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Impacts of Crop-Specific Agricultural Practices on the Accumulation of Heavy Metals in Soil in Kvemo Kartli Region (Georgia): A Preliminary Assessment

Giorgi Gventsadze [1], Giorgi Ghambashidze [1,*], Zaur Chankseliani [1], Ioseb Sarjveladze [2] and Winfried E. H. Blum [3]

[1] Soil Fertility Research Service, Scientific-Research Centre of Agriculture, Marshal Gelovani Avenue 36b, 0159 Tbilisi, Georgia; giorgi.gventsadze@srca.gov.ge (G.G.); zaur.chankseliani@srca.gov.ge (Z.C.)
[2] Department of Agricultural Technology, Faculty of Agricultural Sciences and Biosystems Engineering, Georgian Technical University, Guramishvili Ave. 17, 0192 Tbilisi, Georgia
[3] Institute of Soil Research, University of Natural Resources and Life Sciences, Peter-Jordan-Str. 82, 1190 Vienna, Austria
* Correspondence: giorgi.ghambashidze@srca.gov.ge

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Abstract: Maintaining sufficient levels of plant nutrients in the soil and controlling certain heavy metals, which can be toxic to the environment, are critical to ensure sustainable agricultural production. The study aimed to assess the linkage of crop-specific agricultural practices established by farmers in the Kvemo Kartli region (Georgia) with metal accumulation in soils of agricultural lands being subject to influence from polluted irrigation water in the past. In particular, we tried to identify the primary sources of micro-nutrients, including iron (Fe), copper (Cu), manganese (Mn), nickel (Ni), and zinc (Zn), and toxic elements such as cadmium (Cd) and lead (Pb), and the share of the contaminated irrigation water and other factors related to agricultural practices under different land uses, such as intensive and extensive arable farming, vineyards, orchards, and permanent pastures having the least disturbed soil. Based on principal component analysis, five primary sources were identified and categorized according to farmer interviews and previous studies conducted in the region. The results showed that increased concentrations of plant-available Cu, Zn, Cd, and Pb were mainly associated with irrigation water and intensive use of fungicides; Fe, Mn, and Ni were closely linked to several factors, such as the mineralogical composition of soils, minerals, and organic fertilizers inputs; and atmospheric deposition from diffuse sources, where exhausts from transport are probably the primary source. During our study, we attempted to differentiate irrigation water inputs from fungicides using simulation based on irrigation patterns and irrigation water quality on the one hand and fungicide application rates and their metal contents on the other. The simulation revealed that the intensive application of fungicides, especially in vineyards, is more significant in enriching soils with Cu and Zn than irrigation water. Identification of factorial dependences was supported by statistical analysis and application of several contamination assessment methods: contamination factor (CF), pollution load index (PLI), single-factor pollution index (PI), Nemerow's comprehensive pollution index (PIN), enrichment factor (EF), and geo-accumulation index (Igeo). Applied environmental indices indicate that the soils under the former and existing vineyards are the most enriched with Cu and Zn, highlighting the significance of agricultural practices on heavy metal accumulations in the soils of agricultural lands.

Keywords: soil fertility; soil contamination; heavy metals; agricultural practices; plant nutrients

1. Introduction

Agricultural production heavily depends on the soil fertility level and balanced nutrient supply of crops, affecting the yield [1,2]. In agricultural production, sustainability can be achieved through the introduction of sustainable agricultural practices [3], enabling farmers to maintain adequate soil fertility and improve the crop yield or, at least, ensure stability in production in the long term without negatively impacting the quality traits [4] and safety of a product [5]. Therefore, selecting proper agricultural practices is crucial for achieving the sustainable development of agricultural production systems [6]. The main challenge that agricultural systems face today is determining the advantages and disadvantages of a particular agricultural practice, as their study requires years and sometimes decades. At the same time, a great deal of scientific knowledge has been accumulated from long-term experiments [7,8] and farm-level studies [9,10], demonstrating the impacts of specific agricultural practices on plant nutrients in soil. Numerous studies have shown that soil macro- and micro-nutrient composition changes are associated with agricultural practices [11–13]. Those changes in the nutrient concentrations can be temporal but, in some cases, last longer and often remain detectable even after changes in land use. Therefore, the historical use of the soil and its related management practices are essential predictors of its elemental composition.

Currently, many developments are taking place in the agricultural sector in Georgia [14] as it becomes more market-oriented, which is also causing changes in the types of crops and land. These changes are evident in the regions where agriculture plays an important economic role. Our study was conducted in one of the most active agricultural production regions of Georgia, namely Kvemo Kartli, and we attempted to assess the impacts of the agricultural practices established by farmers and their relationships with the soil micro-nutrients and heavy metal compositions considering the impact of metal-enriched irrigation water in the past. The research was conducted in close cooperation with the farmers to understand their crop-specific management practices and to predict their sustainability in the long term based on the inputs of macro- (N, P, K) and micro-nutrients (Fe, Cu, Mn, Ni, Zn) and toxic heavy metals (Cd, Pb).

2. Materials and Methods

2.1. Study Area

The study was conducted in the Kvemo Kartli region in eastern Georgia (Figure S1). The region is known for producing vegetables, although the lands occupied by cereals and perennial crops represent a considerable share of the total area. Diverse agricultural production is supported by the region's favorable soil and climatic conditions. The foothills of the region, at 500–600 m above sea level, have a moderately humid climate, with moderately cold winters (3–5 °C) and hot summers (23–28 °C). The average annual temperature is 12 °C, and the average annual precipitation is 572 mm. The agricultural lands on the foothills are mainly occupied by cereals (wheat, barley, maize), perennial crops (vine, fruits and nuts), and pastures.

The lowland area has a moderately warm steppe climate, with moderately cold winters and hot summers. The average annual temperature is 12 °C, and the absolute maximum is 40 °C. The average annual precipitation is 400–500 mm. The precipitation is unequally distributed throughout the year, with the maximum precipitation observed in spring, as May is the wettest month, and the minimum in winter, with the driest month being December. Due to this, agriculture, particularly vegetable production, heavily depends on irrigation supplied by the rivers Mashavera and Khrami.

The dominant soils belong to the soil reference group [15] of calcic and calcaric Kastanozems. The slopes at higher elevations are characterized by rendzic Leptosols, and the lowest plains near the rivers are characterized by calcaric Fluvisols.

2.2. Soil Sampling

The soil sampling was conducted in two stages: initial sampling was conducted in 2021 for recognizance purposes, based on which the sampling scheme was elaborated, and final sampling was conducted in 2022, which is presented in the paper. Soil samples were taken from plots occupied by dominant crops in each selected area. Additional samplings were performed in the neighboring plots in which annuals and perennials were cultivated, as well as pastures, which mainly served as a local reference, assumed to be the least disturbed soil, as there are no inputs from farmers, as they are used as communal natural pastures, known as village pastures [16], located in a vicinity of settlements and used almost year-round. The state owns these village pastures, which are common property that local farmers use as grazing land for their animals, mainly for cattle.

The soil samples were taken after the harvest of the main crop at a fixed depth from 0 to 30 cm to ensure the comparability of the results. In each case, five points were sampled using a spade and a shovel, one core sample and four subsamples located 2 m away from the core sample were taken to obtain a composite sample [17], which was used for the laboratory analysis. Samples were collected in plastic bags with appropriate labeling and transported to the laboratory the same day. The full dataset of analytical results is given as Supplementary Materials (Tables S1–S4).

2.3. Farm Survey

The farm survey was conducted in the study area and covered all the fields of agriculture represented in the region. We used questionaries' prepared before the fieldwork and conducted personal interviews with the farmers managing the agricultural lands where soil sampling was performed. The survey was conducted using a mobile application, Collect [18]. In total, 83 sites were assessed, from which 5 orchards, 9 vineyards, 10 former vineyards, 14 arable intensive, 20 arable extensive, and 25 pasturelands. The survey aimed to understand the agricultural management practices established by a given farmer to better interpret the results obtained. In total, 16 farmers managing arable and perennial croplands were interviewed; covering 37 sites, we assessed where farm management practices are established. This allowed us to survey with a margin error of 12% at a 95% confidence level.

2.4. Soil Analysis

The soil samples were analyzed based on the following parameters: the pH, electric conductivity (EC), calcium carbonate, organic matter (OM), bulk density, texture, cation exchange capacity (CEC), mobile phosphorous (P), exchangeable potassium (K), and potentially plant-available and *aqua regia*-extractable forms of copper, cadmium, iron, lead, manganese, nickel, and zinc.

The soil pH was measured in an aqueous solution using a 1:2.5 ratio by the potentiometric method [19] with pH/ion meter (InoLab Multi 9310, WTW, Weilheim, Germany). EC was determined in a 1:5 ratio extract (InoLab Multi 9310, WTW, Weilheim, Germany) [20]. Calcium carbonate was determined volumetrically using a Scheibler calcimeter [21]. The OM was measured colorimetrically using a spectrophotometer (Specord 210 plus, Analytik Jena AG, Jena, Germany) after digestion with potassium dichromate, according to the Walkley–Black method [22]. The soil bulk density was determined in undisturbed soil cores taken using stainless steel cylinders with a volume of 100 mL and dried to a consistent weight using a drying oven (UF160, Memmert, Schwabach, Germany). The texture was determined using a pipette method according to the Kachinskii system [23] and was then transferred to USDA textural classes [24] using the conversion method proposed by Shein [25]. The mobile phosphorous were determined colorimetrically after extraction by sodium bicarbonate, according to the Olsen method [26]. The exchangeable potassium was measured using an atomic absorption spectrometer (AAS) (ZEEnit 700P, Analytik Jena AG, Germany) after extraction by 1 M ammonium nitrate [27]. Cation exchange capacity was measured in 0.01 M barium chloride extract [28] using AAS. The potentially plant-available pool of elements were measured using an AAS after extraction using DTPA [29], and the total forms of the studied elements that can be extracted with *aqua regia* [30] were measured using an AAS.

