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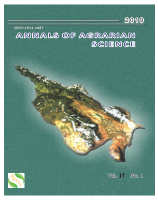

Method of laser diffraction spectra's deconvolution for characteristics strength of soil microaggregates

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A B S T R A C T

Laser diffractometry, yielding exactly, cannot replace the pipette analysis of the soils/sediment particle size distribution. But laser diffractometry can be used to improve soil physical knowledge related with soil structure stability, for example, to assess the degree of microaggregates preservation after their partial dispersion. For this purpose it is necessary to use deconvolution of the laser diffraction curves, with the following analysis of the number of LD-fractions and their properties. It was ppproposed 4 indicators of LD-fractions: theoretical number of fractions (N), the real number of fractions (n), period of fractions (T), and their dispersion (D). Introduced a new indicator of the aggregates strength (RMA), taking into account the role of only 3 independent criteria: N, D and T. According to RMA-indicator, the aggregates in paleosols are stronger than aggregates in recent andosols.

Keywords: Degree of microaggregates preservation, Soil structure stability, LD-fractions. Laser diffractometry, Real number of fraction, Dispersion if fraction.

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Introduction

At present, two methods for analyzing the grain size composition of soils and sediments are common. The older method, a sieve analysis combined with a thin-particle pipette analysis (SPA), is based on determining the mass fraction of individual fractions [1]. Later, a method of laser diffraction analysis (LDA) was developed, based on the determination of the volume part of fractions [2, 3]. Laser diffractometer is provide rapid analysis and do not need a larger sample mass. Another important LDA advantage is the obtaining of a practically continuous spectrum of the dependence of the particle content in % on their size. On the graph of the LD-function, a sequence of minima and maxima is formed. They are interpreted as follows: the position of the minima on the particle diameter axis is the boundary between the fractions, and the magnitude of the (maximum) is proportional to the fraction part in these boundaries.

But the LDA has a serious flaw. Numerous tests have shown that usually the grain size composition determined by the LDA method differs significantly from the composition determined by the SPA method [2, 3, 4-7]. The LDA method is not capable of taking into account the deviation of thin clay particles from the spherical shape [4, 2]. But there is an error in the content of sand particles, if their shape is very different from the ball [5]. In addition, an error makes a difference in the density of minerals within a single sample. As a result, the composition determined by the LDA method may be very different from the true grain size composition determined by the SPA.

To use laser diffraction to determine the grain size composition, much work is being done to align the LDA and SPA data. To do this, they determine the conversion factors for the content of each particle fraction [6]. In this case, the correction factors are valid only for a given series of samples. In the absence of a reliable statistical relationship between the content of the same fractions the determination of correction factors becomes impossible, determined by two methods [6]. This led to limitations on the use [5] and the realization that it is not possible to determine the grain size composition by the LDA method [2].

In general, except for rare cases of accidental coincidence, the LDA method can not determine the grain size composition of soil/sediment. In order to distinguish from the grain size fractions, we will name the fractions revealed by the laser diffraction method as "LDA-fractions". But then the question arises: what can be the use of the LDA method? We will try to answer this question.

We'll give a quote from the very important paper of Buurman et al. “Grain-sizing by laser diffraction cannot replace the classical combination of sieving and sedimentation as long as correlations between the methods have not been established for many populations of samples. Nevertheless, grain-size determination by laser diffraction has a great potential for use in soil science, e.g., for detailed comparison of samples from the same origin to establish homogeneity of parent materials, for the study of texture changes caused by weathering, and for changes in aggregation” [8].

Probably, the significance of this rapid analysis is the characterization of the relative dispergation of soils and sediments. With the new approach, because of the conventionality of the absolute indices of LDA fractions, such as the average particle diameter (d_{aver}) and their content n, the authors use relative dispersity indices.

Let's pay attention to the studies, where relative LDA indicators are used. At the same time, the authors exclude from consideration such absolute indicators of LDA fractions as the average particle diameter (d_{aver}) and their content n. Thus, the advantage of LDA is used as an express analysis of the relative characteristics of different systems.

For example, the difference in loess particle sizes obtained from two models of the LDA function analysis is used: Freinhofer (FH) and Mie (Mie) [9]. Then the relative particle dispersity index ΔGSD is calculated:

$$\Delta GSD = GSD_{FH} - GSD_{Mie}$$

A strong disagreement between the results of the two methods of analysis (SPA and LDA) is noted by many authors [2, 10]. Thus, the composition of loess soils by LDA is strongly depleted of silty particles <2 μm and enriched in dust particles of 2-20 μm [10]. In paper [2], a regression equation was given for 158 samples that bound the content of clay particles thinner than 2 μm, determined by the laser diffraction (Y) method with their content from the pipette analysis (X):

$$Y = 0.361 X - 0.232.$$

As can be seen, on average the sludge content, determined by the LDA, is 2.8 times less than in the classical pipet-analysis. In the same paper [2] on certified samples it was shown that the amount of silt, according to the LDA, is 2/3 below its actual content.

Data on the extremely low shortage in the content of clay particles by the LDA method in one of the samples are given: the content of these particles was 5.5 times lower than for the pipet-method [3].

As can be seen, using the relative characteristics of LD-fractions, new information on the properties of disperse systems is obtained. The relative characteristics of LD-fractions can also be used to solve some soil problems.

One of the problems facing the soil scientist is the need for an operational control of the conservation of soil microaggregates, after chemical preparation for grain size analysis. The degree of safety of microaggregates with the selected preparation for LDA reflects the genetic features of soils.

The most durable microaggregates are formed in volcanic-ash soil, taxonomically Andosol [11, 12]. In Andosol are formed the organo-mineral associations occurring at smaller spatial scales because this soil type holds much higher amounts of organic matter and short-range-order minerals compared to any other soil types [13].

At present, the completeness of the dispergation of microaggregates is estimated by a rather complicated method: using microscopy methods, including expensive electron microscopy. At the same time, a detailed analysis of the LDA-spectra can give an answer to the completeness of the microaggregates dispergation. The fact is that the grain size fractions of elementary particles of soils and sediments have a number of characteristic features that differ from the properties of microaggregates. If the LDA-spectra deviate from standards (extremely dispersed samples), we can speak of the preservation of microaggregates, that is, of incomplete soil dispergation.

But it is not possible to determine directly the fractal indices from the visual analysis of the LDA-spectra. This requires splitting the function of the LD-spectra. The procedure for splitting the spectrum is called as "deconvolution".

Objective: to use deconvolution of laser diffraction spectra as a method of controlling the preservation of microaggregates after chemical preparation of soils.

The method of deconvolution

The meaning of deconvolution (with respect to decoding the energy dispersive X-ray fluorescence spectrum) is described in detail by Savichev and Stepanov [14]. Let us apply this technique for the deconvolution of the grain size spectra of soils.

Since the particle size varies over a wide range, the logarithms of the particle diameters are plotted along the abscissa axis, i.e. spectra are displayed on a semilogarithmic scale. The base of the logarithm does not matter much, it is important that it is greater than one. We adopted the construction of Gaussian curves in natural logarithms. Then the initial distribution looks like this:

$$Y(\ln d), \qquad (1)$$

Where d is the particle diameter. The initial distribution represents the sum of the individual lines whose wings are superimposed on each other. Let us assume that the true contours of the lines have a Gaussian shape. We construct a model distribution representing the Gaussian curves sum:

$$Y_{mod}(\ln d) = \sum_{i=1}^{N} A_j \cdot \exp\{-[(\ln d_j - \ln d)/D_j]^2\}. \qquad (2)$$

Here, the index of the line number j runs through the values 1, 2, 3, ..., K, where K is the quantity of lines, A_j is the amplitude of the j-th Gaussian curve, d_j is the position of the j-th line vertex on the abscissa (μm), D_j is the dispersion of j- th Gaussian curve.

The transition to a discrete distribution for given diameters d_i yields expressions (1) and (2) to the form:

$$Y(\ln d_i) = Y_i\,, \qquad (3)$$

and

$$Y_{mod}(\ln d_i) = Y_{mod\ i}\,. \qquad (4)$$

Here the index i runs through the values 1, 2, 3, ..., N, where N is the quantity of measurement points.

The model distribution is found from the condition for minimizing the deviation of the model distribution from the initial one:

$$\sum_{i=1}^{N} (Y_i - Y_{mod\ i})^2 = \min. \qquad (5)$$

However, expression (5) assumes identical error prices at small and large values, although for small values the error price is higher. To take this into account, we introduce the statistical weight of ordinates:

$$G_i = 10/(Y_i + 1)^{1/2}\,, \qquad (6)$$

and we search for the optimal model distribution from the minimization of the function:

$$\sum_{i=1}^{N} G_i\,(Y_i - Y_{mod\ i})^2 = \min. \qquad (7)$$

From condition (7) we search for all the exponents of each of the Gaussian curves: the amplitude A_j, the position of the vertex d_j (d_{aver}) and the dispersion value D_j.

The problem is linear only in the amplitudes A, but non-linear in the diameters of the maxima d_{aver} and the dispersions D. Therefore, it is necessary to go over the positions of the maxima and dispersions with a small step and to calculate the amplitudes at each step.

The most insignificant fractions with a share of <1%, as unreliable, are excluded from consideration. Examples of two deconvolution LD-spectras are shown in figures 1 and 2.

Objects

We studied recent soils and paleosols in quaternary fluvio-lake sediments in the basin of Bozhano in northern Italy, described in the paper [15]. Recent soils and paleosols were formed as a result of pedogenesis on the products of interaction of pyroclastic material with alluvial clay sediments, some of which are strongly enriched in carbonates.

Recent soils are referred to as andosols, their thickness is 1.5 m. The parent rocks C-1 and C-2 at depths of 80-150 cm are strongly enriched in carbonates: the calcite content reaches 70-77%. Below, up to a depth of 11 m, paleosols are opened, which according to morphology are divided into four solums: Solum I-IV. Their parent rocks are lake sediments, in varying degrees of erosion.

Before the grain size analysis, for dispersing the microaggregates samples <2 mm were treated with H_2O_2 to oxidize the organic matter, and then dithionite-citrate-bicarbonate (DCB) to dissolve the glandular cement. In carbonate rock samples underlying the recent soil (RS-CI and RS-C2 samples), the carbonates were removed by treatment with Na acetate buffered at pH 5.

After this preparation, the soil composition was determined by laser diffraction on a Malvern Mastersizer 2000 analyzer. The analysis parameters are the following: the pump speed is 2500-3000 rpm, the number of measurements is 6-10, the refractive index is 1.52, and the absorption index is 0.1 [15]. The obtained spectra of particle distribution were deciphered by deconvolution.

Calculations of LD-fractions

Main indicators of LD-fractions are their real content in this sample (n), average diameter $d_{average}$, period T, and dispersion (D).

