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Bridhikitti, Arika, Kaewsuk, Jutamas, Karaket, Netiya et al. (5 more authors) (2023) Sources and Magnitude of Heavy Metals in Sugarcane Plantation Soils with Different Agricultural Practices and Their Implications on Sustainable Waste-to-Foods Strategy in the Sugar–Ethanol Industry. Sustainability. 14816. ISSN: 2071-1050

https://doi.org/10.3390/su152014816

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Sources and Magnitude of Heavy Metals in Sugarcane Plantation Soils with Different Agricultural Practices and Their Implications on Sustainable Waste-to-Foods Strategy in the Sugar–Ethanol Industry

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Citation: Bridhikitti, A.; Kaewsuk, J.; Karaket, N.; Somchat, K.; Friend, R.; Sallach, B.; Chong, J.P.J.; Redeker, K.R. Sources and Magnitude of Heavy Metals in Sugarcane Plantation Soils with Different Agricultural Practices and Their Implications on Sustainable Waste-to-Foods Strategy in the Sugar–Ethanol Industry. *Sustainability* **2023**, *15*, 14816. https://doi.org/10.3390/su152014816

Academic Editors: Taghi Miri and Helen Onyeaka

Received: 10 September 2023
Revised: 28 September 2023
Accepted: 9 October 2023
Published: 12 October 2023

Abstract: Driven by Thailand's Bio-Circular Green Economy strategy, this study explores industrial waste utilization as a solution to mitigate the impacts of climate change and economic insecurity. This study involved interviews with farmers and field sampling across 131 sugarcane plantations, primarily in four districts in Kanchanaburi, western Thailand. The investigation aimed to assess heavy metal levels (As, Fe, Mn, Zn, Cu, Cr, Pb, Cd, Hg) in the plantation soils and their accumulations in soils and biomass under various agricultural practices, including the uses of filter cake and vinasse (industrial wastes from sugar–ethanol industries). Spatial analysis showed that As often exceeded national soil-quality standards for agriculture (25 mg kg^{-1}). The Cd, As, and Zn tended to accumulate at a high level in most soils, whereas Pb accumulated locally. Factors such as clay content, soil alkalinity (for As and Mn), soil organic matters (As, Mn, and Hg), and no/minimum tillage (Zn and Cd) promoted the metal accumulation. Factor analysis showed that natural geochemical processes govern the spatial variations of the metals. The application of filter cake led to soils with elevated Cr, Fe, As, Cd, and Mn content and a clayey organic-rich composition, while the vinasse resulted in soils with higher levels of Zn, Cu, Fe, and clayey saline. The bioconcentration factors (BCF) revealed that sugarcane generally accumulated Hg (BCF ~2.32−35.72), whereas Cu (2.67) and As (1.04) tended to accumulate in sandy-soil farmlands. The waste utilization, however, neither contributed significantly to the concern levels of soil metals nor enhanced the bioconcentration of the soil metals into the sugarcane biomass. Utilizing the waste as fertilizer could benefit cane yield, but further studies should focus on proper fertilization rates and food safety.

Keywords: agricultural soils; heavy metals; industrial waste; Bio-Circular Green Economy; bioconcentration factor; geoaccumulation index; soil conservation

1. Introduction

Thailand has approximately 1,763,575 ha of sugarcane plantations and was ranked the second-largest sugar exporter in 2021–22 [1]. In 2022, about 6.62 M tons of cane sugar were exported, generating a national income of about 3100 M USD [2]. Sugar and related products accounted for about 21% of the national gross domestic product in the agricultural sector and affected more than 425,000 households [3]. Given the consequential impact of cane yield on farmers' economic returns, it is customary for farmers to employ mineral fertilizers and pesticides. The chemicals are predominantly sourced through imports, with costs subject to fluctuations tied to petroleum prices and global supply and demand. The recent increases in costs were attributable to supply shortages stemming from the Russia–Ukraine War in 2022. Furthermore, crop yield is also strongly dependent on the amount of rainfall and air temperature; thus, climate change significantly affects cane yields. To cope with climate change and world economic volatility, the Thai Government has introduced the Bio-Circular Green Economy model (BCG) to promote sustainable growth conforming with the sustainable development goals of the UN. The food and agricultural sector is one of the main industries adopting the BCG. The suggested strategies for BCG implementation in this sector include product diversification, waste reduction, efficient resource consumption, technology for optimized waste production, smart farming technology, and food safety [4].

Industrial waste utilization from agricultural production could be one of the options for BCG implementation, but it requires scientific evidence to assure the general population about its insignificant short-term and long-term impacts on human and ecosystem health. The waste from sugar mills and molasses-based ethanol distilleries could possibly be used for fertilization in crop fields, as it is organic, nutrient-rich, and the production processes typically use low-toxic compounds. The chemicals primarily added in the juice clarification process for controlling pH are lime, salts, silicates, amino acids, proteins, enzymes, and organic acids. To adsorb impurities, either lime with carbon dioxide is used to produce calcium carbonate precipitate (or carbonization) or lime with sulfur dioxide to produce calcium sulfite precipitate (or sulphitation) [5–7].

The primary wastes from the sugar mills are bagasse from milling processes, boiler ash from energy production processes, filter cake from juice clarification processes, and wastewater from machine and floor cleanings. The waste produced from the ethanol distilleries is vinasse. Bagasse is mainly wood pulp gained through milling sugarcane. It contains about 45–50% water, 40–45% fibers (cellulose, pentosans, lignin), and dissolved sugar [5]. Though previous literature suggests composting it for organic fertilizers [5], bagasse has more economic potential as a biomass fuel for energy production in sugar mills [8]. The boiler ash is what remains after the incineration of bagasse. The ash is enriched with minerals, such as potassium and phosphate, which can be used as soil fertilizer [5]. Filter cake (or Press Mud) appears soft, spongy, and as a dark brown solid. The cake consists of moisture (50–65%), fiber (20–30%), crude wax (7–15%), crude protein (5–10%), and sugar (5–12%) [9]. In addition, the cake may also contain sulfites (from the sulphitation process), phosphates (added to increase particle settling), organic carbon, macronutrients (C, N, P, K, Mg, Ca, S), and micronutrients (Fe, Mn, and Si) [5,9]. Thus, filter cake has been widely used as fertilizer. Vinasse (the same as stillage and spent wash) is the liquid waste from the sugar–ethanol industry. It is acidic (3.5–5 pH), dark brown (attributed to melanoidin), and high in organic content and potassium content [6]. Using vinasse as fertilizer in fertigation has been widely recommended due to its low cost, improved soil aggregation, and increased crop yield [6,10]. Long-term irrigation by vinasse could promote soil acidification and salinity, change the population of microorganisms in the soil, increase potassium and organic load, and increase soil porosity, resulting in more soil water retention [6,11]. Yin et al. [12] have shown the negligible accumulation of heavy metals in soil with vinasse irrigation.

Agricultural soils have not only been typically contaminated by industrial wastes but also applications of mineral fertilizers and agrochemicals, which contain both recalcitrant organic substances and heavy metals [13–19]. The accumulation of heavy metals in agricultural soils has been widely monitored and assessed in previous studies. However, the findings have been inconsistent among the study areas due to differences in the physical properties of soil, organic and inorganic contents, soil conservation practices, and contributions of both anthropogenic and natural sources [18–23]. High concentrations of heavy metals have been typically found in paddy and vegetable fields, such as in China [13,23], the European Union [24], and Iran [25,26]. Considering that some heavy metals are toxic, even at low concentrations, such as As, Hg, and Cd, the accumulation of the heavy metals in food crops could be an issue of concern.

To consider the bioavailability enhancement of the heavy metals, a bioconcentration factor (BCF) of greater than 1 implies the phytoextraction of heavy metals from soil to biomass. The soil-to-plant transfer of heavy metals was the highest in leafy vegetables, followed by rootstalk/fruit vegetables, rice, and grain [27,28]. Cd was often found with a BCF greater than 1 in many studies, such as in Xi River, NE China [27], and Swat, N Pakistan [29]. In addition, Sharma [30] found that rice and maize grain were hyperaccumulators for Cr, Co, and Cu in Punjab wetlands, in India. Nonetheless, previous studies have also found low BCF (<1) in Bangladeshi rice grains in [31] and Thai sugarcane leaves/shoots/roots [32]. The soil's organic content, heavy metals content, and plant species contribute to different bioavailability and phytoextraction of the heavy metals from soils.

Previous studies often overlooked variabilities in soil physicochemical properties, fertilization practices, and soil conservation efforts within sugarcane plantation areas. These factors significantly influence heavy metal dynamics in soils and biomass. Moreover, there are gaps in the literature regarding investigation of waste utilization sustainability and a lack of comprehensive integration of these factors affecting cane yield, a pivotal aspect for economic sustainability. This study, therefore, investigated diverse soil physicochemical properties, fertilizations (focusing on those using mineral fertilizations, filter cake, and vinasse), and soil conservation practices. This study aims to quantify heavy metal levels and accumulations in sugarcane soils. The transfer of heavy metals from soils to phytomass was also estimated from the BCF. Sources of these soil metals were identified from factor analysis, and the effects of soil metals on cane yield were also assessed and discussed. The findings suggest the potential sustainability of utilizing wastes from the sugar–ethanol industry in sugarcane cultivation. These outcomes have the potential to drive positive changes in agricultural practices, environmental stewardship, food safety assurance, policy formation, and academic knowledge advancement based in agriculture and environmental science. They collectively contribute to the overall sustainability and resilience of sugarcane farming systems.

2. Methodology

2.1. Sampling Sites

The studied area covers primarily, but is not limited to, four districts in the Kanchanaburi province, western Thailand, comprising the Muang Kanchanaburi, Bo Phloi, Tha Muang, and Tha Maka districts (Figure 1). They are situated between latitudes from 13.7 to 14.0° N and longitude from 99.0 to 99.9° E. In these four districts, the predominant land use/cover is agricultural lands (56.3%), of which 17.1% are sugarcane fields and 11.6% cassava fields, followed by urban and built-up land (25.9%) [33]. Sugarcane is the key economic crop in Kanchanaburi, contributing significantly to its gross domestic product [34]. The study location was influenced by the confluences of the Khwae Yai River, Khwae Noi River, and Taphoen Canal that all flow into the Mae Khlong River in the Mae Khlong River watershed. Nonetheless, some of the sampling sites in Tha Maka were in the Tha Chin watershed (see Figure 1).

Geographical characteristics of Muang Kanchanaburi, Tha Muang, and Tha Maka districts are alluvial plains located downstream of Srinagarindra Dam and Vajiralongkorn Dam (18,770 M m^3 and 11,000 M m^3 retention capacities, respectively). Bo Phloi is characterized by an undulating plain. There are a variety of mine types in the Mae Khlong River watershed, such as limestone, dolomite, kaolin, granite, quartz, feldspar, phosphate, tin, fluoride, and tungsten [35].

Soil samples in this study are mostly sediment lying in the valley basin on top of a carbonate platform bedrock with some intrusion of igneous rock. From the Permian period in this region, it is estimated that 300 m thick carbonate rocks had been deposited [36].

