Food and Agriculture Organization of the United Nations

GLOBAL SYMPOSIUM ON SOIL INFORMATION AND DATA

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Harmonisation of methods - the way to implement global initiatives: the case on SOC by Tyurin, Walkley-Black, Loss on Ignition and Dry Combustion methods

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GLOBAL SOIL PARTNERSHIP

Introduction

- Integration of planetary knowledge in the historical period about soil carbon is especially relevant in the era of global warming.
- However, the presence of different scientific schools, which have different, often incomparable results, hinders the creation of common databases and the development of knowledge about soils.
- The availability of non-harmonized data is one of the reasons for the low accuracy of the global SOC map (Peralta et al., 2022). This is especially true for regions such as Eurasia where data are limited.
- A tool for international communication, inventory and monitoring of soil resources is the harmonization of the methods for measuring soil indicators.

SOC measurement methods

"Wet" chemistry (dichromatometry)

- Walkley-Black (**W-B**) method
- Tyurin (**T**) method

"Dry" chemistry

- Loss-on-ignition (**LOI**)
- Dry combustion (**DC**) on the analyzer
- Thermogravimetry
- Gas emission analysis et al
- Differential scanning calorimetry
- Spectroscopy

SOC measurement methods

"Wet" chemistry (dichromatometry)

- Walkley-Black (**W-B**) method
- Tyurin (**T**) method

"Dry" chemistry

- Loss-on-ignition (**LOI**)
- Dry combustion (**DC**) on the analyzer

Which method to choose?

- accuracy

- the time necessary for analysis

- cost

- environmental friendliness (safety for the engineer and the environment),

- the ability to measure other indicators in one soil sample (for example, N, S, O, H)....

"Wet" chemistry

- **Walkley-Black method –** USA, Canada, Australia and other countries
- **Tyurin method –** Russia, some countries in Europe and Asia

Disadvantages:

- Labor intensity
- Need for constant presence of the operator
- Toxicity

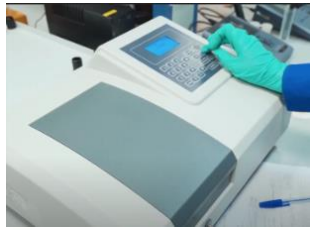
Limitations:

- Presence of Cl^-, Mn^{2+} and Fe^{2+}
- Difficult to oxidize components (pyrogenic C)
- Uncertainty of the conventionally accepted zero oxidation state of C in the reaction:

$$3\,[C]^0 + 2\,Cr_2O_7^{2-} + 16\,H^+ = 3\,CO_2 + 4\,Cr^{3+} + 8\,H_2O$$







"Wet" chemistry. Measurement steps

Tyurin method (Institute of Biology)

Walkley-Black method (Colorimetric Method, GLOSOLAN)

$$3\,[C]^0 + 2\,Cr_2O_7^{2-} + 16\,H^+ = 3\,CO_2 + 4\,Cr^{3+} + 8\,H_2O$$

- **20g** $K_2Cr_2O_7$ + 0,5L H_2O, $c(K_2Cr_2O_7)$= 0,136 M
- **Chromium mixture**: 1V $K_2Cr_2O_7$+1V H_2SO_{4conc} , $c(K_2Cr_2O_7)$= 0,068 M
- **Soil+10 mL "Chromium mixture" (5 mL +5 mL)**

added to the sample $n(K_2Cr_2O_7)$= 0,68 mmol

- **Heating in a water bath (t = 100 °C for 60 min)**
- +15 mL H_2O
- Centrifugation 6000 rpm for 10 min
- Measure the absorbance λ = 590 nm
- Calculation of %SOC

oxidation correction factor f = 1,15 – our research

oxidation correction factor f = 1,0 – traditionally

Tyurin I.V. New modification of the volumetric method for determining humus using chromic acid // Pochvovedenie, 1931. No. 6. P. 36-47.

- **50 g** $K_2Cr_2O_7$ +0,5L H_2O, $c(K_2Cr_2O_7)$= 0,34 M

- **Soil+ 2 mL $K_2Cr_2O_7$ +5 mL $H_2SO_{4\ conc}$ = 7 mL**

added to the sample $n(K_2Cr_2O_7)$= 0,68 mmol

- **Standing for 30 min**
- +20 mL H_2O
- Standing for 24 hours **(without external heating)**
- Measure the absorbance λ = 590 nm
- Calculation of %SOC

oxidation correction factor f = 1,3

Walkley A., Black I.A. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method // Soil Sci., 1934. V. 37. P. 29-38.

"Wet" chemistry. Measurement steps

Tyurin method (Institute of Biology)

- **20g** $K_2Cr_2O_7$
- **Chromium**
- **Soil+10 mL "Chromium mixture"**

added to the sample *n*($K_2Cr_2O_7$)= 0,6

- **Heating in a water bath (*t* = 100 °C**
- +15 mL H_2O
- Centrifugation 6000 rpm for 10 min
- Measure the absorbance λ = 590 nm
- Calculation of %SOC

oxidation correction factor *f* = 1,15 – our research

oxidation correction factor *f* = 1,0 – traditionally

Tyurin I.V. New modification of the volumetric method for determining humus using chromic acid // Pochvovedenie, 1931. No. 6. P. 36-47.

Walkley-Black method (Colorimetric Method, GLOSOLAN)

- **Soil+ 2 mL $K_2Cr_2O_7$ +5 mL $H_2SO_{4\ conc}$ = 7 mL**

)= 0,68 mmol

external heating)

590 nm

oxidation correction factor *f* = 1,3

Walkley A., Black I.A. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method // Soil Sci., 1934. V. 37. P. 29-38.

! In the Walkley-Black method, the amount of $K_2Cr_2O_7$ and H_2SO_4 is equal to the same characteristics as in the Tyurin method, but the concentration of these components of the mixture is 1,5 times higher.

! Heating of the reaction mixture occurs due to the exothermic effect that occurs when a concentrated solution of H_2SO_4 is mixed with distilled water.

