = BOD in time t
k_1, K_1 = rate constant

By integration of this relation from 0 to t we get the equation:

$$L_r = Le^{-klt} = L.10^{-klt}$$

In general it holds good for BOD in time t:

$$y = L(1-10^{-klt})$$

where: y = BOD in time t
L = BOD_t
k_1 = rate constant with dimension per day

Rate constant k_1 can have largely different values. For organic matters of sewage water k_1 = 0.1–0.19 per day, for pure glucose k_1 = 0.87 per day, for peptone 0.74 per day.

The study was supported by MSM grant, id. code MSM 122200002.

The variability of rate constant k_1 documents that BOD_5 is not itself an exact measure of organic contamination of waters. They would have to contain only matters with approximately identical rate of mineralization (Pitter 1981).

The BOD_5:COD ratio (chemical oxygen demand for $K_2Cr_2O_7$ oxidation in H_2SO_4 medium) indicates the measure of organic matter decomposability in hydrochemical analytics. This ratio amounts to 0.5–0.75 in waste waters, and is below 0.1 in clean surface waters. Measurements proved a wide range of this ratio 0.1–0.8 for most clean organic matters (Pitter and Chudoba 1968).

MATERIAL AND METHODS

Dilution method is a traditional way of measuring BOD and rate constants k_1 (Horáková et al. 1989). Another procedure is a gas-measuring analysis with mercury macrovolumetric respirometers. Last year we published a paper describing the use of the labor- and time-consuming dilution method (Kolář et al. 2002).

Currently, the WTW Company (MERCK measuring and analytical instrumentation) offers kits Oxi Top IS 6 and Oxi Top IS 12 for mercury-free measurements of BOD at 6 and 12 measuring places. They consist of patented measuring heads with piezoelectric pressure sensors to measure vacuum and with two buttons – to display instantaneous values and memory-stored values, with double LED indicator for measurements of hPa corresponding to 0–4 000 mg/l BOD. A more sophisticated Oxi Top system designated Oxi Top CONTROL 6 or 12 is equipped with heads where indicators are replaced by infrared interface communicating with controller OC 100 or OC 110 that can control up to 100 measuring heads. Documentation is provided by a PC program ACHAT OC or thermoprinter TD 100. The measuring head will store 180–360 data sentences to its memory that can be transmitted to the controller where they are displayed graphically. Measurements can also be carried out through the thermostat glass or plastic door. It is just this technology that will facilitate the use of BOD method in pedochemical laboratories.

The procedure we adopted in this study was identical with the method recommended by the manufacturer in accordance with the Proposal for German Uniform Procedures, DEV 46 Bulletin 2000 – H 55, also published in BOD instructions (on CD-ROM) of WTW MERCK Company.

Fresh soil samples with original moisture content were disintegrated only mechanically in distilled water, filtered through a 1mm sieve, and 5% soil suspension was prepared (dry matter was determined parallelly at 105°C). The samples were not inoculated, microbiological colonization of samples was indicated by the joint result of mineralization of present organic matters. If pH of soil suspension was lower than 6, the suspension was neutralized with 1M NaOH to pH = 6.

Nitrification inhibitor NTH 600, which is supplied with the kit, was used for nitrification inhibition. Soil samples underwent incubation in Oxi Top Box thermostat at 20°C. Agitating trays IS 6 prevent the settlement of soil suspensions in sample bottles Oxi Top IS 6.

In the second part of the study an Oxi Top Control system was used to determine biological decomposability of organic matters in a complex OECD kit in accordance with DIN EU 29 408 (ISO 9408) OECD 301 F. From our aspect, the procedure did not bring about any new results or any important advantages. The OECD procedure is suitable for isolated organic matters and compounds. This is the reason why the results are not presented.

BOD values were determined for particular days; from these values limit BOD_t was derived and rate constant k_1 at BOD_5 was calculated from the above-mentioned equation. The data were complemented by determination of soil suspension COD using the current bichromate method and by determination of active carbon C_{hws}. The data were processed by the Dean and Dickson method for few-element sets (Eckschlager et al. 1980).