Later, collisions between the Indian and Eurasia plates during the Eocene caused the uplifting, faulting, and folding of basement rock and an intrusion of igneous rock in some areas [37,38]. Two active fault zones in the area are the Three Pagodas Fault Zone (TPFZ) and Sri Sawat Fault Zone (SSFZ). Both TPFZ and SSFZ are dextral strike-slip faults striking NW–SE [38], which also collocate with the Khwae Noi and the Khwae Yai rivers, respectively. Tectonic activities in this area create a complex geological system with a variety of exposed rocks, where the exposed surface rock could range from Precambrian to recently eroded sediment [39].

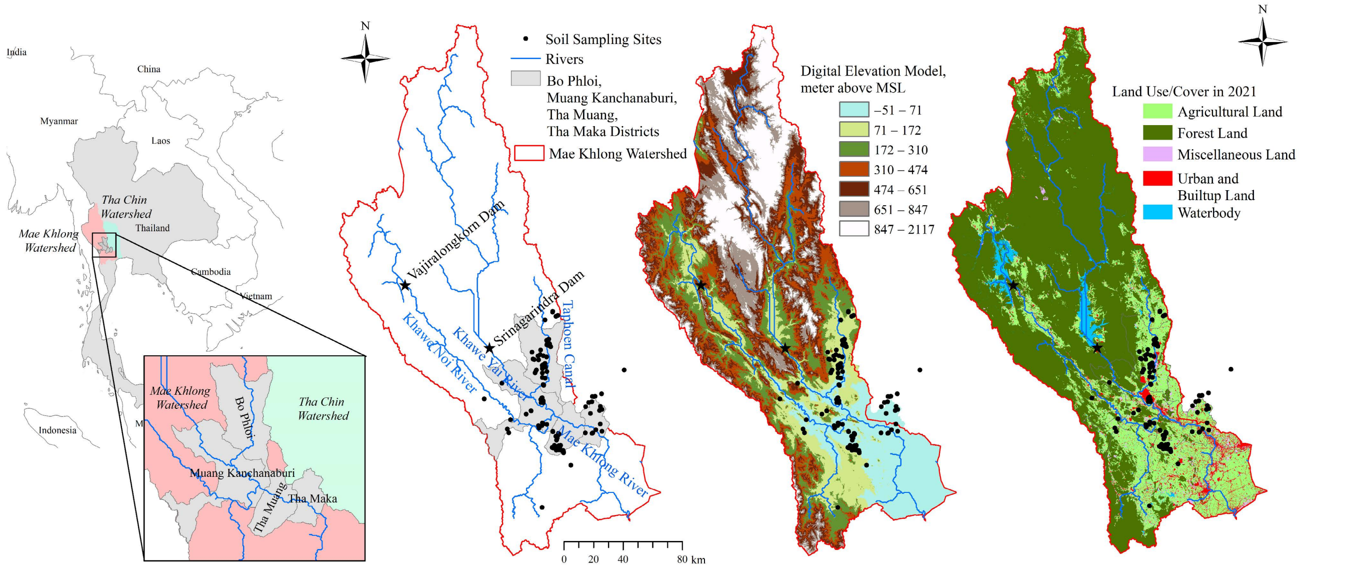

Figure 1. Studied area, soil sampling sites, terrain elevation * and land use/cover in 2021 **. Note: * based on 30 m SRTM DEM, acquired from https://dwtkns.com/srtm30m/, accessed on 18 February 2023. ** acquired from the Land Development Department, Thailand through Open Government Data of Thailand, https://data.go.th/th/dataset?res_format=SHP, accessed on 1 September 2023.

The climate in Kanchanaburi is classified as tropical savanna (AW), according to Köppen's climate classification. The rainy season is from May to October, with an average annual rainfall of 1086.2 mm, influenced by a strong southwesterly monsoon blowing from the Indian Ocean. The summer season is from February to April, with a maximum average daily temperature of 39.39 °C, and winter is from November to January, with a minimum daily temperature of 22.45 °C [33].

2.2. In-Depth Interviews

The in-depth interviews and field sampling were carried out during 20–31 May 2022, in the sugarcane plantations. A total of 207 farmers in the four subdistricts participated in the interviews. The interviews aimed to quantify the cane yield, mineral fertilizer and agrochemical application rates, and identify fertilization processes (mineral fertilizer, vinasse, and filter cake applications) and soil conservation practices. The average plantation area was 38 ha per household, ranging from 0.5 to 384 ha. From the interviews, the average application rate of mineral fertilizers was 674.43 kg ha^{-1} yr^{-1}, applied once to twice a year. The application rate of the filter cake was 99.3 tons ha^{-1} yr^{-1} and applied once every two to four years. Fertigation with vinasse was also used once every two to three years only, due to pungent smells and soil aggregation concerns. The interviews complied with the guidelines of the Human Research Ethics Committee, Mahidol University (Protocol Number MU-CIRB 2022/038.2302 since 28 April 2022).

2.3. Field Sampling

Surface soil (0–15 cm depth) and cane leaf samples were taken from 131 sugarcane plantations. The sampled leaves were the third-top leaves. The sampling locations were wider than just the four districts. Researchers randomly collected samples in zigzag patterns across the fields, and each sample was composited from seven to ten plots, depending on plantation size.

Bagasse, filter cake, and ash samples were taken from a local sugar mill in Tha Maka. In contrast, the vinasse sample was acquired from a molasses-based ethanol distillery in Bo Phloi.

2.4. Sample Preparation and Analysis

After collection, soil samples were immediately air-dried and completely dried within 1 to 3 days. The dried soil samples were ground and sieved using a 2 mm mesh. The prepared soil samples were later used for physicochemical soil determination, including soil color (via Munsell Color Book), soil texture (using the ribbon test), soil pH (1:1 soil:water), and soil electroconductivity (EC) (1:5 soil:water). For quantitative assessment, the soil texture was later classified into five classes based on % clay content, from low to high: 1 = sand, 2 = loamy sand, 3 = sandy loam and sandy clay loam, 4 = sandy clay, and 5 = silt loam, loam, silty clay loam, silty clay, and clay. Furthermore, the soil samples were extracted following the EPA3051 alternative method using an Ethos Up microwave digester. The sugarcane filter cake and ash were also prepared and extracted using the same method as the sol samples.

Leaf and bagasse samples were refrigerated at 4 °C for two days before being chopped to < 5 mm in size and dried in a hot air oven under 70 °C for 2 to 3 days. The dried leaf and bagasse samples were later digested using an Ethos Up microwave digester with 8 mL of HNO_3 and 2 mL of H_2O_2 at 200 °C for 15 min. The 5 -g vinasse sample was digested using 7 mL of HNO_3 and 1 mL of H_2O_2 at 200 °C for 10 min and 200 °C for 20 min using an Ethos Up microwave digester.

The soil, leaf, filter cake, ash, bagasse, and vinasse extracts were filtered and analyzed for heavy metals using inductively coupled plasma–optical emission spectroscopy (ICP–OES) (Perkin Elmer, Avio 500 model). In this study, there are nine metals included in the discussion: Arsenic (As), Iron (Fe), Manganese (Mn), Zinc (Zn), Copper (Cu), Chromium (Cr), Lead (Pb), Cadmium (Cd), and Mercury (Hg). The ICP–OES detection limits are, respectively, 1.0, 0.08, 0.026, 0.07, 0.26, 0.17, 1.3, 0.1, and 1.0 μg L^{-1}. Calibration concentrations ranged from 0.5 μg L^{-1} to 10 mg L^{-1}, resulting in a coefficient of determination, R^2, of 0.999669 or higher.

2.5. Data Analysis

The data analyses in this study were implemented using MATLAB version 9.9 R2020b software under Mahidol University License.

Geoaccumulation index, or I_{geo}, was first introduced by Muller (1969) to assess pollution levels in the soil of individual heavy metals by comparing present and previous contaminations [40]. The I_{geo} can be calculated using Equation (1).

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \tag{1}$$

where C_n = the mass concentration of the metals in sampled soils (mg kg^{-1}), and B_n = the mass concentration of the metals in background soils (mg kg^{-1}).

In this study, the background levels of the soils in Thailand were obtained from Zarcinas et al. [41]. The soils were sampled from forested, uncultivated, and remote from industry areas across the country [41].

Magnitudes of the contamination were classified into six levels, according to I_{geo} figures: $I_{geo} < 0$ = no contamination; $0 < I_{geo} < 1$ = light to moderate; $1 < I_{geo} < 2$ = moderate;

$2 < I_{geo} < 3$ = moderate to strong; $3 < I_{geo} < 4$ = strong; $4 < I_{geo} < 5$ = strong to extremely serious; and $5 < I_{geo}$ = extremely serious.

Bioconcentration factor (BCF) was calculated using Equation (2) to indicate the phytoextraction ability of the sugarcane plant when absorbing metals from the soil to the aboveground biomass [42]. Low BCF (<1) implied poor efficiency for phytoextraction, whereas high BCF (>1) highlighted efficient accumulation of soil metals into the phytomass.

$$BCF = \frac{C_{plant,leaf}}{C_{soil}} \quad (2)$$

where $C_{plant,leaf}$ = concentration of metal in the sugarcane leaf, and C_{soil} = concentration of the corresponding metal in soil

Spearman Correlation Coefficients were calculated to identify any associations between heavy metal contents in soil and the soil's physicochemical properties and between BCF for each metal species and the soil's physicochemical properties.

Factor analysis using the Varimax rotation method was performed on the soil's metals contents and the physicochemical soil properties to assess potential sources of the soil metals. Five factors were estimated from the eigenvectors acquired from principal component analysis (PCA) that explained about 75.8% of the total variance of the observations.

Chi-square test for independence was conducted to indicate significant associations between the soil metals and the soil conservation measures, the amount of herbicides, and the amount of mineral fertilizers applied to the fields.

3. Results and Discussion

3.1. Chemical and Physical Characteristics of the Sugarcane Plantation Soils

The pH levels of most soils in the studied area were slightly basic (pH 7.27–8.73), but those in Tha Maka were slightly acidic (pH 5.06–6.98). Higher soil ECs were found along the Mae Khlong River in Muang Kanchanaburi, Tha Muang, and Tha Maka, with dominant clay content and darker color soils (Figure 2). Conformingly with typical high EC soil found in the other studies [43], the high EC soil in this study was found to have dominant clay content and darker color soils (as shown in Figure 2), implying organic-rich soils. Interestingly, heavy metals content in the soils around the Khwae Noi River connecting to the Mae Khlong River in Muang Kanchanaburi were significantly high for all metal types (Figure 3). In contrast, soil samples collected from nearby areas in Tha Muang exhibited lower metal contents (except for Cr and Hg).

