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Circular Mining Wastes Management for Sustainable Production of *Camellia sinensis* (L.) O. Kuntze

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Abstract: Mining operations have a significant negative impact on the surrounding ecosystems. The operation of mines and quarries creates a large amount of waste that accumulate and are practically unrecyclable in the environment. The involvement of these wastes in economic activity is an extremely urgent task. This can make the economy more sustainable and reduce its influence on ecosystems. This work presents the attempts of using quarry wastes as a fertilizer applied for growing tea crops. The novelty of this research involves revealing the quarry wastes as a fertilizer when growing *Camellia sinensis* (L.) O. Kuntze and assessing changes in the productivity of this plant when applying these calcium wastes. The waste of a quarry intended for extracting crushed stone was studied in this article. The composition of the waste was analyzed. Fertilizers used for manuring the soil were prepared based on the waste. Two experimental sites were selected. One of them was a control, where *Camellia sinensis* (L.) O. Kuntze was grown without using fertilizers. Fertilizers obtained from the waste were applied on the second site. The experimental work proceeded for 10 years. When discussing the results, special attention was paid to climatic conditions. This was caused by the need to show that it was the use of the fertilizer that influenced the change in the yield, not the climatic conditions. As a result of using calcium fertilizers based on the waste, the productivity of *Camellia sinensis* (L.) O. Kuntze was increased. The application of the fertilizers based on the quarry wastes was shown to provide an increase in the yield. The possibility of using calcium fertilizers to overcome unfavorable agroclimatic conditions during the tea cultivation was also demonstrated. To assess the climatic impact of applying new fertilizers, three-dimensional modeling in the "gnuplot v.5.4" software was used. As a result, an increase in the average annual precipitation, from 1000 to 1980 mm/year, in the range of the average annual air temperature, from 14 to 16 °C, was found to lead to an increase (when using a new fertilizer) in the yield of *Camellia sinensis* (L.) O. Kuntze up to 4.8 times (from 20 to 95 centner/ha). The results have shown that applying fertilizers based on the quarry wastes is also possible in unfavorable climatic conditions.

Citation: Malyukova, L.S.; Martyushev, N.V.; Tynchenko, V.V.; Kondratiev, V.V.; Bukhtoyarov, V.V.; Konyukhov, V.Y.; Bashmur, K.A.; Panfilova, T.A.; Brigida, V. Circular Mining Wastes Management for Sustainable Production of *Camellia sinensis* (L.) O. Kuntze. *Sustainability* **2023**, *15*, 11671. https://doi.org/10.3390/su151511671

Academic Editors: Ioannis Mylonas, Fokion Papathanasiou and Elissavet Ninou

Received: 30 June 2023
Revised: 21 July 2023
Accepted: 26 July 2023
Published: 28 July 2023

Keywords: circular economy; sustainable agriculture; mining waste; *Camellia sinensis* (L.) O. Kuntze

1. Introduction

According to the latest data, CO_2 emissions from rivers in the permafrost zone will increase three times over the next 10 years due to climate change [1,2], which can significantly affect life expectancy in certain regions of the world [3]. Differences in the regional policy when constructing the carbon trading market do not always provide a tangible effect of industrial sector decarbonization [4]. Along with the increase in the average annual air temperature, the negative consequences of global climate changes are also manifested in an increased risk of water scarcity, which may exceed USD 2.7 trillion [5]. In subtropical zone conditions of the Caucasus in the last 5 years, a change in the trend of the average annual air temperature towards an increase was traced [6], which deteriorates the growing conditions for crops. In addition, in the spring period (from March to May), climatic factors have been proven to have a dominating effect, causing soil organic carbon growth in the layers of 0–10 cm and 10–30 cm [7]. The temperature of the late rainy season can significantly limit the radial growth of S. superba plantings in the southern rims of the subtropical forests of Southeastern China [8].

The influence of industrial wastes on agriculture. The mining that exploits "brown mining technologies" aggravates the anthropogenic component effect (for example, the influence of landfills of household wastes [9]) on the existing biocenoses [10–12]. The mining of rich ores at shallow depths is replaced by complicated mining conditions, and the transportation of interspersed ores to the extraction is accompanied by an increased consumption of high-tech goods. For example, in the Mufulira River, the presence of the slurry pulp obtained from the Konkola Copper Mines Plc mine tailings led to an increased SO_4^{2}—concentration (1396 mg/L) and dissolved Al (2115 µg/L), Co (909 µg/L), Cu (7405 µg/L), Ni (51.5 µg/L), Pb (161 µg/L), and Zn (346 µg/L), including a decreased pH (2.04). This fact poses a serious threat to agriculture [11]. In the southwest of Spain, a rather long-term extraction of sulfide deposits led to the migration of dissolved and suspended metals and arsenic compounds into surface waters [13]. The authors identified the arsenic concentrations of 80 µg/L As^{3+} and 5 mg/L As^{5+}. At the same time, the concentration of arsenic compounds increases, and the As^{3+}/As^{5+} ratio decreases downstream of the Agua Agria brook (in the Tarsis Mine area). Many authors point to the presence of uneven contamination of the soil and surface waters. For example, in Zambia, the soils in the zone of influence of the Koperbelt mining area (4700 km^2) reflect a significant variability in the geochemical properties of the soils, as well as different contamination degrees (a high proportion of copper in soils equal to 85.5 mg/kg is found even in seemingly uncontaminated areas) [14]. The levels of heavy metals in various fractions of soil particles (>250, 63–250, and <63 microns) of the landscapes in suburban areas of Saudi Arabia are determined by mining (Cd, Cu, Zn, and Pb) [15].

Open-pit mining causes serious damage to land resources and completely transforms the land relief [16]. Land amelioration is mainly aimed at restoring the ecosystem and the value of the land exposed to mining, which is still a difficult task [17]. The results of the high-performance sequencing (using the PIECRUST method) of microbial communities of aluminum quarry soils have shown the efficiency of using yellow rose, lespedeza, and sweet wormwood herb to improve the soil quality [18]. When compared to this fact, spontaneous succession at an abandoned dolomite limestone quarry in Missouri can lead to the emergence of plant communities, including 74 native species (and 21 non-native species), which is close to the species diversity of natural communities [19].

