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Land Use Effects on Organic Carbon in Andean Volcanic Ash Soils

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ABSTRACT

Background: Both organic carbon (OC) stocks and labile OC (LOC) fractions are important indicators of soil health and are sensitive to land use change.

Aims: To study the effects of land use change on these indicators in montane volcanic ash soils, a soil transect was surveyed in northern Ecuador.

Methods: Samples were collected from 0–30, 30–60, and 60–90 cm soil depth at two agricultural sites with different time of cultivation and at three natural vegetation sites (tropical alpine grassland, páramo). LOC was determined as cold and hot water extractable OC (CWEOC and HWEOC). Molar absorptivity at 254 nm was determined in the extracts as a qualitative measure.

Results: Total OC stocks were high at the páramo sites (51.3–60.2 kg C m^{-3}) and the younger agricultural site (50.8 kg C m^{-3}; 20 years of cultivation), but significantly lower (30.1 kg C m^{-3}) at the older agricultural site (at least 100 years of cultivation); CWEOC (0.1%–0.7%) and HWEOC (0.6%–4.1%) represented only a small part of the OC. Both LOC pools decreased with increasing cultivation time, with CWEOC reflecting short-term and HWEOC long-term effects. In contrast, the molar absorptivity was highest at the oldest site (198–307 L mol^{-1} cm^{-1} vs. 36–64 L mol^{-1} cm^{-1} at the other sites), indicating that easily degradable labile C was depleted leaving compounds with higher aromaticity.

Conclusions: The conversion of páramo into agricultural land negatively affects OC stocks and soil health, as indicated by reduced OC storage capacities and lower LOC contents.

1 | Introduction

Changes in land cover due to land use change have profound effects on soil quality, including the ability of a soil to store carbon (C). One component most directly affected by land use change is the labile organic C (LOC) pool. It represents a small but significant fraction of a soil's organic C (OC) content. Typically, the LOC pool contains less than 8% of the total OC content (Landgraf, Leinweber, and Makeschin 2006; Waldrip et al. 2022), although exceptions of up to 21% have been documented (Hamkalo and Bedernichek 2014). However, it has a high relevance for microbial activity and plant growth, as it represents the easily utilizable fraction of OC (Cao et al. 2017; Ghani, Dexter, and Perrott 2003; Li et al. 2017). It consists of microbial biomass, soluble soil carbohydrates, and amines (Ghani, Dexter, and Perrott 2003). Unlike the stable OC pool, which has a long residence time of years to millennia, the LOC pool is used over shorter time periods (Davidson and Janssens 2006).

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A significant fraction of the LOC pool is water-soluble (Hamkalo and Bedernichek 2014). This fraction is derived from novel C sources such as freshly fallen plant litter, microbial biomass, root exudates, and animal excreta (Kalbitz et al. 2003; Sollins, Homann, and Caldwell 1996). Water-soluble OC can be divided into cold and hot water extractable fractions (Ghani, Dexter, and Perrott 2003). The hot water extractable fraction generally exceeds the cold water extractable fraction. They differ in their mineralizability: although cold water extractable OC (CWEOC) is easily mineralized and utilized by microorganisms and plants, hot water extractable OC (HWEOC) represents the more stable component of the LOC pool and is consequently utilized at a slower rate (Cao et al. 2017; Ghani, Dexter, and Perrott 2003).

Andosols are volcanic ash soils that contain unusually high levels of OC compared to other non-organic soils. OC levels in old Andosols of southern Ecuador can reach up to 670 g kg^{-1} (Buytaert et al. 2005). For younger Andosols in northern Ecuador, OC contents are lower, and they reach up to 200 g kg^{-1} (Poulenard, Podwojewski, and Herbillon 2003; Tonneijck et al. 2010). Generally, contents of 100 g OC kg^{-1} are common (Buytaert et al. 2006). Consequently, Andosols contribute significantly to the global C storage (Calispa et al. 2023; Pesántez et al. 2018). Despite covering only 1.0% of the global land surface, Andosols store about 5% of terrestrial OC (Eswaran, Van Den Berg, and Reich 1993; Soil Survey Staff 2015). Given the climate change discourse and the increasing attention to soil health (Baveye 2021; Lehmann et al. 2020), the role of Andosols as C sinks or sources is relevant (Calispa et al. 2023; Pesántez et al. 2018). The capacity of Andosols to store these high amounts of C depends on climatic conditions and land cover. Cold and wet conditions favor the formation of Andosols (Nierop et al. 2007; Pesántez et al. 2018). Andosols are found in volcanic activity zones worldwide, including the páramo region in South America, which includes Colombia, Venezuela, and Ecuador (Buytaert et al. 2006; López-Sandoval 2004).