3.2. Accumulations of Heavy Metals in the Sugarcane Plantation Soils

The average quantities of heavy metals in the soils with conventional fertilization using chemical fertilizers were 48.7, 35,291, 1384, 77.1, 26.1, 72.3, 51.0, 0.67, and 0.018 mg kg^{-1} for As, Fe, Mn, Zn, Cu, Cr, Pb, Cd, and Hg, respectively (Table 1). All the heavy metals were within the satisfactory limits set by the National Soil Standard for Agriculture (Notification of the National Environment Board on Soil Quality Standard, issued on 11 March 2021), except for As. The soil Hg was relatively lower than the typical agricultural soils worldwide, exhibiting the average content of 0.28 mg kg^{-1} [16]. Nonetheless, the soil As and Cd levels were higher than those in the background soils in Thailand [41]. The key concern was that the levels of soil As often exceeded the National Soil Standard for Agriculture, limited to 25 mg kg^{-1}.

As interpreted from the geoaccumulation index (I_{geo}) in Figure 4, accumulations of heavy metals in the agricultural soils were significant for Cd (median of 1.35), As (0.04), and Zn (−0.69), which scatter across the studied site. Two areas are exhibiting significant accumulations of heavy metals. Most notably, Bo Phloi exhibited strong Cd contamination, moderate-to-strong Pb contamination, and moderate As and Zn contamination. The confluence of the Khwae Noi River to the Mae Khlong River at Muang Kanchanaburi also contained strong contamination of Cd and moderate levels of As, Cr, and Zn.

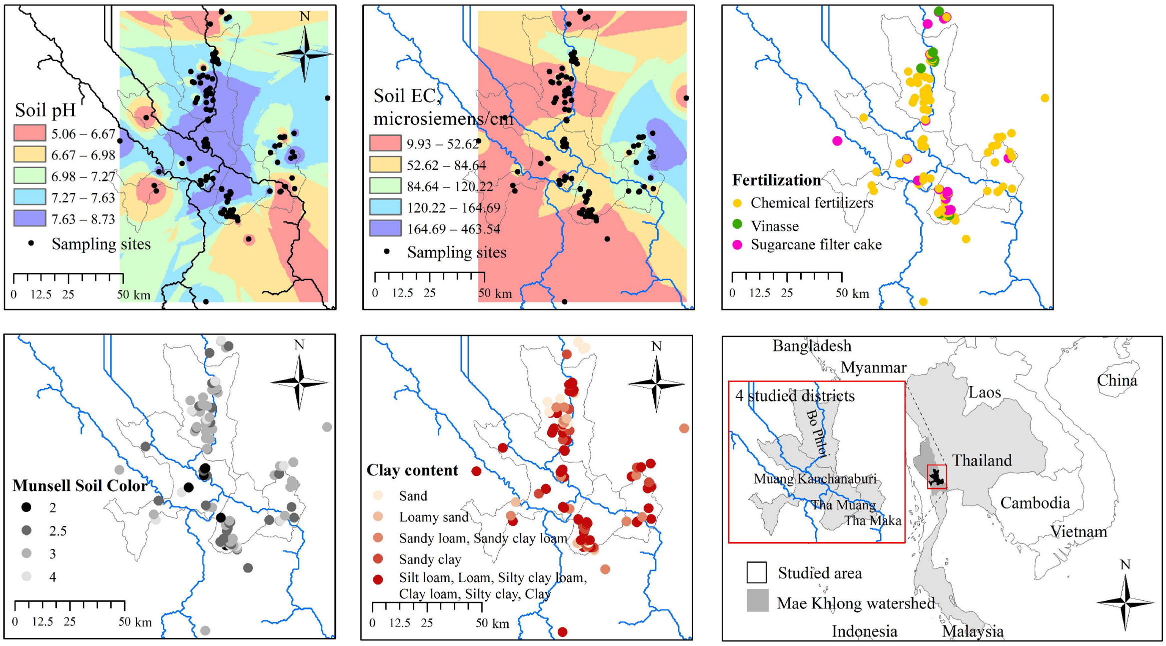

Figure 2. Spatial interpolations of soil pH, EC, color value, soil-texture-based clay content, and type of fertilization acquired from field soil sampling.

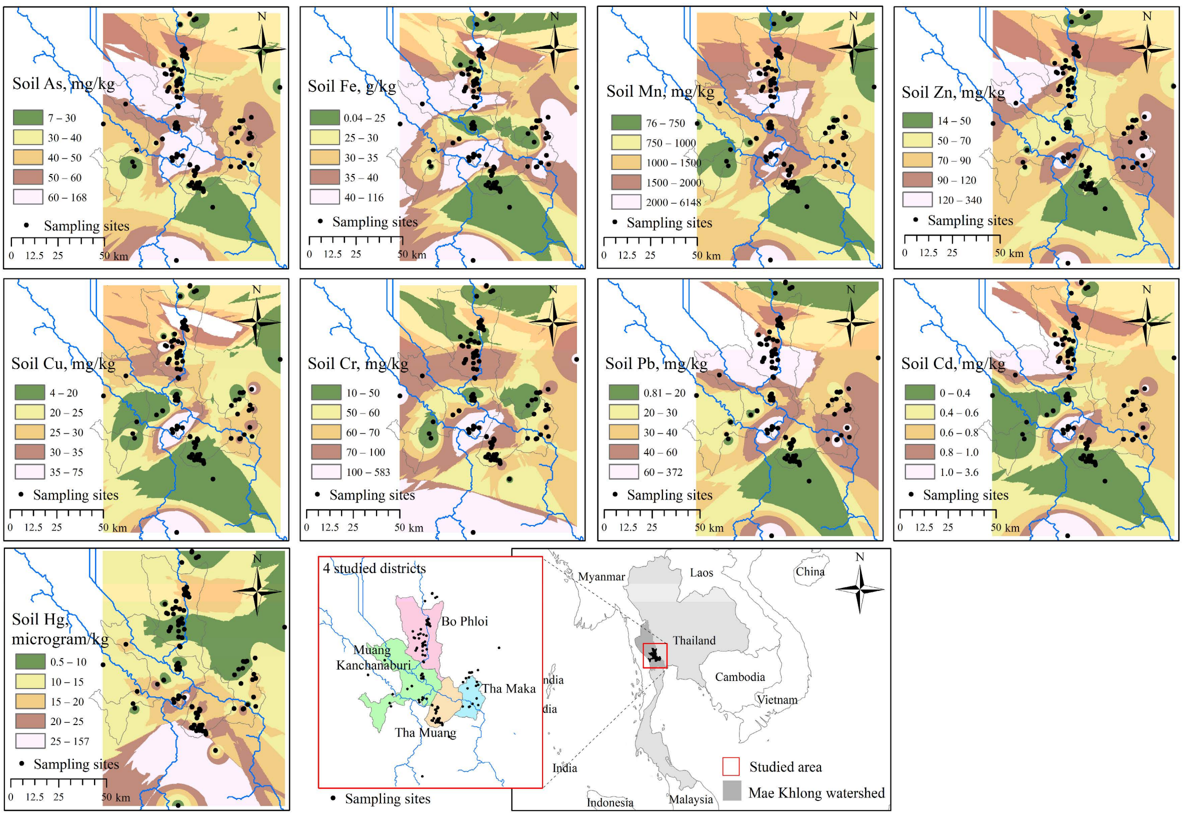

Figure 3. Spatial interpolations of heavy metals content in the agricultural soils.

However, soils along the Taphoen canal in Bo Phloi exhibited lower EC, corresponding with their lighter color and lower clay content (Figure 2). Correspondingly, high amounts of soil metals were found in Bo Phloi for all tested metals except Hg (Figure 3).

Table 1. Physicochemical properties and heavy metals content in agricultural soils for various types of fertilization.

Type of Fertilizer	Mineral Fertilizers	Vinasse from Molasses-Based Distilleries	Filter Cake from Sugar Mills	Typical Range in Agricultural Soils (Su, 2014 [16])	National Soil Standard for Agriculture **	Background Soil in Thailand (Zarcinas et al., 2004 [41])
	Mean ± Standard Deviation (Median)			Min–Max (Mean)		
Number of Observations	102	11	18			
pH	7.42 ± 0.89 (7.79)	7.05 ± 0.87 (6.98)	7.59 ± 0.68 (7.91)			
EC, μS cm^{-1}	69.83 ± 71.10 (54.5)	78.32 ± 53.58 (55)	73.76 ± 47.21 (58.5)			
Color Value	3 *	3 *	3 *			
Color Chroma	1 *	2 *	1 *			
Soil Texture	Clay *	Clay *	Sandy Clay *			
Soil As, mg/kg	48.7 ± 33.0 (44.0)	37.3 ± 26.9 (47.7)	59.6 ± 28.6 (60.2)	0.78–92.7 (21.19)	<25	30
Soil Fe, mg/kg	35,291 ± 21,477 (32,314)	29,691 ± 21,766 (42,344)	39,252 ± 22,444 (30,165)			
Soil Mn, mg/kg	1384 ± 1166 (1075)	1254 ± 849 (1479)	1233 ± 749 (1046)		<19,640	
Soil Zn, mg/kg	77.1 ± 52.2 (64.7)	93.8 ± 64.4 (104.8)	66.0 ± 41.5 (60.5)	4.65–427.8 (117.35)		70
Soil Cu, mg/kg	26.1 ± 18.2 (22.2)	28.2 ± 20.5 (36.2)	23.9 ± 10.8 (21.5)	1.20–107.65 (38.03)	<35,040	45
Soil Cr, mg/kg	72.3 ± 66.8 (59.9)	51.5 ± 23.3 (58.2)	79.2 ± 42.1 (73.4)	1.23–87.73 (46.69)	<212	80
Soil Pb, mg/kg	51.0 ± 66.8 (34.6)	23.1 ± 16.3 (31.7)	28.8 ± 18.6 (22.8)	0.95–213.93 (51.19)	<800	55
Soil Cd, mg/kg	0.67 ± 0.67 (0.49)	0.58 ± 0.55 (0.80)	0.72 ± 0.57 (0.48)	0.05–13.50 (1.5)	<762	0.15
Soil Hg, μg/kg	18.1 ± 33.3 (10.6)	15.4 ± 8.2 (13.5)	14.1 ± 9.7 (14.9)	50–730 (280)	<263,000	100

Note: * Mode. ** Notification of the National Environmental Board: Soil Quality Standard in the *Royal Gazette* on 11 March 2021.