"Wet" chemistry

Modifications of the Tyurin method (Russia)

Conditions for the oxidation		Quantity estimation method		Reference documents
		Cr^{3+}	$Cr_2O_7^{2-}$	
Temperature	Time	Colorimetric	Titrimetric	
100 °C (water bath)	1 hour	λ = 590 nm (Mohr's salt)	-	Turin, 1931; GOST 26213-91
>140 °C (electric stove)	5 min	-	titrant - Mohr's salt solution	Simakov, 1957
>140 °C (electric stove)	5 min	λ = 590 nm (Mohr's salt)	-	Orlov, 1967
20 °C	24 hours	λ = 590 nm (Mohr's salt)	-	Samoilova, Rogiznaya, 2013
>140 °C (water bath)	20 min	λ = 590 nm (sucrose)	-	Simakov, Tsyplakov, 1969
150 °C (drying cabinet)	20 min	λ = 590 nm (sucrose)	titrant - Mohr's salt solution	Nikitin, 1983

"Wet" chemistry

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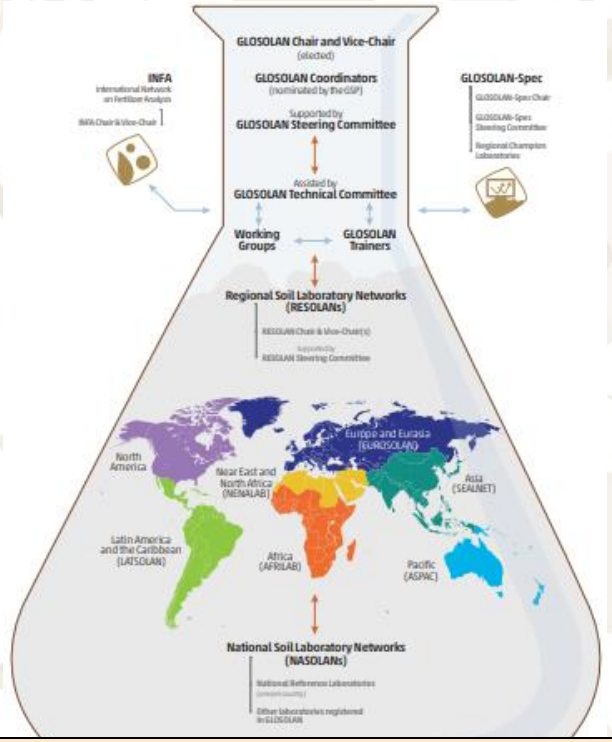
WHAT TO DO?

Global Network of Soil Laboratories (GLOSOLAN)

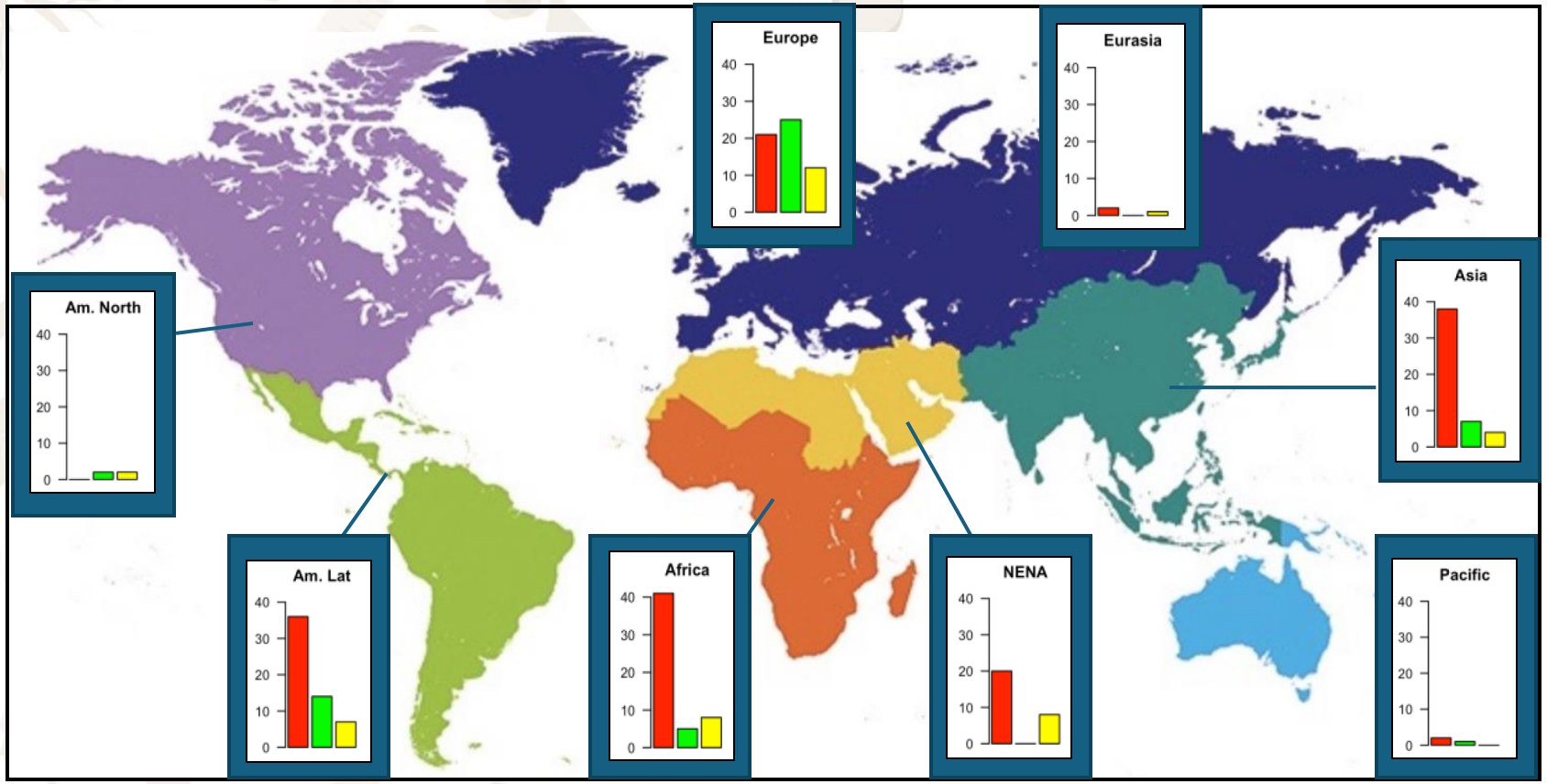


> 1000 laboratories in the world

- The main goal is to harmonize methods for measuring soil parameters
- Unites the efforts of scientists from around the world
- 2017-2024 - **more than 20 protocols** of harmonized methods for measuring soil parameters have been developed and made publicly available

https://www.fao.org/global-soil-partnership/glosolan/

Overview of the methods used to determine carbon from GLOSOLAN PT 2022



- Walkley and Black
- Dumas
- Loss of Ignition

The Institute of Biology of Komi Scientific Center of the Ural Branch (Syktyvkar) **as a member of GLOSOLAN** has decided to go one step forward