Ecuador has undergone significant structural changes, especially since the middle of the 20th century. Rapid population growth is one of the reasons for these changes. Between 1950 and 2024, the population more than quintupled, from 3.52 million to 18.14 million people (United Nations 2024). United Nations projections (2024) predict further increases in the coming years. These demographic shifts require adaptation in the country's economic sectors, particularly agriculture, to meet food and housing needs (López-Sandoval 2004; Stadel 2005). As a result, previously natural land is being transformed, leading to the creation of more agricultural land and increased population density at higher altitudes in the páramo area (López-Sandoval 2004; Poulenard, Podwojewski, and Herbillon 2003). This change in land use puts pressure on the ecosystem and on OC storage capacity and C balance of the soil, thereby affecting soil health.

A significant proportion of soil OC is directly influenced by human activities (Batjes 1996). Especially land-use change plays a prominent role by severely limiting the OC storage capacity of a soil (Buytaert et al. 2006; Pesántez et al. 2018; Poulenard et al. 2001). To date, the literature on changes in labile OC content in Andosols due to land use change is scarce. This study investigates how human-induced land use change affects the OC storage capacity of Andosols in northern Ecuador near the El Ángel Ecological Reserve. Samples from three natural vegetation and two cultivated sites with different durations of agricultural use were analyzed for their total OC content, OC stock, and water-soluble OC content. Both CWEOC and HWEOC were extracted, and qualitative information was obtained through molar absorptivity measurements of dissolved C to identify relationships between land use changes and the two different LOC pools.

2 | Materials and Methods

2.1 | Landscape

The study site was located in the province of Carchi near the town of El Ángel in northern Ecuador, close to the Colombian border (Figure 1a). The El Ángel Ecological Reserve, which includes parts of the Espejo and Tulcán districts, is home to the highest elevation of the reserve, Cerro de Iguán (3967 m above sea level, hereafter asl). The topography bears the imprint of pyroclastic material from the neighboring volcano Chiles (4729 m asl) and Quaternary glacial processes (Buytaert et al. 2006; Poulenard, Podwojewski, and Herbillon 2003). The region is predominantly covered by páramo vegetation, a tropical belt that exists between the upper tree line and the perpetual snow zone of the equatorial Andes (Lopez Sandoval 2004).

For the purposes of this study, sampling was conducted within this native vegetation type and in adjacent areas converted to agricultural land. The term "páramo" denotes a tropical alpine ecosystem, originally classified by Alexander von Humboldt in the early 19th century as part of the upper *Tierra Helada*, which characterizes mountain landscapes by vertical climatic variations (Stadel, 1992). Contemporary definitions rely on different climatic, altitudinal, and vegetational attributes, resulting in different estimates of the páramo extent. Lopez-Sandoval (2004) summarizes global surface estimates ranging from 12000 to 25000 km^2 within the region stretching from Costa Rica to northern Peru, at altitudes of 3000 to 4700 m asl.

The ecological literature defines páramo as "native alpine grasslands" (Farley, Kelly, and Hofstede 2004) or "neotropical alpine ecosystems" (Buytaert et al. 2006; Poulenard et al. 2001) and distinguishes subtypes such as sub-páramo, proper páramo (or grass páramo), and super-páramo (Poulenard, Podwojewski, and Herbillon 2003). The páramo landscape is characterized by a layer of tussocky grasses (mainly *Agrosis* sp., *Calamagrostis* sp., *Festuca* sp., and *Stipa Ichu*) covering the entire ground. The defining feature of this landscape is the endemic plant *Espeletia*, locally called "Frailejones" (Figure 1b). This perennial dwarf shrub of the aster family has a unique water-harvesting mechanism, absorbing water vapor from passing clouds, storing it in its stem, and transferring it into the soil through its root system. In our study area, the species *Espeletia pycnophylla* subsp. *Angelensis* is endemic and found nowhere else in the country (Cross 2001). For the purposes of this study, the term "páramo" distinguishes the monitored native landscape from other forms of land cover in converted and cultivated areas.

Climatically, the sites are classified as a Köppen–Geiger climate type Cfb (warm temperate climate, no dry season, warm summer) (Kottek et al. 2006). The mean annual precipitation and air