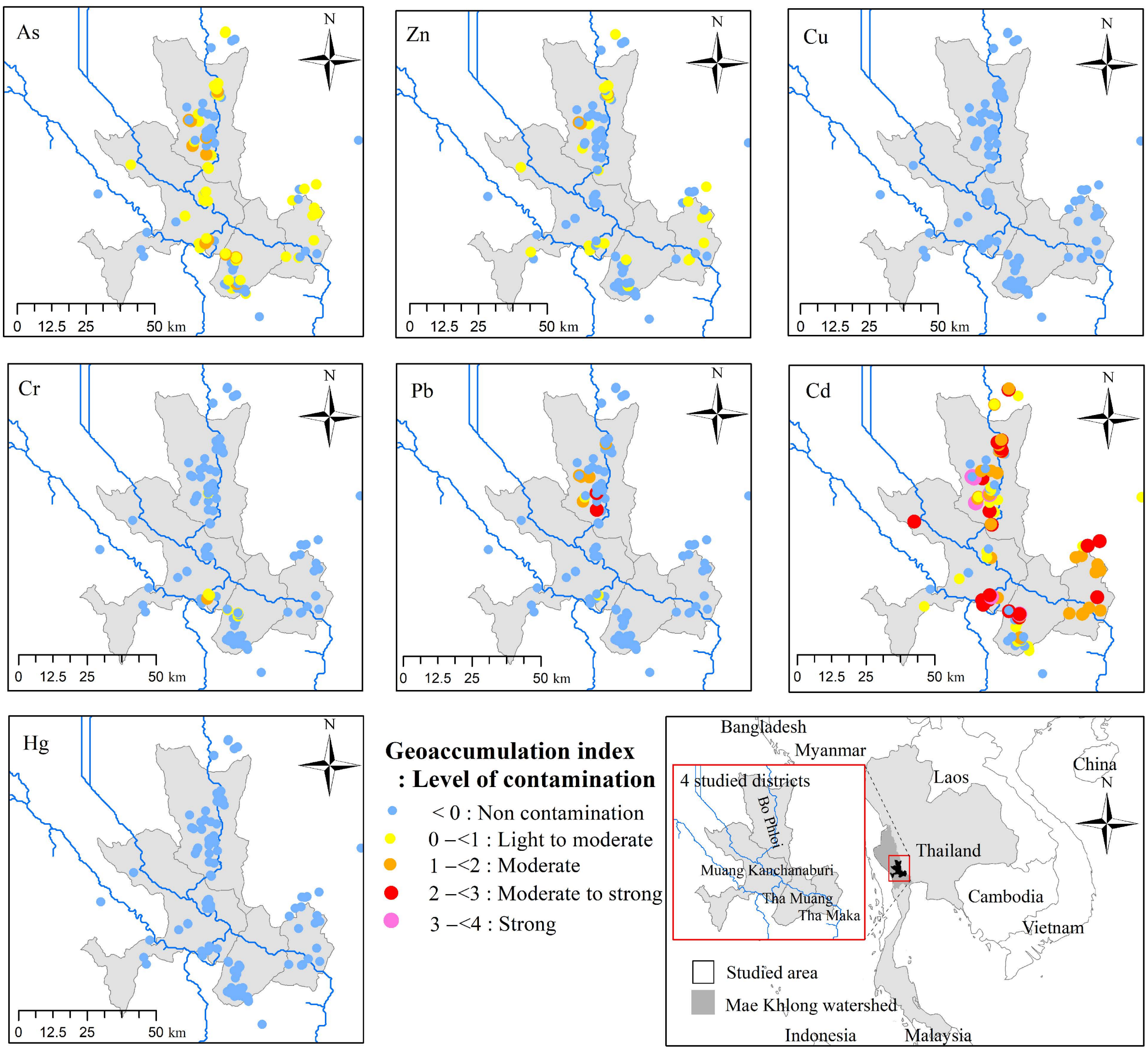

Figure 4. Spatial distributions of geoaccumulation index at the sampling sites.

3.3. Factors Associating Heavy Metal Accumulation in the Soils

3.3.1. Soil Texture

Clay fraction positively correlated with all metals in soils ($p \leq 0.05$), indicating that metal concentrations are controlled by clay fraction (see Table 2). Therefore, the metals-bound clayey soil grain could have transported downstream from the upper Mae Khlong River watershed and accumulated at the confluence of the Khwae Yai River, Khwae Noi River, and the Mae Khlong River [21].

Table 2. Spearman correlation coefficients among soil physicochemical properties and soil heavy metals.

	EC	Color Value	Chroma	Clay Fraction	As	Fe	Mn	Zn	Cu	Cr	Pb	Cd	Hg
pH	0.38 [a]	−0.23 [a]	−0.22 [b]	0.12	0.21 [b]	0.03	0.26 [a]	0.01	0.04	0.02	0.11	−0.04	−0.09
EC		−0.14	−0.22 [b]	0.39 [a]	0.42 [a]	0.32 [a]	0.35 [a]	0.39 [a]	0.36 [a]	0.09	0.27 [a]	0.30 [a]	0.21 [b]
Color Value			0.40 [a]	−0.16	−0.26 [a]	0.02	−0.21 [b]	0.02	0.06	−0.06	−0.02	−0.01	−0.15
Chroma				−0.09	−0.14	−0.06	−0.17	−0.13	−0.13	−0.14	−0.10	−0.02	−0.28 [a]
Clay fraction					0.54 [a]	0.53 [a]	0.44 [a]	0.45 [a]	0.42 [a]	0.39 [a]	0.41 [a]	0.41 [a]	0.18 [b]
As						0.78 [a]	0.73 [a]	0.61 [a]	0.68 [a]	0.66 [a]	0.59 [a]	0.77 [a]	0.26 [a]
Fe							0.68 [a]	0.78 [a]	0.82 [a]	0.73 [a]	0.79 [a]	0.85 [a]	0.25 [a]
Mn								0.63 [a]	0.72 [a]	0.51 [a]	0.68 [a]	0.64 [a]	0.22 [b]
Zn									0.72 [a]	0.46 [a]	0.72 [a]	0.73 [a]	0.42 [a]
Cu										0.56 [a]	0.75 [a]	0.83 [a]	0.32 [a]
Cr											0.53 [a]	0.63 [a]	0.17
Pb												0.74 [a]	0.17
Cd													0.22 [b]

Note: [a] $p < 0.01$, [b] $p < 0.05$.

3.3.2. Soil Electroconductivity (EC)

Most soil metals (except for Cr) were also significantly associated with soil EC. This could suggest that most metals were likely sorbed onto the surface and concentrated in clay size fraction (<2 mm), allowing easy transport along the river and runoff. The sorbed metals could be desorbed via leaching. The higher the metals desorption, the more metals mobilization, and the higher soil EC.

3.3.3. Soil pH and Soil Organic Content

In this study, slightly alkaline and organic-rich soils significantly corresponded with As and Mn contents in soil, suggested by the negative correlations between the soil metals and color value ($r = -0.26$ and -0.21, respectively), and the positive correlations between the soil metals and soil pH ($r = 0.21$ and 0.2, respectively), as shown in Table 2. The soils with pH > 7 could result in the mobilization of As(V) due to the conversion of $H_2AsO_4^-$ to $HAsO_4^{2-}$ along with increasing negative surface charges of soils, resulting in electrostatic repulsion [44]. However, Moreno-Jiménez et al. [45] reported that high pH in the presence of sulfates and carbonates can produce either a co-precipitation of arsenic in the form of metal oxides/hydroxides and sulfates, or a precipitate such as calcium arsenate. Bia et al. [46] investigated As in natural carbonates and found that As(V) was likely adsorbed onto calcite.

The studied area is located in western Thailand, where Permian carbonate rocks are predominant [36,47]. Therefore, carbonate-inducing arsenic precipitation and adsorption could play a role in As immobilization in this area. Furthermore, the significant correlation between soil As and Fe/Mn ($r = 0.78$ for Fe and 0.73 for Mn) found in Table 2 confirms that Fe and Mn oxides/hydroxides represent the primary sorbing agents for As in the soils. A similar finding was also reported by Fitz and Wensel [44].

Various soils may yield differing conclusions regarding metal speciation. A study in Turkey on agricultural sedimentary soil demonstrated that As was predominantly found in residual non-exchangeable fraction, followed by binding with organic matrices and less prone to exchangeability [48]. Conversely, Verbeeck et al. [49] investigated clayey Luvisol soils from agricultural grasslands in France, and they reported that organic matter could enhance the mobility of AsO_4 (tetrahedral arsenates). Dousova et al. [50] also demonstrated that As(V) exhibited stronger adsorption to metal oxides/hydroxides compared to organic horizons. The adsorption, however, depended on the competitive affinity of the other metals or compounds in soils and the ionic strength of the aqueous phase above soil surfaces [49,50]. Further studies on the As adsorption on the surface reactive organic matters could be performed to quantify the As transformation in soils [49].

Mercury (Hg) exhibited high sorption capacities and <1% desorbed [51]. In Hg-soil systems, Hg tends to be immobilized due to its affinity for mineral surfaces and bonding to organic matter [52]. In this study, a significant negative correlation between soil Hg and soil Chroma ($r = -0.28$, $p < 0.01$, see Table 2)—the lower value, the lesser saturated color, and the more organic content [53]—suggests that low mobility Hg in the soils was strongly associated with non-labile organic carbon [52].

3.3.4. Soil Conservation Measures

The concept of soil conservation has been introduced widely to maintain soil quality and minimize adverse impacts on agroecosystem health. Several soil conservation measures have been implemented in many sugarcane plantations, including no open burning (n = 92), drip irrigation (n = 88), applying organic fertilizers (n = 72), retention reservoirs (n = 62), mulching (n = 60), terracing (n = 52), ridging (n = 35), alternative cropping (n = 25), intercropping (n = 18), checking dam installations (n = 14), and no-tillage or minimum tillage (n = 11). Among these measures, no-tillage/minimum tillage was associated with the agricultural soil heavy metals content, whereas the other measures did not have any significant association.

No-tillage or minimum tillage was significantly found with high soil Zn and Cd accumulations, as suggested by the Chi-square test for independence ($p = 0.02$ and 0.047, respectively) in Figure 5. The effect of a tillage system was also found in arable sandy loam soils in Poland [20]. The study found decreases in total Zn, Cu, Mn, and Fe in soils with full-inversion tillage and strip tillage compared with those with minimum tillage. The effects of tillage were also significant for soil heavy metals content in a wheat–soybean/corn cropping field in Buenos Aires province, Argentina [54]. The no-till or minimum tillage could be beneficial for the retention of water in the soil, less inversion of subsoil to the surface, and reducing the leaching of soil organic matter, nutrients, and metals from soils [55].

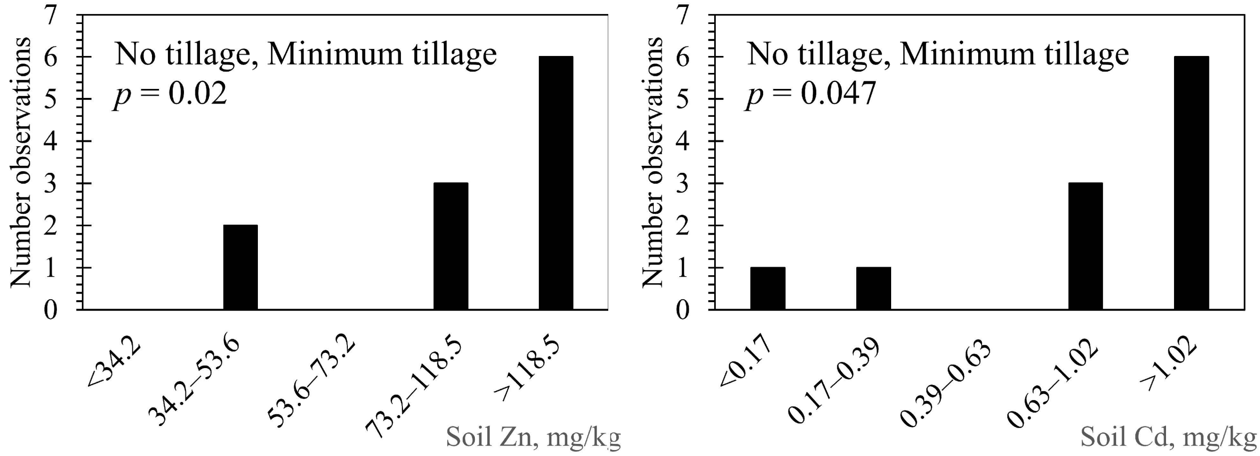

Figure 5. Frequency of the observations with no-tillage or minimum tillage for different soil Zn and Cd contents.