2.5. Statistical Analysis

Descriptive statistical parameters, including mean, median, standard deviation, and coefficients of variation, were calculated using the MS Excel Data Analysis Tool. A Kruskal–

Wallis test (KWT) was used to evaluate the impact of crop-specific agricultural practices on changes in the studied soil macro- and micro-nutrients and toxic heavy metals accumulation in soils. The Spearman correlation coefficient was used to determine the correlation between studied elements and other properties of soil (Table S5). Spearman correlation coefficient was preferred as some studied parameters were not normally distributed. In such a case, Spearman's rank correlation coefficient is recommended as being more robust than the Pearson product-moment correlation coefficient [31], which is also widely used. Principal component analysis (PCA) was used to identify the primary sources of metal inputs, focusing on those affecting their availability to plants. It was categorized according to the farmer interviews and previous studies conducted in the region.

2.6. Baseline Content

The regional baseline contents of studied elements were estimated based on median values $\pm$ one standard deviation, as proposed by Salminen and Tarvainen [32]. A similar approach was practiced in many studies worldwide where median or mean values were used [33–35] and applied in Georgia [36]. Median values were taken from soils studied on pastures, as it was considered a land use type with minimum anthropogenic impact compared to other agricultural land use forms. Median values were preferred over the mean, as the median is less influenced by extremely high or low values, which was also avoided by eliminating outliers from baseline content calculations. Instead of defining a baseline as a range, as suggested by Salminen and Tarvainen [32], we reported it as an upper limit of that range to obtain a single maximum baseline concentration, which could be easily used in calculations.

2.7. Soil Contamination Assessment

Most micro-nutrients (such as Cu, Mn, Ni, and Zn) measured in soils in our study belong to heavy metals like Cd and Pb. Therefore, in parallel to evaluating the impact of crop-specific agricultural practices, we assessed the degree of heavy metal accumulation in the soil using various indices frequently applied in monitoring and assessing harmful contaminants in different environmental media. In this study, we used contamination factor (CF), pollution load index (PLI) [37–39], single-factor pollution index (PI), Nemerow's comprehensive pollution index (PIN) [40,41], enrichment factor (EF), and geo-accumulation index (Igeo) [38,42,43], which are described in detail in the corresponding subchapters.

2.7.1. Contamination Factor (CF) and Pollution Load Index (PLI)

The contamination factor (CF) is often used to express soil contamination levels with some aspects in combination with the pollution load index (PLI) [37–39]. CF is calculated using a ratio of the measured concentration of an element (C_i) and its baseline content (C_b) using the following equation:

$$CF = C_i/C_b \quad (1)$$

PLI represents the total contamination level by considering the CFs of all observed elements [38,39].

$$PLI = (CF1 \times CF2 \times CF3 \cdots\cdots CFn)^{1/n} \quad (2)$$

The scale of the classes for CF and PLI are shown in Table S6.

2.7.2. Nemerow's Comprehensive Pollution Index Method

The comprehensive pollution index method developed by Nemerow (PIN) is widely applied to assess pollution caused by multiple elements [40,41] based on compositing results obtained from single-factor pollution index (PI) assessments. The corresponding equations to calculate PI (3) and PIN (4) are as follows:

$$PI_i = C_i/S_i \quad (3)$$

$$PIN = \{[(PI_{mean})^2 + (PI_{max})^2]/2\}^{0.5} \quad (4)$$

C_i is the observed concentration of element *i*; S_i is the standard referential value for evaluating this element. In our study, we used threshold values established in Georgia based on a legislative norm to evaluate soil quality on agricultural land [44]. Threshold values are established for Cu, Zn, Mn, Ni, Cd, and Pb. Therefore, PI and PIN were calculated only for these elements.

In the equation for estimating PIN (4), PI_{mean} corresponds to the single-factor pollution index, and PI_{max} is the maximum single-factor pollution index observed. Table S7 shows the scale of the classes for PI and PI_N.

2.7.3. Enrichment Factor (EF)

The enrichment factor (EF) is another commonly applied index to assess the degree of contamination in different environmental media [38,42,43]. It is used to determine the trend of geochemical characteristics at a local or regional scale. An EF index can be used to see whether certain elements in soils or sediments are related to anthropogenic activities or have a natural origin [45]. The equation for estimating EF (5) relies on the local reference element for normalization, which is essential to distinguish the anthropogenic impact from natural origins [38,45]. In this research, we selected Fe, as it has the highest baseline content and is the most uniformly distributed element in the study area, with the lowest coefficient of variation of 34% among the studied elements (Table S1) and it is potentially less affected by anthropogenic activities.

$$EF = (C_i/C_{ref})/(B_i/B_{ref}) \quad (5)$$

where C_i is the concentration of a measured element, C_{ref} is the concentration of the measuring element in the reference environment, B_i is the concentration of the reference element in the study area, and B_{ref} is the concentration of the reference element in the reference environment. Table S8 shows the scale of the classes for EF.

2.7.4. Geoaccumulation Index (Igeo)

The geoaccumulation index (Igeo) method was initially developed to assess the contamination level of river sediments by Muller [46], but it was widely used to evaluate urban [33,34] and agricultural soils [47]. It is calculated with the following equation:

$$Igeo = \log_2 [C_i/1.5 \times C_b] \quad (6)$$

where C_i is the concentration of a measured element *i* in soil, C_b is a baseline value of a measured element in the study area, and 1.5 is a correction factor for the background matrix [38] to normalize the fluctuation of the element in the baseline value as well as possible minimal anthropogenic influences and/or inputs [45]. The scale of the classes for Igeo is shown in Table S8.

2.7.5. Maximum Permissible Total Addition

According to the legislative act [44], which sets environmental quality criteria for soils in Georgia, it is necessary to estimate the maximum permissible total addition of fertilizer or soil improver based on Equation (7), where the concentration of a specific element in a material to be added and the baseline content and threshold values of respective element are used. Equation (7) calculates the maximum permissible amount of material added per hectare of agricultural land. It is calculated with the following equation:

$$D = [(0.8 \times MPC\text{-}BS) \times 3000]/[C] \quad (7)$$

where D is the maximum permissible amount of material in t/ha; MPC is the maximum permissible concentration or threshold value of an element in soil, in mg/kg; BS is the actual content of an element in the soil of agricultural land where the material is to be applied, in mg/kg; 0.8 is a coefficient limiting the increase in concentration of an element above 80% of its threshold value; 3000 is an average mass of soil of ploughed layer per hectare, in tones; and C is the concentration of an element in the material applied to soil.

In our study, we slightly modified Equation (7) and used it to estimate the possible inputs of the elements on polluted soils. The modified equation is as follows:

$$D = [(Cmean - Cmin) \times 3780]/[C] \quad (8)$$

where D is the maximum amount of material in t/ha, which could be applied based on existing agricultural practices; Cmean is an average concentration of an element in soil where the material was applied, in mg/kg; Cmin is a minimum content of an element in soil of agricultural land where the material is applied, in mg/kg; 3780 is an average mass of 0–30 cm soil layer per hectare, in tones, based on an average bulk density 1.26 g/cm^3, measured in soils formerly used for vineyards (Table 1), which were used for calculations in our study; and C is a concentration of an element in material applied to soil. The modified Equation (8) gives an understanding of whether inputs made in the past could contribute to the accumulation of certain elements in soil and that a mean concentration of a certain element observed under different land use types could be reached from its minimum value whichis used as an initial condition and found under the same land use.

Table 1. Mean values of basic soil properties and major nutrient concentrations in soil.

Land Use	Number of Sampling Sites	pH	SOM (%)	Bulk Density (g/cm^3)	CEC (cmol$_c$/kg)	$CaCO_3$ (%)	EC (dS/m)	P_2O_5 (mg/kg)	K_2O (mg/kg)
Orchard	5	7.70 ±0.74 *	5.73 ±1.09	1.25 ±0.07	55.64 ±1.09	4.35 ±4.17	0.16 ±0.05	40.98 ±52.48	661.30 ±386.82
Vineyard	9	8.05 ±0.41	5.31 ±0.97	1.24 ±0.13	63.19 ±9.83	4.08 ±2.76	0.20 ±0.11	38.94 ±21.82	955.09 ±692.28
Former vineyard	10	8.11 ±0.37	4.72 ±1.34	1.26 ±0.09	60.05 ±10.77	5.36 ±5.10	0.16 ±0.04	27.96 ±24.42	736.85 ±768.54
Arable, intensive	14	8.21 ± 0.37	3.74 ±0.97	1.23 ±0.12	52.18 ±13.91	4.39 ±2.90	0.18 ± 0.06	38.13 ±25.30	630.05 ±431.95
Arable, extensive	20	8.08 ±0.44	4.46 ±1.20	1.18 ±0.13	59.22 ±13.24	4.70 ±5.18	0.14 ±0.03	22.96 ±15.30	404.45 ±181.19
Pasture	25	8.14 ± 0.46	6.12 ±2.36	1.23 ±0.16	55.29 ±10.90	11.45 ±10.69	0.20 ±0.15	15.89 ±9.91	485.37 ±522.70

* Standard deviation.