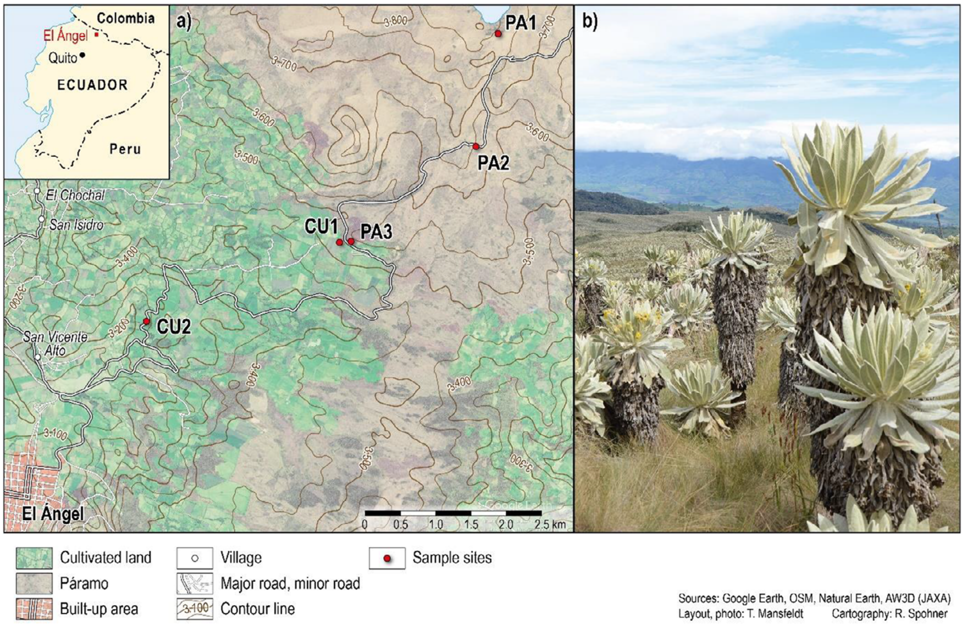

FIGURE 1 | The study site in northern Ecuador with three páramo (PA) and two cultivated (CU) sites (a) and the páramo vegetation dominated by the endemic plant *Espeletia pycnophylla* subsp. *Angelensis* locally known as "Frailejones" (b).

TABLE 1 | The five sampling sites in northern Ecuador.

Site	Coordinates	Altitude (m asl)	Land cover	Soil type
PA1	N00°40.824′ W77°52.719′	3817	Páramo	Aluandic Andosol
PA2	N00°39.957′ W77°52.890′	3570	Páramo	Aluandic Andosol
PA3	N00°39.228′ W77°53.846′	3422	Páramo	Aluandic Andosol
CU1	N00°39.221′ W77°53.933′	3390	Pasture–potato cropping system	Silandic Andosol
CU2	N00°38.614′ W77°55.410′	3232	Dairy pasture	Hortic Anthrosol

[a] *Source:* IUSS Working Group WRB (2022).

temperature at the El Voladero weather station, located at 3400 m asl near the El Ángel Reserve, are approximately 1150 mm and 9°C, respectively (Poulenard, Podwojewski, and Herbillon 2003). However, it is important to note that both temperature and precipitation are strongly dependent on altitude. An approximate temperature gradient of 0.6°C per 100 m is observed (Poulenard, Podwojewski, and Herbillon 2003). No specific data are available on the effect of altitude on local precipitation, where fog may play an important role.

2.2 | Sites

Sampling was conducted at five sites ranging in elevation from 3232 to 3817 m asl (Table 1). Of these, three sites had páramo vegetation (hereafter referred to as PA sites), whereas two sites were cultivated areas (hereafter referred to as CU sites). PA3, located on the border between páramo and agricultural zones, showed slight alterations due to illegal burning. CU2 represented an area that had experienced natural vegetation loss over a century ago and was later covered by grassland used for permanent pasture. In contrast, CU1 was historically used for agriculture and lost its páramo vegetation in the late 1990s (Figures S1 and S2). Since then, it has been subject to a crop rotation system of annual potato cultivation with two harvests, followed by 3 years of cattle grazing. At the time of sampling, this field had just been freshly seeded for pasture farming. The soil properties of the PA sites are used as a reference for the soil before its conversion to agriculture.

2.3 | Soil Sampling and Sample Preparation

Sampling was conducted on 2 consecutive days in September 2017. Each site was divided into three 5 × 5 m plots designated for random sampling, with approximately a 50 m distance between plots. Within each plot, five individual subsamples were collected at soil depths of 0–30, 30–60, and 60–90 cm using a hand auger set (S10, Stitz, Gerden, Germany). Sampling depths were chosen to compare the sites with respect to the influence of agricultural activities on the soils, such as plowing. Each subsample was collected by individual drilling to ensure independent sampling data for subsequent statistical analysis. Therefore, a total of 15 holes were drilled at each plot. The subsamples within each plot were pooled on the basis of the three different soil depths. Visible plant roots and debris were removed from the collected samples in the field.

In the laboratory, samples were manually homogenized and sieved (<2 mm). No soil skeleton was present as all material passed through the sieve. Samples were air-dried at 20°C room temperature for a week (until dry) and stored in the dark until further analysis. Subsamples of the air-dried material were then finely ground using a zirconia ball mill (MM 400, Retsch, Haan, Germany).

2.4 | Soil Analysis

Total C (TC) and nitrogen (N) in the ground samples were determined by dry combustion using a CNS analyzer (Vario EL cube, Elementar, Hanau, Germany). In the case of agricultural soils, the presence of inorganic C (IC) was checked due to regular liming. These specific samples were treated with hydrochloric acid (10% HCl), and their OC content was measured. As IC was consistently undetectable, OC was equal to TC for all sites. Soil pH was measured potentiometrically using a glass electrode in a solution of 0.01 M $CaCl_2$ mixed in a 5:1 ratio with soil (v/v).