3.4. Potential Sources of the Heavy Metals in the Sugarcane Plantation Soils

Five factors were obtained from factor analysis using Varimax rotation that can imply five significant sources of the heavy metals in the soils. The five factors could explain about 75.8% of variances of the original observations, including soil properties and heavy metals contents, based on principal component analysis. Factor loadings on the original parameters are shown in Table 3, and potential sources of the heavy metals in the soils are discussed following.

Table 3. Factor loading matrix for soil physicochemical properties and heavy metals content using Varimax rotating method and mean factor scores for different types of fertilization.

Soil Properties	Factor Loading					Specific Variances
	F1	F2	F3	F4	F5	
pH	0.10	0.06	0.02	**−0.52**	−0.07	0.71
EC	−0.01	0.08	**0.46**	−0.10	0.07	0.77
Color Value	−0.02	−0.03	0.06	**0.75**	−0.18	0.40
Color Chroma	0.11	0.07	−0.21	**0.57**	−0.11	0.60
Clay fraction	0.25	**0.31**	**0.37**	**−0.27**	−0.01	0.63
Soil As	**0.69**	**0.53**	0.16	−0.18	**0.22**	0.13
Soil Fe	**0.55**	**0.68**	**0.46**	0.04	−0.01	0.03
Soil Mn	**0.81**	0.23	0.07	**−0.24**	**−0.33**	0.11
Soil Zn	**0.60**	0.08	**0.66**	0.10	**0.20**	0.15
Soil Cu	**0.55**	0.27	**0.50**	0.01	0.04	0.37
Soil Cr	0.27	**0.72**	0.10	0.00	−0.03	0.40
Soil Pb	**0.75**	0.16	0.03	0.01	0.06	0.41
Soil Cd	**0.80**	**0.43**	0.21	0.10	**0.35**	0.005
Soil Hg	0.05	0.00	0.10	−0.17	**0.24**	0.90
Fertilizations			Average factor scores			
Mineral Fertilizers (n = 95)	0.045	−0.029	−0.019	0.001	−0.047	
Vinasse (n = 10)	0.179	−0.739	**0.560**	0.523	−0.136	
Sugarcane Filter Cake (n = 17)	−0.310	**0.651**	−0.316	**−0.298**	0.291	

Note: Bold numbers represent high loading with the original variables.

3.4.1. Parent Rock Materials

Natural geochemical processes could respond to high As, Fe, Mn, Zn, Cu, Pb, and Cd contents, as suggested by the positive loadings for F1. Agricultural fertilization did not strongly influence this factor (F1) since the F1 scores were not obviously high for soils with particular fertilization. High levels of these metals were also found in the Pb–Zn mining in limestone karst nearby this studied area [21]. In that study, As, Zn, Cu, Pb, and Cd were influenced by mining activities and metal adsorption onto the Fe- and Mn-oxides, and the clay minerals were thought to be pathways for these metals in this environment [21]. Tropical karst weathering of the mineral limestone and soil erosion during the rainy season could potentially drive the distribution of these metals in the soils [21]. Furthermore, it has been documented that sediment from natural chemical weathering of the basaltic host rock, which is dominant in the studied area, could affect heavy metal accumulation in the area. Eroded sediment from basaltic rock significantly enriched Cd, As, and Pb [56].

3.4.2. Addition of Sugarcane Filter Cake

The filter cake is cane pulp obtained during the purification of sugar by sulphitation or carbonation processes, resulting in richness in sulfate or carbonate [7]. Filter cake has an abundance of both macronutrients (C, N, P, K, Mg, Ca, S) and micronutrients (Fe, Mn, and Si) [9]. Due to high amounts of complex organic compounds, filter cake decomposition requires the aid of microbes, fungi, bacteria, and some actinomycetes [7].

Application of filter cake into agricultural plantations could cause prominent accumulations of Cr, Fe, As, and Cd in the clay fraction of soils, as suggested from the positive loadings for F2. The F2 score was higher for the soils with filter cake applications than for the other treatments. As shown in Table 4, soils with filter cake addition had Cr, Fe, As, and Cd of approximately 79.2, 39,252, 59.6, and 0.72 mg kg^{-1}, respectively, higher than soils with the other treatments. The metal contents in the filter cake were also high (79.98, 34,955, 49.46, and 0.69 mg kg^{-1} for Cr, Fe, As, and Cd, respectively, as shown in Table 1).

Table 4. Elemental compositions of bagasse, ash, and filter cake taken from the sugar mill in Kanchanaburi, Thailand.

	As	Fe	Mn	Zn	Cu	Cr	Pb	Cd	Hg
	mg/kg								µg/kg
Bagasse	5.26	2060	89	18.16	3.27	6.65	2.68	0.20	4.17
Ash	38.86	24,159	1063	136.04	29.81	56.07	19.97	0.49	10.82
Filter Cake	49.46	34,955	1566	138.85	42.02	79.98	29.53	0.69	15.26
Organic Fertilizer Standards *	<50				<500	<300	<500	<5	<2000

Note: * Announcement of the Department of Agriculture on Organic Fertilizer Standards, B.E. 2548.

In addition, high organic contents in the filter cakes, relating to darker soil color (low soil Color Value and Chroma), could respond to Mn accumulated in the clay fraction of soils, as suggested by F4 factor loadings. Under such high pH and organic-rich conditions, the Mn could be immobilized and accumulated in soils via precipitations in the form of carbonate or hydroxide and form complexes with organic substances [21].

3.4.3. Addition of Treated Vinasse from Molasses-Based Ethanol Distillery

Vinasse is the wastewater from the molasses-based ethanol distillery [57]. After treatment, typically via anaerobic digestion, it still contains high organic matter and nutrients [58]. Some farmers apply the treated vinasse to the agricultural field to fertilize the soils and reduce the burden of costly mineral fertilizers.

The vinasse could also be the source of Zn, Cu, Fe, and soil salinity (implied from high soil EC) in the sugarcane plantation soils. As implied from F3 factor loadings in Table 3, significantly positive loadings were found for Zn, Cu, Fe, soil EC, and clay fraction in the soil, and a high positive F3 factor score (0.56) was found for the soils with vinasse treatment. Rajkishore and Vignesh [59] also report that vinasse could be a significant source of micronutrients, including Zn, Cu, and Fe. In addition, Mahimairaja and Bolan [60] showed that high salt in the vinasse could increase soil salinity. The high contributions of Cu and Zn from the vinasse were similar to those obtained from phosphate fertilizer, livestock manure, or sewage sludge [14,19,61,62]. Furthermore, excess Fe was typically found in soils irrigated with industrial wastewater [28].

3.4.4. Applications of Mineral Fertilizers and Agrochemicals

High contributions of Cd, Hg, As, and Zn, found in positive F5 factor (see Table 3), could be attributed to fertilizers, pesticides, and liming [19]. Predominant levels of Cd could be the signature of the agricultural soils, as found in many agricultural environments, including in the Hun-Taizi River watershed, China [63], Xi River watershed, NE China [27], Wuqing, Tianjin, China [61], Shouguang city, Shandong, China [64], Ropar wetland, Punjab, India [30], Swat, N Pakistan [29]. The rising Cd and Zn in agricultural soils could be due to fertilizing using phosphate fertilizers [18,41]. Su [16] and Alengebawy et al. [15] also reported high Cu, Zn, Cd, and Pb in phosphate fertilizers. The heavy metals naturally occur with phosphate rock in nature. Previous studies have also reported that pesticides could be responsible for high Cd, As, Hg, Pb, Zn, and Cu in agricultural soils [14,15].

Based on the farmer interviews and the soil sampling in this study, herbicides have been regularly applied to control the weeds during tillering and elongation periods of crop growth from March to July. The applications can be twice or more per cropping cycle, depending on the number of weeds. The types of herbicides typically applied to the fields were phenoxy carboxylic acids (e.g., 2,4-D), triazines (e.g., ametryn, atrazine), and ureas (e.g., diuron). Herbicides contain higher As (151 times), Cu (639 times), and

Zn (83 times) content than in agricultural soils [65]. The insecticides and fungicides were applied periodically when experiencing insect and plant disease outbreaks, respectively.

The agricultural soils in this study significantly responded to the increasing level of Cu in the soil from the addition of pesticides in the sugarcane plantations. As shown in Table 5, the Chi-square test for independence between the soil Cu and the amount of the pesticides applied revealed significant dependence between both factors (p = 0.023). The test, however, did not show significance for the other metals.

Table 5. Observations of soil Cu content corresponding to the amount of herbicides applied.

Soil Cu, mg kg^{-1}	Amount of Herbicides Applied, kg ha^{-1} yr^{-1}			
	0–3.12	3.12–6.25	6.25–12.5	>12.5
<11.4	11	6	3	3
11.4–17.9	7	8	7	3
17.9–26.8	11	6	3	3
26.8–38.6	5	3	5	12
>38.6	9	3	8	3

Apart from natural origins, high Cu could be found in agricultural soils with excessive addition of fungicides [66–68]. However, the fungicides were not applied in the sampling year due to no plant disease outbreak. Thus, long-term accumulative doses of the herbicides should play a role in responding to soil Cu level.

3.5. Bioconcentration Factor (BCF) of Heavy Metals from the Soils to the Sugarcane Leaves

BCFs from the soils to sugarcane leaves were the highest for Hg, followed by Cu, As, Zn, Mn, Cr, Fe, Pb, and Cd, respectively (Table 6). A BCF > 1 suggests a significant accumulation of the soil metals in the biomass (leaves), or phytoextraction, for Hg (~2.32–35.72, depending on soil clay content). Furthermore, the phytoextraction ability of the sugarcane was also found for Cu (~2.67) and As (~1.04), exclusively in sandy soils. Similarly, the high absorptions of Hg and Cu in food crops were previously found in crop fields near an industrial park in Ayutthaya, Thailand. The Hg and Cu were from irrigated water [69]. High concentrations of the Hg in leaves were typical for vascular plants, such as rice plants and lavender plants [70]. The Hg in the plant leaves may have either originated from soil and translocated after root uptake or stomatal uptake of gaseous Hg emitted from soils or atmospheric deposition [70].