The average diameter (d_{aver}) of all fractions allows us to determine the period of the function T:

$$T = (d_{aver})_{i+1} : (d_{aver})_i \quad (8)$$

This makes it possible to compare the T values of the soils with the periodicity of the sediment fractions: T = 3-4 [16, 17]. For vrtisols period received us is T ~ 3.3 [18]. The larger the value of T, the stronger the fractions are differentiated.

Another important indicator of the differentiation of LDA fractions: the dispersion of Gaussian curves D. The smaller the value of D, the more pronounced the differentiation of the fraction. By the value of D, one can judge the homogeneity of the particle distribution in a given fraction.

As additional characteristics of LD-fractions, you must enter the new indicators; one of them is the theoretical number of LD-fractions (N). In the range 0-2000 µm, it is allocated 9 classic size fractions of differing mineralogy of the dominant particles. Each faction is marked the index. The faction fc: 0-0.2 µm; mC: 02-0.63 µm; cC: 0.63-2.0 µm; fSi: 2.0-6.3; mSi: 6.3-20 µm; cSi: 20-63 µm; fS: 63-200 µm, mS: 200-630 µm and cC: 630-2000 µm [9]. Similarly it is calculated the period E, based on the borders between the factions. According to [9] the period of classical size fractions T ~ 3.1.

Thus, each of the groups: clay (c), silt (Si) and sand (S) are subdivided into 3 factions: fine (f), medium (m) and large (c), total 9 classic fractions. It is possible that each grain fraction is meet a real set of particles, whose distribution is described by the Gauss-curve. The reality of individual solid fractions is confirmed by the results of rock crushing. The close number of factions was identified with the spraying rocks by Sadovsky [17, 14]. It is proved that when the dispersion of particles is formed are not arbitrary, but quite specific sizes. In the interval 0 - 2000 µm are identified 8 fractions. A small difference among the factions is so classic width slightly narrower than fractions resulting after the experimental crushing of rocks. The proximity of a number of theoretical and a number of real-world factions is confirm the possibility of using borders classic fractions to analyze fractions identified in the result of LD-deconvolution.

Thus, the average diameter (d_{aver}) of the LD-fractions, you can identify this LD-fractions by placing this faction in the classical borders of one of the 9 groups of clay, silt and sand. This will examine the nature of distribution of LD-fractions within the classical scale size [9].

For example, in the sample of RS-A were identified four factions, n = 4. In accordance their average diameters (d_{aver}) the factions are fall into the following classic groups: cC (coarse clay), mSi (middle silt), cSi (coarse silt) and mS (middle send). Will be denoted by symbol "N" is the total number of classic fractions ranging from very thin to very large fraction of the sample. As you can see, the sample RS-A in the interval from cC to mS are contains six classic fractions, then N = 6. The difference: N-n = 6-4 = 2, this means two spaces in the distribution of LD-fractions of sample RS-A.

In the future it will be shown that in all samples of Italian andosols and paleosols: N > n. The inequality (N > n) is the important difference of aggregates andosols and paleosols from the grain-size composition of previously studied soils. For them equality (N = n), then there are no gaps in the distribution of graine size fractions on the scale of classical groups. Thus, there is a possibility to identify gaps in continuum of classic size groups. In the case of incomplete soil dispersion, the gap reflects the increased aggregation of related, coarser, aggregates.

Results and discussion

The number and properties of LD-fractions

Insufficiently complete energy impact in the preparation of soils for LDA appears as a dignity, allowing to assess the strength of the surviving micro-aggregates.

We propose several indicators of the microaggregates safety, which can be derived from the LD-spectra. This is the number of fractions of N and their characteristics. Comparing the data on the number of LD-fractions and their properties in a given soil with data on LD-fractions of reference samples that are known to be completely dispersed, it is possible to determine the strength of the surviving microaggregates.

Absolute indices of the fractions determined by the LDA, such as the average particle diameter (d_{aver}) and their content, have no physical meaning, due to the already mentioned deficiencies of the LDA. Repeat that only relative (dimensionless) indices have meaning: 1) the real number of fractions (n), 2) the theoretical number of fractions (N), 3) period (T) of the function n = f (d), and 4) the dispersion of an fraction (D).

The results of counting these five criteria are given in the table. 1.

The number of LD-fractions. The real number of LDA fractions (n) in andosol and in the paleosols of the fluvio-lake sediments of northern Italy is from 2 to 4.

In reference soils and rocks, the real number of LDA fractions in the range 0-2000 µm, is n = 8 [10, 11]. A small number of fractions (n = 2-4) mean that the processing of DCB did not completely disintegrate the recent andosols and paleosols of northern Italy.

Maximum theoretical number of LD-fractions is detected the particles or aggregates with size medium from clay (mC) to the large sand (cS), i.e., Nmax = 8. For our andosols and paleosols are N = 3-6. All samples have the difference: (N-n) = 1-2. Inequality (N > n) is due to omissions in the content of 1-2 classic fractions.

Reasons for skipping of the fractions: 1) natural heterogeneity in composition of sedimentary rocks, 2) preservation aggregates due to incomplete dispersion of soil or sediment. It should be noted that previously studied vertisols in Stavropol (South Russia) after processing the ultrasound respected equality: N = n [18]. When the same processing in some specimens vertisols in Texas (USA) (N-n) = 1, while most samples (N = n).

Thus, all specimens of Italian andosols have inequality (N > n) occurs due to omissions in the content of 1 or even 2 fractions. One possible reason is preservation of aggregates due to incomplete dispersion of soil.

Characteristics of the preserved microaggregates: T and D. Another relative index of soils is the period T of adjacent fractions (table 1). The average values of the period T for six samples vary from 5.5 to 13.3. Meanwhile, according to Sadovsky average values of T for rocks 3-4 [16, 17], and according to our data for vertisols $T_{(aver)}$ = 3.3 [18]. Explicitly overestimated values of T in Italian andosols indicate an incomplete dispersion of microaggregates. There are especially large periods T in the samples of vertisols (Stavropol and Texas) [18].

The next relative index of LD-fractions is dispersion D. The studied Italian andosols and paleosols differ by an increased dispersion of the fractions: the D value reaches 1.5, while the dispersion of the fractions after complete dispersion of the samples of vertisols $D_{(aver)}$ = 0.6 [18]. Very high values of the variance indicate the heterogeneity of the LD-fractions in the studied soils, possibly including particles of different sizes. Thus, an abnormally high dispersion also indicates the preservation of microaggregates. The safety of microaggregates makes it possible to assess the strength of cement in different layers of this profile.

Micro-aggregates strength criteria, reflecting both: the content preserved units and their relative strength, have five LD-fractions indicators. For some indicators maximum strength is translated into maximum values (D) and (T), for other indicators maximum strength is translated into minimum values (N and n). Specific extreme values of LD-fractions and soil indexes, are given in the table. 2.

As you can see, the strongest aggregates have the paleosol SIV-1 with extreme values of the three indicators (N, N, and D). The strength aggregates have the paleosol SIII-1 with two indicators (N and n). Also the strength aggregates have the paleosols: SI-1 (with H) и SII-1 (with T).

Since the LD-factions depend on each other, their informative value is not the same. Most high informative value has the criteria that correlate with other related very weakly.

Statistical connection with indexes. We have calculated the correlation coefficients between pair of the five indicators: n, N, D and T (table 3).

Then we are calculated the average value of the correlation coefficient excluding characters on r-coefficients. The average values of the r-coefficient are increase in the sequence: 0.39 (T) < 0.45 (N) < 0.54 (D) < 0.68 (n). Most high information has first three indexes (T, N and D). These three indexes were used to create a new, integral indicator of the strength of the persevered resistance of micro-aggregates (RMA).

It is the averaged sum of the ratios of the three indicators of the LD-fractions in the given soil in comparison with the parameters of the reference LD-fractions obtained after complete dispersal of the microaggregates; N = 8, D = 0.6 and T = 3.3. This RMA index is determined from the expression:

$$RMA = [(8/N) + (D_{aver}/0.6) + (T_{aver}/3.3)] : 3 \qquad (9)$$

Knowing this index, we determine the total strength of microaggregates that survived after a given chemical dispergation. In a fully dispersed sample RMA is 1. But if the aggregates are preserved the value RMA is higher. We will consider samples with RMA = 1-2 as containing aggregates of low strength, and samples with RMA > 2 with aggregates of high strength.

On average, in recent andosols RMA = 1.91 ± 0.20, while in paleosols, the average RMA index rises to 2.28 ± 0.10, the difference in the mean is significant at P = 80%. Thus, in paleosols the strength of microaggregates is higher than that of recent andosols. Probably, in the course of time, the strength of cement cementing the particles of the pyroclastic material of andosols increases. The strongest of aggregate are designs in paleosols: SIV-1 (RMA = 2.56) and SII-1 (RMA = 2.50).

The reasons for preserving part of the microaggregates in andosol

Strong micro aggregates are cemented with cement, for the destruction of which the application of considerable energy is required. Microaggregates are destroyed by physical or chemical methods. Ultrasound is one of the most often method used; consumable energy depends on the power of the dispergator and the time of exposure.

It is more difficult to estimate the energy consumed during chemical dispergation of microaggregates. Most often perhydrol for oxidation of humus is used and dithionite is used to reduction Fe^{3+} in the composition Fe-(hydr)oxides to Fe^{2+}. In the first case, the released energy can be calculated by the reaction of the decomposition of H_2O_2, in the second case the energy for the decay reaction of dithionite. In the surviving microaggregates, the energy necessary for the destruction of cement exceeds the energy spent on dispergation.

The mineralogical composition of andosols in a neutral medium is determined by the hydrolysis of volcanic glass [19]. This leads to the formation of typical minerals of andosols: clay minerals (allophane and imogolite) and Fe-hydroxide: ferrihydrate $2Fe_2O_3 \cdot FeOOH \cdot 4H_2O$) [19]. The role of mineral cement in andosols is performed by active particles of allophone, imogolite and ferrihydrate, connected with organic matter [11].

Allophane and imogolite are nano-sized aluminosilicate with hollow spherule and tube structures with the diameter varies from 3 to 5.5 nm and have high cation/anion exchange capacity as well as extensive, variable-charged surfaces [11, 12]. Together with Fe-bearing short-range-order minerals which can easily dissolve and precipitate upon redox changes, these nano-sized short-range-order minerals and the organic matter bound to them may act as strong binding agent for aggregate formation. In addition, Al-organic (and, to less extent, Fe-organic) complexes formed via covalent bonding between monomeric Al and Fe ions with organic functional groups are also relatively abundant in Andisols [11, 12].

DCB effectively dissolves Fe-cement in strongly ferruginized soils, for example, in ferrallitic soils [20]. Feature of these soils is high content of gross iron, mach more above the Clarke of the lithosphere - 6.2% [21]. But the gross iron content in the Italian andosols and paleosols is very low: 0.7-2.8%. This already indicates a weak ferrigination of andosols.

The most of thin microaggregates of Andosol have very high strength. Maximum dispersion was achieved only after sodium saturation pretreatment followed by the sonication at the energy level 5–10 folds higher than normally required for non-volcanic soils (Alfisol, Molisol, Oxisol and other) and reaches – 5 kJ /mL [11]. It is obvious that DCB is not able to completely destroy solid microaggregates of Andosols.