3. Results

3.1. Land Use Types

The farm survey results and analysis of the old topographic maps were used to group the agricultural plots based on the agricultural practices established for the dominant crops, as a crop rotation system was not in place. Usually, the farmers focus on a single crop in a specific field, considering the practice that would best suit that crop. Therefore, we defined six land use forms with similar management practices and cultivated crop types, as the survey showed that crop-specific agricultural practices were the main drivers of farm-to-farm differences. In particular, wheat, barley, and oats were grouped in the category of extensive arable farms; fruit (stone and seed fruits) and nut crops were grouped in the category of orchards; and legumes (alfalfa and bean), vegetables (potato and onion), maize, and sunflowers were combined in intensive arable farms category. Grapevines were separated as vineyards, and pastures and haylands were separated as pastures, the last serving as a reference to estimate the impact of agricultural practices as the primary source of anthropogenic impact on agricultural lands. Besides that, we separated an additional group of former vineyards, which are currently under different land use forms, including intensive and extensive arable farming and pastures. Previous land use forms were identified on the topographic maps created during the last century in 1942 (Figure S2), 1969–1973 (Figure S3), and 1982–1984 (Figure S4), meaning that vineyards already existed during those periods on those plots, mainly as state-owned farms, which remained unchanged at least until 1996, when land privatization took place [48] and some land owners decided to replace vines with more profitable crops; although, not all plots were privatized and there are still some plots with abandoned vineyards currently used as pastures. The region has a very long history of agricultural production; the southeastern part of the region was already known for viticulture in the early Neolithic Period, during 6000–5800 BC [49]. The active development and expansion of commercial vineyards and fruit orchards occurred in the region's central part in 1819 [50]. In 1930, state collective farms were established, replacing existing private farms, and most agricultural lands were managed by the state for 60 years until the collapse of the Soviet Union. Collective farm management was organized centrally, and all operations followed guidelines for specific crops and soil-climatic conditions. These guidelines include so-called "agrotechnical norms" of pesticides and fertilizers to be applied annually, which helps to make proximate the quantification of their regular inputs [51].

Consequently, here, we present our results on a land use category basis, providing a better understanding of crop-specific agricultural practices and their impacts on the concentration of plant nutrients and toxic elements in soil. The following subchapters discuss the results for each nutrient and toxic element for the abovementioned land use categories. The attempt is made to assess the degree of impact of agricultural practices on the changes of concentrations of heavy metals and their availability to plants, as well as potential risks to human health and the environment, comparing regional baselines to existing threshold values [44] using statistical methods and various indices.

3.2. Organic Matter

Although organic matter (OM) is not included among the plant nutrients, it plays an essential role in soil fertility. It represents the primary nitrogen source available to the plant [52]. Therefore, we assessed the OM distribution through a method similar to that used for nutrient and toxic elements to determine the changes caused by agricultural practices and land use. Table 1 clearly shows that the pasture soils had the highest potential fertility. The average concentration of OM in their soils was 6.12%, which was expected because soils under pasture are not tilled and no fertilizers were applied; therefore, the conditions required to accelerate OM mineralization are absent, except on several occasions with excessive grazing on specific areas and the development of erosion.

After the pastures, the highest content of OM was found in the soils occupied by orchards, which equaled 5.73% on average, followed by the soils in vineyards, which amounted to 5.31%. In the case of the orchards and vineyards, the relatively high levels of organic matter were probably related to less intensive tillage and, in some cases, the maintenance of inter-row grass cover, which is an effective means of erosion protection. The lowest concentration was recorded in soils under intensive arable farming, amounting to 3.74%, which indicates the intensification of the production of these crops and the combination of factors contributing to the mineralization of OM, whereby farmers ploughed the soil several times per year to obtain two or three yields from the crops per plot by cultivating crops with shorter vegetation that can be gown after harvesting the main crop. OM mineralization can develop more intensively in such cases, as it benefits from the warm season when microbial activity is high [53]. Furthermore, some farmers apply the surface burning practice of crop residues after harvest, which reduces organic inputs to soil and, at the same time, accelerates organic matter mineralization.

The impact of agricultural practices on OM concentrations in soil was assessed using KWT, which showed that the difference between land use types was statistically significant ($p = 0.003$), confirming a substantial influence from crop-specific management.

3.3. Phosphorous

The results showed that the plant-available pool of one of the major nutrients, phosphorous (P), was highest in the soils under orchards (Table 1), amounting to 40.98 mg/kg on average, which was caused by a single high concentration found in one orchard soil (Table S1), due to the consistent input of synthetic mineral fertilizers, as confirmed by our interview with the farmer, and relatively low removal compared to other crops, as the orchard is still young and the optimal yields have not yet been reached. These differences are expressed in a high standard deviation (±52.48), numerically exceeding the mean value. Vineyard was the second land use type to which P-containing fertilizers were applied, and its average content in the soil reached 38.94 ± 21.82 mg/kg, which is very similar to soils under intensive arable farming—38.13 ± 25.30 mg/kg. The lowest values, as expected, were found in pasture soils, as the current nutrient management practices established by the farmers do not consider any fertilizer application for pastures, and its use is also minimal under extensive arable farming conditions, showing the second lowest content of P in soils.

According to KWT, the impact of agricultural practices on P concentration under different land use types was significant ($p = 0.016$), showing that variations between land uses are more significant than within each land use type.

P has a weak but statistically significant ($p < 0.01$) negative correlation ($\varrho = -0.322$) with calcium carbonate content in soil (Table S5), which often restricts its availability to plants.

3.4. Potassium

A different pattern was exhibited by the exchangeable potassium (K), where the highest values were found in vineyards, reaching 955.09 mg/kg on average (Table 1). In two vineyards, the level of exchangeable K exceeded 2000 mg/kg (Table S1), which could also result from high organic and inorganic fertilizer input. However, as farmers do not usually have records of the exact amount of each type of fertilizer they applied more than five years ago, it is difficult to estimate their contributions precisely. However, historical inputs during state collective farms may still have an effect, as the annual recommended input based on agrotechnical norms was 100 kg K/ha/y in the form of mineral fertilizer plus potential additions from manure applications with a rate of 12.5 t/ha/y (50 t/ha in every 4 years) [51], around 40 kg K/ha/y, assuming 0.32% of total K content in manure [54].

The soils under former vineyards had the highest concentrations of K with a mean value of 736.85 ± 768.54 mg/kg, showing a legacy of high K inputs in the past. Similar high K content was observed in orchards with an average of 661.30 ± 386.82 mg/kg, which is also considered very high. Despite the vital role of K in plant growth and development, its high concentration in soil can inhibit the uptake of calcium [55] and magnesium [56]. High K availability can result from the continued application of complex NPK fertilizers containing equal amounts of the three major nutrients (N, P, K). Complex NPK fertilizers are often applied based on the soil P levels, which are usually deficient in these soils, resulting in the accumulation of K in excess quantities. Despite this, most of the farmers interviewed during the field studies stated that they prefer to use one type of fertilizer containing all the major nutrients (N, P, K), as they have high nutrient content, and this practice reduces transportation and application costs.

Systematic use of complex NPK fertilizers can be a cause of a statistically significant ($p < 0.01$) moderate positive correlation ($\varrho = 0.456$) between P and K (Table S5), meaning that concentration changes of those macro-nutrients are partially interdependent.

The lowest K content was observed in soils under extensive arable farming (404.45 mg/kg on average), which can be influenced by the low input production system established for winter cereals, the dominant crop types in these farms.

The impact of agricultural practices on K concentration in soil was confirmed using KWT, showing a statistically significant difference ($p = 0.001$) between land use types.

3.5. Copper

The level of potentially plant-available copper (Cu) was observed to be highest in the former vineyard and current vineyard soils, reaching on average 46.95 and 41.66 mg/kg, respectively (Table 2), which can be considered as a high value and indicates an excessive availability of Cu to plants. Cu is an essential micro-nutrient for plants [57], but it is needed in small quantities [58], and its optimal range for most crops in the soil varies from 0.9 to 2.5 mg/kg extracted by DTPA [59]. It is reported that DTPA-extractable Cu concentrations higher than 20 mg/kg in soil can be toxic to crops [60] and cause considerable yield reduction [58]. This is the case for all soils from former vineyards and nearly 67% of soils studied in current vineyards (Table S3). Cu availability sharply decreases in soils of other land use types and exceeds the abovementioned toxic level (20 mg/kg) only in one sample taken from the pastures. Cu is generally a less mobile nutrient due to its strong fixation in soil. However, metals of an anthropogenic origin have higher mobility in soil than those of a natural origin [61]. Statistically significant differences between land use forms in potential plant-available Cu content are confirmed by KWT results ($p < 0.001$) and its very high variability in studied soils (CV = 111%).