Residual-water content of air-dried samples was determined gravimetrically after exposing the samples to 105°C for 24 h. All chemical results are presented on the basis of the oven-dried soil mass. Soil bulk density for the respective soil depths was calculated by dividing the oven-dry soil mass of the disturbed samples by the hand auger's volume of the corresponding depth. The bulk density was then used to calculate OC stocks from the OC contents. To provide OC stocks for 1 m sampling depth, the bulk density for 90–100 cm was extrapolated from the 60–90 cm layer.

2.5 | Extraction of LOC

Soil extraction followed the protocol outlined by Ghani, Dexter, and Perrott (2003) and consisted of two sequential steps. First, readily soluble C, possibly derived from recent soil liming, animal excreta, or soluble plant residues, was removed by agitating the soil with cold water for 0.5 h. Second, labile C components were targeted using hot water at 80°C for 16 h. The first fraction is referred to as CWEOC, and the subsequent fraction is referred to as HWEOC. Briefly, 3 g of soil (on a dry matter basis) was weighed into 50-mL polypropylene centrifuge tubes, followed by the addition of 30 mL of demineralized water. The tubes were agitated on a horizontal shaker (GFL, Burgwedel, Germany) at 30 rpm for 0.5 h at 20°C and then centrifuged at 2500 *g* for 20 min. The supernatants were filtered through 0.45 mm cellulose nitrate membrane filters. An additional 30 mL of demineralized water was added to the tubes, shaken on a vortex shaker for 10 s to suspend the soil, capped, and left in a hot water bath at 80°C for 16 h. After the extraction period, each tube was shaken briefly on a vortex shaker to ensure complete suspension of the HWEOC released from the soil OC in the extraction medium. The tubes were then centrifuged at 2500 *g* for 20 min, and the supernatants were again filtered through 0.45 mm cellulose nitrate membrane filters.

TC in both extracts was determined on a liquid C analyzer by high-temperature catalytic oxidation to CO_2 at 900°C, followed by quantification using a nondispersive infrared detector (Dimatok 2000, Dimatek Analysentechnik, Essen, Germany). Injection volumes of 100 µL were used for the analysis. Samples were analyzed in triplicate. Standard deviations were <3%.

Qualitative information on the extracted OC was obtained by determining its molar absorptivity at 254 nm. Ultraviolet absorbance was measured using a Lambda 25 UV/VIS double beam spectrophotometer (PerkinElmer, Rodgau, Germany) in a 1 cm path length quartz cuvette, with deionized water as a blank. At sufficiently low concentrations, Lambert–Beer's law can be applied as follows:

$$A = \varepsilon b c, \tag{1}$$

where A is the absorbance (dimensionless), c is the concentration (mol L^{-1}), b is the path length (in cm), and ε is the molar absorptivity (L mol^{-1} cm^{-1}). The molar absorptivity of both CWEOC and HWEOC was calculated by rearranging Equation (1).

2.6 | Statistical Analysis

The soil sampling plan used a simple random system, where each sample was selected separately, randomly, and independently of the others. All statistical analyses were performed with R, version 4.3.1 (R Core Team 2023), and RStudio, version 2023.09.1 (Posit Team 2023). Descriptive summary statistics, such as the calculation of mean and standard error of the mean for soil properties in each sample, were performed. A one-way analysis of variance (ANOVA) followed by Tukey's post hoc test implemented in the *multcompView* package (Graves et al. 2023) was used to assess significant differences between samples. A significance level of alpha = 0.05 was used. Data were grouped according to (1) replicate per plot, (2) site, and (3) soil depth. A Spearman correlation was conducted using the stats package in R, version 4.3.1 (R Core Team 2023). All figures were created with the *ggplot2* package, version 3.4.3 (Wickham 2016).

3 | Results

3.1 | General Soil Properties

Table 2 presents the main soil properties of the five sites at three soil depths. For simplicity, the 0–30 cm depth will be referred to as topsoil, whereas the other two depths are grouped as subsoil (in the broader sense, as there is no strong gradient in OC content between topsoil and subsoil here), unless otherwise stated.

In terms of pH, OC content, and the C:N ratio, the sites can be categorized into three groups: The site with the longest agricultural history (CU2) had the significantly highest pH values (5.0–5.1) across all soil depths. However, it had the lowest OC contents (30.9–48 g kg^{-1}) and, restricted to the two upper depths, the closest ratios of C:N (10 and 12). On the other hand, site CU1 showed a more acidic pH (4.5) and higher OC contents (107 g kg^{-1}). In comparison, in the uncultivated sites, pH values ranged from 4.0 to 4.3, and OC contents from 98.6 to 170 g kg^{-1}. Particularly in the topsoil, the PA sites can be clearly differentiated from the CU sites. Among the PA sites (sites with typical páramo vegetation),

TABLE 2 | General soil properties of the páramo (PA) and the cultivated (CU) sites with mean and standard error of the mean (±).