Finally, it is to note that the values of BOD determination in decomposable fraction of soil organic matter by the traditional dilution method and by the Oxi Top Control procedure are not comparable. The former method measures oxygen concentration while the latter procedure records vacuum values.

RESULTS AND DISCUSSION

Table 1 shows the characteristics of soil samples collected in the area of Šumava Mts., Třeboň and České

Table 1. Characteristics of soil samples

Sample group No.	Place of sampling	Soil type	Geological petrographic substratum	Soil granularity	Elevation (m)	Production potential of soils	pH/KCl	Sorption capacity (mgekv/kg)
1	Koryto	KM	orthogneisses	sandy loam	918	low	5.92	116
2	Křišťanov	KP	orthogneisses	sandy loam	925	very low	5.85	108
3	Skříněřov	PG	acid polygenetic loams	sandy loam	940	low	5.67	120
4	Hosín	LM	paragneisses	sandy loam	472	higher	6.00	174
5	Lišov	LMg	parargneisses and migmatites	loamy	496	higher	5.95	165
6	Libín	PG	acid polygenetic loams	sandy loam	451	high	5.98	185

Table 2. Characteristics of organic matters and oxidation kinetics of a decomposable part of soil samples from Table 1

Sample group No.	C$_{org}$ (%)	C$_{hws}$ (mg/1000 g)	BOD$_t$ (mg O$_2$/1000 g)	BOD$_5$ (mg O$_2$/1000 g)	Reaction rate constant k_1/24 hrs	Chemical oxygen demand COD (mg O$_2$/1000 g)	BOD$_5$:COD
1	1.72	530	594 ± 57	243 ± 22	0.338 ± 0.027	$51.52.10^3$	$4.72.10^{-3}$
2	2.85	1 060	1 195 ± 143	194 ± 23	0.238 ± 0.028	$85.40.10^3$	$2.27.10^{-3}$
3	3.26	850	810 ± 80	211 ± 21	0.270 ± 0.027	$85.77.10^3$	$2.46.10^{-3}$
4	1.65	200	220 ± 16	101 ± 8	0.370 ± 0.030	$32.16.10^3$	$3.14.10^{-3}$
5	1.49	400	380 ± 34	194 ± 18	0.410 ± 0.037	$44.60.10^3$	$4.35.10^{-3}$
6	1.28	460	465 ± 56	293 ± 35	0.540 ± 0.065	$38.30.10^3$	$7.65.10^{-3}$

Budějovice. Table 2 indicates data on these samples describing their decomposable part of soil organic matter. The amount of active carbon expressed as C$_{hws}$ is considerably higher in all samples from higher locations than is the optimum for loam-sandy soils of Šumava Cambisol CA (formerly brown soils), i.e. 500–550 mg/kg. It is explained by the lower stability of soil organic matter at higher locations on lighter Cambisols in relation to Chernozem and Orthic Luvisol at lower locations (Kubát et al. 1999). Similar results were reported by Weigel et al. (1998), who studied C$_{hws}$ at Lukavec in comparison with other localities. Some exceptions were found in Šumava localities (Kolář et al. 2000). It is to note that BOD$_t$ values of soil suspensions faithfully follow C$_{hws}$ contents of soil samples from which they were prepared. But the rate constant k_1 of biochemical oxygen demand kinetics varies and does not depend on the amount of C$_{hws}$. Hence it indicates the rate of mineralization in the decomposable part of soil organic matter and specifies static data on active carbon expressed by the value C$_{hws}$. The independence of k_1 on the amount of C$_{hws}$ corresponds with the important finding of Kubát et al. (1999) that with increasing concentration of soil organic mater its mineralization rate does not increase although it looks paradoxical according to Guldberg-Waag law of reaction kinetics.

BOD$_5$:COD ratios of soil suspensions are regularly consistent with the values of rate constant k_1, that means these ratios could also be used to express an estimate of mineralization kinetics in the decomposable part of soil organic matter. But it is not necessary because if Oxi Top Control and OC 100 (110) controller are used, technical determination of BOD$_t$ and k_1 is faster and easier than COD determination.

REFERENCES

Eckschlager K., Horsák I., Kodejš Z. (1980): Vyhodnocování analytických výsledků a metod. SNTL, Praha.