Table 2. Potentially plant-available forms of nutrients (Cu, Zn, Fe, Mn, Ni) and toxic elements (Cd, Pb) in soil.

Land Use	Cu (mg/kg)	Zn (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Cd mg/kg)	Pb (mg/kg)
Orchard	4.53 ±2.40	1.25 ±1.19	59.43 ±88.85	50.80 ±26.16	2.68 ±1.45	0.20 ±0.08	1.24 ±0.25
Vineyard	41.66 ±40.61	11.23 ±19.89	37.89 ±23.54	28.68 ±20.89	1.72 ±0.66	0.60 ±0.76	1.32 ±0.49
Former vineyard, currently with different land use	46.95 ±16.14	18.17 ±17.85	23.86 ±18.40	55.81 ±47.88	2.26 ±0.85	0.74 ±0.48	2.00 ±0.84
Arable, intensive	9.11 ±8.33	2.11 ±3.72	21.42 ±25.07	56.21 ±35.92	2.61 ±0.82	0.34 ±0.15	1.49 ±0.73
Arable, extensive	4.97 ±4.64	0.97 ±1.24	12.35 ±7.33	86.65 ±72.23	3.89 ±2.02	0.26 ±0.12	2.03 ±0.58
Pasture	5.30 ±8.15	1.09 ±1.89	16.34 ±14.94	75.49 ±46.15	2.50 ±0.95	0.23 ±0.13	0.93 ±0.40

The accumulation of copper in vineyard soils is a well-known issue that is often reported worldwide [60–63] and is mainly associated with the long-term application of copper-based fungicides [61]. It could be a primary source of Cu input to vineyard soils in our study sites also, although several studies conducted in the Kvemo Kartli region showed the impact of contaminated irrigation water [64–68], which is taken into account in our study, considering that irrigation is an integral part of agricultural practices, as the amount of water and frequency depends on crop water demands and methods of irrigation. To estimate the possible contribution from irrigation water, we used the maximum concentration of Cu found in samples (0.1076 mg/L) taken from irrigation canals reported by Withanachchi et al. [38] from the study region. The amount of irrigation water applied was estimated using the FAO-CROPWAT model [69], as it is often used to estimate irrigation requirements of grapevines [70,71]. Climate data of the region was extracted from the TerraClimate high-resolution global dataset [72]. As the CROPWAT model uses average annual data and rainfall distribution can vary from year to year during vegetation season, we did not consider rainfall in calculations, and total crop water requirements were taken as irrigation water. According to the results, the grapevines in the study requires 3860 m^3 of water per year, which was used to calculate the possible input of Cu through irrigation water using Equation (8). The calculation was performed for former vineyard soils, where the minimum Cu concentration (138.77 mg/kg) was taken as a baseline (Table S4) and the mean Cu concentration (300.01 mg/kg) as a target to be reached (Table 3). According to the results, it would require more than 1400 years to increase Cu concentration using irrigation water only by applying an equal amount of irrigation water with the same quality. In addition, we made calculations, including sediments, which usually contain a higher concentration of metals and can be delivered to soil with irrigation water.

Table 3. Total forms of nutrients (Cu, Zn, Fe, Mn, Ni) and toxic elements (Cd, Pb) in soil.

Land Use/Main Crop Type	Cu (mg/kg)	Zn (mg/kg)	Fe (g/kg)	Mn (mg/kg)	Ni (mg/kg)	Cd mg/kg)	Pb (mg/kg)
Orchard	48.89 ±16.24	80.58 ±12.35	38.42 ±14.08	671.40 ±157.58	73.64 ±34.01	3.16 ±0.93	20.70 ±11.09
Vineyard	184.08 ±155.85	324.31 ±353.34	45.09 ±13.09	747.53 ±185.63	114.70 ±100.09	3.79 ±2.21	14.36 ±11.21
Former vineyard, currently with different land use	300.01 ±131.64	310.86 ±166.27	36.90 ±8.48	1157.21 ±612.52	137.06 ±103.21	6.96 ±9.39	25.03 ±12.22
Arable, intensive	76.99 ±35.84	108.40 ±54.58	34.91 ±11.04	1039.76 ±617.75	74.65 ±23.56	3.21 ±0.81	22.96 ±13.74
Arable, extensive	63.71 ±22.05	115.63 ±49.96	29.81 ±7.92	1645.57 ±748.74	77.96 ±17.52	2.60 ±0.92	30.10 ±13.91
Pasture	56.83 ±28.45	79.78 ±24.32	26.27 ±8.16	784.91 ±626.94	82.75 ±16.05	2.28 ±1.14	21.33 ±9.91
Baseline content *	52.86	81.86	25.60	1057.64	93.69	3.01	28.49

* Baseline content values are estimated based on pasture soils.

Similarly, we took the average values of the maximum concentration of Cu (410.03 mg/kg) found in irrigation water sediments reported by Withanachchi et al. [38]. We estimated an average of 1000 mg sediments per liter, corresponding to high turbidity, which is rarely observed in the region. Based on the results, it would require about 305 years to add a sufficient amount of Cu to reach a 300.0 mg/kg concentration in the soil from the baseline value of 138.77 mg/kg. The calculations showed that Cu addition from the irrigation water and its sediments is obvious. However, there were other sources of Cu, as the Cu mining site located in the region is the source of water contamination and has operated since 1975 [73]. Time was insufficient to raise Cu concentrations to the level found in this study.

Therefore, at the beginning of our research, we hypothesized that the influence of crop-specific agricultural practices play a major role in soil nutrient concentrations, which is evident based on the historical land use and the statistical analysis of the results. Furthermore, in our study, total Cu contents in existing and former vineyards soils vary from 67.35 to 582.97 mg/kg (Table 3) and are in the same range reported from different countries having no issues with irrigation water quality, indicating that such accumulation can be reached based on copper-based fungicides only [74–76]]. Cu-based fungicides have been used in vineyards for more than 150 years, and in the 1950s, their annual application amounted to 20–30 kg/ha, sometimes reaching 80 kg/ha [77,78]. Nowadays, due to raised concerns about Cu accumulation in soils [50], its application is limited to 6 kg/ha/year in organic agriculture, which mainly relies on Cu-based fungicides, and in some countries, down to 3–4 kg/ha/year [60,61].

We applied a similar approach to estimate the potential inputs of Cu from the most widespread fungicide—the Bordeaux mixture (containing 20% of elemental Cu)—based on agrotechnical norms [51] used in state collective farms during the Soviet period; its addition could reach 9.6 kg Cu per year, with potential further additions during wet seasons. This amount could increase Cu concentrations in soil from the baseline value of 138.77 mg/kg to 300.0 mg/kg in about 60 years. This indicates that Cu-based fungicides have the most significant share in the accumulation of Cu in soil.

Dependency of Cu accumulations in soil on the application rate of Cu-based fungicides and thus its crop-specific character is confirmed by KWT results showing statistically significant differences between land use forms ($p < 0.001$). Those differences are also indicated by very high variations in Cu content in the studied soil samples (CV = 105%).

Based on factorial analysis using PCA, Cu accumulation is mainly influenced by a single factor, which we assume to be a combined effect of irrigation water and fungicides (Table S9).

According to the CF index, 77.8% of the existing vineyard soils (Figure S6) and 20.0% of the former vineyard soils (Figure S7) are categorized as moderately contaminated (CF value = 1–3). Contamination is considerable for 11.1% of the vineyard and 50.0% of the former vineyard soils (CF value = 3–6). In 11.1% of cases of the vineyard and 33.0% of the former vineyard soils, contamination is very high (CF value > 6). The CF index does not exceed the value of 3 for all remaining land use types (Figures S5 and S8–S10) and has the following order based on the moderately contaminated category: arable, intensive (78.6%) > arable, extensive (60%) > orchards (40%) > pastures (20%).

The soils in the existing and former vineyards are the most heavily enriched with Cu, based on the EF index assessment (Figures S11–S16). Only those two land use forms showed significant enrichment (EF value = 5–20) with Cu, corresponding to 40.0% of the former vineyards (Figure S13) and 11.1% of the existing vineyards (Figure S12). The soils under other land use types are moderately (EF value = 2–5) or minimally enriched (EF value = 0–2) with Cu. Typically, EF values from 0.05 to 1.5 are considered to result from natural processes or have a crustal origin, while EF > 1.5 is related to anthropogenic activities [33]. Based on this consideration, we can conclude that Cu in all orchard soils (Figure S11), the absolute majority of pastures (Figure S16), and intensive (Figure S14) and extensive arable farms (Figure S15) in our study area can be mainly of natural origin, whereas the soils in the existing and the former vineyards experience significant enrichment from anthropogenic activities.

The metal enrichment with Cu, based on Igeo index, showed the highest values (Igeo value = 2–3) in soils of the former (25.0%) and existing vineyards (11.1%) only, classified as moderately to strongly polluted (Figures S18 and S19). A total of 41.7% of the soils of the former and 11.1% of the existing vineyards are moderately polluted (Igeo value = 1–2). Igeo index values remain below 1 on all other land use types soils corresponding to unpolluted to moderately polluted category (Figures S17 and S20–S22) and have the following order according to the percentage of occurrence: existing vineyards (66.7%) > former vineyards (33.3%) > arable, intensive (28.6%) > arable, extensive (20%) > pastures (4%). The orchards were categorized as unpolluted with Cu (Figure S17).