1. The information provided by GLOSOLAN members was used as a reference

Laboratory Submission Forms

Please provide the following information on the procedure you are using to assess **soil organic carbon by Tyurin Method**. *Complete only the information corresponding to the method / equipment used in your laboratory.*

Please do not complete the form if you are not using this method in your laboratory

Deadline: 28 February

Colorimetric Method

Modifications of the Tyurin Method

Full Name	E-mail Address	Country	Institute name	Particle Size, mm	Mass of Sample, mg (range)	Dishes (test tubes, conical flasks)	"Chrome mixture", V = 1 L: $K_2Cr_2O_7$ Concentration, M	"Chrome mixture", V = 1 L: Volume of $K_2Cr_2O_7$, mL	"Chrome mixture", V = 1 L: Volume of Concentrated H_2SO_4 Added + $K_2Cr_2O_7$	Volume of the "Chrome mixture" added to the Sample, mL	1. GOST (Russia): Boiling in a water bath at T = 100°, min	1. GOST (Russia): Standing Time, min	2. Modification of Nikitin: Boiling in an oven at T = 150°, min	2. Modification of Nikitin: Standing Time, min	3. Modification of Orlov-Grindel: Boiling in a sand bath, T = 100°, min	3. Modification of Orlov-Grindel: Standing Time, min	4. Modification of Tsyplenkov: Boiling in a salt bath CaCl2 (1.3 M), T = 140°, min	4. Modification of Tsyplenkov: Standing Time, min	5. Modification of Antonova: Standing Time (T=20°), min
xxxx	xxxx	xxxx		≤0,25	0,100-0,700	test tubes	m(K2Cr2O7)=40g, V=1L, c(K2Cr2O7)=0,1359M	500	500	10.0	60.0	until the particles completely settle, time is not indicated (not more than 48 hours)								

2. The harmonized method was developed to ensure comparability of the results from new modification the Tyurin, Walkley-Black and Dry Combustion methods
3. SOC by Combustion method is taken as a reference value

WHAT TO DO?

Soil samples (%CaCO3 = 0)

- Reference materials of soils and bottom sediments (Elemental Microanalysis Limited, UK)
- 7 quality control soils (Russia)
- 3 control soils from GLOSOLAN
- More than 220 field soil samples

Organic carbon content of the quality control soil samples selected for the study.

	Quality control soil samples	Measurement characteristics	
		Organic carbon	Relative error ($P = 0.95$), $\pm\delta$
		%	
The Russian Federation*			
1	OSO 18911	1.55	3.2
2	GSO 10413	2.00	5.5
3	OSO 10904	2.62	3.1
4	OSO 11201	3.73	1.1
5	OSO 21401	6.10	0.8
6	OSO 39002	5.80	2.9
7	OSO 29106	7.44	2.7
GLOSOLAN**			
8	A	1.34	7.5
9	B	2.60	4.6
10	C	5.39	5.0

Note. * The consensus values obtained from the results of Tyurin method from GOST 8.315–2019 (2019) ** The consensus values obtained from the results by Walkley-Black method (FAO, 2020a).

Methods / Equipment

Methods:

- Tyurin method
- Walkley-Black method
- Loss-on-ignition
- Dry Combustion method - a reference method

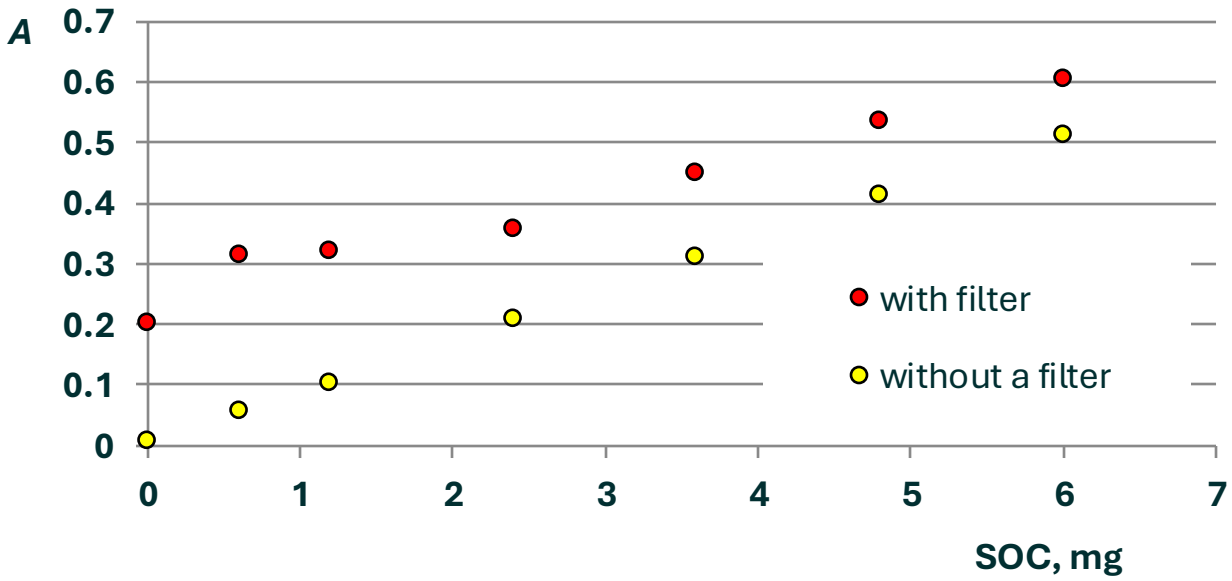
Equipment:

- Carlo Erba EA-1110 HCNS-O analyzer (Italy)
- Spectrophotometers UNICO 2100 (USA) and KFK-3 (Russia)
- Centrifuge SIGMA 2-16P (Russia)
- Muffle furnace (L9/11P330 C3E, Germany)

Tyurin method (Institute of Biology)