Soil depth (cm)	Site	Bulk density (kg L^{-1})	pH (0.01 M $CaCl_2$) [–]	OC (g kg^{-1})	N (g kg^{-1})	C:N (–)	OC stock (kg OC m^{-2})
0–30	PA1	0.33 ± 0.02c	4.0 ± <0.1b	167 ± 4.4b	10.2 ± 0.19bc	16bc	16.7 ± 1.02ab
	PA2	0.35 ± 0.01c	4.1 ± <0.1b	170 ± 3.7b	10.6 ± 0.08b	16b	17.7 ± 0.39ab
	PA3	0.38 ± 0.01bc	4.1 ± 0.1b	167 ± 2.6b	9.79 ± 0.16c	17d	19.0 ± 0.24a
	CU1	0.46 ± 0.02b	4.5 ± 0.1c	107 ± 2.5c	6.44 ± 0.12d	17cd	14.9 ± 0.70b
	CU2	0.77 ± 0.02a	5.1 ± <0.1a	48.0 ± 2.8a	4.85 ± 0.24a	10a	10.99 ± 0.15c
30–60	PA1	0.49 ± 0.02b	4.2 ± <0.1b	117 ± 1.5bc	7.27 ± 0.09bc	16b	17.2 ± 0.83a
	PA2	0.45 ± 0.02b	4.3 ± <0.1b	126 ± 8.9bc	8.00 ± 0.42b	16b	16.8 ± 0.18a
	PA3	0.49 ± 0.01b	4.3 ± 0.1b	137 ± 21.1b	8.17 ± 1.13b	17b	20.1 ± 2.16a
	CU1	0.53 ± 0.01b	4.3 ± 0.1b	93.1 ± 1.6c	5.60 ± 0.12c	17b	14.6 ± 0.14a
	CU2	0.88 ± 0.03a	5.0 ± 0.1a	32.1 ± 0.6a	2.69 ± 0.15a	12a	8.5 ± 0.16b
60–90	PA1	0.50 ± 0.01b	4.3 ± <0.1bc	109 ± 4.0bc	6.30 ± 0.31b	17a	16.4 ± 0.77a
	PA2	0.42 ± 0.004b	4.3 ± <0.1b	113 ± 0.8b	7.08 ± 0.08c	16a	14.1 ± 0.14a
	PA3	0.54 ± 0.003b	4.3 ± <0.1b	98.6 ± 3.3c	5.86 ± 0.25b	17a	15.9 ± 0.37a
	CU1	0.44 ± 0.01b	4.2 ± 0.1c	121 ± 6.3b	6.18 ± 0.10b	20b	15.9 ± 0.35a
	CU2	0.85 ± 0.09a	5.0 ± 0.1a	30.9 ± 1.6a	1.94 ± 0.16a	16a	7.9 ± 0.9b

Note: The letters denote significant differences among samples of the corresponding soil depth (pairwise ANOVA followed by Tukey's post hoc test).
Abbreviation: OC, organic carbon.

the differences in pH, OC contents, and C:N ratios were mostly small and not significant.

Soil bulk densities in páramo sites varied from 0.33–0.38 kg L^{-1} (mean 0.35 ± 0.025) in 0–30 cm, 0.45–0.49 kg L^{-1} (mean 0.47 ± 0.02) in 30–60 cm, and 0.42–0.54 kg L^{-1} (mean 0.48 ± 0.06) in 60–90 cm. In the cultivated sites, topsoil bulk densities were significantly higher (0.46–0.77 kg L^{-1}, except for CU1 vs. PA3). In particular, the oldest cultivated site had higher densities in both lower depths (0.85–0.88 kg L^{-1}). Organic C stocks were significantly lower in all depths of the oldest site (7.9–11.0 kg C m^{-2}) but showed no significant differences between the páramo sites and CU1 (14.6–20.1 kg C m^{-2}), except for site PA3, which had significantly higher stocks than CU1. Cumulative summation of the OC stocks in the three soil depths (0–90 cm) resulted in the following site order: CU2 (27.4 ± 2.3 kg C m^{-2}) << CU1 (45.5 ± 1.6 kg C m^{-2}) < PA2 (48.5 ± 1.0 kg C m^{-2}) < PA1 (50.2 ± 5.4 kg C m^{-2}) < PA3 (55.0 ± 4.6 kg C m^{-2}).

3.2 | Labile Organic Carbon

Table 3 summarizes the data for the CWEOC and HWEOC fractions. CWEOC contents ranged from 93.2 to 1261 mg kg^{-1}, representing 0.08%–0.74% of the total OC, whereas HWEOC contents ranged from 428 to 4882 mg kg^{-1}, representing 0.69%–3.99% of OC. Together, both fractions accounted for a proportion of LOC ranging from 0.77% to 4.66% of OC.