The PI index was used to evaluate the risks associated with environmental and human health threats; the total Cu concentrations found in the soils were compared to the guide values established by the legislative norms in Georgia [44]. PI values showed that the Cu concentrations exceeded the established threshold (132 mg/kg) in soils under the existing and the former vineyards by more than three times. Consequently, 11.1% of vineyards (Figure S24) and 30.0% of former vineyards (Figure S25) are classified as heavily polluted with Cu according to the PI index (PI value > 3), while orchards (Figure S23), extensive arable farms (Figure S27), and pastures soils (Figure S28) are classified as pollution-free (PI value < 1). The soils under intensive arable farms also remain pollution-free (Figure S26) in the case of 88.9% of farms, and only 11.1% have light pollution (PI value = 1–2).

Such elevated Cu concentrations are mainly a consequence of the use of copper-based fungicides, which persist for decades, and the time required to reach critical levels depends on the initial Cu content in the soil and annual Cu input based on the farmer-established practices. According to the farmers interviewed during our study, the minimum amount of Cu input as a fungicide in the vineyards varied from 2 to 5 kg/ha/year. However, it was nearly twice as high during the Soviet period in state collective farms [51], as mentioned above.

Cu accumulation is also typical in orchard soils due to the use of Cu-based fungicides [79,80], but their input is relatively lower than in vineyards. It should be noted that most fruit orchards studied were relatively young and established on less intensive arable lands or former pasturelands. Therefore, these soils had not been subject to substantial anthropogenic influence.

Cu exhibited a statistically significant ($p < 0.01$) strong positive correlation (Table S5) with Zn ($\varrho = 0.732$) and a moderate correlation with Cd ($\varrho = 0.465$), which potentially had a common source of origin that, based on our studies, may have included both Zn- and Cu-based fungicides and fertilizers. Cu's statistically significant moderate correlation with K ($\varrho = 0.418$) and a weak but still significant correlation with P ($\varrho = 0.345$) can be related to Cu input through K- and P-containing fertilizers. Potential plant-available DTPA-extractable Cu levels are highly dependent on total Cu level in the soil expressed in a very strong correlation ($p < 0.01$, $\varrho = 0.885$). Furthermore, the soil enrichment with total Cu increases the availability of DTPA-extractable Zn. This phenomenon is observed in previous studies [81] and confirmed with a statistically significant strong correlation ($p < 0.01$, $\varrho = 0.709$) in our study.

3.6. Zinc

Zn followed a similar pattern as that observed for Cu, and the highest values were found in soils of the former and existing vineyards. The mean value of the potentially plant-available concentration of Zn equaled 18.17 ± 17.85 mg/kg in the soils of the former vineyards and 11.23 ± 19.89 mg/kg in the existing vineyards (Table 2). These concentrations of DTPA-extractable Zn indicate a very high availability [59] and can be toxic to plants. Zn toxicity was observed in wheat at 7 mg/kg concentrations and in maize at 11 mg/kg [82]. The lowest concentrations were found in extensive arable farms soils with a value of 0.97 ± 1.24 mg/kg, which can be deficient to crops [59], especially on calcareous and alkaline soils, which are dominant in the study region, where Zn bioavailability is reduced due to increased sorption in soils [58]. Significant variation in Zn availability is evident through KWT results ($p < 0.001$), showing statistically significant differences between crop-specific management practices under different land use forms and very high variability of DTPA-extractable Zn in studied soils (CV = 244%).

Likewise, for DTPA-extractable Zn, the highest concentrations of total Zn were observed in soils under the existing and former vineyards, 324.31 ± 353.34 and 310.86 ± 166.27 mg/kg, respectively (Table 3). The variability of total Zn in studied soils is also very high (CV = 109%), and it also shows more considerable variability between studied land use forms based on the KWT ($p < 0.001$).

Based on factorial analysis using PCA, Zn accumulation has a pattern similar to Cu and is mainly influenced by irrigation water and fungicides (Table S9).

CF index shows a similar distribution of contamination classes among land use forms as observed in the case of Cu. A total of 33.3% of vineyards (Figure S6) and 30.0% of former vineyards (Figure S7) have very high contamination levels (CF value > 6) with Zn. CF index is below 3 for all remaining land use types (Figures S5 and S8–S10) and has the following order for the moderately contaminated category: arable, intensive (71.4%) > arable, extensive (70%) > orchards (40%) > pastures (16%).

According to EF, only soils under the existing and former vineyards soils have significant enrichment (EF value = 5–20) with Zn, corresponding to 33.3% of vineyards (Figure S12) and 10.0% of former vineyards (Figure S13). The soils under extensive (18.2%) and intensive arable (7.1%) lands are moderately enriched (EF value = 2–5) with Zn. All soils under orchards (Figure S11), nearly all of the pastures (Figure S16), and majority of the intensive (Figure S14) and extensive arable lands (Figure S15) in our study area have an EF < 1.5, which can be of natural origin. In contrast, soils in the existing and former vineyards soils experience significant enrichment from anthropogenic sources.

A total of 33.3% of the existing and 25.0% of the former vineyards (Figures S18 and S19) belong to the moderately to strongly polluted category based on the Igeo index (Igeo value = 2–3). A total of 33.3% of the soils of the former vineyards and 5.0% of the extensive arable lands (Figure S20) are moderately polluted (Igeo value = 1–2). Igeo values remain below 1 in soils of all other land use types, except one site from extensive arable farms, corresponding to 5% of the total number of this land use form is classified as moderately polluted (Igeo value = 1–2). Based on Igeo index, the least Zn accumulation is observed under orchards (Igeo value ≤ 0), followed by pastures (Figure S22) with 4% in the unpolluted to moderately polluted category (Igeo value = 0–1), the former vineyards with 8.3% and intensive and extensive arable farms, 28.6% and 35%, respectively (Figures S20 and S21).

PI index was used to evaluate the risk associated with environmental and human health threats; the total Zn concentrations found in the soils were compared to the guide values established by the legislative thresholds [44]. PI values showed that the Zn concentrations exceeded the established threshold (220 mg/kg) more than three times (PI value > 3) in soils of 33.3% of the vineyards and are classified as heavily polluted according to PI index (Figure S24). The soils under 30.0% of the former vineyards (Figure S25) have medium pollution levels (PI value = 2–3) with Zn. Single cases of light pollution are observed in soils under intensive and extensive arable farms (Figures S26 and S27), corresponding to 5.0 and 5.6%, according to PI index. In contrast, soils under orchards (Figure S23) and pastures (Figure S28) are classified as pollution-free (PI value < 1) with Zn.

As reported by previous studies use of Zn-based plant protection products to control fungal diseases [83], organic and mineral fertilizers, and polluted irrigation water can result in a high accumulation of Zn in soils [64–66],.

We evaluated possible contributions from irrigation water using the same method as for Cu. We used the maximum concentration of Zn found in irrigation water (0.1218 mg/L) and the average value of maximum concentrations of Zn (863.7 mg/kg) found in irrigation water sediments by Withanachchi et al. [38] from the study region. The calculation was conducted using Equation (8) for the soil of the former vineyards, where minimum the Zn concentration (104.9 mg/kg) was taken as a baseline (Table S4) and the mean Zn concentration (310.9 mg/kg) as a target to be reached (Table 3). According to the results, it would require more than 1650 years to increase Zn concentration using irrigation water and more than 200 years to increase Zn concentration from the baseline value of 104.9 mg/kg to 310.9 mg/kg through the sediments delivered with irrigation water. As in the case of Cu, Zn addition from the irrigation water and its sediments is significant, but it could only enrich soils to such a level with the existence of other sources.

We estimated Zn inputs from another wide-spread fungicide—Zineb (containing 23.7% of elemental Zn), used as an alternative to the Bordeaux mixture—based on agrotechnical norms [51] elaborated from state collective farms during the Soviet period, its addition could reach minimum 4.3 kg Zn per year, with potential additions in rainy seasons, when repeated treatments are typical. This amount could increase Zn concentration in soil from the baseline value of 104.9 mg/kg to 310.9 mg/kg in about 130 years. This indicates that Zn-based fungicides represent the major input source in the accumulation of Zn in soil.

3.7. Iron

The total iron content is usually never deficient in soil, although there are frequent cases of inadequate supply in the case of the plant-available forms [84]. The average values of the concentrations of the DTPA-extractable Fe in the soils subjected to the studied agricultural practices were the highest in soils from the orchards, on average 59.43 $\pm$ 88.85 mg/kg (Table 2). It should be noted that high Fe availability is not characteristic of all orchards but is a result of the single highest concentration found in one orchard soil, under slightly acidic (pH = 6.5) conditions free from carbonates, which probably is the leading cause of greater availability of Fe. The dependency of DTPA-extractable Fe on soil pH and carbonate content is also expressed in statistically significant ($p < 0.01$) moderate negative correlations with pH ($\varrho = -0.432$) and $CaCO_3$ ($\varrho = -0.404$). The vineyards are the richest land use form in plant-available Fe, with an average of 37.89 $\pm$ 23.54 mg/kg. In both cases, the given values correspond to the very high iron content in the soil, which can be explained by relatively higher inputs of organic fertilizers supporting higher extractability of Fe in alkaline calcareous soils [85]. The lowest iron content was recorded in soils of extensively used arable lands, on average 12.35 ± 7.33 mg/kg, and is considered a moderate level of Fe [59].