A thorough research carried out using near-edge X-ray absorption fine structure was shown that organic matter forms a weak connection with the smooth surface of large crystals [12]. This explains the reason not to attend such minerals like kaolinite, hematite, goethite in the formation of microaggregates in andosol. But organic matter is formed a strong connection with unordered minerals such as allophone, imogolite and ferrihydrite [12].

In [15], the authors randomly used a reagent (DCB) that is not very selective to andosols. But this allowed us to obtain new information on the composition of soil microaggregates. In the future, it is possible to deliberately apply soft processing to obtain information about firmly connected soil microaggregates, not only in Andosol.

Conclusion

Andosols have possessed special properties which distinguish them from the many other soils. The role of durable cement in andosol is not Fe-oxides (as in oxysol), but organo-mineral complexes based on short-range-order minerals (allophone, imogolite and ferrihydrite). This is not to prejudge the effectiveness of DCB as a chemical to destroy solid microaggregate in andosol. This leads to the conservation of the andosols aggregates after processing by DCB.

For the determination of soil grain size and micro aggregates are using 2 methods: classic pipet-analysis and a new more powerful analysis using laser diffraction. Recent studies have shown that the composition determined by the laser diffraction method differs greatly from the grain size composition according to the pipet method.

But the laser diffraction data is possible to use for another purpose: to characterize strength of microaggregates preserved after chemical treatment of soils. For this purpose it is necessary to use deconvolution of the laser diffraction curves, with the following analysis of the number of LD-fractions and their properties. It was pproposed 4 indicators of LD- fractions: theoretical number of fractions (N), the real number of fractions (n), period of fractions (T), and their dispersion (D).

We analyzed recent andosols and paleosols in northern Italy, which studied be Colombo et al. [15]. The theoretical number of andosols and paleosols fractions is N = 3-6, whereas in standard, completely dispergated sedimentary rocks, the number of grain size fractions in the range up to 2000 μm is higher and is 8. The real number of LD-fractions in andosols and paleosols is n = 2-4, whereas in standard, completely dispergated vertisois and oxisols n = 4-5.

Additional information on the degree of dispersion of the samples is given by the period T of adjacent fractions. In Italian andosols and paleosols T = 12-14, which is much higher than the values of T for sedimentary rocks (3-4) and for soils T ~ 3. In addition, the fractions of Italian andosols and paleosols are characterized by increased dispergation, the D value reaches 1.5, whereas the dispersion of the granulometric fractions after complete dispergation of the samples is usually below: ~0.5. All this indicates partial preservation of microaggregates after treatment of soils with dithionite-citrate-bicarbonate.

Introduced a new indicator of the aggregates strength (RMA), taking into account the role of only 3 independent criteria: N, H and T. According to RMA, the aggregates in paleosols are stronger than aggregates in recent andosols. The strongest of aggregate are designs in solums: 1-SIII and SIV-1.

References

[1] A.D. Voronin, Fundamentals of Soil Physics, Lomonosov Moscow State University, Moscow, 1986 (in Russian).

[2] M. Konert, J. Vandenberghe, Comparison of laser grain size analysis with pipette and sieve analysis: a solution for the underestimation of the clay fraction, Sedimentology, 44 (1997) 523-535.

[3] A. Kun, O. Katona, G. Sipos, K. Barta, Comparison of pipette and laser diffraction methods in determining the granulometric content of fluvial sediment samples , J. Environ. Geography 6 (2014) 49-54.

[4] P. Buurman,, Th. Pape,, J.A. Reijneveld, F. de Jing, E. van Grlder, Laser- diffraction and pipette-method grain sizing of Dutch sediments: correlation for fine fractions of matine, fluvial, and loess samples, Netherlands J. Geosc. 80 (2001) 49-57.

[5] J.R. Campbell, Limitations of laser particle sizing of soils, in "Adv. in Regolith" (2003) 38-42.

[6] C. Di Stefano, V. Ferro, S. Mirabile, Comparison between grain-size analyses using laser diffraction and sedimentation methods, Biosystems Engineering 106 (2010) 205-215.

[7] R. Xu, A. Di Guida, Comparison of sizing small particles using different technologies, Powder Technol. 132 (2003)145-153.

[8] P. Buurman, Th. Pape, C.C. Muggier, Laser grain-size determination in soil genetic studies 1. Practical problems, Soil Science 162 (1997) 211-218.

[9] P. Schulte, F. Lehmkuhl, The difference of two laser diffraction pattern as an indicator for post-depositional grain size reduction in loess-paleosol sequence, Paleogeography, Paleoclimatology, Paleoecology, 509 (2017) 126-136.

[10] X. Yang, Q. Zhang, X. Li, X. Jia, X. Wei, M. Shao, Determination of Soil texture by Laser Diffraction Method, Soil Sc. Soc. Am. J. 79 (2015) 1556-1566.

[11] M. Asano, R. Wagai, Evidence of aggregate hierarchy at micro- to submicron scale in an allophonic Andisol, Geoderma 216 (2014) 62-74.

[12] M. Asano, R. Wagai, N. Yamaguchi, et al., In search of a binding agent: nano-scale evidence of preferential carbon associations with poorly-crystalline mineral phases in physically-stable, clay-sized aggregates, Soil Systems 2 (2018) 32.

[13] R.A. Dahlgren, M. Saigusa, F.C. Ugolini, The nature, properties and management of volcanic soils, Adv. Agron. 82 (2004) 113–182.

[14] A.T. Savichev, S.S. Stepanov, Allowance for superimposition of lines and approximation of background radiation in X-ray fluorescent and microprobe energy-dispersive analyzes, Surface. X-ray, synchrotron and neutron studies 2 (2007) 85-89.

[15] C. Colombo, G. Palumbo, E. Di Iorio, F. Russo, F. Terribile, Z. Jiang, Q. Liu, Soil development in a Quaternary fluvio-lacustrine paleosol sequence in Southern Italy, Quaternary Int. 418 (2016) 195-207.

[16] M.A. Sadovsky, On the distribution of the solid dimensions, Reports of the Academy of Sciences of the USSR 269(1) (1983) 69-72 (in Russian).

[17] M.A. Sadovsky, L.G. Bolkhovitinov, V.F. Pisarenko, On the properties of the discreteness of rocks, Izvestiya of the Academy of Sciences of the USSR, series of physics of the Earth 312 (1982) 318 (in Russian).

[18] Yu.N. Vodyanitskii, E.Yu. Milanovskii, E.G. Morgun, A.T. Savichev, Deconvolution of the spectra of the drain size composition for the characterization of fine soil fractions, Eurasian Soil Sci. (in Press).

[19] Referentiel Pedologique, Inst. Nat. Resch. Agron. (1995) Paris.

[20] Yu.N. Vodyanitskii, The effect of dithionite-containing reagents on soil minerals, Eurasian Soil Sci. 35(5) (2002) 552-563.

[21] N.N. Greenwood, A. Earnshaw, Chemistry of the elements, (1997) Elsevier Sc. Kidlington, England.

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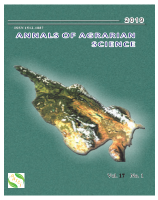
Journal homepage: http://journals.org.ge/index.php



Improving of Copper (II)-Ions Phytoextraction by Using Glycolipid Biosurfactants

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A B S T R A C T

Pollution of soil with heavy metals is a dangerous issue that endangers both the environment and human health. Phytoextraction, that implies planting contaminated area by previously selected species of plants having the potential to extract heavy metals from the soil, is common used technology. Some limitations of this technology revealed in difficulty to absorb the heavy metals, usually being in form of insoluble. For aim to increase the phytoextraction efficiency it is necessary to use agents able of solubilization of heavy metals. The aim of presented work is to test some biosurfactants for enhancing copper(II) phytoextraction by different plant species. For this purpose, the model experiments for cleaning of water and soils artificially contaminated with copper(II) ions have been carried out. The obtained results show that rhamnolipids and trehalose lipids increase the phytoextraction effectiveness significantly (2-3 times). Alfalfa with trehalose lipids are the most effective tools for cleaning soils contaminated with copper(II) ions. In this case removal of heavy metal from soil is achieved by 75%, and main part of removed copper(II) ions (approximately 60%) is translocated in upper ground parts of plant that is very important for performing phytoextraction process successfully.

Keywords: Heavy metals, Copper, Phytoremediation, Phytoextraction, Biosurfactants, Pollution

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Introduction

Heavy metals existing in environment cause the gross violation of natural equilibrium and processes of contamination of life importance ecosystems – ground and surface waters, soils, atmospheric air, vegetation (including cultivated verdure) get irreversible character, which reflects directly on the condition of health of population.

Especially dangerous and complex are the contaminations with persistent toxic substances, among which are petroleum products, heavy metals, chlorinated organic substances etc. [1]. They cause a violation of the structure, aeration, water exchange in soils, lead to changes in ecosystems and impossibility of their use in industry and agriculture.

Biological methods of restoration the environment (bioremediation, phytoremediation), that is the treatment with microorganisms and plants, are priority ones among the most promising and environmentally acceptable methods. Due to the great power of natural detoxification processes, interest in the ecological potential of microorganisms and plants has increased in the last decades [2-6]. Microorganisms that transform organics play an important role in maintaining the ecological balance in various ecosystems and, due to their high degradation and transformation power, are successfully used for sewage and soil purification. Plants actively participate in soil and air remediation processes. Plants and microorganisms, together or individually, mainly through their powerful oxidative enzyme systems are capable to remediate environment polluted by a wide spectrum of contaminants.

Phytoremediation is a unique cleanup strategy [3-6]. The realization of phytoremediation technologies for cleaning of environment polluted with heavy metals (phytoextraction) implies planting contaminated area by previously selected species of plants having the potential to extract heavy metals from the soil. Some limitations of this technology revealed in difficulty to absorb the heavy metals, usually being in form of insoluble. For increasing efficiency of phytoextraction, it is necessary to use agents able of solubilization of heavy metals and improve their absorption by plants. Some preparations of biological origin, such as surface-active compounds bacterial origin (biosurfactants) possess metal-chelating properties that enable their application in phytoextraction of heavy metals [7].

The aim of presented work is to test some glycolipid biosurfactants for enhancing copper(II) phytoextraction by different plant species.

Materials and methods

Microbial synthesis of biosurfactants was conducted using the strains-producers of the genera *Pseudomonas, Rhodococcus and Bacillus* on optimized liquid medium with glycerol, mannitol, hexadecane and plant oil industry wastes (20 g/l) [8-11]. Monocolonial selection of the strains has been carried out for the enhancement of their activity and the improvement of the surfactant synthesis. Rhamnolipids were isolated from cultural broth via acid precipitation (10% HCl to pH 3) and following extraction of the obtained precipitate with Folch mixture (chloroform : isopropanol – 2 : 1). Trehalose lipids were isolated with the same extragent from cell mass. Polysaccharides were isolated from cultural broth via precipitation with 2 volumes of ethanol. The solvent was evaporated under vacuum. The lipids were analyzed via thin layer chromatography and HPLC. The content of rhamnolipids was determined using orcinol method, trehalose lipids – using antron method.