A BCF < 1 was generally found, and the lowest BCF was found in Pb and Cd, followed by Fe, Cr, Mn, and Zn, respectively. This finding suggests that the sugarcane did not perform phytoextraction well for these metals. The findings in this study agreed with the previous works of Akkajit et al. [32], showing that applications of sugar mills' boiler ash, filter cake, and a mixture of ash and vinasse did not significantly affect BCF in sugarcane plantations for Cd and Zn. The limited phytoextraction of Cd in this study may be attributed to the prevalence of alkaline soils, which restrict the assimilation of Cd into vegetables [71]. Pandey et al. [72] also found BCF < 1 for all metals (Cr, Cu, Cd, Pb, Zn, Ni, Fe, and Mn) in sugarcane juice from the plantations irrigated with industrial effluent in India. Nonetheless, some herbal plants in soils fertilized with molasses-based distillery waste acted as hyperaccumulators of heavy metals [73].

The BCF for As exhibited strong soil texture dependence. It was higher for sandy soil (low clay content) and lower for those having more clay content (see Table 7). The As in natural carbonates was more favorable to be adsorbed on calcite, co-precipitate in the form of metal oxides/hydroxides and sulfates, or precipitate in the form of calcium arsenate than adsorbed on the organic substances [45,46]. Thus, the more As adsorbs onto the metal complexes, the more As is found in sandy soil and accumulates in the sugarcane biomass.

Table 6. Bioconcentration factors (BCF) of the metals from soils to plants.

Clay Content Level	As	Fe	Mn	Zn	Cu	Cr	Hg	Pb	Cd
1 (n = 3–14)	1.04 ± 0.77 (0.81) *	0.013 ± 0.009 (0.012)	0.29 ± 0.22 (0.24)	0.78 ± 0.28 (0.77)	2.67 ± 4.09 (1.12)	0.15 ± 0.16 (0.12)	10.25 ± 11.90 (6.41)	Very low **	Very low **
2 (n = 2–6)	0.73 ± 0.45 (0.76)	0.007 ± 0.003 (0.007)	0.17 ± 0.07 (0.16)	0.49 ± 0.00 (0.49)	0.90 ± 0.53 (0.71)	0.06 ± 0.05 (0.03)	25.55 ± 35.67 (25.55)		
3 (n = 7–23)	0.47 ± 0.37 (0.39)	0.011 ± 0.011 (0.006)	0.27 ± 0.63 (0.09)	0.57 ± 0.62 (0.32)	1.33 ± 2.08 (0.50)	0.16 ± 0.27 (0.06)	5.03 ± 10.22 (1.44)		
4 (n = 3–18)	0.40 ± 0.24 (0.34)	0.013 ± 0.021 (0.007)	0.11 ± 0.09 (0.08)	0.83 ± 0.87 (0.57)	0.60 ± 0.40 (0.56)	0.06 ± 0.04 (0.06)	35.72 ± 59.44 (1.87)		
5 (n = 13–64)	0.35 ± 0.63 (0.22)	0.008 ± 0.009 (0.004)	0.08 ± 0.07 (0.06)	0.37 ± 0.24 (0.32)	0.86 ± 1.57 (0.35)	0.11 ± 0.19 (0.06)	2.32 ± 4.61 (0.41)		

Note: * mean ± standard deviation (median), ** Very low BCF is due to lower Pb and Cd concentrations in cane leaves than the detection levels.

Table 7. Spearman correlation coefficients between soil physicochemical properties, soil heavy metals, bioconcentration factor (BCF) of the metals from soils to plants (leaves), and cane yield.

	BCF from Soils to Plants (Cane Leaves)								
	As	**Fe**	**Mn**	**Zn**	**Cu**	**Cr**	**Hg**		
Soil pH	−0.11	−0.11	−0.29 [a]	−0.09	−0.05	0.08	0.15		
Soil EC	−0.36 [a]	−0.21 [b]	−0.35 [a]	−0.27	−0.34 [a]	0.10	0.15		
Color Value	0.17	0.12	0.21 [b]	0.04	0.06	0.12	0.10		
Chroma	0.13	−0.01	0.20 [b]	0.05	0.10	0.00	0.12		
Clay Content	−0.50 [a]	−0.34 [a]	−0.45 [a]	−0.31 [b]	−0.31 [a]	−0.11	−0.27		
Cane Yield	−0.04	−0.09	−0.10	−0.41 [a]	−0.06	0.17	−0.11		
	Soil Heavy Metals								
	As	Fe	Mn	Zn	Cu	Cr	Hg	Pb	Cd
Cane Yield	0.09	0.28 [a]	0.19 [b]	0.34 [a]	0.27 [a]	0.09	−0.05	0.42 [a]	0.26 [a]

Note: [a] $p < 0.01$, [b] $p < 0.05$.

As shown in Table 7, high (low) levels of BCF for the sugarcane leaves could be attributed to low (high) soil pH for Mn; low (high) soil EC for As, Fe, Mn, and Cu; light (dark) soil color—indicating low (high) organic content—for Mn; and low (high) clay content for As, Fe, Mn, Zn, and Cu. Based on this finding, organic-rich clayey soils resulted in poor bioavailability for Mn, whereas clay fraction alone could suppress bioavailability for As, Fe, Zn, and Cu. No significant association of soil properties was found on the BCF for Hg and Cr.

Though soil organic matter was found to be significantly associated with soil As, Mn, and Hg contents, discussed in Section 3.3, the role of soil organic matter in accumulating the metals in the sugarcane leaves was the inverse for Mn and not significant for the other metals. A previous study also reported significant adsorption of heavy metals by soil organic matter on the sugarcane plantations fertilized by sugarcane waste [32]. This finding suggests that soil organic matters could adsorb the metals, resulting in immobilization of the metals in agricultural soils and minimizing the bioconcentration of the metals in agricultural products.

3.6. Effects of Soil Heavy Metals on the Sugarcane Yield

The Spearman correlation coefficients shown in Table 7 suggest that high cane yield was significantly associated with higher soil Fe, Mn, Zn, Cu, Pb, and Cd contents. Tamez et al. [74] found higher Chlorophyll A content in sugarcane with the addition of a Cu-based fungicide in the soil. Nonetheless, higher uptake of Zn from the soils to sugarcane biomass responded to lower cane yield (see Table 7). Jain et al. [75] confirmed that applying excess Zn to sugarcane cultivar could suppress sugarcane growth.

3.7. Implications on Sustainability of Utilizing Wastes from Sugar–Ethanol Industry for Sugarcane Cultivation

The filter cake is the waste from sugar mills, and vinasse is from molasses-based ethanol distilleries. Both wastes contain a significant amount of macro- and micro-nutrients for plant growth. Thailand's economy relies vitally upon agricultural production. Industrial waste utilization could reduce waste generation and promote efficient resource consumption as the strategy for the Bio-Circular Green Economy. Nonetheless, utilizing the waste for agricultural production could raise public concerns about food safety.

According to the observation-based studies, adding filter cake to the agricultural soils could increase soil Cr, Fe, As, Cd, and Mn and alter soil properties toward organic-rich clayey soil. The additions of vinasse via fertigation could increase soil Zn, Cu, and Fe and alter soil properties toward saline clayey soil.

By considering the bioconcentration of the metals from the soils to the sugarcane leaves, the sugarcane markedly absorbed the Hg for all soil textures (BCF >> 1) and absorbed soil Cu and As in sandy soils. Based on the factor analysis, mineral fertilizers and agrochemicals should be the source of both Hg and As in soil. Furthermore, soil As is highly attributed to natural lithological sources, as found in the high level for all fertilization treatments.

High bioconcentration of Zn was associated with low yield. High cane yield, however, was found with high soil Fe, Mn, Zn, Cu, Pb, and Cd. Thus, increasing soil metal contents and enhancing the immobility of the soil metals should be implemented to optimize the cane yield. No-tillage or minimum tillage is also recommended to enhance the immobility of soil metals, as found significant for soil Zn and Cd in this study.

Based on the evidence from this study, the waste utilization neither contributed significantly to the concern levels of soil metals nor enhanced the bioconcentration of the soil metals into the sugarcane biomass. Moreover, the additions of vinasse together with filter cake could be beneficial for increasing the cane yield since the vinasse acted as the sources of soil Zn, Cu, and Fe (essential for yield promotion), and filter cake could be the sources of soil Mn and organic matter, adsorbing the metals. Vinasse and filter cake also promote higher clay fraction, enhancing soil surface adsorption and minimizing bioconcentration for Zn. Nonetheless, the proper combination of both materials should be further studied to minimize the impacts of soil salinity and satisfy physicochemical soil properties. Furthermore, an additional study on the accumulation of toxic substances in the cane biomass could be conducted to clarify the possible impacts on food safety.

3.8. Limitations

It is noted that this study carries certain weaknesses and limitations. The study was focused on the sugarcane fields in western Thailand. Although it addresses diverse soil properties, it may not capture the full spectrum of soil conditions found in various regions. The study also provides limited exploration of socioeconomic factors and may not fully account for seasonal variations. The emphasis on short-term outcomes might overlook longer-term trends. These limitations present opportunities for future research to enhance understanding of heavy metal dynamics in sugarcane plantation systems.

4. Conclusions

Thailand, a major sugar exporter, heavily relies on cane sugar for its economy. However, most sugarcane farmers use costly agrochemicals, such as mineral fertilizers and pesticides, to boost yield. To align with the national strategy for sustainable growth, there is a growing emphasis on using industrial waste, driving the Bio-Circular Green Economy. This study examines heavy metals levels in the sugarcane plantation soils, considering various fertilization methods, including industrial wastes from sugar–ethanol industries (filter cake and vinasse). We also assess the impact of soil properties and conservation practices on metal accumulations, bioaccumulation in sugarcane leaves, and the promotion of sustainability through waste-based fertilizers.

The study covers 131 sampling sites in four districts in Kanchanaburi, western Thailand, dominated by sugarcane plantations. Spatial analysis revealed that Arsenic (As) often exceeded the national soil quality standard for agriculture of 25 mg kg^{-1}. According to the geoaccumulation index (I_{geo}), soil accumulations of Cd, As, and Zn (median I_{geo} values of 1.35, 0.04, −0.69, respectively) were scattered across the studied area, whereas Pb was concentrated in the Bo Phloi subdistrict. Factor analysis highlighted natural geochemical processes' substantial influence on spatial variations in soil metal distribution. Applications of mineral fertilizers and agrochemicals elevated levels of Cd, Hg, As, and Zn in soil. The use of filter cake increased the soil content of Cr, Fe, As, Cd, and Mn and altered the soil physicochemical properties towards an organic-rich clayey composition. The molasses-based vinasse enriched soils with more Zn, Cu, and Fe, along with alterations in soil properties towards saline clayey soil.

Spearman correlation analysis indicated that inorganic ions and complexes of clay fraction significantly accounted for the high metal accumulations in soils, primarily through adsorption or precipitation processes. Alkaline and organic-rich soils were strongly associated with As and Mn accumulations, whereas organic matter was solely correlated with soil Hg accumulation. No-tillage or minimum tillage practices strongly associated with high soil Zn and Cd levels, whereas other conservation measures showed less pronounced effects.