Separation of solid and liquid phases

1. Filtration was not used in our studies

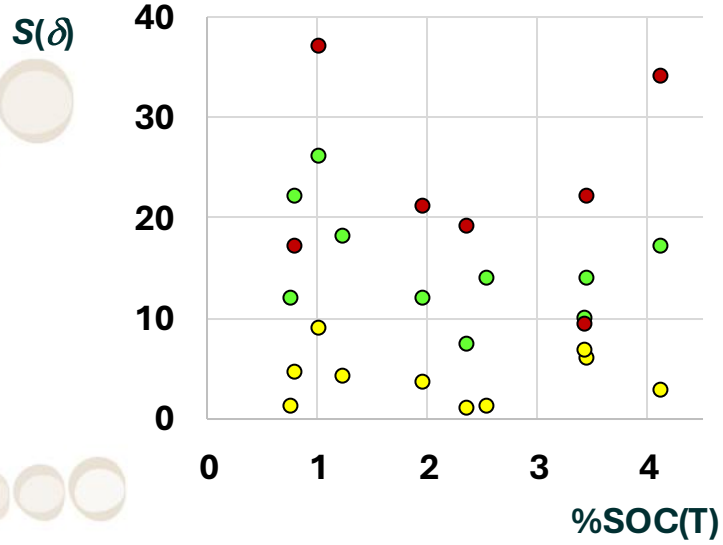


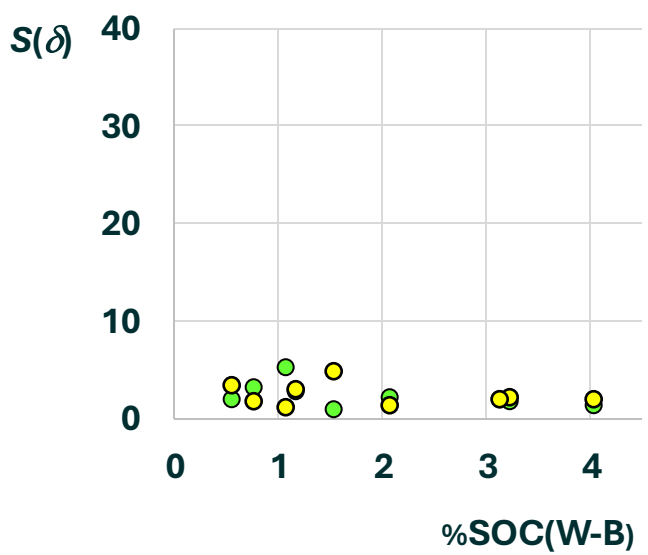
Tyurin method (Institute of Biology)

Separation of solid and liquid phases

2. Centrifugation instead of settling

Each value is the average of 5 parallel measurements





S(δ)			
	Settling, hours		● - Centrifugation
	● - 24	● - 48	
T	26	37	>> 9
W-B	4.7	-	~ 5

S(δ) – the relative value of the standard deviation of a single measurement result, %

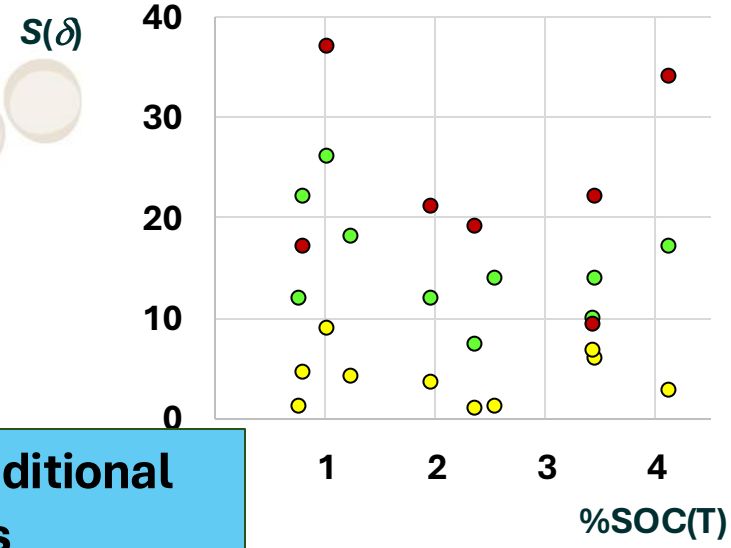
Tyurin method (Institute of Biology)

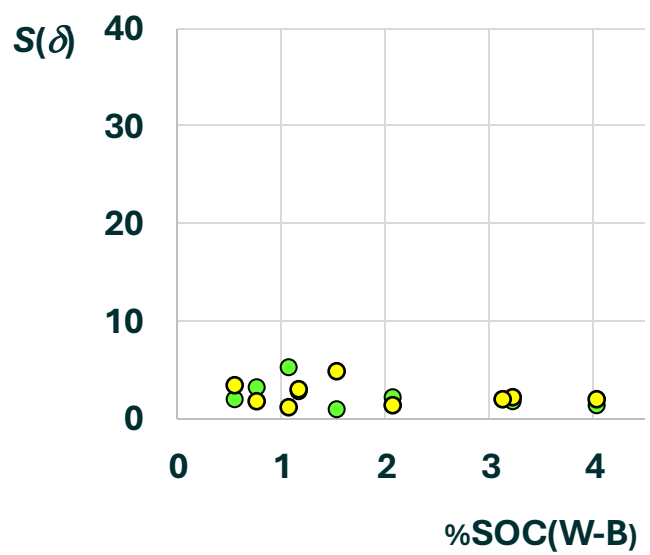
Separation of solid and liquid phases

2. Centrifugation instead of settling

In the Tyurin method, compared to W-B, additional dispersion of the solid phase occurs