The isolated biosurfactants we investigated by the following parameters: surface tension of solutions, critical micelle concentration (CMC), emulsification index (E24), thin layer chromatography, UV- and IR-spectroscopy.

The following preparations of biosurfactants were prepared:

- Rhamnolipids,
- Trehalose lipids,
- Rhamnolipid biocomplex PS,
- BR1 – complex of biosurfactants produced by strain of *Rhodococcus* sp. 50,
- BP1 – complex of biosurfactants produced by strain of *Pseudomonas* sp. 6R67,
- BB1 – complex of biosurfactants produced by strain of *Bacillus* sp. 3Zu9.

Plants. The following plant species: rape (*Brassica napus*), soybean (*Glycine max*) and alfalfa (*Medicago sativa*) were used as phytoremediators.

Model experiments. In the model experiments the soil samples contaminated artificially, as well as polluted as a result of oil pipeline accidental spills, were used.

The model experiments were carried out according to the following scheme: the suspension of microorganisms and solutions of biosurfactants was inoculated in the contaminated soil in the beginning of experiment. After different incubation times the plants were sowed in separate samples of soil. The conditions and details of each experiment are described in legends of figures.

Analysis of copper(II) ions. For analysis of Cu2+ content in plant and water samples have been determined sphectrophotometrically by measuring the absorption of the Cu(II)-dithizone (1,5-Diphenylthiocarbazone) complex at 553 nm, according to Kumar et al. [12].

Results and Discussions

For selection of biosurfactants and polysaccharides, chelating heavy metals to increase efficiency of their absorption by root system and transportations in upper ground parts of plants, 7 preparations of biosurfactants were tested.

The following plants and biosurfactants were tested in the model experiments:

- Plants - soybean, alfalfa and rape (growing on hydroponic area);
- Copper(II) ions as model heavy metal (concentrations –100 and 200 ppm);
- Preparations of biosurfactants (concentration – 0.1 g/l):
  - o Rhamnolipids
  - o Trehalose lipids
  - o Rhamnolipid biocomplex PS
  - o BR1 – complex of biosurfactants produced by strain of Rhodococcus sp. 50
  - o BP1 – complex of biosurfactants produced by strain of Pseudomonas sp. 6R67 and
  - o BB1 – complex of biosurfactants produced by strain of Bacillus sp. 3Zu9
  - o BB2 – complex of biosurfactants produced by strain of Baccilus spp.

For carrying out of experiments, seedlings of the plants were placed in special tubes on hydroponic media containing different concentrations of copper(II) ions and tested biosurfactants. After 7 days from the start of experiments, copper(II) contents were measured in growing medium and plant seedlings (separately in roots and upper parts). The obtained results are presented on Figures 1-4.

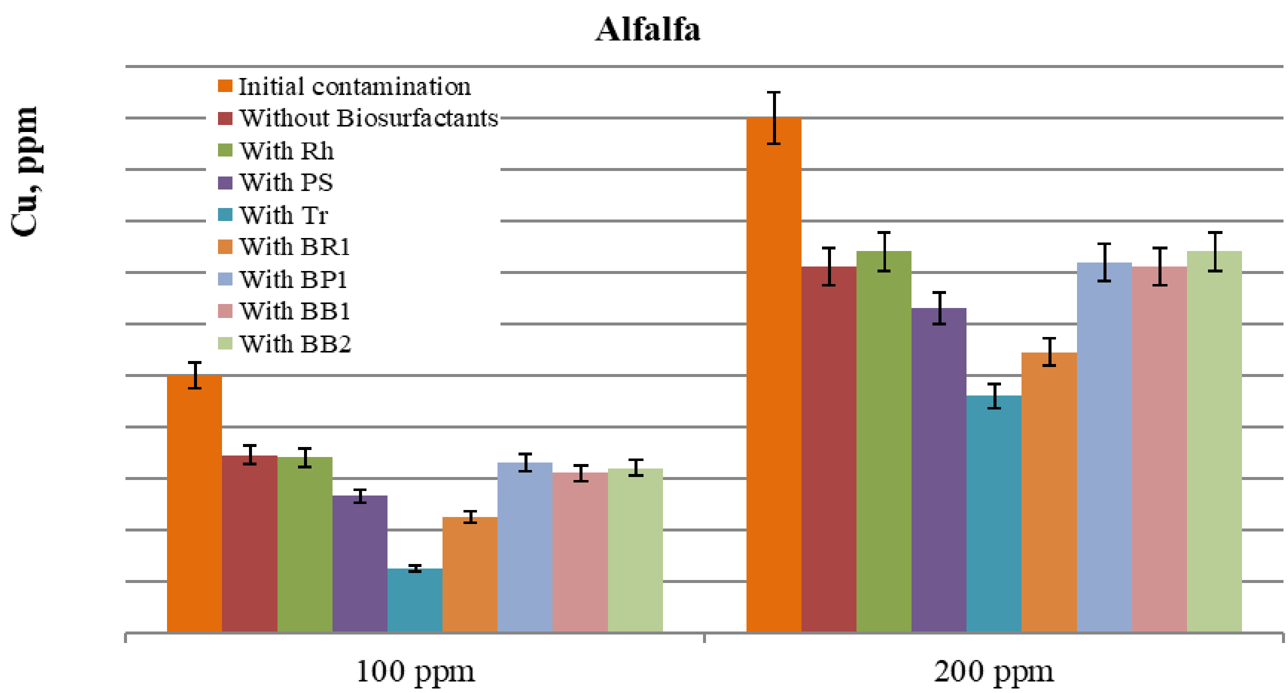

Fig. 1. The absorption of copper(II) ions from hydroponic media by alfalfa seedlings and the influence of different preparation on this process. Preparations: Rh – Rhamnolipids; PS – Rhamnolipid biocomplex PS; Tr – Trehalose lipids; BR1 – complex of biosurfactants produced by strain of Rhodococcus sp. 50; BP1 – complex of biosurfactants produced by strain of Pseudomonas sp. 6R67; BB1 – complex of biosurfactants produced by strain of Bacillus sp. 3Zu9; BB2 – complex of biosurfactants produced by strain of Baccilus spp. Initial concentration of Cu2+ – 100 and 200 ppm; concentration of preparations – 0.01%; duration of experiment – 7 days.

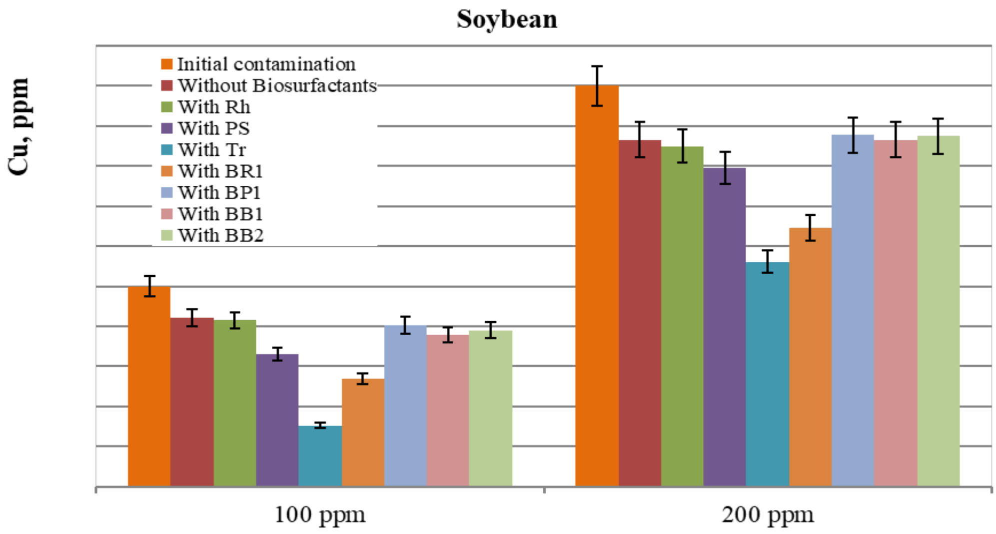

Fig. 2. The absorption of copper(II) ions from hydroponic media by soybean seedlings and the influence of different preparation on this process. Preparations: Rh – Rhamnolipids; PS – Rhamnolipid biocomplex PS; Tr – Trehalose lipids; BR1 – complex of biosurfactants produced by strain of Rhodococcus sp. 50; BP1 – complex of biosurfactants produced by strain of Pseudomonas sp. 6R67; BB1 – complex of biosurfactants produced by strain of Bacillus sp. 3Zu9; BB2 – complex of biosurfactants produced by strain of Baccilus spp. Initial concentration of Cu2+ – 100 and 200 ppm; concentration of preparations – 0.01%; duration of experiment – 7 days.

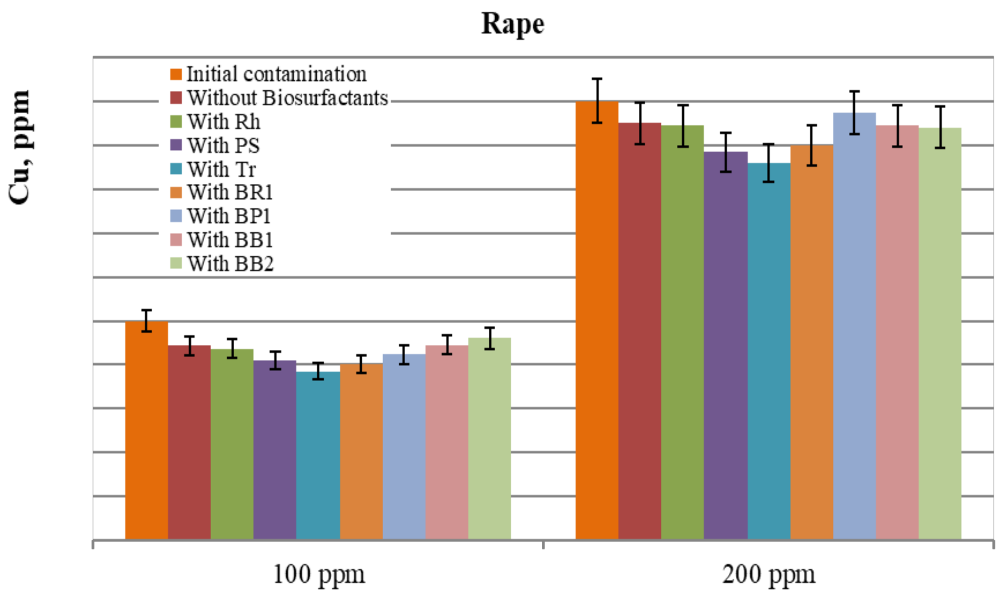

Fig. 3. The absorption of copper(II) ions from hydroponic media by rape seedlings and the influence of different preparation on this process. Preparations: Rh – Rhamnolipids; PS – Rhamnolipid biocomplex PS; Tr – Trehalose lipids; BR1 – complex of biosurfactants p roduced by strain of Rhodococcus sp. 50; BP1 – complex of biosurfactants produced by strain of Pseudomonas sp. 6R67; BB1 – complex of biosurfactants produced by strain of Bacillus sp. 3Zu9; BB2 – complex of biosurfactants produced by strain of Baccilus spp. Initial concentration of Cu2+ – 100 and 200 ppm; concentration of preparations – 0.01%; duration of experiment – 7 days.