Bioconcentration factor (BCF) revealed that the sugarcane generally acted as an Hg accumulator (BCF ~2.32 to 35.72), while the biomass accumulation for Cu (~2.67) and As (~1.64) tended to be prominent in sandy soil. Mineral fertilizers and agrochemicals were the main contributors to these metal accumulations. The BCFs for the other metals in sugarcane leaves were generally < 1, indicating limited phytoextraction potential.

Based on the findings of this investigation, the waste utilization did not significantly impact soil metal levels or enhance the bioconcentration in sugarcane biomass. The combined application of vinasse and filter cake, as a source of organic matter, showed dual benefits by increasing soil metal content and reducing Zn bioconcentration, thereby enhancing cane yield. Additionally, reduced reliance on chemical fertilizers contributes to a diminished Hg bioconcentration, consequently mitigating health risks. However, further research is needed to determine optimal waste application quantities for optimizing cane yield, ensuring food safety, and safeguarding environmental health.

Author Contributions: A.B.: conceptualization, methodology, collecting data, formal analysis, writing, funding acquisition; N.K.: co-writing, field sampling; J.K.: field surveying, field sampling, project administration; K.S.: co-writing; R.F.: supervision; B.S.: sample analysis; J.P.J.C.: supervision; K.R.R.: co-writing, supervision, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the British Council Research Environment Links in joint venture with the Program Management Unit for Human Resources and Institutional Development, Research and Innovation (PMU-B), Thailand for the year 2021/22.

Institutional Review Board Statement: The project has been approved by the Human Research Ethics Committee, Mahidol University (Protocol Number MU-CIRB 2022/038.2302 on 28 April 2022).

Informed Consent Statement: All farmers who participated in the interviews had signed a consent form to participate. The work described in this manuscript has not been published before and is not under consideration for publication anywhere else. It has been approved by all co-authors for publication.

Data Availability Statement: All data generated or analyzed during this study are included in the manuscript.

Acknowledgments: This research received financial support from the British Council Research Environment Links in joint venture with the Program Management Unit for Human Resources and Institutional Development, Research and Innovation (PMU-B), Thailand, for year 2021/22. The Research and Academic Service, Mahidol University Kanchanaburi Campus, provided support for laboratory services. Special thanks is given to Peerata Khunoth, the laboratory scientist, for her service. We appreciate the kind assistance from the Cane Planters Association Zone 7 (Naratip Anuntasuk), Thamaka Sugar Industry (Karunchai Taksin), and KSL (Bo Phloi) Sugar Industry.

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

References

1. Office of the Cane and Sugar Board. Report on the Situation of Sugarcane Planting, Production Year 2021/2022. Available online: http://www.ocsb.go.th/upload/journal/fileupload/13813-1585.pdf (accessed on 26 February 2023).
2. Office of Agricultural Economics. Export statistics. Available online: https://impexpth.oae.go.th/export (accessed on 26 February 2023).
3. Preecha, R.J.M.; Srikongphet, K.; Ratchatawechkul, W. Step into the new context of Thai Cane and Sugar Industries. In Proceedings of the Bank of Thailand Symposium 2017, Centara Grand, Bangkok, Thailand, 18–19 September 2017.
4. Office of National Higher Education Science Research and Innovation Policy Council. BCG in Action. Available online: https://www.nxpo.or.th/th/en/bcg-in-action/ (accessed on 19 February 2023).
5. Sahu, O. Assessment of sugarcane industry: Suitability for production, consumption, and utilization. *Ann. Agrar. Sci.* **2018**, *16*, 389–395. [CrossRef]
6. Christofoletti, C.A.; Escher, J.P.; Correia, J.E.; Marinho, J.F.U.; Fontanetti, C.S. Sugarcane vinasse: Environmental implications of its use. *Waste Manag.* **2013**, *33*, 2752–2761. [CrossRef] [PubMed]
7. Raza, Q.-U.-A.; Bashir, M.A.; Rehim, A.; Sial, M.U.; Ali Raza, H.M.; Atif, H.M.; Brito, A.F.; Geng, Y. Sugarcane industrial byproducts as challenges to environmental safety and their remedies: A review. *Water* **2021**, *13*, 3495. [CrossRef]
8. Wakamura, Y. Utilization of bagasse energy in Thailand. *Mitig. Adapt. Strateg. Glob. Change* **2003**, *8*, 253–260. [CrossRef]
9. Dotaniya, M.; Datta, S.; Biswas, D.; Dotaniya, C.; Meena, B.; Rajendiran, S.; Regar, K.; Lata, M. Use of sugarcane industrial by-products for improving sugarcane productivity and soil health. *Int. J. Recycl. Org. Waste Agric.* **2016**, *5*, 185–194. [CrossRef]
10. Hoarau, J.; Caro, Y.; Grondin, I.; Petit, T. Sugarcane vinasse processing: Toward a status shift from waste to valuable resource. A review. *J. Water Process Eng.* **2018**, *24*, 11–25. [CrossRef]
11. Murillo, J.M.; Cabrera, F.; López, R. Effect of beet vinasse on germination and seedling performance of ryegrass (*Lolium multiflorum* Lam cv Barwoltra). *J. Sci. Food Agric.* **1993**, *61*, 155–160. [CrossRef]
12. Yin, J.; Deng, C.-B.; Wang, X.-F.; Chen, G.-l.; Mihucz, V.G.; Xu, G.-P.; Deng, Q.-C. Effects of long-term application of vinasse on physicochemical properties, heavy metals content and microbial diversity in sugarcane field soil. *Sugar Technol.* **2019**, *21*, 62–70. [CrossRef]
13. Huang, Y.; Wang, L.; Wang, W.; Li, T.; He, Z.; Yang, X. Current status of agricultural soil pollution by heavy metals in China: A meta-analysis. *Sci. Total Environ.* **2019**, *651*, 3034–3042. [CrossRef]
14. Gall, J.E.; Boyd, R.S.; Rajakaruna, N. Transfer of heavy metals through terrestrial food webs: A review. *Environ. Monit. Assess.* **2015**, *187*, 1–21. [CrossRef]
15. Alengebawy, A.; Abdelkhalek, S.T.; Qureshi, S.R.; Wang, M.-Q. Heavy metals and pesticides toxicity in agricultural soil and plants: Ecological risks and human health implications. *Toxics* **2021**, *9*, 42. [CrossRef] [PubMed]
16. Su, C. A review on heavy metal contamination in the soil worldwide: Situation, impact and remediation techniques. *Environ. Skept. Crit.* **2014**, *3*, 24.
17. Baranowska, I.; Barchanska, H.; Pyrsz, A. Distribution of pesticides and heavy metals in trophic chain. *Chemosphere* **2005**, *60*, 1590–1599. [CrossRef] [PubMed]
18. Peris, M.; Recatalá, L.; Micó, C.; Sánchez, R.; Sánchez, J. Increasing the knowledge of heavy metal contents and sources in agricultural soils of the European Mediterranean region. *Water Air Soil Pollut.* **2008**, *192*, 25–37. [CrossRef]
19. Nicholson, F.A.; Smith, S.R.; Alloway, B.; Carlton-Smith, C.; Chambers, B. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Total Environ.* **2003**, *311*, 205–219. [CrossRef] [PubMed]
20. Kobierski, M.; Jaskulska, I.; Jaskulski, D.; Debska, B. Effect of a tillage system on the chemical properties of sandy loam soils. *J. Elem.* **2020**, *25*, 1463–1473. [CrossRef]
21. Intamo, P.; Suddhiprakarn, A.; Kheoruenromne, I.; Tawornpruek, S.; Gilkes, R. Geomorphic significance on distribution of heavy metals in soils affected by Pb-Zn mining in a limestone karst, western Thailand. *Thai J. Agric. Sci.* **2015**, *48*, 187–197.
22. Micó, C.; Recatalá, L.; Peris, M.; Sánchez, J. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere* **2006**, *65*, 863–872. [CrossRef]
23. Huang, S.-W.; Jin, J.-Y. Status of heavy metals in agricultural soils as affected by different patterns of land use. *Environ. Monit. Assess.* **2008**, *139*, 317–327. [CrossRef]
24. Tóth, G.; Hermann, T.; Da Silva, M.R.; Montanarella, L. Heavy metals in agricultural soils of the European Union with implications for food safety. *Environ. Int.* **2016**, *88*, 299–309. [CrossRef]