The hydroseeding of *Leguminosae*, *Poaceae*, and *Cyperaceae* is effectively used on the landscapes to reclaim sites and reduce soil erosion in the post-mining period [20]. The increase in the related environmental problems [21–23] actualizes not only the need to develop a green mining strategy [24], green technologies for mineral enrichment [25], involving other sustainable technologies [26] but also a transition to a sustainable use of mineral resources based on circular economy models [27–29]. A circular economy implies the closure of resource flows without forming associated wastes [30–32]. This direction is the dominant tool in developing national strategies used for sustainable development all over the world [33]. The process of zero fluid discharge used for extracting struvite and regenerating the drinking water obtained from wastewater is quite a promising direction when introducing a closed-cycle economy [34]. When forming sustainable agricultural processes, a circular economy is most often used in the context of the life cycle assessment (LCA) theory [35], while waste management issues remain insufficiently studied. Circular waste management is the most efficient method of soil reclamation. In this regard, a rather promising direction in solving the problem of waste is developing the directions for their use in agriculture or closure in the in-house technological cycle. For example, using composted sewage sludge of an organic fertilizer in sugar cane fertilizers increases soil fertility and reduces the need for mineral fertilizers [36]. The wastes obtained from a highly acidic dump in the form of soil substitutes obtain a nutrient medium with the following parameters: (N (0.37–0.51%), P (0.23–0.47%), K (1.78–3.17%), Ca (4.93–8.39%), and Mg (1.16–1.71%)). This allows their use for agricultural purposes [37]. In some cases, for example, using waste drilling mud ($\geq$6%) has a negative effect on the germination of Maize seeds (*Zea mays* L.), which does not yet allow it to be used for sustainable agriculture purposes [38,39]. In another study, the influence of using organic wastes on the physical properties of the soil in arid regions affected by the negative consequences of coal mining was established [40].

One example of involving the calcium wastes obtained from quarries in the production process is adding them to cement [41,42] or the thermochemical modification of granular copper slag [43] for using it as a binder substitute. At the same time, in the regions of the agricultural or recreational-tourist specialization, their use as fertilizers is more productive. Investing in innovations of this kind [44,45] will allow the achievement of the carbon neutrality of individual industries [46], in addition to minimizing the anthropogenic impact.

Meteorological conditions for growing the plants. Tea cultivation in the subtropics of different regions of the world, as a rule, is associated with the risks of yield losses in dry years. In the end, the yield losses in adverse meteorological conditions can be 50–60% or more. According to a number of researchers [47,48], hydrothermal stress leads to the loss of more than 50% of the tea harvest during rain-fed cultivation. For example, in the case of chickpeas or soybeans, drought can pose a serious threat [49–52], causing the need to ensure sustainable agribusiness [53–55]. In this regard, it is interesting to develop the possibility of cleaning ponds for sedimentation tanks followed by their subsequent use in agriculture [56] or to use the synergy of agricultural and energy production [57]. The progressive aridization of the climate actualizes the task of increasing the plants' resistances to drought. In this regard, much attention in the research devoted to the tea culture is paid to studying the mechanisms of its drought resistance, searching for the most informative markers of drought resistance, as well as creating new resistant varieties and the influence of exogenous inducers, including mineral fertilizers. Therefore, the influence of applying the calcined fertilizers on the tea yield is an urgent specific research issue in circular waste management when ensuring sustainable agriculture. This study hypothesis consisted in the fact that the introduction of calcium-containing quarry wastes would increase the tea yield despite the insufficient rainfall.

In this connection, the aim of this study is to assess the productivity of growing *Camellia sinensis* (L.) O. Kuntze in conditions of the cyclic management of calcium wastes.

2. Materials and Methods

2.1. Properties of Calcium-Containing Wastes

The object of research and the source of the calcifying fertilizer is the "Kamensky" quarry, which is located at 43°32′04.5″ N 39°58′59.4″ E (Figure 1). To characterize the chemical composition of the sample material, the gross content of the chemical elements was determined with quantitative methods. They are mass spectrometric and atomic emission analyzers using inductively coupled plasma (ICP-MS and ICP-AES) according to the certified NSAM methodology. The 499-NPP/MS method, "Determination of the elemental composition of rocks, soils and bottom sediments using the atomic emission method, having inductively coupled plasma, and the mass spectral method involving inductively coupled plasma", was used to conduct these studies [58]. The equipment included the inductively coupled plasma mass spectrometer Elan-6100 ("Perkin Elmer", Waltham, MA, USA) and the atomic emission inductively coupled plasma spectrometer Optima-4300 DV ("PerkinElmer", Waltham, MA, USA).