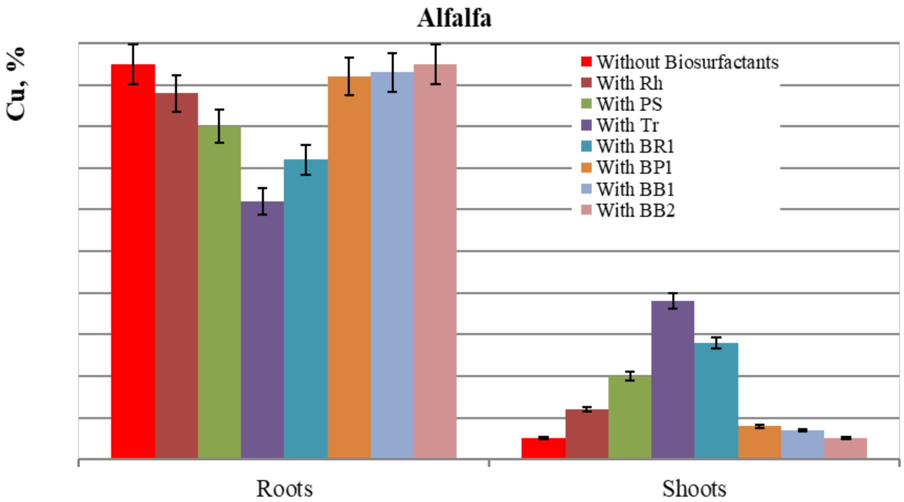

Fig. 4. The distribution of absorbed from hydroponic media copper(II) ions between roots and shoots of alfalfa seedlings and the influence of different preparations on this process. Preparations: Rh – Rhamnolipids; PS – Rhamnolipid biocomplex PS; Tr – Trehalose lipids; BR1 – complex of biosurfactants produced by strain of Rhodococcus sp. 50; BP1 – complex of biosurfactants produced by strain of Pseudomonas sp. 6R67; BB1 – complex of biosurfactants produced by strain of Bacillus sp. 3Zu9; BB2 – complex of biosurfactants produced by strain of Baccilus spp. Initial concentration of Cu2+ – 100 and 200 ppm; concentration of preparations – 0.01%; duration of experiment – 7 days.

The obtained results show that after penetration in plants, copper(II) ions are located mainly in the roots of the plant. Among the tested plants, alfalfa revealed the highest ability to uptake copper(II) ions (coefficient of bioaccumulation equals 78 mg per kg of dry biomass). After alfalfa, came soybean (64 mg/kg) and rape (37 mg/kg).

Trehalose lipids sharply increase the process of translocation of copper(II) ions in the upper parts of plants, but in case of high concentrations of copper (100 and 200 ppm), so much quantity of heavy metal penetrates into plants that it becomes lethal to them. In case of using rhamnolipid biocomplex PS similar results are observed only at 200 ppm concentration of copper(II) ions. In case of biopreparation BP1 the increasing of uptake of copper(II) ions and intensification of their translocation in upper parts of plants is observed. Other 4 preparations do not affect absorption of copper(II) ions by plants and their translocation.

The optimal concentration of tested biosurfactants equals 0.1 g/l.

The model remediation experiments in laboratory and greenhouse conditions for cleaning of soils artificially contaminated with heavy metals (copper(II) ions) have been carried out.

The model experiments were carried out according to the following scheme:

1. The soil samples were dried, sieved and artificially contaminated with different concentrations of heavy metals (50 and 200 ppm according to content of metal ions in dried mass of soil). Heavy metals were added on soil in the form of copper(II) acetate water solution.

2. The plants (soybeen and alfalfa) were sowed in separate samples of soil.

3. For intensification of copper phytoextraction, after 3 weeks from the beginning of experiments, the following preparations were added to soil samples (concentration 0.1 g/l) as metal chelating agents:

a. Rhamnolipid biocomplex PS

b. Trehalose lipids

c. Biopreparation BP1 (complex of biosurfactants produced by strain of Pseudomonas sp. 6R67)

d. EDTA (for comparison of biopreparations effects with chemical chelating agent)

The model experiments were carried out during 30 days at greenhouse conditions (temperature 22-27°C). On 10th, 20th and 30th days of experiment the content of copper in soil samples was measured. After finishing the experiments, copper contents were measured also in plant seedlings (separately in roots and upper parts) (Table).

Table. *Concentration of copper(II) ions in soil during remediatin experiments by using alfalfa and different chelating agents. Initial concentration of copper(II) ions was equaled 50 ppm*

Chelating agent	Concentration of copper(II) ions in soil, ppm				Concentration of copper(II) ions in dried plant organs, ppm	
	Initial	After 10 days	After 20 days	After 30 days	In roots	In shoots
Control[1]	50	44	35	27	21	n.d.[2]
PS[3]		37	30	24	18	7
Tr[4]		18	15	12	11	16
BP1[5]		42	37	32	12	5
EDTA[6]		6	3	1	5	42

[1] – without chelating agents
[2] – n.d. – not detected
[3] – PS – Rhamnolipid biocomplex PS
[4] – Tr – Trehalose lipids
[5] – BP1 – complex of biosurfactants produced by strain of Pseudomonas sp. 6R67
[6] – EDTA – Ethylenediaminetetraacetic acid

As it seen from obtained results, using plants as phytoextractors without chelating agents has less effectiveness in case of contamination of soil with copper(II). Chelating agents increase the effectiveness of cleaning the soil from heavy metals significantly (2-3 times). The effectiveness of tested preparations for their application for enhancing of copper phytoextraction increases in the following order:

Biopreparation BP1 < Rhamnolipid biocomplex PS < Trehalose lipids < EDTA.

It is worth noting that tested biopreparations are much less effective than chemical chelating agent EDTA.

Alfalfa with biopreparation of trehalose lipids are the most effective tools for cleaning soils contaminated with copper(II) ions. In this case 75% removing of heavy metal from soil is achieved, and main part of removed copper(II) ions (approximately 60%) is translocated in upper ground parts of alfalfa.

Conclusion

The obtained results allow drawing following conclusions:

- Among the tested plants, alfalfa revealed the highest ability to uptake copper(II) ions (coefficient of bioaccumulation equals 78 mg per kg of dry biomass).
- Rhamnolipids and trehalose lipids increase the phytoextraction effectiveness of copper(II) ions significantly (2-3 times).
- Alfalfa with trehalose lipids are usable for cleaning soils contaminated with copper(II) ions, because effective phytoextraction of heavy metal from soil is achieved, and main part of removed copper(II) ions is translocated in upper ground parts of plant.

Acknowledgment

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References

[1] F. Korte, M. Behadir, W. Klein, J.P. Lay, H. Parlar, I. Scheunert, Lehrbuch der okologischen chemie. Grundlagen and Konzepte fur die Okologische Beureilung von Chemikalien. Suttgart, Georg Thieme Verlag, 1992.

[2] C.C. Lai, Y.C. Huang, Y.H. Wei, J.S. Chang, Biosurfactant-enhanced removal of total petroleum hydrocarbons from contaminated soil. Journal of Hazardous Materials, 167 (1–3) (2009) 609–614.

[3] E.L. Arthur, J.R. Coats. Phytoremediation, in: P. Kearney, T. Roberts (Eds.) Pesticide Remediation in Soils and Water, Wiley, Washington, DC, 1998, pp. 251-281.

[4] D.E. Salt, M. Blaylock, P.B.A. Nanda Kumar, V.P. Dushenkov, B.D. Ensley, I. Chet, I. Raskin. Phytoremediation: a novel strategy for the environment using plants, Biotechnology, 13 (1998) 468-474.

[5] D.T. Tsao, Phytoremediation. Advances in biochemical engineering and biotechnology, Springer, Berlin, Heidelberg, New York, 2003.

[6] G. Kvesitadze, G. Khatisashvili, T. Sadunishvili, J.J. Ramsden, Biochemical Mechanisms of Detoxification in Higher Plants. Basis of Phytoremediation, Springer, Berlin, Heidelberg, New York, 2006.

[7] A.J. Das, S. Lal, R. Kumar, C. Verma, Bacterial biosurfactants can be an ecofriendly and advanced technology for remediation of heavy metals and co-contaminated soil, Intern. J. Environ. Sci. Technol. 14 (2017) 1343–135

[8] E.V. Karpenko, T.Ya. Pokin'broda, R.G. Makitra, E.Ya. Pal'chikova, Optimal Methods of Isolation of Biogenic Ramnolipid Surfactants, Zhurnal Obshchei Khimii, 79 (2009) 2637–2640

[9] O. Karpenko, M. Prystay, B. Datsko, G. Gafijchuk, T. Nogyna, Optimization of biosynthesis of surfactants and exopolysaccharides by strain Gordonia rubripertincta UKM AC-122 by mathematical methods. Biotechnology (Ukrainian), 4 (2009) 39-44.

[10] O.V. Karpenko, M.V. Prystay, R.G. Makytra, O.Y. Palchykova, Optimization for isolation of surface-active compounds synthesized by bacteria of the genus Rhodococcus. Naukovi praci DNTU, Chem. Chem. Technol, 17 (2011) 124-128.

[11] V. Yerokhin, O. Karpenko, E. Karpenko. Optimization of Parameters of Biosynthesis of Surface-Active Rhamnolipids by the Strain Pseudomonas sp. PS-17 in the Bioreactor with Injection-Vortex Aeration System, Journal of Microbiology Research, 4 (2014) 1-5.

[12] B. Kumar, H.B. Singh, M.Katyal, R.L. Sharma, Spectrophotometric and derivative spectrophotometric determination of copper(II) with dithizone in aqueous phase. Microchimica Acta, 105 (1991) 79-87.

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Major Agricultural Crops in the XVI Century Samtskhe-Javakheti

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A B S T R A C T

The paper represents a study of the XVI century historical document, known as the 'The Great Defter of Gurcistan Vilayet' and shows the agricultural image of the time. The document contains data describing Samtskhe-Javakheti region, which is located in the southern part of Georgia and unites six administrative municipalities. Above, mentioned historical source contains the information about the population, settlements, agricultural crops and taxes imposed on them. The paper focuses on the rye, millet, broad bean, cicer and lentil crops, which were widespread in described area, in the second half of the XVI century, but disappeared later. Research included land-use mapping, also creation of databases. The work also shows the results of the analysis of agricultural censuses from XX and XXI centuries, which revealed the major factors of disappearance of the crops.