The HWEOC content consistently exceeded the CWEOC content by at least 3.4 times at all locations and depths. A clear differentiation of the sites into two groups is apparent: the PA sites and the CU sites. Both cultivated sites generally had significantly lower CWEOC contents compared to the PA sites (172 and 321 vs. 821 to 1261 mg kg^{-1} in the topsoil; 101 and 134 vs. 311 to 573 mg kg^{-1} in the 30–60 cm layer; 93.2 and 110 vs. 196 to 364 mg kg^{-1} in the 60–90 cm layer). This trend was also observed for the HWEOC fraction (1480 and 1913 vs. 4310 to 4882 mg kg^{-1} in the topsoil; 640 and 857 vs. 1889 to 2303 mg kg^{-1} in the 30–60 cm layer; 428 and 830 vs. 1164 to 1483 mg kg^{-1} in the 60–90 cm layer). Notably, site CU1 consistently had the lowest values for both CWEOC (0.08% to 0.16%) and HWEOC (0.69% to 1.38%) fractions in terms of their relative contribution to the total OC content. In addition, a strong depth gradient was observed for both fractions, with subsoil contents approximately one-quarter to one-half lower than those in the topsoil (Table 3).

At site CU2, the molar absorptivity for both LOC fractions (CWEOC: 306–432 L mol^{-1} cm^{-1}; HWEOC: 198–307 L mol^{-1} cm^{-1}) was remarkably high, up to 13 times higher than at any other site, including the young cultivated site (Table 3). In addition, a significant difference between CU2 and all other sites was observed: The molar absorptivity for both CWEOC and HWEOC increased with increasing sampling depth at CU2, whereas no significant trend was observed at the PA sites (Table 3). In contrast, at CU1, the molar absorptivity decreased with increasing soil depth for both LOC fractions (Table 3).

To identify relationships between the LOC fractions and soil parameters, a correlation analysis was performed (Figure 2, Table 4). Both the content (r_s = 0.936) and the absorptivity (r_s = 0.948) of the two LOC fractions showed a significant positive correlation with each other (Figure 2a,b). Considering the soil properties, the most significant positive influences on CWEOC and HWEOC were observed for soil OC and N contents (r_s = 0.728–0.865). Due to the wide range of soil OC contents

TABLE 3 | Cold- (CWEOC) and hot-water extractable organic carbon (HWEOC) and their molar absorptivity at 254 nm of the páramo (PA) and the cultivated (CU) sites with mean and standard error of the mean (±).

Soil depth (cm)	Site	CWEOC			HWEOC			Sum of CWEOC and HWEOC (%)
		C (mg kg^{-1})	CWEOC/OC (%)	Molar absorptivity (L mol^{-1} cm^{-1})	C (mg kg^{-1})	HWEOC/OC (%)	Molar absorptivity (L mol^{-1} cm^{-1})	
0–30	PA1	1114 ± 122b	0.67 ± 0.08	43 ± 7b	4882 ± 276b	2.93 ± 0.23	44 ± 1bc	3.60 ± 0.31
	PA2	1261 ± 29b	0.74 ± 0.01	32 ± 1b	4310 ± 51c	2.54 ± 0.05	38 ± 1b	3.28 ± 0.05
	PA3	821 ± 59c	0.49 ± 0.04	76 ± 7c	4398 ± 138c	2.64 ± 0.11	53 ± 2cd	3.13 ± 0.14
	CU1	172 ± 13a	0.16 ± 0.01	97 ± 3d	1480 ± 50a	1.38 ± 0.04	64 ± 2d	1.54 ± 0.03
	CU2	321 ± 5a	0.67 ± 0.03	306 ± 6a	1913 ± 65a	3.99 ± 0.11	198 ± 6a	4.66 ± 0.14
30–60	PA1	457 ± 67bc	0.39 ± 0.06	39 ± 6bc	2046 ± 180b	1.74 ± 0.15	37 ± <1b	2.13 ± 0.20
	PA2	573 ± 69b	0.45 ± 0.03	35 ± 3b	2303 ± 229b	1.82 ± 0.08	36 ± 1b	2.28 ± 0.11
	PA3	311 ± 29c	0.23 ± 0.02	60 ± 2cd	1889 ± 49b	1.41 ± 0.19	43 ± 1b	1.64 ± 0.21
	CU1	101 ± 7a	0.11 ± 0.01	64 ± 6d	857 ± 49a	0.92 ± 0.05	50 ± 2b	1.03 ± 0.06
	CU2	134 ± 10a	0.42 ± 0.02	375 ± 13a	640 ± 75a	2.00 ± 0.25	298 ± 42a	2.41 ± 0.24
60–90	PA1	250 ± 38c	0.23 ± 0.03	39 ± 6b	1272 ± 135b	1.16 ± 0.08	38 ± <1b	1.39 ± 0.11
	PA2	364 ± 30d	0.32 ± 0.03	33 ± 2b	1483 ± 64b	1.31 ± 0.08	37 ± 1b	1.64 ± 0.10
	PA3	196 ± 30ac	0.20 ± 0.03	60 ± 7b	1164 ± 152bc	1.18 ± 0.15	45 ± 2b	1.38 ± 0.18
	CU1	93.2 ± 8b	0.08 ± 0.01	54 ± 4b	830 ± 17c	0.69 ± 0.05	45 ± 2b	0.77 ± 0.06
	CU2	110 ± 3ab	0.36 ± 0.02	432 ± 102a	428 ± 31a	1.38 ± 0.03	307 ± 24a	1.74 ± 0.01

Note: The letters denote significant differences among samples of the corresponding soil depth (pairwise ANOVA followed by Tukey's post hoc test).
Abbreviation: OC, organic carbon.