Each value is the average of 5 parallel measurements



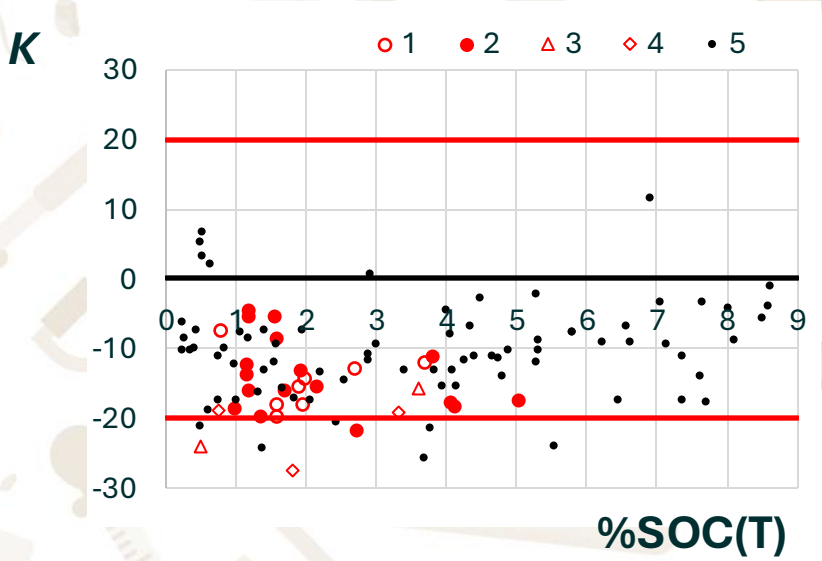


S(δ)			
	Settling, hours		● - Centrifugation
	● - 24	● - 48	
T	26	37	>> 9
W-B	4.7	-	~ 5

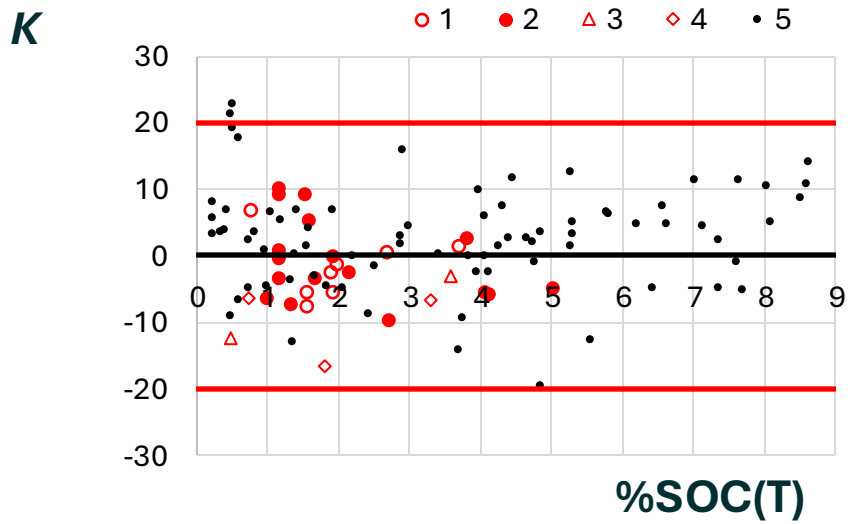
S(δ) – the relative value of the standard deviation of a single measurement result, %

Quality control of measurements %SOC(Tyurin)

without taking into account the *f* = 1,15



taking into account the *f* = 1,15



%SOC(T)	*K*, % (*P* = 0,95)
0,170 - 8,7	20

$$K = 100\% * \frac{|\%SOC(T) - \%SOC(DC)|}{\%Corg(DC)}$$

W-B · 1,3 = Tyurin · 1,15 = Dry Combustion (*P* = 0,95)

The Institute of Biology of Komi Scientific Center of the Ural Branch (Syktyvkar) **as a member of GLOSOLAN** has decided to go one step forward

1. The information provided by GLOSOLAN members was used as a reference

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
1	**Laboratory Submission Forms**																			
2																				
3	Please provide the following information on the procedure you are using to assess **soil organic carbon by Tyurin Method**. *Complete only the information corresponding to the method / equipment used in your laboratory.*																			
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5	**Deadline: 28 February**																			
6																				
7		**Colorimetric Method**										**Modifications of the Tyurin Method**								
8												**1. GOST (Russia)**		**2. Modification of Nikitin**		**3. Modification of Orlov-Grindel**		**4. Modification of Tsyplenkov**		**5. Modification of Antonova**
9	**Full Name**	**E-mail Address**	**Country**	**Institute name**	**Particle Size, mm**	**Mass of Sample, mg (range)**	**Dishes (test tubes, conical flasks)**	**"Chrome mixture", V = 1 L**			**Volume of the "Chrome mixture" added to the Sample, mL**	**Boiling in a water bath at T = 100°, min**	**Standing Time, min**	**Boiling in an oven at T = 150°, min**	**Standing Time, min**	**Boiling in a sand bath, T = 100°, min**	**Standing Time, min**	**Boiling in a salt bath CaCl2 (1.3 M), T = 140°, min**	**Standing Time, min**	**Standing Time (T=20°), min**
10								**$K_2Cr_2O_7$ Concentration, M**	**Volume of $K_2Cr_2O_7$, mL**	**Volume of Concentrated H_2SO_4 Added + $K_2Cr_2O_7$**										
	xxxx	xxxx	xxxx		≤0,25	0,100-0,700	test tubes	m(K2Cr2O7)=40g, V=1L, c(K2Cr2O7)=0,1359M	500	500	10.0	60.0	until the particles completely settle, time is not indicated (not more than 48 hours)							

МИНИСТЕРСТВО НАУКИ И ВЫСШЕГО ОБРАЗОВАНИЯ РОССИЙСКОЙ ФЕДЕРАЦИИ
ФЕДЕРАЛЬНОЕ ГОСУДАРСТВЕННОЕ БЮДЖЕТНОЕ УЧРЕЖДЕНИЕ
АДМИНИСТРАТИВНО-ХОЗЯЙСТВЕННОЕ УПРАВЛЕНИЕ
УРАЛЬСКОГО ОТДЕЛЕНИЯ РОССИЙСКОЙ АКАДЕМИИ НАУК
Центр метрологии и сертификации «СЕРТИМЕТ»
(Центр «СЕРТИМЕТ» АХУ УрО РАН)

СВИДЕТЕЛЬСТВО

ОБ АТТЕСТАЦИИ МЕТОДИКИ (МЕТОДА) ИЗМЕРЕНИЙ

№ 88-17641-001-RA.RU.310657-2020

Почвы, грунты, почвообразующие породы, донные отложения. Методика измерений массовой доли углерода органических соединений и органического вещества фотометрическим методом (методы Тюрина и Уолкли-Блэка).

разработанная Институтом биологии Коми научного центра Уральского отделения Российской академии наук Федерального государственного бюджетного учреждения науки Федерального исследовательского центра «Коми научный центр Уральского отделения Российской академии наук» (г. Сыктывкар, ГСП-2, ул. Коммунистическая, д. 26).