Keywords: Retrospective cartography, Crops, Landscape change, Agricultural crops, Samtskhe- Javakheti, Georgia.

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Introduction

A crop diversity is a foundation for agricultural development of a country. To study and understand the traditional agricultural crops is strategically important to the states similar to Georgia. The existence of such crops in the area is an indicator of ancient traditions, maintenance and development of which can contribute to the food security and strengthening of agricultural sector. This can lead to the economic stability and empowerment of communities.

The officials of the Ottoman Empire prepared 'The Great Defter of Gurcistan Vilayet'in order to spread the influence over the territory of Georgia, and resulting from the developed political processes several historical regions of Georgia got under its command [1, 2]. The tax system of the Ottoman Empire itself implied the census and assessment of subjugated territories aimed to the tax collection. The imposed taxes entailed human custom duties (the military service of the Ottoman Empire) and a chief rent [1, 3, 4]. made in natural form, similar to the monetary one. The main concern of the Empire was to get the taxes. The way the goal would be reached did not matter. The region of Samtskhe-Javakheti was well developed from an agricultural standpoint. The tax data presented in 'The Great Defter of Gurcistan Vilayet' is the source that confirms the distribution of agricultural crops. The cereal crops are still in majority [5, 6]; The substantial part has disappeared from agricultural crops. In particular, this fact refers to millet and rye crops, as well as the legumes. Among the bean family, broad beans, lentil and cicer crops were traditional here and played quite an important role in the regional agriculture over the past centuries, however today a kidney bean replaced the other legumes.

By means of the historical materials, we have tried to study and assess the crops spread in the region and their state several centuries ago. Based on the available basic sources (The Great Defter of Gurcistan Vilayet, results of 1923, 2002, 2014 agricultural inventories), we have assessed the distribution of the mentioned crops in the region and changes in the course of several centuries.

Objectives and methods

The 'Gurcistan vilayet' included the territory of modern Samtskhe-Javakheti, Kvabliani gorge adjacent to it and was extended to the territory of present-day Turkey, where it included the surroundings of Chrdili (Childir) lake, the Potskhovi River valley, as well as the upper part of Mtkvari River flowing through the Artaani plateau and the upper part of Oltisi River. Our research covers the part of the 'vilayet', which is in the limits of the modern Georgia that corresponds to the military-administrative unit of the present-day Samtskhe-Javakheti. The region under the study (Fig. 1.) includes six administrative units – Borjomi, Akhaltsikhe, Adigeni, Aspindza, Akhalkalaki and Ninotsminda municipalities [7]. The area of the region is 6412.8km2 [6]. Its population is 160, 5 thousand people [8]. The Didi Abuli Mountain (3301m) at the Samsari ridge is its highest point. The region is mountainous, with alternation of hollows, volcanic canyons, tablelands and mountain ranges. Here are represented Akhaltsikhe (Samtskhe) structural basin, the Lesser Caucasus mountain system, in a form of Arsiani, Adjara-Imereti and Trialeti ridges and volcanic highlands in form of Javakheti, Borjomi-Thori-Tsikhisjvari plateaus and Erusheti highland, as well as in form of Samsari and Javakheti ridges situated between volcanic plateaus, which borders with the region under study from the east. The regional climate transforms from moderate chilly subtropical one into a cold and the dry subtropical climate of mountain hollows, dry climate of mountain tablelands and cold climate of high mountains [9]. The amount of precipitation at the Javakheti tableland is within 500-600 mm, which is roughly similar within the limits of the hollow, while on the slopes of Trialeti, Arsiani and Adjara-Imereti ridges it increases and reaches the maximum of 1400-1500 mm in its upper part, approximately at 2200-2500 m height.

We have used the following materials to execute this work: 'The Great Defter of Gurcistan Vilayet', historical sources of the XVI-XX centuries, 1897 and 1923 census documents, as well as the results of a newest census in the form of the 2014 Geostat materials. As for cartographic documents, we made use of the map compiled by Jikia and Aslanikashvili in 1953, and large-scale 1:50000, 1:25000 maps and satellite images. In order to execute the work, we have used the method of retrospective mapping, the historiographic analysis and the statistical analysis, that assisted us in the manifestation of the situation revealed resulting from the processing of available archive documents and other sources.

The time interval of statistical materials is quite large. The numbers given in 'The Great Defter of Gurcistan Vilayet' providing us with information about what tax was imposed on different settlements; the equivalent of the chief rent was also calculated in kind, measured in weight and volume (so-called Qila), which slightly differed from each other in weight in case of various crops [1].

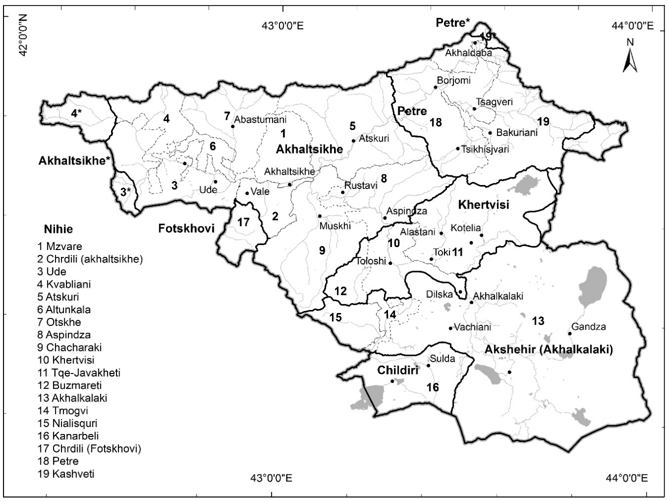

Fig. 1. *Map of the study area.*

The following materials were used as a basis of the map: large-scale 1:50000, 1:25000 maps and satellite images., By means of GIS-technology, we have selected the satellite images a zone of arable lands, which are suitable for agricultural crops, taking into account soils, slope inclinations, aspect and altitude above the sea level. We have composed GIS-layers of arable lands and perennial plantings, i.e. a zone, where the mentioned crops were cultivated.

The expedition method envisaged the visual study of land fund, directly in the field (on-site) and current state assessment. Field works foresaw an intensification of agricultural crop distribution area, and their verification with the outlines drawn from satellite images. We conducted GEO-information map compilation and analysis afterwards, when the tables calculated using Excel and reflecting the quantity of agricultural crops under study, sorted according the rural settlements, were transferred to GIS databases. The extrapolation was made for each settlement, according to arable lands. Thus, we got the map of the distribution of the above-mentioned crops for the second part of the XVI century, based on which we can conduct a comparative analysis and figure out what changes have happened during this time period and what trends exist as of today.

Results

Rye crop is still rare and occasionally found in Georgia. In the second part of the XVI century, the rye plantings were widely spread in the whole region under study. The five main areas of their concentration were identified, resulting from the mapping (Fig. 2.): 1. Samtskhe structural basin; 2. Uraveli gorge and Greli-Uraveli-Sakhudabeli band; 3. Javakheti highland; 4. Mtkvari valley from Aspindza to the south, in the Tolerta-Erkota-Atskvita band; 5. Niali fields, Buzmareti basin and its adjacent settlements, and according to administrative units of that time two peaks of their concentration are clear: Chacharaki district (Nihie) in Akhaltsikhe Liva (Sanjak) and Akhalkalaki district in the Liva (Sanjak) having the same name.

In total, the rye harvest was equal to 2356.96 tons, rye was sowed in 400 locations, other settlements were deprived of its plantings, including all those settlements, information on which is scarce. The zone of mentioned crops occupied far more areas than those where its actual plantings are distributed (Fig. 2.). Rye plantings occupy more than half of inhabited localities. However, today the plantings are available in singular experimental farms only.

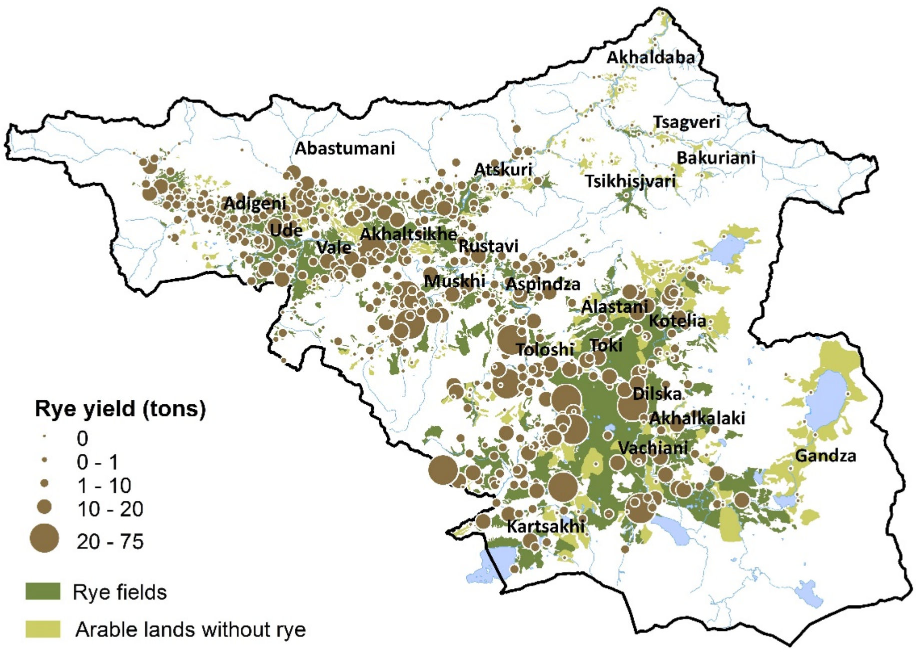

Fig. 2. *Rye plantings in Samtskhe-Javakheti in the second half of the XVI century.*

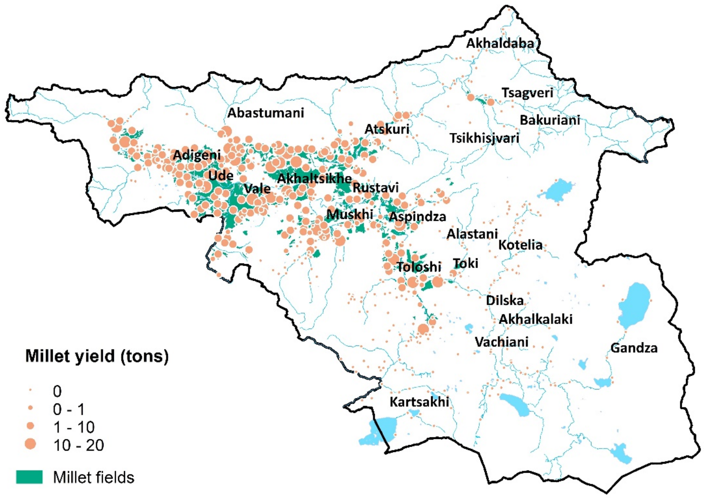

Fig. 3. *Millet plantings in the second halfof the XVI century.*

Millet plantings in the XVI century occupied far less areas, than in case of rye, since the millet was not the main food crop, as a wheat and barley. Its plantings ended at the approximately, 1500-1600 meters height above the sea level, which on one hand can be referred to its less productivity in highest belts, or else there could be another reason, e.g. that other crops were prioritized at the Javakheti plateau and Niala-Buzmareti volcanic fields, since it is not considered to be the best zone for millet plantings (Fig. 3.). The distinct concentration of their plantings in the millet distribution area is observed in the Samtskhe hollow; a relatively small area of its concentration is represented by Uraveli gorge. They are also concentrated on the Uraveli-Anda-Tskordza section and in the Aspindza-Saro-Nijgori-Toloshi band, from Tmogvi village to Nakalakevi. In total, 857.89 tons were harvested. The millet was sowed with 236 locations, other settlements were deprived of its plantings, including all settlements, information on which is scarce, since these villages were depopulated and their prescribed taxes, similar to rye plantings, are reflected in total monetary (Akce). The millet crop occupied a substantial sector in a third part of settlements identified in the area.