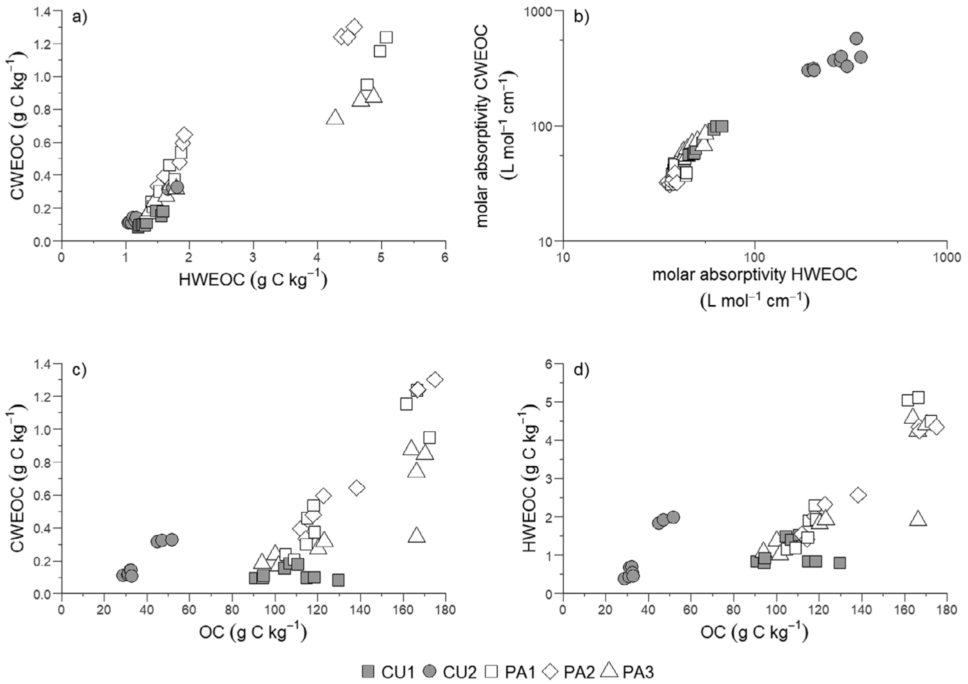

FIGURE 2 | Relationship between (a) contents of cold-water extractable organic carbon (CWEOC) and hot-water extractable organic carbon (HWEOC), (b) molar absorptivity at 254 nm of CWEOC and HWEOC, (c) contents of CWEOC and organic carbon (OC), and (d) contents of HWEOC and OC of the páramo (PA) and the cultivated (CU) sites.

TABLE 4 | Correlation matrix for labile organic carbon fractions and soil properties (the Spearman rank correlation, $n = 44$).

	CWEOC	HWEOC	MA-CWEOC	MA-HWEOC	pH	OC	N
CWEOC	—	0.936***	−0.550***	−0.527***	0.551***	0.728***	0.830***
HWEOC	—	—	−0.497**	−0.463**	0.609***	0.795***	0.865***
MA-CWEOC			—	0.948***	−0.632***	−0.621***	−0.669***
MA-HWEOC				—	−0.562***	−0.594***	−0.645***
pH					—	0.890***	0.814***
OC						—	0.962***
N							—

Abbreviations: CWEOC, cold-water extractable organic carbon; HWEOC, hot-water extractable organic carbon; MA, molar absorptivity at 254 nm; OC, organic carbon.
**$p < 0.01$.
***$p < 0.001$.

across different land uses, an additional correlation analysis was performed only for the PA sites (Figure 2c,d, Table 5), as the other statistical population only comprises two sites. It was observed that the r_s values increased from 0.728 to 0.866 for CWEOC and from 0.795 to 0.886 for HWEOC.

4 | Discussion

4.1 | General Soil Properties

Our results clearly illustrate the influence of agriculture on the cultivated sites. Long-term liming resulted in significantly elevated pH values in both the topsoil and subsoil of CU2. At CU1, where the liming period was much shorter (≤20 years), the effects on pH were evident in the topsoil. In contrast, the pH values observed at the páramo sites were <4.5, a characteristic associated with aluandic properties in Andosols according to the WRB classification (IUSS Working Group WRB 2022). Soil aeration and disruption of soil aggregates caused by tillage have accelerated the mineralization process of OC in Andosols (Buytaert et al. 2006; Pesántez et al., 2018; Podwojewski et al. 2002). This is manifested in the degradation of OC across all sampling depths of CU2 and the topsoil of CU1. At the natural sites, OC contents (170 g kg^{-1} in the topsoil) are similar to other sites near El Angél (Poulenard, Podwojewski, and Herbillon 2003; Tonneijck et al. 2010). In comparison to other sites in northern Ecuador outside the El Ángel region, our OC levels are slightly higher. Topsoils on the western slopes of Antisana volcano revealed 110 g kg^{-1} OC (Páez-Bimos et al. 2022) and 130 g kg^{-1}

TABLE 5 | Correlation matrix for labile organic carbon fractions and soil properties of the páramo sites (Spearman rank correlation, $n = 27$).