предназначенная для измерений массовой доли углерода органических соединений и органического вещества в почвах, грунтах, почвообразующих породах, донных отложениях

и регламентированная в документе № 88-17641-001-2020 «Почвы, грунты, почвообразующие породы, донные отложения. Методика измерений массовой доли углерода органических соединений и органического вещества фотометрическим методом (методы Тюрина и Уолкли-Блэка)», утвержденная в 2020 г., на 51 л.

Методика измерений аттестована в соответствии с приказом Минпромторга России от 15.12.2015 г. № 4091 и ГОСТ Р 8.563.

Аттестация осуществлена по результатам экспериментальных исследований и метрологической экспертизы материалов по разработке методики измерений.

В результате аттестации установлено, что методика измерений соответствует предъявляемым к ней метрологическим требованиям и обладает показателями точности, приведенными в приложении.

Приложение: показатели точности методики измерений на 1 листе.

Дата выдачи свидетельства 11 сентября 2020 г.

Начальник АХУ УрО РАН Р. В. Зиновьев

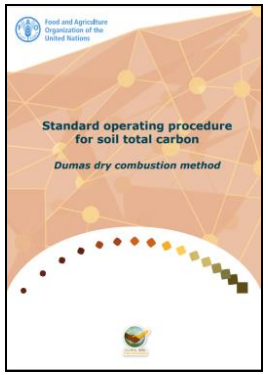
Руководитель Центра «СЕРТИМЕТ» АХУ УрО РАН А. А. Исаченков

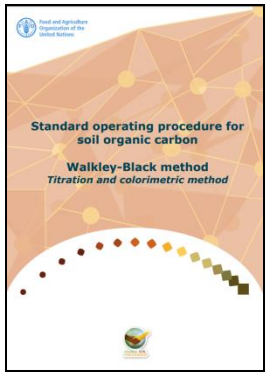
СертиМет

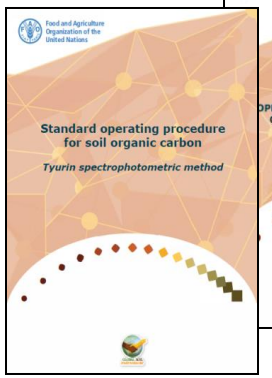
2. We have certified new modification of the Tyurin method and the Walkley-Black method at the Center for Metrology and Certification "Sertimet" (No. 88-17641-001-2020).

GLOBAL SOIL PARTNERSHIP

https://www.fao.org/global-soil-partnership/glosolan/



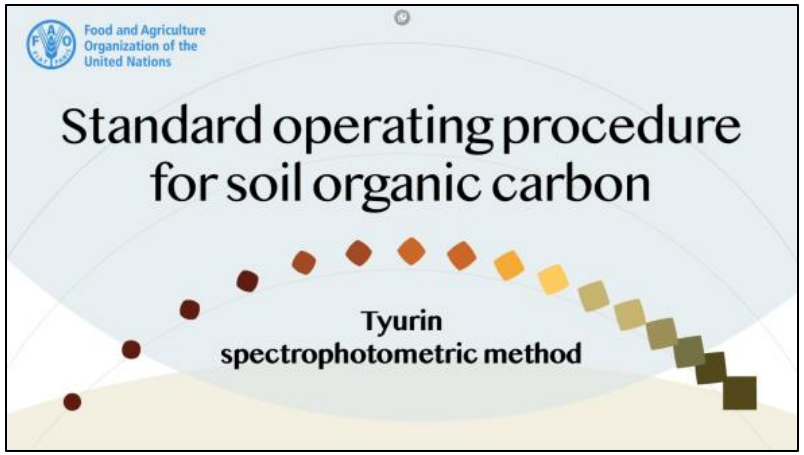




Organic carbon

Carbon, as soil organic matter, alters the physical (e.g. structure), chemical (e.g. cation exchange capacity), and biological (e.g. microbial activity) properties of soils with impacts on plant growth and yield, biodiversity and the soil water retention capacity. The content of organic carbon of mineral horizons can be used also in soil classification, taking the textural class into account. However, the inferred organic carbon status of a soil should always be locally checked as it is only a rough estimate.

The methods to measure organic carbon are rather easy to run but a special effort should be made by soil analysis laboratories to provide the best possible quality data. This will allow monitoring of changes in SOC at both local and regional scales and also give a better idea of the future scenarios, not only for SOC content but also for atmospheric CO_2 evolution. Did you know that the Global Soil Partnership launched a series of activities on soil organic carbon? For more information click here.



The methods to quantify SOC already harmonized by GLOSOLAN are the following:

SOP Walkley-Black method – titration and colorimetric method (**EN** | **ES** | **RU**)