The millet plantings are concentrated in Udi, Mzvare and Chacharaki districts, while in the number of regions (Akhalkalaki, Tke-Javakheti, Kanarbeli, Nialiskuri, Kashveti, Kvabliani) its plantings are almost unavailable; The Kvabliani district is almost depopulated. The Kanarbeli, Nialiskuri, Akhalkalai and Tke-Javakheti districts avoided their sowing due to chilly climate, since in the Buzmareti district available settlements are almost in the same climate and edaphic conditions, as those of Nialiskuri and Kanarbeli. Millet plantings in small quantities were available there.

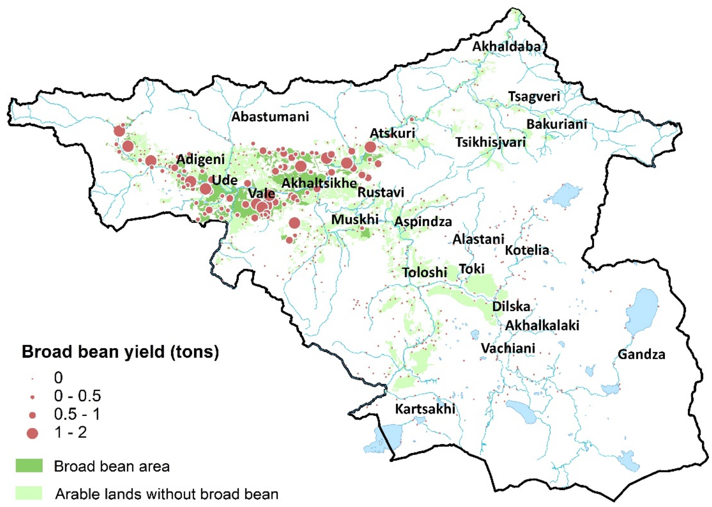

Fig. 4. *Broad bean plantings in the second part of the XVI century.*

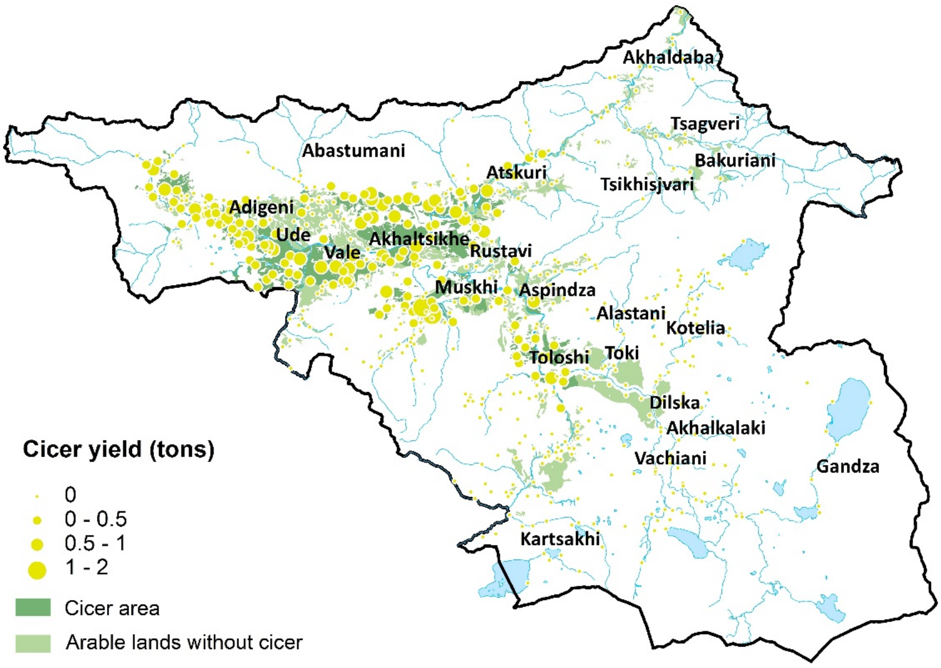

Fig. 5. *Cicer plantings in the second part of the XVI century.*

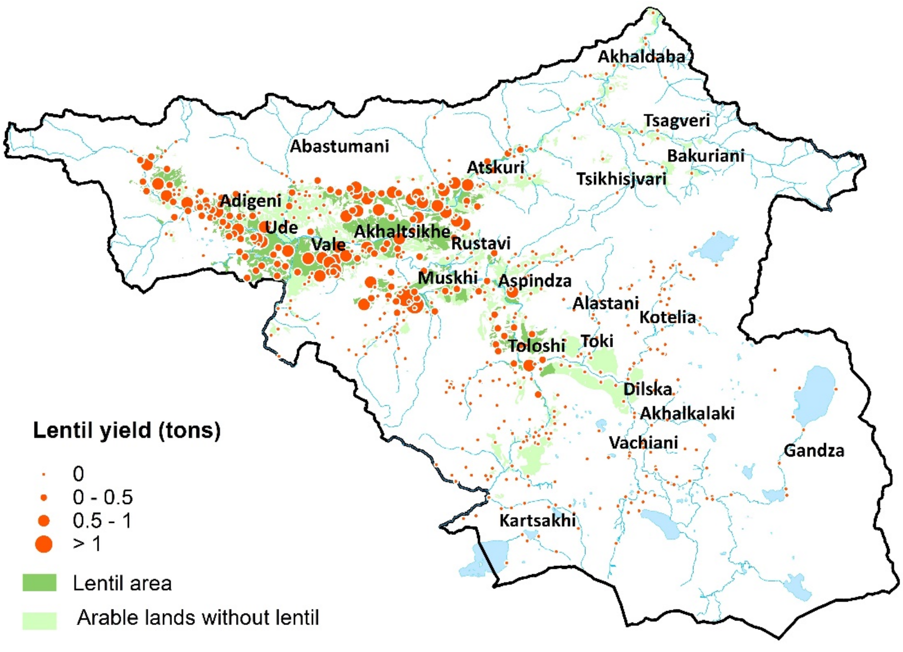

Fig. 6. *Lentil plantings in the second part of the XVI century.*

Broad bean (Fig. 4.) and cicer (Fig. 5.) plantings almost repeat the same zone, and their basic area coincides with each other as well as lentil (Fig. 6.) plantings repeat the distribution limits of other legume crops. The major part of them are, again, concentrated on the Samtskhe structural basin and in case of all three crops their harvest is getting smaller from the west of the hollow to its east. A top yield was obtained in Use district; the slightly less harvest is peculiar to Mzvare, Atskuri and Chacharaki districts; but the latter substantially lags behind other districts by broad bean plantings.

Table 1. *Administrative units entering into 'Gurcistan vilayet' at the present-day territory of Samtskhe-Javakheti and agricultural crops vanished today, as of the second part of the XVI century.*

Administrative units	Agricultural crops	Number of settlements with crops	Yield, Tons
Akhaltsikhe Liva			
Mzvare Nihie	Rye	18	97.9
	Millet	18	100.76
	Broad-bean	18	7.650
	Lentil	18	6.757,5
	Cicer	18	7.778
Chrdili (In Akhaltsikhe Liva)	Rye	22	113.52
	Millet	21	89.76
	Broad-bean	21	11.985
	Lentil	21	9.053
	Cicer	21	6.630
Ude	Rye	51	215.93
	Millet	51	171.27
	Broad-bean	39	16.575
	Lentil	50	15.81
	Cicer	50	13.388
Kvabliani	Rye	6	11.55
	Millet	1	2.2
	Broad-bean	0	0
	Lentil	1	0.765
	Cicer	1	0.255
Otskhe	Rye	18	113.3
	Millet	18	83.93
	Broad-bean	1	0.383
	Lentil	2	0.638
	Cicer	2	0.638
Atsk'uri	Rye	38	156.42
	Millet	26	77
	Broad-bean	14	8.16
	Lentil	21	9.18
	Cicer	21	7.65
Altunkala (Okrotsikhe)	Rye	14	87.45
	Millet	13	64.02
	Broad-bean	2	0.893
	Lentil	4	1.53
	Cicer	4	1.403
	Rye	35	147.18

Aspindza	Millet	25	45.98
	Broad-bean	1	0.255
	Lentil	7	2168
	Cicer	7	1785
Ch'ach'araki	Rye	40	326.15
	Millet	24	106.15
	Broad-bean	0	0
	Lentil	16	6.12
	Cicer	16	5.865
Total, in Akhaltsikhe Liva	Rye	242	1269.4
	Millet	197	741.07
	Broad-bean	96	45.9
	Lentil	140	52.02
	Cicer	140	45.392
Khertvisi Liva			
Khertvisi	Rye	29	242.11
	Millet	22	68.97
	Broad-bean	0	0
	Lentil	13	4.208
	Cicer	13	4.208
Tqe-Javakheti	Rye	35	226.6
	Millet	0	0
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Buzmareti	Rye	8	51.15
	Millet	0	0
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Total, in Khertvisi Liva	Rye	72	519.86
	Millet	22	68.97
	Broad-bean	0	0
	Lentil	13	4.208
	Cicer	13	4.208
Akshehir (Akhalkalaki) Liva			
Akshehir (Akhalkalaki)	Rye	43	355.3
	Millet	0	0
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Tmogvi	Rye	10	72.05
	Millet	2	12.1
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Nialisquri	Rye	15(5 Outside of Georgia)	96.8 (42.45 Outside of Georgia)
	Millet	0	0
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0

Total, in Akhalkalaki Liva	Rye	68	469.8
	Millet	2	12.1
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Childiri Liva			
Kanarbeli	Rye	15 (7 Outside of Georgia)	94.05 (37.95 Outside of Georgia)
	Millet	0	0
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Total, in Childiri Liva	Rye	15 (7 Outside of Georgia)	94.05 (37.95 Outside of Georgia)
	Millet	0	0
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Fotskhovi Liva			
Chrdili (In Fotskhovi Liva)	Rye	3 (9 Outside of Georgia)	3.85 (10.45 Outside of Georgia)
	Millet	12 (7 Outside of Georgia)	30.25 (27.5 Outside of Georgia)
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Total, in Fotskhovi Liva	Rye	3 (9 Outside of Georgia)	3.85 (10.45 Outside of Georgia)
	Millet	12 (7 Outside of Georgia)	30.25 (27.5 Outside of Georgia)
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Petre liva			
Petre	Rye	0	0
	Millet	2	5.5
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Kashveti	Rye	0	0
	Millet	1	2.75
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Total, in Petre Liva	Rye	0	0
	Millet	3	8.25
	Broad-bean	0	0
	Lentil	0	0
	Cicer	0	0
Total, in Region	Rye	400	2356.96
	Millet	236	857.89
	Broad-bean	96	45.901
	Lentil	153	56.23
	Cicer	153	49.6

The role and importance of the mentioned crops was high in the past, which was a good precondition for agriculture diversification and for a new introduction of a variety of crops (Table 1). In case, we compare the state of agricultural crops described in the 'Defter' with the current state, the change is obvious. It was interesting to figure out, what was the crucial moment, when the society stopped cultivating them. Was this fact related to any natural (climate, edaphic) or human factors?