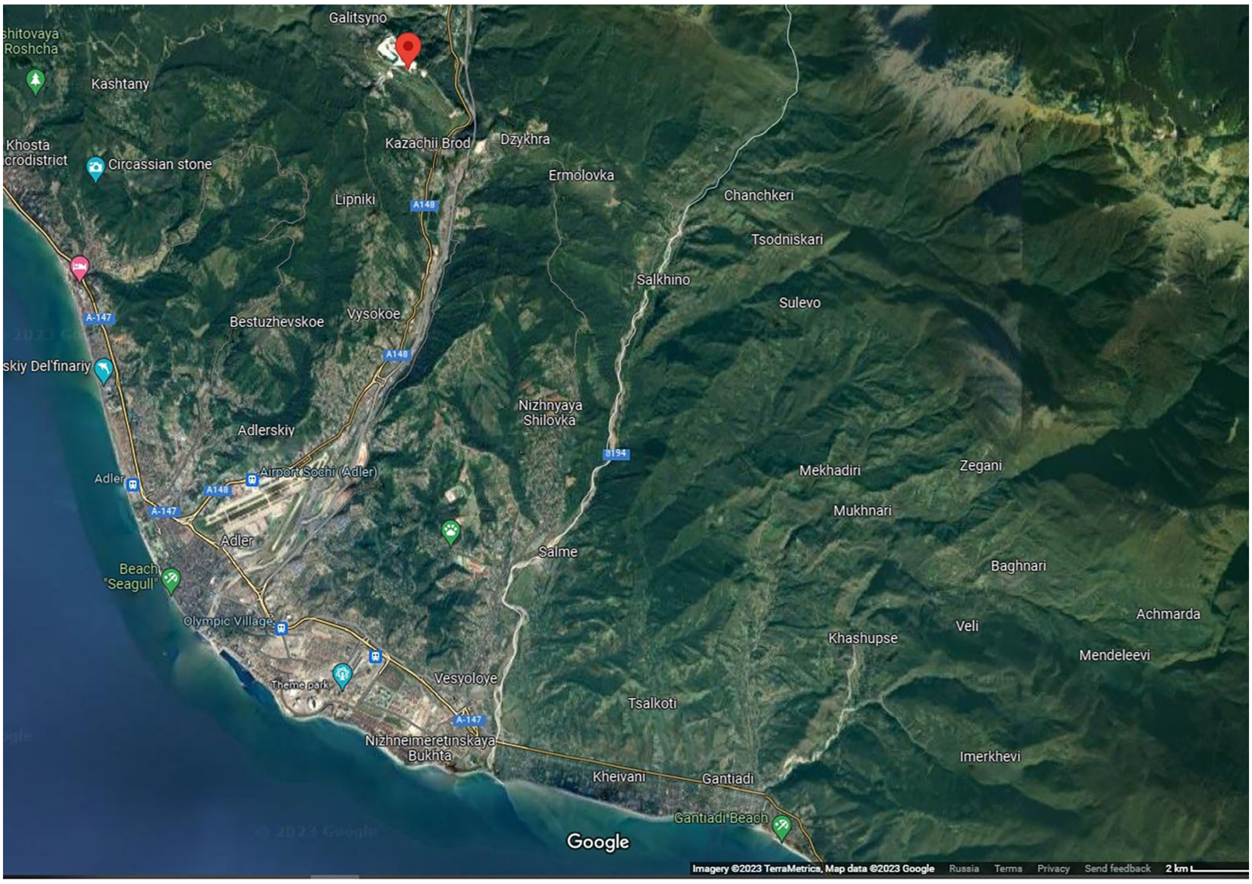


Figure 1. Location of the waste collection (43.534586, 39.983163 Copyright © Google Earth).

Limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) crushed stone are mined at the facility, whose sludge waters flow along the streams into the Mzymta river (Figure 2). The sampling was carried out as follows. During the license revocation period, the facility was examined to determine the oversized tailing at the industrial site where the rock was crushed (Figure 2a). To ensure the sample representativeness, the material was selected once (in three stages). Approximately 2000 kg of the small rocks was filled into bags (45–50 kg each). As a result, 142 bags were filled for the sampling and then transported to the warehouse of the scientific center (FRC SSC RAS). Later, before each application, the packed material was additionally prepared (ground in a laboratory mill) and sieved up to a grinding thickness of 0.25 mm. The material is characterized by a slightly alkaline reaction in water (pH_{H_2O} = 8.2).

(**a**) (**b**)

Figure 2. Functioning "Kamensky" quarry: (**a**)—view of the quarry; (**b**)—its sludge water drains flowing into the Mzymta river (**b**).

The obtained results of the elemental composition of the bulk wastes are presented in Table 1. The data presented in Table 1 are the average values for 10 measurements. The maximum deviation for the content of the elements over 400 µg/g was 6.3%, for the content of the elements within 1–400 µg/g it was 8.7%%, for the content of the elements within 0.1–1 µg/g it was 0.05 µg/g, and for the values less than 0.1 µg/g it was 0.02 µg/g. This substance is characterized by a slightly alkaline reaction of an aqueous suspension (pH is 8.20). It contains calcium in an exchange form (10.9 mmol (eq)/100 g) and a smaller amount of magnesium of 2.2 mmol (eq/100 g). The calcium-containing natural material is the clay-lime waste formed when crushing the limestones into small fractions of the crushed stone.

Table 1. Chemical composition of the Ca-containing mining waste.

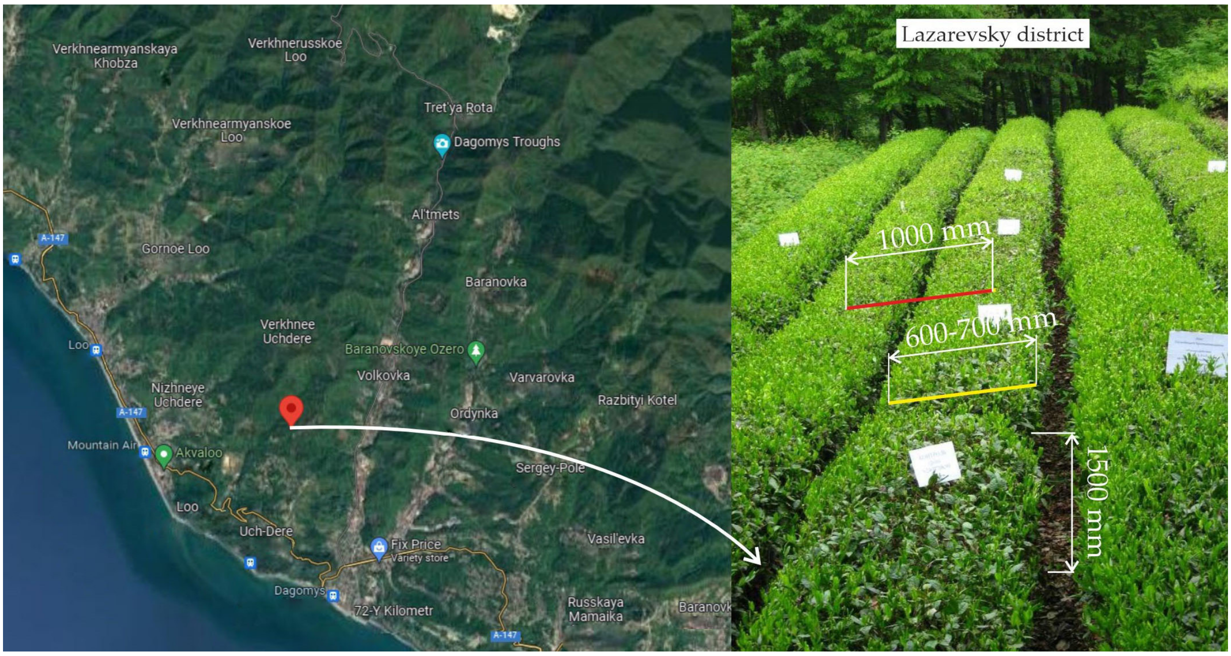
Elements	Concentration µg/g	Elements	Concentration µg/g	Elements	Concentration µg/g	Elements	Concentration µg/g
Li	5.76	Sr	709.80	Tb	0.15	Th	0.84
Be	0.15	Nb	1.23	Dy	0.58	U	0.19
Sc	1.43	Mo	0.07	Ho	0.28	Na	783
V	3.71	Sn	1.84	Er	0.56	Mg	3848
Cr	2.22	Sb	0.02	Tm	0.04	Al	3870
Co	1.21	Ba	19.50	Yb	0.41	K	2086
Ni	12.60	Pr	0.62	Lu	0.12	Ti	114.80
Cu	1.920	Nd	2.52	Hf	0.27	Mn	421
Zn	11.13	Sm	0.89	Ta	0.72	Fe	1485
Ga	0.54	Eu	0.17	Pb	4.40	Cd	0.36
Rb	7.50	Gd	0.89	Bi	0.04	I	0.72
As	0.59						