Total Fe has the lowest degree of variation among studied elements (CV = 34%) and was considered a reference element in this study. Nevertheless, according to KWT results, both DTPA-extractable and total forms of Fe show statistically significant differences ($p < 0.001$) between crop-specific management practices.

Based on factorial analysis using PCA, total Fe content is mainly a result of soil mineralogical composition, and DTPA-extractable Fe is more affected by organic fertilizer inputs (Table S9).

3.8. Manganese

The situation was different from that of iron in the case of manganese, for which the highest concentrations were recorded in soils of extensive arable farms. The average plant-available Mn concentration is 86.65 ± 72.23 mg/kg (Table 2) and 1645.57 ± 748.74 mg/kg for total Mn forms (Table 3). In the case of the mobile forms, the lowest rate was recorded in vineyards, on average 28.68 ± 20.89 mg/kg, and the lowest total content was in orchard soils, 671.40 ± 157.58 mg/kg.

According to the CF index, 65.0% of the soils of extensive arable lands (Figure S9), 30.0% of former vineyards (Figure S7), 28.6% of intensive arable lands (Figure S8), and 12.0% of pastures (Figure S10) are categorized as moderately contaminated (CF value = 1–3). Soils in the orchards (Figure S5) and vineyards (Figure S6) have low Mn contamination levels (CF value < 1).

A total of 22.7% of soils under the intensive arable lands (Figure S14), 7.1% under the extensive arable lands (Figure S15), and 4% under the pastures (Figure S16) are moderately enriched with Mn based on an EF index. Soils of all other land use forms show minimal enrichment (EF value = 0–2), where the absolute majority have EF value < 1.5 (Figures S11–S13) and can be the result of natural processes or have crustal origin.

Based on the assessment with the Igeo index, 65.0% of the soils of extensive arable lands (Figure S21), 25.0% of former vineyards (Figure S19), 21.4% of intensive arable lands (Figure S20), and 12% of pastures (Figure S22) are placed in the unpolluted to moderately polluted category (Igeo value = 0–1). All other land use forms are categorized as unpolluted (Figures S17 and S18) with Mn (Igeo value < 0).

Despite the low toxicity of Mn in soils under near natural and alkaline conditions, we have assessed the risk related to its accumulation according to the PI index (Figures S23–S28). The total Mn concentrations found in the soils were compared to the maximum permissible concentration values established by the legislative norm [44]. PI values showed that the Mn concentrations exceeded the established threshold (1500 mg/kg) more than two times in 4% of pastures classified as moderately polluted (Figure S28) according to the PI index (PI value = 2–3). A total of 65% of the soils of extensive arable farms (Figure S27), 30% of former vineyards (Figure S25), 16.7% of intensive arable farms (Figure S26), and 8.0% of pastures are lightly polluted (PI value = 1–2). In contrast, the orchards (Figure S23) and the vineyards (Figure S24) remain free from Mn pollution (PI value < 1).

Total forms of Mn are characterized by a moderate degree of variation (CV = 66%), indicating some influence from anthropogenic sources. This is confirmed by KWT results, where both DTPA-extractable Mn and total forms of Mn show statistically significant differences between crop-specific management practices. The difference is greater in the case of total Mn ($p < 0.001$) than in the case of DTPA-Mn ($p = 0.005$), which can be caused by a rapid fixation of Mn in alkaline soils.

Based on factorial analysis using PCA, total Mn content is conditioned by atmospheric deposition from diffuse sources and soil mineralogical composition. In addition to those two factors, organic fertilizer inputs significantly affect DTPA-extractable Mn (Table S9).

3.9. Nickel

Nickel is often described as one of the heavy metals and a potential contaminant. However, studies have confirmed the functions of nickel as a micro-nutrient, and the problems caused by its deficiency have been widely studied in the case of nut crops [86]. Therefore, in this paper, nickel is considered a micro-nutrient and a heavy metal, similar to copper, zinc, and manganese.

The results showed that the highest average concentration of nickel in the plant-available form was found in soils of the extensive arable farms, on average 3.89 ± 2.02 mg/kg (Table 2), and the highest values of the total forms were observed in soils of the former vineyards, 137.06 ± 103.21 mg/kg on average (Table 3). In the case of the mobile forms, the lowest content was found in vineyards soils, 1.72 ± 0.66 mg/kg, and the lowest total content was found in soils under the orchards, 73.64 ± 34.01 mg/kg.

Based on the CF index, 40.0% of orchards (Figure S5) and former vineyards (Figure S7), 33.3% of vineyards (Figure S6), 28.6% of intensive arable lands (Figure S8), 15% of extensive arable lands (Figure S9) and 12% of pastures (Figure S10) are moderately contaminated (CF value = 1–3). The remaining sites of the studied land use types show low contamination with Ni (CF value < 1).

A total of 20% of the soils of former vineyards (Figure S12) and 11.1% of existing vineyards (Figure S13) are moderately enriched with Ni by the evaluation by EF index (EF value = 2–5). The soil of all other land use forms and the remaining parts of the existing and the former vineyards are minimally enriched with Ni (EF = 0–2). All soils from orchards (Figure S11), intensive (Figure S14) and extensive arable lands (Figure S15), and pastures (Figure S16) have an EF < 1.5, indicating a natural origin of Ni.

According to the Igeo index (Figures S17–S22), 33.3% of soils of former and existing vineyards (Figures S18 and S19) are classified as unpolluted to moderately polluted (Igeo value = 0–1) with Ni. In contrast, the soils of orchards (Figure S17), extensive and intensive arable lands (Figures S20 and S21), and pastures (Figure S22) are unpolluted (Igeo value ≤ 0).

In order to assess the risk associated with Ni accumulation in soil, the total Ni concentrations found under different land-use soils were compared to the guide values established by the legislation [44]. PI values showed that the Ni concentrations exceeded the established threshold (120 mg/kg) more than two times (PI value = 2–3) in 30.0% of soils of former vineyards (Figure S24) and 22.2% of existing vineyards (Figure S25), marking a medium pollution level. Light Ni pollution is observed in the soils of 11.1% of existing vineyards, 10.0% of former vineyards, and 5.0% of extensive arable lands (Figure S27) (PI value = 1–2). In contrast, soils in orchards (Figure S23), pastures (Figure S28), intensive arable lands (Figure S26), and 95.0% of extensive arable lands are classified as pollution-free (PI value < 1) according to PI index (Figures S23–S28).

Notably, the statistical analysis of the data showed a weak but statistically significant ($p < 0.01$) correlation (Table S5) of total nickel with soil–clay fraction ($\varrho = 0.286$). At the same time, DTPA-extractable Ni strongly correlates to the soil–clay fraction ($\varrho = 0.619$). Those relationships of Ni with soil texture indicate its possible crustal origin, as predicted also according to the EF index for most land use forms (Figures S11–S16). Total forms of Ni have one of the lowest degrees of variation after Fe (CV = 59%) and show insignificant anthropogenic impact on its contents in soils under agricultural use, which is confirmed by KWT results ($p = 0.566$). In contrast, DTPA-extractable Ni show statistically significant ($p < 0.001$) differences between crop-specific management practices.

Based on factorial analysis using PCA, total Ni content is mainly affected by irrigation water and fungicides. In contrast, DTP-extractable Ni is linked to atmospheric deposition from diffuse sources and soil mineralogical composition and, to a lesser extent, with organic and mineral fertilizer inputs (Table S9).

3.10. Cadmium

The soils of former vineyards contained high amounts of the mobile and total forms of cadmium, on average 0.74 ± 0.48 mg/kg (Table 2) and 6.96 ± 9.39 mg/kg (Table 3), respectively. One of the known sources of Cd in agriculture is phosphorous fertilizers, which may contain variable concentrations of Cd. Considering the systematic application of these fertilizers, they can be considered a significant contributor.

Based on the CF index, the highest contamination with Cd (CF value > 6) among land use forms is observed in 10.0% of soils of former vineyards (Figure S7). CF index is less than 3 in soils for all of the remaining land use types (Figures S5, S6, and S8–S10) and has the following order for those in the moderately contaminated category: existing vineyards (77.8%) > former vineyards (70.0%) > orchards (60.0%) > arable, intensive (50.0%) > pastures (24.0%) > arable, extensive (20.0%).

Soils of the former vineyards show a significant enrichment (EF value = 5–20) with Cd according to EF index (Figure S13), corresponding to 10.0% of this land use form and 11.1% of soils currently used under the vineyards (Figure S12) are moderately enriched (EF value = 2–5). The soils of other land use forms have minimal or no enrichment with Cd, and their absolute majority have EF < 1.5 (Figure S11 and S14–S16), indicating the natural origin of Cd without substantial impact from anthropogenic sources. This statement is supported by a moderate ($\varrho = 0.560$) but statistically significant ($p < 0.01$) correlation of Cd with Fe, which is the least affected element in our study (Table S5).