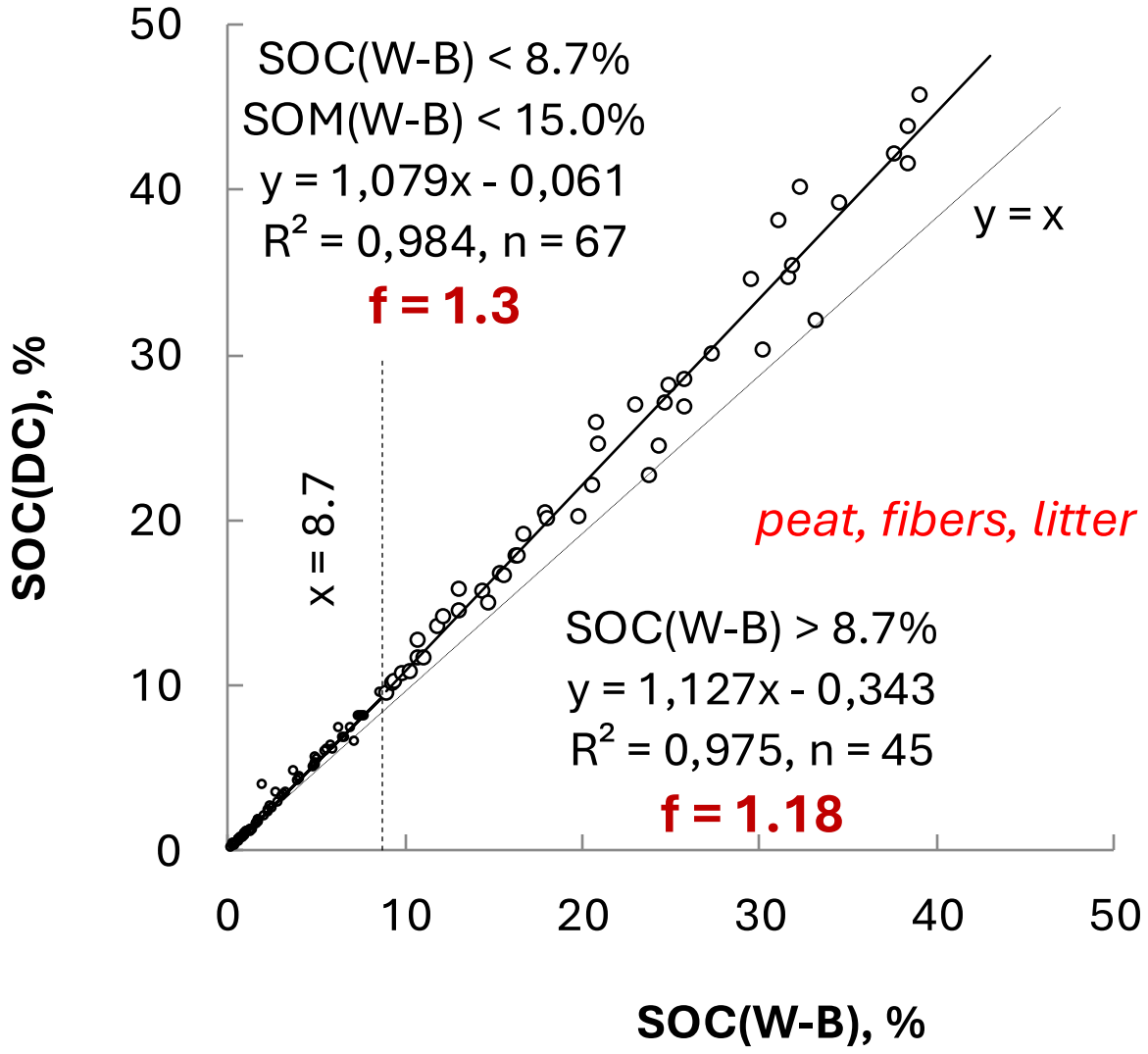
Soil organic carbon – Tyurin spectrophotometric method (**EN** | **RU**)

Training video: Walkley and Black - **titration** and **colorimetric** method

Training video: **Tyurin method**

Soil Organic Carbon methods : Sustainability of methods

Method	Risk for human health related to the use of chemicals and the overall implementation of procedure by staff	Environmental risk (waste disposal)	Level of technology required	Average duration of the analysis	Global median price of the analysis (for the customers)
Walkley & Black	High	High	Low	Up to one working day	6 USD
Tyurin	High	High	Low	Up to one working day	7.6 USD



- SOC(DC) and SOC(W-B) are linearly related at SOC 8.7-45%
- organic matter with SOC > 15 % is more easily oxidized by the chromium mixture than at low %SOC

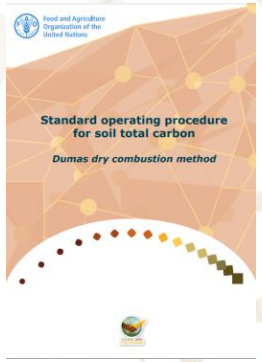
"Dry" chemistry

Dry combustion on the analyzer – gold standard

Advantages:

- SOC measurement range from 0.1 to 100%
- High measurement accuracy
- Complete SOC oxidation
- Availability of control samples for calibration
- Expressivity (batch up to 100 samples)
- Selectivity

Limitations: Expensive for many labs



Loss-on-ignition

- Many modifications (*T* 450-550 °C, *t* = 4-9 hours),
- SOP of GLOSOLAN in progress

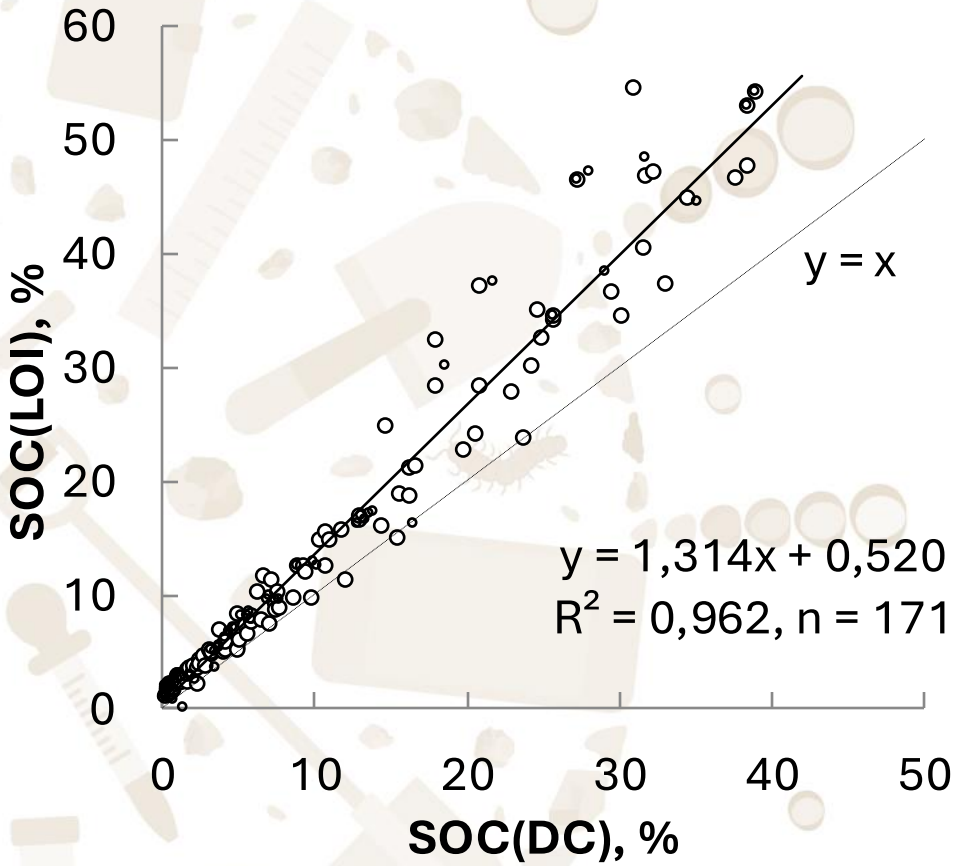
Advantages:

- Eco-friendly
- Expressivity
- Simple
- Cheap

Limitations:

- Presence of other compounds that decompose at T = 105-550 °C with the release of gaseous products
- Multiple weighing of the soil, leading to a systematic error

Loss-on-ignition (T = 550 °C, t = 7 hours)



1. Limitations:

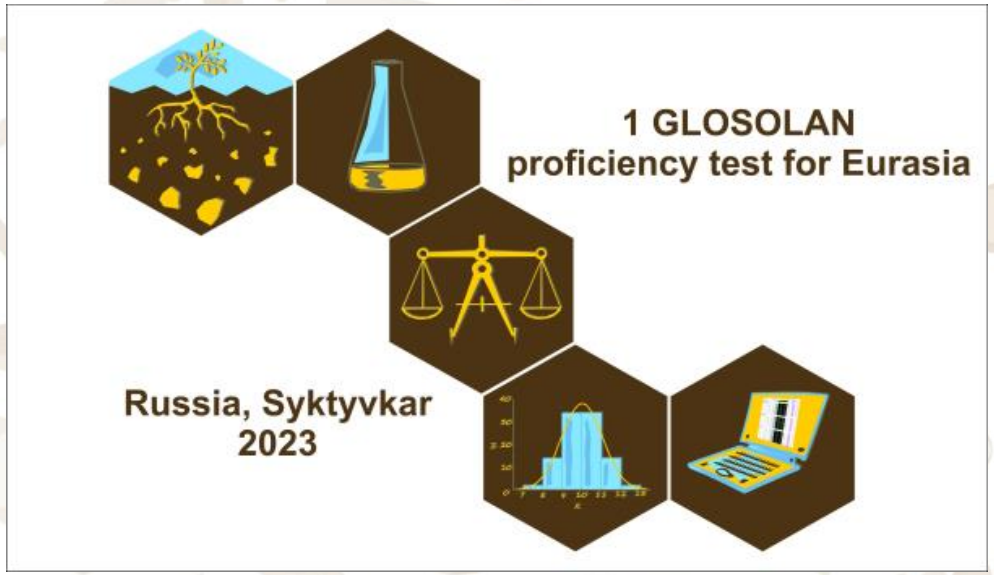
- Presence of other compounds that decompose at T = 105-550 °C with the release of gaseous products
- Multiple weighing of the soil, leading to a systematic error

2. k = SOC / SOM = 0.58 (1/1.724)

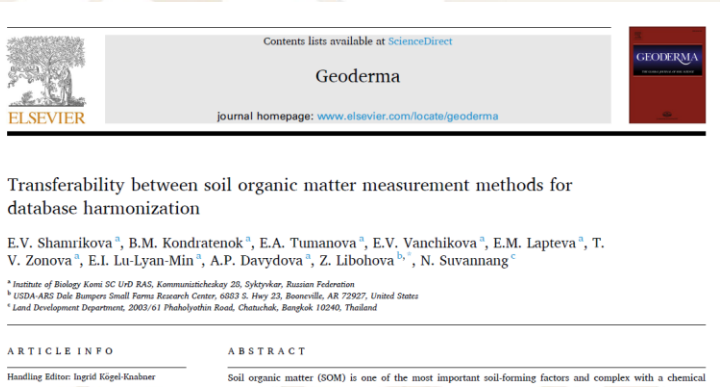
In the literature k = 0.4-0.71

(Kamara et al., 2007; Pribyl, 2010; Roper et al., 2019).

In our research k = 0.43 (Organic carbon content 43%)



The 1st Euro-Asian professional test GLOSOLAN-2023/2024 on measuring SOC confirmed these conclusions.



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Transferability between soil organic matter measurement methods for database harmonization

E.V. Shamrikova [a], B.M. Kondratenok [a], E.A. Tumanova [a], E.V. Vanchikova [a], E.M. Lapteva [a], T. V. Zonova [a], E.I. Lu-Lyan-Min [a], A.P. Davydova [a], Z. Libohova [b,*], N. Suvannang [c]

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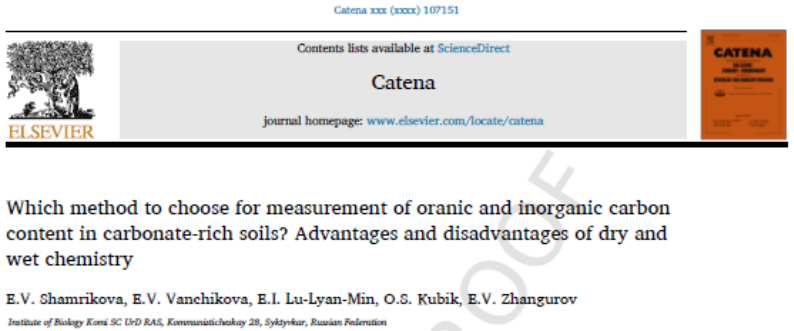
ABSTRACT

Soil organic matter (SOM) is one of the most important soil-forming factors and complex with a chemical



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Catena

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Which method to choose for measurement of oranic and inorganic carbon content in carbonate-rich soils? Advantages and disadvantages of dry and wet chemistry

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Conclusion

- A comparative study of quality control samples and field soil samples by the Tyurin, Walkley-Black and Dry Combustion methods confirmed the possibility of taking into account incomplete organic carbon oxidation. For this, it is necessary to enter a coefficient of 1,15 for the Tyurin method and 1,3 for the Walkley-Black method.

W-B · 1,3 = Tyurin · 1,15 = Dry Combustion (*P* = 0,95)

- The accumulated large array of SOC measurements by the Tyurin method can be included in the global soil quality monitoring network with the introduction of this coefficient.
- In our opinion, the Walkley-Black method is less laborious than the Tyurin method. The rejection of the procedure for heating soil suspensions with a chromium mixture less pollutes the working areas, therefore, *it is more environmentally friendly and less harmful to the performers*.
- The LOI method is “waiting” for harmonyization. We invite interested groups to participate in this process. The scope of soil studies should be expanded to confirm our results.

Acknowledgments

We would like to express our gratitude to **GLOSOLAN** for supporting our initiative to carry out this work, as well as for providing soil samples for research.

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Food and Agriculture Organization of the United Nations

THANK YOU

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GLOBAL SOIL PARTNERSHIP