After checking the fact that individual chemical elements did not exceed the specified critical concentrations, a standard biotesting method was applied to them. The studied quarry wastes turned out to be chemically neutral, as a result of biotesting its extracts [59] using the single-celled algae *Chlorella Vulgaris*. The test results showed no significant deviations from the control in either acute or chronic experiments. This proves that they do not have reliable toxic properties and can be used in agriculture.

2.2. Experiment Parameters and Possible Limitations

The basis for choosing the plant type was the fact that tea is an industrially significant crop for this region, which has been grown in the Black Sea coastal area of the Krasnodar

Territory for more than 100 years. Due to the favorable conditions of tea cultivation in the subtropics, as well as the presence of experimental plantations, the existing full-aged tea plantation *Camellia sinensis* (L.) O. Kuntze (Colchis variety) was chosen to be used for further experiments (Figure 3).



a b

Figure 3. Influence of calcium wastes on the yield of tea leaves in different meteorological conditions (ZAO "Dagomyschai" Copyright © Google Earth): (**a**)—a variant of using calcium wastes obtained from a quarry; (**b**)—a basic variant of cultivation (N250P70K90).

The studies were conducted for nine years, from 2011 to 2020. The object was 2 variants of the field experiment: (1) control (background) was N240P70K90 (in kg d.v./ha) as a traditional fertilizer system; (2) background + natural calcium-containing material, whose description is provided in [60]. Tea grew on chernozem (black soil) soil with a humus content of 6.5%. The granulometric composition of the soil was generally uniform along the profile. There was no noticeable movement of silt particles. The predominance of silty–silty fractions in the soil caused a high absorption capacity and moisture capacity.

The material was sieved to obtain a fractional composition of less than 0.25 mm in fineness. The area of the experimental plots was 100 m^2. The tea plantation was founded in 1983 with a high-yielding variety of Colchis in subtropical conditions (Dagomys, Russia); the experiment scheme was imposed in 2003. The tea plantation plots are located at 43°41′04.8′′ N 39°38′14.0′′ E (43.684655, 39.637222). Annual fertilization in the amount of 250 kg/ha of the wastes in the form of a dry white-grayish powder was conducted in the spring period. The fertilizer was evenly applied to the root zone (manually). The crop yield was recorded (manual harvesting) during the periods approaching the tea leaf harvesting, according to agricultural regulations [61]. When designing the experiment plan, the following problems were taken into account, which could affect the obtained results. In this case, the factors of "uncontrolled environmental parameters" and insignificant climatic anomalies were not observed, and the intra-annual variability was conditionally stable for the entire observation period. The variability factor of the calcium-containing waste products, due to the uneven distribution of the conditions of the processed rock formations on the ledges, could significantly affect the results. To neutralize this factor, the material was taken once from one source, while the composition for the chemical analysis was taken from the random 10 bags. The "experiment duration" factor was undoubtedly of significant interest in the context of assessing the duration of a positive effect (which was one of the main research issues this time). In this regard, the observation period was approaching ten years.

During the study period, the soil was analyzed in a standard way. The exchange acidity of the soils was determined with the potentiometric method using the ionometer "pH-121 EKOSTAB" (OOO "EKOINSTRUMENT", Moscow, Russia). Easily hydrolyzable nitrogen was determined with the Tyurin–Kononova method (colorimetric method involving the Nessler reagent), including mobile phosphorus (with Oniani having a colorimetric ending according to Deniges) using the "USF-01" spectrophotometer (FSUE All-Russian Research Institute of Optical and Physical Measurements, Moscow, Russia). Mobile potassium was determined with Oniani using an atomic-absorption spectrometer "KVANT-AFA" (OOO "KORTEK", Moscow, Russia). The content of the exchange forms of Ca^{2+} and Mg^{2+} was determined with the trigonometric method.

2.3. Mathematical Processing of the Results

When choosing the methods for processing arrays of three-dimensional data, we proceeded from the experience of solving such types of problems in the relevant fields of knowledge [62–65]. The closest analog is the spatial–temporal problems of geoecology: the assessment of the aerogas regime of the surface layer (earth breathing) [66–69], forecasting the long-term time series of data [70], geostatistical modeling using GIS technologies [71–73], applying fractal models [74], deep learning [75,76], or perceptrons [77,78]. In contrast to using splines [79,80] or the local polynomial regression (LOESS) method [81,82], the primary data were not smoothed in this work due to the small sample size. The primary data were processed using Microsoft Excel 2010 software; three-dimensional models (using R. Renka algorithm implemented as a Python script) were formed based on a standard sequence of built-in commands: "gnuplot v.5.4" software and "Scilab 6.1.1" software for searching the regression equations.