25. Hani, A.; Pazira, E. Heavy metals assessment and identification of their sources in agricultural soils of Southern Tehran, Iran. *Environ. Monit. Assess.* **2011**, *176*, 677–691. [CrossRef] [PubMed]
26. Doabi, S.A.; Karami, M.; Afyuni, M.; Yeganeh, M. Pollution and health risk assessment of heavy metals in agricultural soil, atmospheric dust and major food crops in Kermanshah province, Iran. *Ecotoxicol. Environ. Saf.* **2018**, *163*, 153–164. [CrossRef] [PubMed]
27. Lian, M.; Wang, J.; Sun, L.; Xu, Z.; Tang, J.; Yan, J.; Zeng, X. Profiles and potential health risks of heavy metals in soil and crops from the watershed of Xi River in Northeast China. *Ecotoxicol. Environ. Saf.* **2019**, *169*, 442–448. [CrossRef] [PubMed]
28. Ullah, N.; Ur Rehman, M.; Ahmad, B.; Ali, I.; Younas, M.; Aslam, M.S.; Rahman, A.-u.; Taheri, E.; Fatehizadeh, A.; Rezakazemi, M. Assessment of heavy metals accumulation in agricultural soil, vegetables and associated health risks. *PLoS ONE* **2022**, *17*, e0267719. [CrossRef] [PubMed]
29. Khan, K.; Lu, Y.; Khan, H.; Ishtiaq, M.; Khan, S.; Waqas, M.; Wei, L.; Wang, T. Heavy metals in agricultural soils and crops and their health risks in Swat District, northern Pakistan. *Food Chem. Toxicol.* **2013**, *58*, 449–458. [CrossRef] [PubMed]
30. Sharma, S.; Nagpal, A.K.; Kaur, I. Heavy metal contamination in soil, food crops and associated health risks for residents of Ropar wetland, Punjab, India and its environs. *Food Chem.* **2018**, *255*, 15–22. [CrossRef] [PubMed]
31. Mahmud, U.; Salam, M.T.B.; Khan, A.S.; Rahman, M.M. Ecological risk of heavy metal in agricultural soil and transfer to rice grains. *Discov. Mater.* **2021**, *1*, 1–13. [CrossRef]
32. Akkajit, P.; DeSutter, T.; Tongcumpou, C. Short-term effects of sugarcane waste products from ethanol production plant as soil amendments on sugarcane growth and metal stabilization. *Environ. Sci. Process Impacts* **2013**, *15*, 947–954. [CrossRef]
33. Land Development Department. Agri-Map Kanchanaburi. Available online: https://www.ldd.go.th/Agri-Map/Data/C/kri.pdf (accessed on 1 September 2023).
34. Kanchanaburi Provincial Statistical Office. Kanchanaburi Provincial Statistical Report. 2022. Available online: https://kanchanaburi.nso.go.th/reports-publications/provincial-statistics-report.html (accessed on 1 September 2023).
35. Department of Primary Industries and Mines. Information on Mining Concessions Nationwide. Available online: https://www1.dpim.go.th//mne/mn.php (accessed on 27 February 2023).
36. Diehl, P.; Kern, H. Geology, mineralogy, and geochemistry of some carbonate-hosted lead-zinc deposits in Kanchanaburi Province, Western Thailand. *Econ. Geol.* **1981**, *76*, 2128–2146. [CrossRef]
37. Morley, C.K. Geometry and evolution of low-angle normal faults (LANF) within a Cenozoic high-angle rift system, Thailand: Implications for sedimentology and the mechanisms of LANF development. *Tectonics* **2009**, *28*. [CrossRef]
38. Pananont, P.; Wechbunthung, B.; Putthapiban, P.; Wattanadilokkul, D. Seismic activities in Kanchanaburi: Past and present. *Songklanakarin J. Sci. Technol.* **2011**, *33*, 355–364.
39. Choowong, M. Quaternary geology and sapphire deposits from the BO PHLOI gem field, Kanchanaburi Province, Western Thailand. *J. Asian Earth Sci.* **2002**, *20*, 119–125. [CrossRef]
40. Kowalska, J.B.; Mazurek, R.; Gąsiorek, M.; Zaleski, T. Pollution indices as useful tools for the comprehensive evaluation of the degree of soil contamination–A review. *Environ. Geochem. Health* **2018**, *40*, 2395–2420. [CrossRef] [PubMed]
41. Zarcinas, B.A.; Pongsakul, P.; McLaughlin, M.J.; Cozens, G. Heavy metals in soils and crops in Southeast Asia 2. Thailand. *Environ. Geochem. Health* **2004**, *26*, 359–371. [CrossRef] [PubMed]
42. Koptsik, G. Problems and prospects concerning the phytoremediation of heavy metal polluted soils: A review. *Eurasian Soil Sci.* **2014**, *47*, 923–939. [CrossRef]
43. Corwin, D.L.; Lesch, S.M. Apparent soil electrical conductivity measurements in agriculture. *Comput. Electron. Agric.* **2005**, *46*, 11–43. [CrossRef]
44. Fitz, W.J.; Wenzel, W.W. Arsenic transformations in the soil–rhizosphere–plant system: Fundamentals and potential application to phytoremediation. *J. Biotechnol.* **2002**, *99*, 259–278. [CrossRef] [PubMed]
45. Moreno-Jiménez, E.; Esteban, E.; Peñalosa, J.M. The fate of arsenic in soil-plant systems. In *Reviews of Environmental Contamination and Toxicology*; Springer: New York, NY, USA, 2012; pp. 1–37.
46. Bia, G.; García, M.; Rueda, E.S.; Mors, R.; Mlewski, E.; Gomez, F.; Borgnino, L. Arsenic in natural carbonates: The role of the biogeochemical conditions in its solid speciation. *Chem. Geol.* **2021**, *583*, 120477. [CrossRef]
47. Fontaine, H.; Kavinate, S.; Hoang, T.T.; Vachard, D. Permian limestone of peninsular and western Thailand in Khao Yoi, Cha-am and Thong Pha Phum areas. *Nat. Hist. Bull. Siam Soc.* **2012**, *58*, 39–47.
48. Demir, A. Speciation, risk assessment and bioavailability of metals in the agricultural soils of the Göksu Delta, Turkey. *Soil Sediment Contam. Int. J.* **2021**, *30*, 292–313. [CrossRef]
49. Verbeeck, M.; Hiemstra, T.; Thiry, Y.; Smolders, E. Soil organic matter reduces the sorption of arsenate and phosphate: A soil profile study and geochemical modelling. *Eur. J. Soil Sci.* **2017**, *68*, 678–688. [CrossRef]
50. Dousova, B.; Buzek, F.; Herzogova, L.; Machovic, V.; Lhotka, M. Effect of organic matter on arsenic (V) and antimony (V) adsorption in soils. *Eur. J. Soil Sci.* **2015**, *66*, 74–82. [CrossRef]
51. Liao, L.; Selim, H.; DeLaune, R. Mercury adsorption-desorption and transport in soils. *J. Environ. Qual.* **2009**, *38*, 1608–1616. [CrossRef] [PubMed]
52. O'Connor, D.; Hou, D.; Ok, Y.S.; Mulder, J.; Duan, L.; Wu, Q.; Wang, S.; Tack, F.M.; Rinklebe, J. Mercury speciation, transformation, and transportation in soils, atmospheric flux, and implications for risk management: A critical review. *Environ. Int.* **2019**, *126*, 747–761. [CrossRef] [PubMed]

53. Konen, M.; Burras, C.; Sandor, J. Organic carbon, texture, and quantitative color measurement relationships for cultivated soils in north central Iowa. *Soil Sci. Soc. Am. J.* **2003**, *67*, 1823–1830. [CrossRef]
54. Lavado, R.S.; Porcelli, C.A.; Alvarez, R. Nutrient and heavy metal concentration and distribution in corn, soybean and wheat as affected by different tillage systems in the Argentine Pampas. *Soil Tillage Res.* **2001**, *62*, 55–60. [CrossRef]
55. Busari, M.A.; Kukal, S.S.; Kaur, A.; Bhatt, R.; Dulazi, A.A. Conservation tillage impacts on soil, crop and the environment. *Int. Soil Water Conserv. Res.* **2015**, *3*, 119–129. [CrossRef]
56. Wu, W.; Qu, S.; Nel, W.; Ji, J. The influence of natural weathering on the behavior of heavy metals in small basaltic watersheds: A comparative study from different regions in China. *Chemosphere* **2021**, *262*, 127897. [CrossRef]
57. Fito, J.; Tefera, N.; Van Hulle, S.W. Sugarcane biorefineries wastewater: Bioremediation technologies for environmental sustainability. *Chem. Biol. Technol. Agric.* **2019**, *6*, 1–13. [CrossRef]
58. Fito, J.; Tefera, N.; Kloos, H.; Van Hulle, S.W. Physicochemical properties of the sugar industry and ethanol distillery wastewater and their impact on the environment. *Sugar Technol.* **2019**, *21*, 265–277. [CrossRef]
59. Rajkishore, S.; Vignesh, N. Distillery spentwash in the context of crop production-a review. *Bioscan* **2012**, *7*, 369–375.
60. Mahimairaja, S.; Bolan, N. Problems and prospects of agricultural use of distillery spentwash in India. *Magnesium* **2004**, *1715*, 2100.
61. Wang, J.; Yu, D.; Wang, Y.; Du, X.; Li, G.; Li, B.; Zhao, Y.; Wei, Y.; Xu, S. Source analysis of heavy metal pollution in agricultural soil irrigated with sewage in Wuqing, Tianjin. *Sci. Rep.* **2021**, *11*, 17816. [CrossRef] [PubMed]
62. Zhang, Q.; Zou, D.; Zeng, X.; Li, L.; Wang, A.; Liu, F.; Wang, H.; Zeng, Q.; Xiao, Z. Effect of the direct use of biomass in agricultural soil on heavy metals—Activation or immobilization? *Environ. Pollut.* **2021**, *272*, 115989. [CrossRef] [PubMed]
63. Zhang, W.; Liu, M.; Li, C. Soil heavy metal contamination assessment in the Hun-Taizi River watershed, China. *Sci. Rep.* **2020**, *10*, 8730. [CrossRef] [PubMed]
64. Tian, K.; Li, M.; Hu, W.; Huang, B.; Zhao, Y. Environmental capacity of heavy metals in intensive agricultural soils: Insights from geochemical baselines and source apportionment. *Sci. Total Environ.* **2022**, *819*, 153078. [CrossRef] [PubMed]
65. Qi, Y.; Donahoe, R.J. The environmental fate of arsenic in surface soil contaminated by historical herbicide application. *Sci. Total Environ.* **2008**, *405*, 246–254. [CrossRef] [PubMed]
66. Li, X.; Zhang, J.; Gong, Y.; Liu, Q.; Yang, S.; Ma, J.; Zhao, L.; Hou, H. Status of copper accumulation in agricultural soils across China (1985–2016). *Chemosphere* **2020**, *244*, 125516. [CrossRef]
67. Heijerick, D.G.; Van Sprang, P.A.; Van Hyfte, A.D. Ambient copper concentrations in agricultural and natural European soils: An overview. *Environ. Toxicol. Chem. Int. J.* **2006**, *25*, 858–864. [CrossRef]
68. Vavoulidou, E.; Avramides, E.; Papadopoulos, P.; Dimirkou, A.; Charoulis, A.; Konstantinidou-Doltsinis, S. Copper content in agricultural soils related to cropping systems in different regions of Greece. *Commun. Soil Sci. Plant Anal.* **2005**, *36*, 759–773. [CrossRef]
69. Kladsomboon, S.; Jaiyen, C.; Choprathumma, C.; Tusai, T.; Apilux, A. Heavy metals contamination in soil, surface water, crops, and resident blood in Uthai District, Phra Nakhon Si Ayutthaya, Thailand. *Environ. Geochem. Health* **2020**, *42*, 545–561. [CrossRef] [PubMed]
70. Beckers, F.; Rinklebe, J. Cycling of mercury in the environment: Sources, fate, and human health implications: A review. *Crit. Rev. Environ. Sci. Technol.* **2017**, *47*, 693–794. [CrossRef]
71. Zwolak, A.; Sarzyńska, M.; Szpyrka, E.; Stawarczyk, K. Sources of soil pollution by heavy metals and their accumulation in vegetables: A review. *Water Air Soil Pollut.* **2019**, *230*, 1–9. [CrossRef]
72. Pandey, B.; Suthar, S.; Singh, V. Accumulation and health risk of heavy metals in sugarcane irrigated with industrial effluent in some rural areas of Uttarakhand, India. *Process Saf. Environ. Prot.* **2016**, *102*, 655–666. [CrossRef]
73. Tripathi, S.; Sharma, P.; Singh, K.; Purchase, D.; Chandra, R. Translocation of heavy metals in medicinally important herbal plants growing on complex organometallic sludge of sugarcane molasses-based distillery waste. *Environ. Technol. Innov.* **2021**, *22*, 101434. [CrossRef]
74. Tamez, C.; Morelius, E.; Hernandez-Viezcas, J.; Peralta-Videa, J.; Gardea-Torresdey, J. Biochemical and physiological effects of copper compounds/nanoparticles on sugarcane (*Saccharum officinarum*). *Sci. Total Environ.* **2019**, *649*, 554–562. [CrossRef]
75. Jain, R.; Srivastava, S.; Solomon, S.; Shrivastava, A.; Chandra, A. Impact of excess zinc on growth parameters, cell division, nutrient accumulation, photosynthetic pigments and oxidative stress of sugarcane (*Saccharum* spp.). *Acta Physiol. Plant.* **2010**, *32*, 979–986. [CrossRef]