Horáková M., Lischke P., Grünwald A. (1989): Chemické a fyzikální metody analýzy vod. SNTL, Praha.

Kolář L., Gergel J., Ledvina R., Kužel S., Šindelářová M. (2000): Agrochemická charakteristika půd horských a podhorských oblastí jihovýchodní Šumavy. Rostl. Výr., *46*: 533–542.

Kolář L., Gergel J., Šindelářová M., Kužel S. (2002): Impact of farming intensity reduction in the Šumava foothills region on changes in soil organic matters and surface water quality. Rostl. Výr., *48*: 377–381.

Körschens M. (1980): Beziehungen zwischen Feinanteil, C$_t$ und N$_t$ – Gehalt des Bodens. Arch. Acker-Pfl. Boden., *24*: 585–592.

Körschens M., Schulz E., Behm R. (1990): Heisswasserlöslicher C und N im Boden als Kriterium für das N-Nachlieferungsvermögen. Zbl. Mikrobiol. Jena, *145*: 305–311.

Kubát J., Nováková J., Mikanová O., Apfelthaler R. (1999): Organic carbon cycle, incidence of microorganisms and respiration activity in long-term field experiment. Rostl. Výr., *45*: 389–395.

Kubát J., Veselý L. (1986): Further possibilities of the determination of the decomposable part of humus in different soils. Rostl. Výr., *32*: 643–648.

Kubát J., Vrzáková E. (1984): Determination of the decomposable part of humus in different soils. Rostl. Výr., *30*: 1145–1149.

Pitter P. (1981): Hydrochemie. SNTL, Praha.

Pitter P., Chudoba J. (1968): Stanovení biologické čistitelnosti průmyslových vod. Chem. Prům., *18*: 604–607.

Schulz E. (1990): Die heisswasserextrahierbace C-Fraktion als Kenngröse zur Einschätzung des Versorgungszustands mit organischer Substanz. Tag.-Ber., Akad. Landwirtsch. Wiss. Berlin, *295*: 269–275.

Schulz E. (1997): Charakterisierung der organischen Bodensubstanz nach dem Grad ihrer Umsetzbarkeit und ihre Bedeutung für Transformationsprozesse für Nähr- und Schadstoffe. Arch. Acker-Pfl. Boden., *41*: 465–483.

Weigel A., Kubát J., Körschens M., Powlson D., Mercik S. (1998): Determination of the decomposable part of soil organic matter in arable soils. Arch. Acker-Pfl. Boden., *43*: 123–143.

Received on October 3, 2002

ABSTRAKT

Metoda ke stanovení kinetiky mineralizace rozložitelné části půdní organické hmoty v půdě

Byla navržena nová metoda, doplňující údaj o aktivním uhlíku v půdě, vyjádřeném jako v horké vodě rozpustný uhlík C_{hws}. Metoda je založena na podtlakovém měření biochemické spotřeby kyslíku BSK (BOD = biochemical oxygen demand) půdních suspenzí systémem Oxi Top Control firmy WTW Merck, určené pro hydrochemickou analýzu organicky znečištěných vod. Měřením lze získat BOD v jednotlivých dnech inkubace, z těchto údajů zjistit celkovou limitní BOD_t a vypočítat rychlostní konstantu k_1 mineralizace rozložitelné části půdní organické hmoty, která je charakteristická pro půdní organickou hmotu (SOM = soil organic matter) daného půdního vzorku a srovnatelná s poměrem BOD_5 : CHSK (chemická spotřeba kyslíku), jenž v hydrochemické analytice slouží k posuzování odbouratelnosti organického znečištění vod.

Klíčová slova: půdní organická hmota (SOM); rozložitelná část SOM; kinetika mineralizace; analytická metoda

---

Corresponding author:

Prof. Ing. Ladislav Kolář, DrSc., Zemědělská fakulta, Jihočeská univerzita v Českých Budějovicích, Studentská 13,
370 05 České Budějovice, Česká republika
tel.: + 420 387 772 410, fax: + 420 385 300 122, e-mail: kolar@zf.jcu.cz