3. Results

The essence of the experiment was a long (more than 5–7 years) introduction of a constant volume of the technogenic fertilizer (whose 40% of the weight was Ca) to confirm the effectiveness of its application in situ. The main effect of its application in the subtropical zone was to restore soil fertility and to assist in overcoming unfavorable climatic conditions of growing *Camellia sinensis* (L.) O. Kuntze. For this purpose, up to 2000 kg of the primary fine-dispersed material was selected at the quarry, which after storage, was periodically sifted and, in a spring period, was manually introduced into the root zone of tea rows. The material consumption in each period was 250 kg per hectare of the tea plantation. The three-leave flush was harvested manually; the average yield of tea is provided in Table 2. The experimental field was divided into nine land plots from which the tea was harvested. The table provides the average values based on the measurement results. The maximum deviation from the average value was 3.2%. In our work, we carried out mathematical processing of the obtained results and for each of the years determined the values of Student's *t*-test—t_S. Based on the obtained values of the criterion for each of the years, we accepted the null hypothesis at a significance level of 0.001. The only exception was in 2012. This year the average temperature was minimal, and there was little rainfall. This year, the Student's *t*-test passed with a significance level of 0.05. By a null hypothesis, we mean that the samples are not equivalent, which in turn, indicates a statistically proven effect of fertilizers on productivity. In most cases, the significance level was less than 0.01. This indicates that there was no relationship between the results.

Table 2. Results of tea yield when Ca was applied to the soil as a fertilizer (ZAO "Dagomyschai").

Time Period, (Year)	Control, Kg/ha (Centner/ha)	Control, Standard Deviation	Yield When Ca Is Introduced in the Soil, Kg/ha (Centner/ha)	With Ca, Standard Deviation	t_S	Percentage Increase, %s	Average Annual Air Temperature, (°C/Year)	Total Precipitation, (mm/Year)
2011	5860 (58.6)	81	6373 (63.73)	93	12.5	9	14.6	1825.5
2012	2610 (26.1)	39	2563 (25.63)	41	2.5	3	14.1	1396.8
2013	9150 (91.5)	98	11,656 (116.56)	150	42.0	27	15.5	1927.8
2014	6510 (65.1)	74	8241 (82.41)	81	47.3	27	15.2	1433.9
2015	2900 (29.0)	35	4040 (40.40)	46	59.2	39	15.3	1325.6
2017	4470 (44.7)	51	5683 (56.83)	56	48.0	27	14.3	1439.3
2018	4560 (45.6)	58	6210 (62.10)	68	55.4	36	16.0	1671.1
2019	4930 (49.3)	67	6110 (61.10)	78	34.4	24	15.3	1653.2
2020	3520 (35.2)	38	3730 (37.30)	45	10.7	6	15.9	1029.8

In the period of study (2011–2020), there were years when the meteorological conditions were relatively favorable, as when the yield varied from 6500 to 11,700 kg/ha (65 to 117 centner/ha). And it was commensurate with the potentially achievable yield for this variety (9000–11,000 kg/ha or 90–110 centner/ha) and relatively unfavorable conditions, in which the yield decreased by an average of 50% and was 26–40 kg/ha (26–40 centner/ha).

The application of modern methods of three-dimensional interpolation has revealed the nature of the relationship between the culture cultivation parameters and the culture yield level (Figure 4).

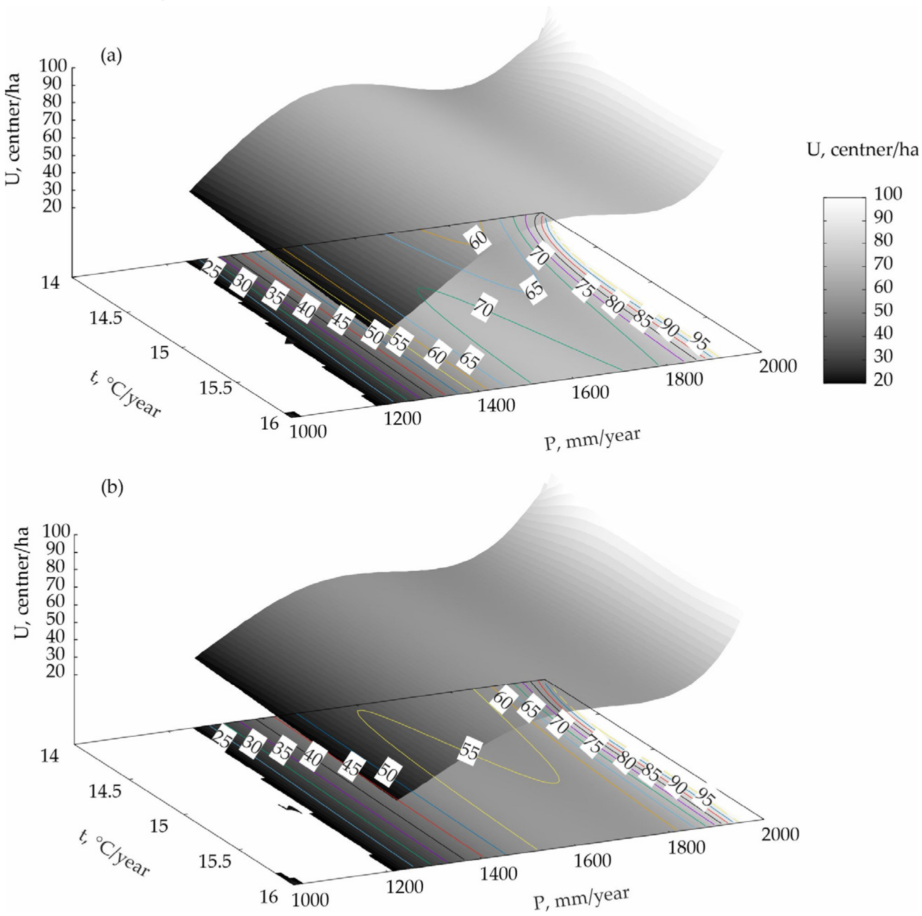


Figure 4. Influence of calcium wastes on the yield of tea leaves in various meteorological conditions: (**a**)—variant of using calcium wastes obtained from the quarry; (**b**)—basic variant of cultivation (N250P70K90).