Based on the Igeo index, 8.3% of the former vineyards (Figure S19) are moderately to strongly polluted (Igeo value = 2–3). Igeo values remain below one on all other land use types soils and have the following order for those in the unpolluted to moderately polluted category: former vineyards (16.7%) (Figure S19)> existing vineyards (11.1%) (Figure S18)) > arable, extensive (10.0%) (Figure S21) > arable, intensive (7.1%) (Figure S20). Pastures (Figure S22) and orchards (Figure S17) are free from Cd pollution (Igeo value ≤ 0).

According to the PI index, the risks associated with environmental and human health are the highest in soils of the former and existing vineyards (Figures S24 and S25). Cd concentration is more than three times higher than the maximum permissible concentration (2 mg/kg) established by the legislative norm [44] in 20.0% of the former and 11.1% of the existing vineyards. The land use forms based on the medium pollution level (PI value = 2–3) with Cd have the following order: former vineyards (40.0%) > vineyards (22.2%) > orchards (20.0%) (Figure S23) > arable, intensive (14.3%) (Figure S26) > arable, extensive (10.0%) (Figure S27) > pastures (4.0%) (Figure S28). All the remaining soils experience light (PI value = 1–2) or no pollution (PI value < 1) of Cd.

The possible input of Cd through the irrigation water was calculated using the same method as for Cu and Zn. We used the maximum concentration of Cd found in irrigation water (0.0003 mg/L) and the average value of maximum concentrations of Cd (3.29 mg/kg) found in irrigation water sediments by Withanachchi et al. [38] from the study region. The calculation was conducted using Equation (8) for former vineyard soils, where minimum Cd concentration (2.4 mg/kg) was taken as the baseline (Table S4) and mean Cd concentration (6.96 mg/kg) as the target to be reached (Table 3). According to the results, it would require more than 14,900 years to increase Cd concentration using irrigation water and nearly 1250 years to increase Cd concentration from the baseline value of 2.4 mg/kg to 6.96 mg/kg through the sediments delivered with irrigation water. As in the case of Cu and Zn, Cd addition from the irrigation water and its sediments is considerable, but it could not be sufficient to increase Cd concentration without the existence of other anthropogenic sources.

Total Cd content shows the highest variability among studied elements in studied soils (CV = 111%). Consequently, there are statistically significant differences between crop-specific management practices under different land use forms, which is more evident for total Cd ($p < 0.001$) than for DTPA-extractable Cd ($p = 0.006$).

Based on factorial analysis using PCA, total and DTPA-extractable Cd content is mainly affected by irrigation water and fungicides. An additional factor affecting total Cd concentration is mineral fertilizer inputs, most probably phosphorous fertilizers (Table S9).

3.11. Lead

The highest content of the mobile and total forms of Pb was found in the soils under the extensive arable land use, on average 2.03 ± 0.58 and 30.10 ± 13.91 mg/kg, respectively. The lowest values of the DTPA-extractable Pb content were observed in pastures, on average 0.93 ± 0.40 mg/kg, and the total Pb content in vineyards was 14.36 ± 11.21 mg/kg.

According to the CF index, soils in the study region do not significantly increase Pb concentration on agricultural lands. The land use types assessed in our study has the following order based on CF index (CF value = 1–3) corresponding to the moderately contaminated category (Figures S5–S10), which is the highest contamination level observed for Pb: arable, extensive (55.0%) > former vineyards (30.0%) > arable, intensive (28.6%) > orchards (20.0%) > pastures (16.0%) > vineyards (11.1%). The rest of the investigated soils have low pollution levels (CF value = 1).

Only 4.5% of soils of the extensive arable land (Figure S15) show a moderate enrichment (EF value = 2–5) with Pb. The remaining part of the extensive arable land soils and all the soils of other land use forms have minimal or no enrichment with Pb, and their absolute majority have EF < 1.5, indicating a natural origin of Pb (Figures S11–S14 and S16), without significant influence from anthropogenic sources.

The former and existing vineyards (Figure S18), as well as orchards (Figure S17), are unpolluted with Pb according to the Igeo index (Igeo value < 0). Igeo values remain below 1 in soils of all other land use types and have the following order in unpolluted to moderately polluted category: arable, extensive (25.0%) (Figure S21) > arable, intensive (11.1%) (Figure S20) > pastures (4.0%).

Based on the PI index, the risks associated with environmental and human health are relatively low in all studied soils (Figures S23–S28). Pb concentration in soils exceeds the maximum permissible concentration (32 mg/kg) established by the legislative norm [44] experiencing light pollution (PI value = 1–2) and have the following order: arable, extensive (40.0%) > orchards (25.0%) > former vineyards (20.0%) > arable, intensive (11.1%) = vineyards (11.1%) > pastures (4.0%). All the remaining soils are not polluted (PI value < 1) by Pb.

The possible addition of Pb through the irrigation water was assessed similarly for Cu, Zn, and Cd. We used the maximum concentration of Pb measured in irrigation water (0.0055 mg/L) and the average value of maximum concentrations of Pb (34.25 mg/kg) found in irrigation water sediments by Withanachchi et al. [38] from the study region. The calculation was conducted using Equation (8) on the example of the former vineyard soils, where the minimum Pb concentration (5.5 mg/kg) was taken as the baseline (Table S4) and the mean Pb concentration (25.03 mg/kg) as the target to be reached (Table 3). According to the results, it would require more than 3470 years to increase Pb concentration using irrigation water and more than 480 years to increase Pb concentration from the baseline value of 5.5 mg/kg to 25.03 mg/kg through the sediments delivered with irrigation water. Pb addition through the irrigation water and its sediments can contribute to soil enrichment with Pb. However, increasing Pb concentration without substantial addition from other anthropogenic sources could not be sufficient.

The total form of Pb has the slightest variation after Fe (CV = 53%). It shows the low anthropogenic impact on its contents in soils under agricultural use, confirmed by KWT results ($p = 0.086$). In contrast, DTPA-extractable Pb shows statistically significant differences between crop-specific management practices ($p < 0.001$). The behavior of Pb is quite similar to that of total Ni, which is expressed in their moderate ($\varrho = 0.410$) but significant ($p < 0.01$) two-tailed correlation (Table S5).

Based on factorial analysis using PCA, total Pb content is mainly affected by atmospheric deposition from diffuse sources and, to a smaller extent, by irrigation water and fungicides. However, DTPA-extractable Pb is nearly equally associated with applying irrigation water, fungicides, and atmospheric deposition from diffuse and relatively less influenced by soil mineralogical composition (Table S9).

4. Discussion

The results for each studied element showed that crop-specific management practices greatly influence the contents of nutrients and toxic elements in soils. The changes in the major nutrient contents, such as P and K, are conditioned by the crop requirements and soil management practices established by the farmers. This finding is in line with the information collected during the interviews. Moreover, although the farmers could only provide some details regarding the amount and type of fertilizers used for the last five years, they still provided valuable data that helped to explain the results obtained. The substantial contribution of fertilizer application practices can be seen in the statistical analysis, in which the application of complex NPK fertilizers, confirmed in the interviews as the farmers' preferred choice, was identified as a cause of P and K interdependencies, with a statistically significant ($p < 0.01$) positive correlation ($\varrho = 0.456$). In some cases, namely those involving extremely high concentrations of K found in the soil in vineyards, it is evident that organic fertilizers in the form of manure were used in combination with synthetic mineral fertilizers. According to agrotechnical norms [51], this practice was common during the Soviet period in state collective farms. In the case of vineyards, on average, 130 kg N, 100 kg P, and 100 kg K were applied as synthetic mineral fertilizers, plus 50 t/ha of manure every 4 years. Nowadays, this is mainly observed in the plots near settlements, where livestock farms are located, as the farmers attempt to reduce transportation costs, as it is costly to apply manure to large plots in remote areas.

The impacts of agricultural practices are even more visible in the case of micro-nutrients and toxic elements, especially Cu, Zn, Cd, and Ni. The existing and former vineyards show high accumulation rates of Cu and Zn and, to a lesser extent, of Cd and Ni, which, according to our study, are closely linked to crop-specific management practices. Those relationships can be seen based on different environmental assessment indices, like CF, EF, Igeo, and PI, used in our study and results obtained from KWT, CV, and Spearman's correlation coefficient. Based on factorial analysis using PCA, increased concentration of plant-available Cu, Zn, Cd, and Pb were mainly associated with irrigation water and intensive use of fungicides; Fe, Mn, and Ni were closely linked to several factors, such as the mineralogical composition of soils, mineral and organic fertilizers inputs, and atmospheric deposition from diffuse sources, where exhausts from transport are probably the primary source.

Soil contamination under different land use forms was additionally assessed using the pollution load index (PLI) and Nemerow's comprehensive pollution index (PIN) to evaluate the cumulative effect of all studied elements (Figures S5–S10), except Fe, which was used as a reference. According to PLI, 80.0% of former vineyards, 57.1% of intensive arable lands, 55.0% of extensive arable lands, 33.3% of vineyards, 20.0% of orchards, and 7.7% of pastures are qualified as polluted. The remaining sites are considered to be at a baseline level, according to PLI.

Based on Nemerow's comprehensive pollution index (PIN), soils at the former and existing vineyards experience heavy pollution (PIN > 3) in 10.0% and 11.1% of the cases, respectively. A total of 10.0% of the former vineyards have medium pollution levels (PIN = 2–3). Most of the studied areas fell under precaution level according to the PIN index in the following order: arable, intensive (92.9%) > former vineyards (80.0%) > existing vineyards (77.8%) > arable, extensive (75.0%) > orchards (60.0%) > pastures (44.0%).