According to the census conducted in 1923 (Table 2, 3), rye crop was still intensely cultivated in both Samtskhe structural basin and Javakheti plateau. The area under crops is small in Borjomi gorge. However, the reasons are different, from the present-day territory of Borjomi municipality is heavily devastated in the Defter, which cannot be said about the data of the 1923 census. The lack of arable lands, on one hand, and the functional change of this territory by the early XX century related to its use for recreation and health-

Table 2. *Agricultural plantings registered according to 1923 census [10]*

Mazra (administrative	N N	Community	Agriculture				
			Rye (ha)	Millet (ha)	Broad bean (ha)	Lentil (ha)	Cicer (ha)
Akhalkalaki	1	Alastani	108.56	0	1.853	0	0
	2	Baraleti	614.65	0	13.298	0.327	8.066
	3	Gorelovo	0	0	0	0	0
	4	Dilska	104.64	0	0	0	0
	5	Eshtia	5.886	0	0	0	0
	6	Kondura	85.238	0	0	0	0
	7	Kulikami	59.623	0	0	0	0
	8	Okami	251.57	0	0	0	0
	9	Sathkhe	26.596	0	0	0	0
	10	Khertvisi	105.95	0	0	0	0
		All	1362.7	0	15.151	0.327	8.066
Akhaltsikhe	1	Adigeni	32.373	2.507	0	0	0
	2	Ats'kuri	15.696	0.327	0	0	0
	3	Vale	86.219	0.327	0	0.109	0
	4	Varkhani	9.701	2.071	0	0	0
	5	Idumala	10.355	0.654	0	0	0
	6	Klde	1.635	0	0	0	0
	7	Lepisi	59.296	0	0	0	0
	8	Ude	14.933	1.308	0	0	0
	9	Uraveli	65.182	0	0	0	0
		All	295.39	7.194	0	0.109	0
Gori (Communities according of 'Gurjistan Villaiet' territory)	4	Akhaldaba	0	0	0	0	0
	7	Bakuriani	0	0	0	0	0
	8	Borjomi	0	1.962	0	0	0
	11	Gujareti	0	0	0	0	0
	12	Dviri	0	0	0	0	0
	32	Kvishkheti	0	0.327	0	0	0
	36	Tsagveri	1.09	0	0	0	0
		All	1.09	2.289	0	0	0
Total			1659.1	9.48	15.15	0.44	8.07

promoting purposes, on the other, are probable reasons for this fact. This region became the resort center of Romanovs' imperial family, and, respectively, the crops that took hold in the Russian Empire with high intensity (corn, potato) that was more rapidly distributed there. Distribution of potato has begun after 1840 and is chronologically related to the migration of different people groups of the Russian Empire (Dukhobors, Ukrainian, Polish and German migrants). The widespread replacement of local, traditional crops with the higher yielding and easy cultivated crops became a precondition for the encouragement towards the development of one-crop (monoculture) system in the Soviet Union and a major part of Javakheti was covered with potato plantings. Similar to the rye, the millet crop was of frequent occurrence in the Akhaltsikhe structural basin. The difference is that it had already been vanished from the Khertvisi community for this period. Roughly, the same took place regarding the lands of Borjomi Municipality.

Table 3. *The productivity of agricultural crops (in tons) registered according to the 1923 census [10]*

Mazra (administrative	N N	Community	Agriculture				
			Rye (ha)	Millet (ha)	Broad bean (ha)	Lentil (ha)	Cicer (ha)
Akhalkalaki	1	Alastani	271.41	0	3.706	0	0
	2	Baraleti	1536.62	0	26.596	0.654	16.132
	3	Gorelovo	0	0	0	0	0
	4	Dilska	261.6	0	0	0	0
	5	Eshtia	14.715	0	0	0	0
	6	Kondura	213.095	0	0	0	0
	7	Kulikami	149.057	0	0	0	0
	8	Okami	628.93	0	0	0	0
	9	Sathkhe	66.49	0	0	0	0
	10	Khertvisi	264.87	0	0	0	0
		All	3406.79	0	30.302	0.654	16.132
Akhaltsikhe	1	Adigeni	80.9325	6.2675	0	0	0
	2	Ats'kuri	39.24	0.8175	0	0	0
	3	Vale	215.547	0.8175	0	0.218	0
	4	Varkhani	24.2525	5.1775	0	0	0
	5	Idumala	25.8875	1.635	0	0	0
	6	Klde	4.0875	0	0	0	0
	7	Lepisi	148.24	0	0	0	0
	8	Ude	37.3325	3.27	0	0	0
	9	Uraveli	162.955	0	0	0	0
		All	738.475	17.985	0	0.218	0
Gori (Communities according of 'Gurjistan Villaiet' territory)	4	Akhaldaba	0	0	0	0	0
	7	Bakuriani	0	0	0	0	0
	8	Borjomi	0	4.905	0	0	0
	11	Gujareti	0	0	0	0	0
	12	Dviri	0	0	0	0	0
	32	Kvishkheti	0	0.8175	0	0	0
	36	Tsagveri	2.725	0	0	0	0
		All	2.725	5.7225	0	0	0
Total			4147.99	23.71	30.3	0.87	16.13

There was a very extensive and centralized agricultural policy of the USSR period. This policy was focused on the receipt of maximally abundant product and therefore the specialization envisaged growing such crops by ‘Kollhozes’ (collective farms) that could give higher yields. The development of this strategy caused the rooting of the crops that could bring higher yields for a specific territorial unit that is why those replaced traditional crops, which were distinguished by high crop yield and at the same time, which were more easily cultivated.

Table 4. *Crop areas for cereals in the middle of the XX century (thousand hectares) [12]*

	Years		
Agricultural crops	1966	1968	1970
Autumn wheat	8.9	7.4	7
Autumn Barley	0.2	0.1	0.2
Spring Barley	19.6	16.3	15.8
Oats	1.1	1.4	2.2
Corn	3	2.4	1.9

In the category of ‘cereals and grain legume crops’ of crop areas the legume crops were in the minority and mainly the kidney bean plantings are meant here, while the rest is occupied by the cereals. However, if we judge by the ensuing table (Table 4): rye and millet crops were no more sowed and, therefore, they had no part in the region everyday life, as agricultural crops [11].

These five agricultural crops had already been totally vanished from the explored region by that time. In addition, this process was developed just in several dozens of years. The crops that have thousand-year traditions disappeared in just dozens of years. The crops, which were successfully cultivated for thousand years, could not disappeared in several dozen years without an outside interference and this process is directly related to the agricultural policy pursued in the mentioned time period.

Conclusion

Based on the research outcomes, we can conclude the following: 1. Today, the presence of annual agricultural crops of the second part of the XVI century, except for cereals, cannot be felt in the region. Among traditionally existing cereal crops, only wheat and barley remain here; legume cultures are completely replaced by kidney beans; 2. The change of rules for the society and such distinct substitution of one agricultural crop by another could not have happened so simply, even due to recommendatory measures. The state-planned economy and collectivization of agriculture of the USSR period envisaged a centralization of farms and region’s focus on a monoculture and planning of agricultural directions. These plans envisaged the receipt of maximally high yields emphasized the species that were aimed at quantitative indices and became a characteristic pattern of Soviet collective farms; 3. This trend caused an invasion of potato and corn crops in the 50-60s of the XX century and enlargement of their plantings at the expense of wheat, barley, rye, and millet plantings, as well. Today we reap the results of the mentioned state-planned economy that are expressed in the reduction of agricultural product diversity that makes up the traditional life and complicates the restoration-preservation of agricultural crops; 4. The comparative analysis conducted for the mentioned period gives us a good opportunity to be guided by the available information, should the local population, farmers and agribusiness sector of the mentioned branch of agriculture be interested in it. Since the traditional local agriculture, its crop species are part of regional traditions and culture, one of the forms of heritage, restoration and renewal of which is an important component of regional development.

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References

[1] M. Svanidze, From the History of Georgian-Ottoman Relations in XVI-XVII Centuries, Metsniereba, Tbilisi, 1971.

[2] Sh. Lomsadze, Samtskhe-Javakheti: from the Middle of XVIII to Middle of XIX Centuries, Metsniereba, Tbilisi, 1975.

[3] S. Jikia, Great Book of Gurjistan Vilaiet, part II, Mnatobi, Tbilisi, 1941.

[4] S. Jikia, Great Book of Gurjistan Vilaiet, part III, Publishig of the Georgian Academy of Sciences of Soviet Republic of Georgia, Tbilisi, 1958.

[5] GEOSTAT. http://geostat.ge/cms/site_images/_files/georgian/census/2002/II%20tomi%20.pdf, 2002 (accessed 2.11.2018).

[6] GEOSTAT. http://census.ge/files/results/agriculture/AG%20Census%20Release_ENG.pdf, 2014 (accessed 2.11.2018).

[7] R. Maisuradze, M. Elizbarashvili, T. Khardziani, M. Tatishvili, Landscapes of Samtskhe-javakheti region, transformation degree and forms, SGEM2018 Conference Proceedings. 18 (2018) 487- 494.

[8] UNFPA. https://georgia.unfpa.org/en/publications/population-dynamics-georgia-factographs, 2018 (accessed 2.11.2018).

[9] N. Beruchashvili, Caucasus: Landscapes, Models, Ecsperiments, Tbilisi State University Press, Tbilisi, 1995.

[10]] Agricultural Census of Georgia (1923), Community sums, 1925 (in Georgian).

[11] FAOSTAT. http://www.fao.org/faostat/en/#data/QC, 2018 (accessed 2.11.2018).

[12] Vakhushti Institute of Geography, Southern economic region of Georgia, Metsniereba, Tbilisi, 1978.