The analysis of Figure 4 implies the fact that the surface of the distribution of crop yield parameters has pronounced nonlinearities, which determines the presence of three pronounced extremes (two maxima and one minimum). At the same, the overall appearance of the response surface is the same in both cases; in the case of waste use, the overall trend is clearly higher relative to the *Z*-axis.

As to the base case, a logarithmic-type dependence has been revealed (the solution is shown in Figure 5), whose formula has the following view ($R^2 = 0.84$):

$$U = -646558.11(\ln t)^2 + 79331.38(\ln t)^3 - 0.23P - 0.006P^2, \quad (1)$$

where U—tea yield in the control version of the experiment using NPK, centner/ha; t—average annual air temperature (from October of the previous year to September of the current year), C/year; P—annual precipitation (for the same period), mm/year.

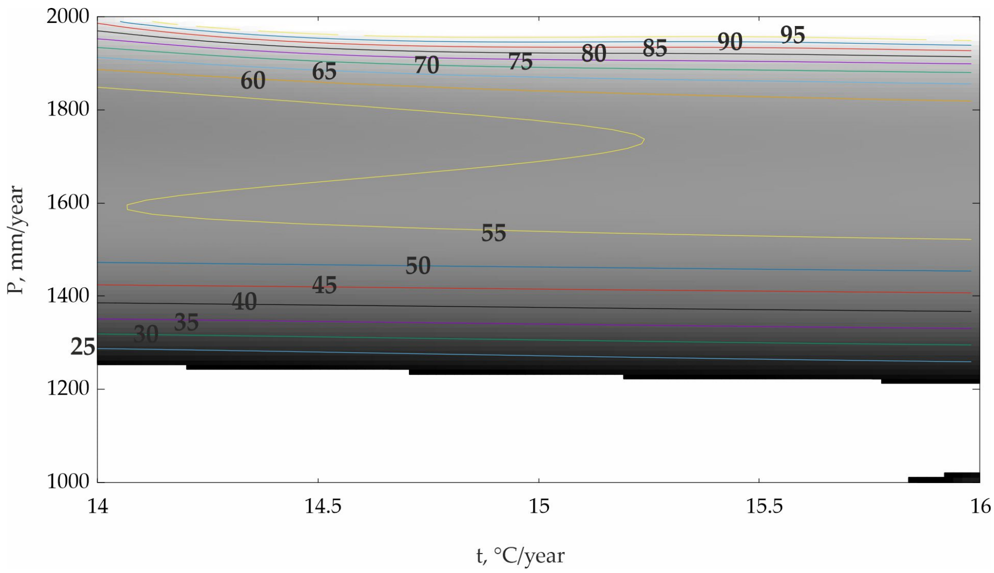


Figure 5. Projection of the logarithmic dependence of the tea yield (1) onto the t—P plane in the case of the basic variant of growing over a period of 2011–2020.

Figure 5 shows that a precipitation (P) increase from 1230 to 2000 mm/year at an average annual temperature of T = 14 °C increases the yield of green tea leaves from 20 to 90 centner/ha (4.5 times along a nonlinear trajectory). Simultaneously, a logarithmic increase from 20 centner/ha is traced up to forming a local maximum (54 centner/ha) within 1580 and 1600 mm/year, followed by a slight decline (at the level of 46–48 centner/ha) in the range of 1670–1800 mm/year, and subsequent growth to maximum values (90 centner/ha) when P = 2000 mm/year.

In turn, a temperature increase of up to 16 °C against the same background of precipitation leads to a similar pattern of yield changes from 20 centner/ha (starting from P = 1200 mm/year) to a maximum of ≥100 centner/ha (at P = 2000 mm/year), providing a five-time increase in the yield. A change in the air temperature from 14 to 16 °C results in a minimum rate of crop growth from 20 centner/ha (14 °C) up to 23 centner/ha (16 °C). In the case of a high amount of precipitation (2000 mm/year), in the same range of changes in the average annual air temperature, the tea yield gradually increases by 25%.

In general, a favorable combination of the average annual temperature and the sum of the precipitations intended for tea cultivation (control, traditional fertilizer system) based on the data analysis is the ranges of T = 14–16 °C and P = 1800–2000 mm/year, when the yield is approximately more than 80 c/ha. The green tea leaf increase in optimal weather conditions when using the traditional fertilizer system is 17.0%.

The introduction of calcium wastes obtained from the quarry into the soil can significantly improve the dynamics of its yield due to the growth in the resistance of the tea plants (*Camellia sinensis* (L.) O. Kuntze) to adverse meteorological conditions. As a result of approximating the experimental data, a logarithmic-type dependence has been established (its solution is shown in Figure 6), whose formula has the following view (R^2 = 0.83):

$$U = 144095.12(\ln t)^3 + 0.90P - 0.009P^2, \tag{2}$$

where U—tea yield when using a calcium-containing material, centner/ha; the other designations are the same as they are in Formula (1).

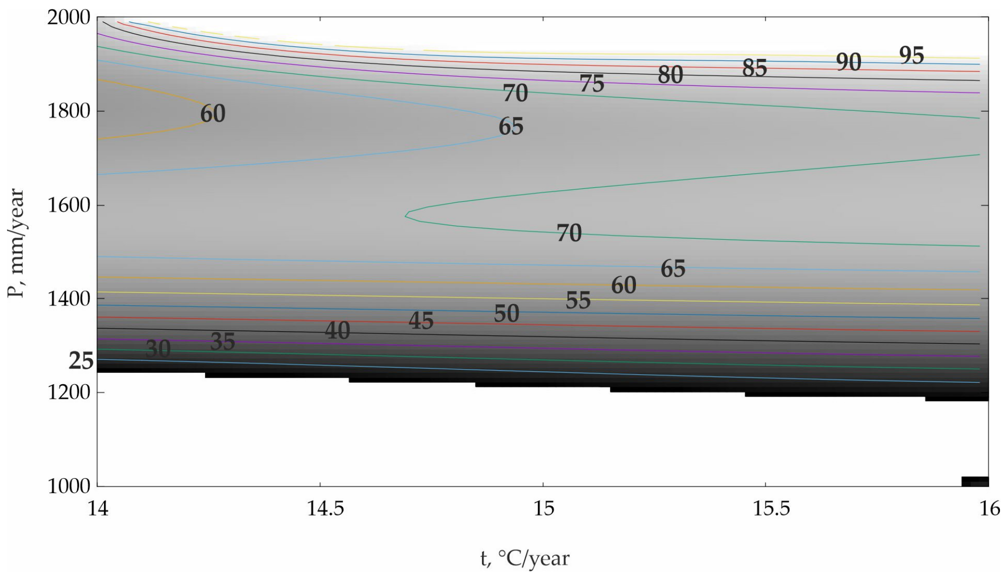


Figure 6. Projection of the logarithmic dependence of the tea yield (2) onto the t—P plane in the case of using the calcium wastes obtained from the quarry.