According to different assessment methods, Cu and Zn are the most affected elements among the micro-nutrients in our study, as in most cases, they determine the severity of anthropogenic influence on the soils. They show the highest degree of variation between different land use types and highlight differences in crop-specific management practices established by farmers.

There are multiple anthropogenic sources of those elements in the environment. However, agricultural management practices seem dominant on agricultural lands, where inputs from plant protection substances play a significant role, especially for Cu. This study underlines the significance of fungicides as a leading contributor to the accumulation of Cu and Zn in access amount in soil, as the highest values were found in soils of vineyards and former vineyards, where Cu- and Zn-based fungicides are regularly applied, and an annual application rate is much higher than in case of other land use types. According to the farmers interviewed during our study, the Cu input as a fungicide in the vineyards can reach 5 kg/ha/year, while Zn can be applied up to 1 kg/ha/year. However, based on historical data from the Soviet period (1921–1991), most agricultural lands were owned and directly managed by state authorities following guidelines of agricultural practices elaborated for a specific crop, region, and soil type. These guidelines include plant protection measures and application norms of fertilizers. Despite some deviations from the written rules due to local agronomists' corrective changes at the farm level, these norms [51] give a good estimation of the types and application rates of fungicides and fertilizers, which continued for about 60 years in the region starting from 1930.

Another source of input is the use of organic and synthetic mineral fertilizers. According to the values in the literature [87], high Cd contents are characteristic of P fertilizers. Assuming an average input rate of 100 kg/ha P fertilizer, based on farmer interviews, their use could introduce an average of 0.009 kg Cd/ha/year. In addition, organic fertilizers in the form of manure could contribute on average 0.310 kg Cu/ha/year, 1.325 kg Zn/ha/year, 0.006 kg Cd/ha/year, and 0.189 kg Ni/ha/year, assuming an annual application of 10 t/ha, which is the average amount typically applied by farmers according to our survey. It should be noted that organic fertilizers, including manure, are not regularly applied by farmers, and they are practiced mainly in vineyards, orchards, and on intensive arable lands.

Considering previous studies [64–68], irrigation water is one of the soil's anthropogenic sources of Cu, Zn, and Cd elevation. Considering irrigation patterns and irrigation water quality on one hand and fungicide application rates and their metal content on the other hand, a simulation study has revealed that intensive application of fungicides, especially in vineyards, is a more significant factor in enriching soils with Cu and Zn than irrigation water. Cu, Zn, Cd, and Pb were selected as leading elements in the soil pollution in the region. The impact of contaminated agricultural water is substantial for Cu and Zn but is negligible for Cd and Pb. In particular, irrigation water in an amount of 3860 m^3, estimated as the maximum possible volume applied per year, including suspended contaminated sediments, could add about 1.998 kg Cu/ha/year, 3.804 kg Zn/ha/year, 0.153 kg Pb/ha/year, and 0.014 kg Cd/ha/year. Despite that, other inputs are needed to reach the current contamination level with irrigation water, as it would require more than 385, 200, 480, and 1250 years for Cu, Zn, Pb, and Cd, respectively. On the other hand, the same irrigation water is applied to other soils for different land uses. However, the highest accumulation rates are found mainly under former and existing vineyards, which is one of the indications of the impact of crop-specific management practices.

Furthermore, the studied elements could be added to the soil through atmospheric deposition, which was not measured in the study region but identified as one of the factors based on PCA factorial analyses affecting Mn, Pb, and Ni. According to the values in the literature [88,89], they may reach 0.638 kg Cu/ha/year, 2.485 kg Zn/ha/year, 0.18 kg Ni/ha/year, 0.611 kg Pb/ha/year, 0.022 kg Cd/ha/year, 0.04 Mn/ha/year, where Pb and Cd addition is much higher than from other sources. However, as a diffuse source of pollution, atmospheric deposition is distributed more or less equally despite land use types and farmers' management practices.

5. Conclusions

Based on our study, the following conclusions can be made:

(1) The impact of crop-specific management practices on plant nutrient concentrations in the soil is substantial. The Kruskal–Wallis test showed statistically significant differences in the contents of all studied macro-nutrients (P, K), micro-nutrients (Fe, Mn, Cu, Zn), and toxic elements (Cd, Pb) between land use forms. The differences are also evident in organic matter content, an essential prerequisite for soil fertility. The agricultural practices established in the vineyards have the most significant impact on

soil nutrient status and toxic element content, followed by intensive and extensive arable lands and orchards. In contrast, soils in pastures, as expected, are relatively less affected, as they experience no direct input from the farmers' side;

(2) The soils in the former and existing vineyards are the most enriched with Cu and Zn. This likely results from the long-term intensive application of Cu- and Zn-based fungicides, especially during the Soviet period in state-owned collective farms, which were already present in 1930 and substantially expanded in the 1940s and 1960s, accelerating the industrialization of agricultural production, with possible additions from metal-contaminated irrigation water and fertilizers. DTPA-extractable Cu and Zn concentrations in those soils reach toxic levels for crops and can deteriorate the quality and quantity of the agricultural produce;

(3) Increased concentrations of plant-available Cu, Zn, Cd, and Pb were mainly associated with irrigation water and intensive use of fungicides; Fe, Mn, and Ni were closely linked to several factors, such as the mineralogical composition of soils, mineral and organic fertilizers inputs, and atmospheric deposition from diffuse sources, where exhausts from transport are probably the primary source. During our study, we attempted to differentiate irrigation water inputs from fungicides using simulations based on irrigation patterns, irrigation water quality, and fungicide application rates and their metal content. The simulation revealed that the intensive application of fungicides, especially in vineyards, is more significant in enriching soils with Cu and Zn than irrigation water, with an average annual input of 9.6 kg/ha/year of Cu and 4.3 kg/ha/year of Zn. Nowadays, those amounts are reduced to 5 kg/ha/year of Cu and 1 kg/ha/year of Zn;

(4) Organic fertilizer inputs are affecting Fe, Mn, and Ni availability to plants, while mineral fertilizers are linked with total Ni and Cd accumulation and, to a smaller extent, the Ni plant-available pool;

(5) Cd is the element of concern among toxic elements studied. Its concentration exceeds the MPC level set by the legislative norm in Georgia (2 mg/kg) in 76% of samples. However, according to the EF index, in the majority (96%) of the samples, Cd can have a natural origin without substantial impact from anthropogenic sources. In contrast, Cd availability to plants is affected by contaminated irrigation water and fungicide application;

(6) Pb rarely exceeds its legislative threshold level and is less affected by agricultural practices, but its plant-available pool is nearly equally affected by irrigation water and fungicide applications and atmospheric deposition from diffuse sources;

(7) Maintenance of OM content in soil and its improvement by the application of organic fertilizers, green manures, and crop residue management, especially changing surface residue burning practices, would benefit agricultural production and reduce the availability of heavy metals to plants;

(8) This study indicates the necessity of understating the cumulative impact of agricultural practices, including irrigation, fertilizer, and pesticide applications and raising awareness among farmers to minimize inputs of harmful substances while improving soil fertility or protecting crops from diseases and pests.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su16104244/s1, Table S1: Basic soil properties and major nutrients concentrations in soil; Table S2: Particle size distribution of soil; Table S3: Potentially plant-available forms of nutrients (Cu, Zn, Fe, Mn, Ni) and toxic elements (Cd, Pb) in soil; Table S4: Total forms of nutrients (Cu, Zn, Fe, Mn, Ni) and toxic elements (Cd, Pb) in soil; Table S5: Spearman's correlation coefficients; Table S6: The classes for CF and PLI; Table S7: The classes for PI and PIN; Table S8: The classes for EF and Igeo; Table S9: Principal component analysis; Figure S1: Map of study area; Figure S2: Map of study area based on topographic map from 1942; Figure S3: Map of study area based on topographic maps from 1969 to 1973; Figure S4: Map of study area based on topographic maps from 1982 to 1984; Figure S5: CF, PLI, and PIN indices for the orchards; Figure S6: CF, PLI, and PIN indices for the vineyards; Figure S7: CF, PLI, and PIN indices for the former vineyards; Figure S8:

CF, PLI, and PIN indices for the intensive arable lands; Figure S9: CF, PLI, and PIN indices for the extensive arable lands; Figure S10: CF, PLI and PIN indices for the pastures; Figure S11: EF index for the orchards; Figure S12: EF index for the vineyards; Figure S13: EF index for the former vineyards; Figure S14: EF index for the intensive arable lands; Figure S15: EF index for the extensive arable lands; Figure S16: EF index for the pastures; Figure S17: Igeo index for the orchards; Figure S18: Igeo index for the vineyards; Figure S19: Igeo index values for the former vineyards; Figure S20: Igeo index for the intensive arable lands; Figure S21: Igeo index values for the extensive arable lands; Figure S22: Igeo index values for the pastures; Figure S23: PI index for the orchards; Figure S24: PI index for the vineyards; Figure S25: PI index for the former vineyards; Figure S26: PI index for the intensive arable lands; Figure S27: PI index for the extensive arable lands; Figure S28: PI index for the pastures.

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