The nonlinearities typical of Figure 5 are also inherent in the studied Figure 6 (when using quarry wastes), but their parameters have specific features, namely the stable optimal productivity zone is located higher (along the Z-axis) than that in the base case.

Figure 6 shows that during the same research period, an increase in the amount of precipitation from 1200 to 2000 mm/year at an average annual temperature above 14 °C ensures a yield increase in the tea culture from 20 to more than 100 centner/ha. At the same time, the logarithmic increase from 20 centner/ha is traced to the formation of a local maximum (68 centner/ha) when P = 1600 mm/year. This is then replaced by a slight decline (at the level of 53 centner/ha) in the range of 1800–1823 mm/year and a subsequent increase up to the maximum values (78 centner/ha) when P = 2000 mm/year.

In turn, a temperature increase of up to 16 °C against the same background of precipitations leads to a similar pattern of yield changes from 20 centner/ha (starting from P = 1180 mm/year) to a maximum of $\geq$100 centner/ha (when P $\geq$ 1900 mm/year), providing a yield increase of more than five times. An air temperature change from 14 to 16 °C results in a minimum rate of crop growth ranging from 20 centner/ha (14 °C) to 28 centner/ha (16 °C). In general, a combination of the average annual temperature and precipitations that are favorable for the tea cultivation (control, traditional fertilizer system) proceeding from the data analysis is the ranges of T = 14–16 °C and P = 1800–2000 mm/year, when the yield is about more than 95 centner/ha. The crop increase in the green tea leaves in optimal weather conditions and using the calcium wastes obtained from the quarry increase the maximum productivity area by 50% (when T = 16 °C and P = 2000 mm/year) compared to the base case.

The combined profiles of the two variants are shown in Figure 7 to visually assess the additional effects that the wastes have on tea cultivation efficiency.

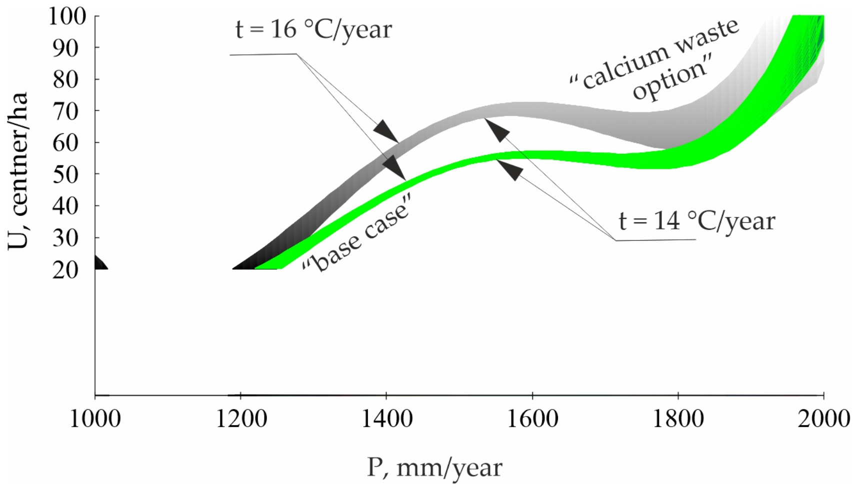


Figure 7. Profile surfaces of the productivity of growing *Camellia sinensis* (L.) O. Kuntze when adding the calcium wastes obtained from the "Kamensky" quarry over the period of 2011–2020.

The analysis of the productivity dynamics of the tea cultivation shown in Figure 7 implies the fact that when using a differentiated calculation of the areas under the average profiles of the two surfaces, the difference is about 22%, which determines a direct effect gained from using the wastes in these microclimatic conditions. The initial agrochemical characteristic of pH_{KCl} was 3.75 ± 0.14. On average, over the period, the variation range for the base case was 2.95–3.3, and in the case of the experimental site, it was in the range of 3.2–3.4. The value of mobile phosphorus (P_2O_5) was 294 ± 37; in the case of the base case, it equaled 780–1100, and it was 560–890 mg/kg when applying the fertilizers. The value of exchangeable potassium (K_2O) was 273 ± 25 and for the base case was 300–450, and in the case of the fertilization, it was 400–660 mg/kg. The value of easily hydrolyzable nitrogen (N_{lg}) was 48 ± 6; in the case of the base case, it was equal to 55–270, and in the case of the fertilization, it was 110–450 mg/kg. The value of the fractions of exchangeable calcium and magnesium ($Ca^{2+} + Mg^{2+}$) was 8.40 ± 1.40; in the case of the base case, it was 2.9–4.5, and when applying the fertilizers, it amounted to 3.9–5.3 mmol (eq)/100 g.

4. Discussion

The main factor studied in this work is undoubtedly the drilled fertilizers based on the waste obtained from the quarries where crushed stone was extracted. Conducting a study on the influence of the fertilizers on productivity requires the consideration of climatic conditions. The climatic conditions are the most important factor influencing both the productivity of plants and the work of the fertilizer itself. The absence of precipitation entails the absence of the fertilizers' influence since it will not be dissolved in water, being in the soil. In this regard, considerable attention is to be paid to climatic conditions. Firstly, this demonstrates the fact that it was the fertilizer that influenced the productivity increase of the tea culture under study. Secondly, this fact clarified the difference in the productivity of the tea culture when applying the fertilizers in different years.

The influence of meteorological conditions on the yield of tea plantations was analyzed throughout the entire period of tea cultivation in the subtropics [83–85]. P.M. Bushin [84] established the temperature factor influence on the 1 May harvesting of tea leaves. The subsequent harvestings (6–8th) depended on the precipitation amount. L.S. Malyukova had previously found that the unfavorable thermal regime of the spring period (in particular, frosts in March–April) leads to a significant loss in the first and, accordingly, the gross yield of tea leaves [86]. Insufficient precipitation (less than 700 mm over the period of April–October) during the growing season additionally inhibits the shoot formation process, reducing shoot activity. An average daily temperature increase in the leaf-harvesting period up to 23–25 °C—conditioned, as a rule, by a significant increase in daytime temperatures up to the values that reduce the photosynthesis process intensity—led to a drop in the tea plantation yield. At the same time, the precipitation of 390 mm over the leaf-harvesting period was of critical value for the shoot-forming activity of the tea plant. The regularities obtained in this study allowed for the detailing of the optimal ranges of the average annual temperature and annual precipitation specified for tea cultivation: in the case of the traditional fertilizer system, T = 14.76–16 °C and P = 1575–1780 mm/year; in the case of using the calcium wastes obtained from the "Kamensky" quarry, T = 14–16 °C and P = 1500–1830 mm/year. The revealed increase in the tea yield against the background of applying the calcium-containing material in the case of different combinations of climatic factors was 22%. Similar to the study of conditions in Southwestern Ethiopia [87], fluctuations in yield in specific years seem to be associated with seasonal climate fluctuations (their influence on the resulting yield values is the topic of further research). In the case of the rather arid tea-growing conditions in the subtropical zone of the Caucasus (compared to the optimal range of 2500–3000 mm/year [88]), a slight change in precipitation leads to significant deviations in the tea yield.

The obtained results do not contradict the studies conducted for the Indian tea variety, where the presence of the seasonal variability of biochemical compounds in the samples of *Camellia sinensis* (L.) O. Kuntze has been convincingly proven [89,90]. In such climatic growing conditions, the increase in applying the fertilizer from 0 to 300 kg/ha can significantly improve the final product quality due to the improved ability of the tea leaf to inhibit antioxidants [91]. According to the literature data, the material concentration change in the *cytosol* represents the first stage in the cell's recognition of external influences and launches a *signal transduction* system for causing a feedback response [92–94]. The reason may be the influence of abiotic stresses on the growth of *metabolites* in tea [95]. An important group of sensors involved in the cascade of calcium ion signals in the cells of higher plants is *Ca-dependent protein kinases* [96,97]. Under the action of calcium, there are changes in the growth, photosynthesis, and water–air regime of the plants, the work of stomata, as well as the accumulation of stress proteins [98,99]. The influence of calcium-entailed changes was noted in the growth, photosynthesis, and water–air regime of the plants, stomata functioning, as well as the antioxidant system induction [100,101]. This contributed to an increase in the tea plant's resistance to the combined effects of stress factors by maintaining the enzymatic activity of the leaves at a higher level, *induction of secondary metabolites synthesis*—the adaptive restructuring of the pigmentary fund, which on the whole, provided a higher functional activity of the plants during subsequent *rehydration*.

When cultivating tea on brown acidic soils, the use of the calcium-containing material was determined by the need to verify the hypothesis of a possible replenishment of the calcium content (when leaching it in acidic conditions) and, accordingly, to improve the resistance of *Camellia sinensis* (L.) O. Kuntze to abiotic stresses. But at the same time, it became possible to identify the existence of the pH shift towards the acidic interval accompanied by a simultaneous increase in the content of exchangeable calcium and magnesium (see the results of Section 3). This conditions the hypothesis, in which the mechanism explaining these changes in improving the nutritional regime of the tea plants in conditions of insufficient water supply is the intensification of the respiratory and enzymatic activity of soils. Verifying this hypothesis is a prospect for further research.

5. Conclusions

In conditions of humid subtropics and high variability of microclimatic cultivation parameters, the calcium wastes obtained from quarries can be successfully applied by agricultural enterprises cyclically when growing tea plants. At the same time, the effect of using the wastes in these microclimatic conditions when growing *Camellia sinensis* (L.) O. Kuntze is about 22%. Finally, the conducted studies have established the fact that an increase in the average annual precipitation from 1000 to 1980 mm/year, in the range of the average annual air temperature from 14 to 16 °C, leads to the 4.8-time yield growth of *Camellia sinensis* (L.) O. Kuntze with the logarithmic dependence (from 20 to 95 centner/ha). The work made it possible to reveal for the first time that the crop yield of *Camellia sinensis*

(L.) O. Kuntze increases more than five times with the logarithmic dependence (from 20 to more than 100 centner/ha) when adding the wastes obtained from the "Kamensky" quarry. At the same time, the zone and absolute values of the region of productive tea cultivation increase, and the maximum productivity is achieved in the case of less precipitation.

The practical significance of applying mining wastes as a non-traditional type of fertilizer for forming sustainable agriculture may consist in the subsequent development of the technological regulations of their use, including transportation, storage, and introduction into the soil.

The obtained data have confirmed the positive role, previously revealed by a set of biophysiochemical indicators, of the calcium-containing natural material in adapting tea plants to drought and the efficiency of its use in tea plantations. The above-mentioned conclusions and recommendations are valid only for the range of conditions of the subtropical zone of the Caucasus (acidic soils, P ranging from 1000 to 2000 mm/year, and t varying between 14 and 16 °C). Further research should be focused on identifying within-year climate variability during the growing season and the productivity of the fertilizer application when cultivating tea.

Author Contributions: Conceptualization, L.S.M., N.V.M. and V.B.; methodology, V.V.T. and V.V.K.; software, K.A.B. and T.A.P.; validation, K.A.B. and T.A.P.; formal analysis, V.V.T. and V.V.K.; investigation, V.V.B. and V.Y.K.; resources, V.V.T. and V.V.K.; data curation, V.V.B. and V.Y.K.; writing—original draft preparation, L.S.M., N.V.M. and V.B.; writing—review and editing, L.S.M., N.V.M. and V.B.; visualization, K.A.B. and T.A.P.; funding acquisition, V.V.B. and V.Y.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data of this work are given in the text of the article.

Conflicts of Interest: The authors declare no conflict of interest.

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