	CWEOC	HWEOC	MA-CWEOC	MA-HWEOC	pH	OC	N
CWEOC	—	0.932***	−0.272	−0.014	0.790***	0.866***	0.930***
HWEOC		—	−0.045	0.208	0.809***	0.886***	0.917***
MA-CWEOC			—	0.834***	−0.007	0.024	−0.107
MA-HWEOC				—	0.219	0.191	0.095
pH					—	0.825***	0.971***
OC						—	0.971***
N							—

Abbreviations: CWEOC, cold-water extractable organic carbon; HWEOC, hot-water extractable organic carbon; MA, molar absorptivity at 254 nm; OC, organic carbon.
***$p < 0.001$.

OC at the Pichincha Mountain (Poulenard, Podwojewski, and Herbillon 2003). Site-specific factors such as elevation and related temperature differences (585 m and around 3.5°C between the lowest and highest site) can be considered minor influences on OC contents in comparison to land use. Minaya et al. (2015) discovered an inverse trend of OC content and elevation for natural vegetation due to a more homogenous plant cover and more stable inputs at lower elevations. For our sites, CU1 and PA3 differ by 32 m in elevation (less than 0.2°C temperature gradient), yet OC contents vary considerably. This suggests that changes in vegetation strongly affect the composition of soil OC by altering both the quality and quantity of organic inputs from the soil surface and subsurface C sources (Berendse 1998; Jiang et al. 2011; Sun et al. 2013). This change is evidenced by the decrease in the native C:N ratio in the upper two sampling depths of CU2 (potatoes, grasses). A decline in the C:N ratio indicates the advanced stage of C decomposition in the soil, potentially leading to an accelerated mineralization of OC (Cai et al. 2022). Site CU1 did not show a distinct C:N ratio compared to the páramo sites, possibly due to the shorter period of agricultural impact. Our páramo C:N ratios are similar to those found by Becker et al. (2019), who studied Tanzanian Andosols at similar elevations.

4.2 | Carbon Stocks

Soil tillage, that is, cultivation, typically leads to an increase in soil bulk density (Don, Schumacher, and Freibauer 2011; Jiang et al. 2011; Shete et al. 2016). This compaction effect was particularly evident at the oldest cultivated site. However, the other sites retained their low bulk densities, which are characteristic of volcanic ash soils, and a criterion used in their classification (Batjes 1996; IUSS Working Group WRB 2022).

Regarding OC stocks, two considerations need to be addressed. First, the bulk density was determined using a hand auger rather than steel cylinders as required. Although the volume of the auger can be accurately calculated, there was a small loss of soil when the auger was removed. As a result, the bulk densities presented here may be slightly underestimated. However, the comparison of these data with a soil profile under páramo vegetation, where undisturbed volumetric samples were collected with steel cylinders (100 cm^3) in 2016 near site PA2, shows a close agreement with the páramo (0.39 ± 0.014 kg L^{-1} in 0–30 cm, 0.52 ± 0.048 kg L^{-1} in 30–55 cm, and 0.48 ± 0.013 kg L^{-1} in 55–160 cm for the soil profile; mean and standard error of the mean of seven replicates, unpublished data). Second, organic C stocks are conventionally calculated for a soil depth of 1 m, whereas our presentation considered a depth of 90 cm. To facilitate comparison with other studies, we extrapolated C stocks for the missing 90–100 cm depth by assuming identical bulk densities and organic C contents as found in the overlying layer (i.e., the 60–90 cm depth). Because the subsoils are highly homogeneous down to ≈160 cm, where the unweathered volcanic ash layer begins (a finding from the 2016 soil profile), we believe that this approach is appropriate for estimating OC stocks for a 1 m depth. Consequently, this results in OC stocks of 30.1 kg C m^{-2} for CU2, 50.8 kg C m^{-2} for CU1, 53.3 kg C m^{-2} for PA2, 55.6 kg C m^{-2} for PA1, and 60.2 kg C m^{-2} for PA3. The mean OC stock of the páramo sites averaged at ≈55 kg C m^{-2}, about 10% less than the stocks from the aforementioned soil profile (≈62 kg C m^{-2}, unpublished data) and another nearby páramo site (≈60 kg C m^{-2}; Poulenard, Podwojewski, and Herbillon 2003). Batjes (1996) estimated the global OC stocks of Andosols (according to FAO–UNESCO soil units) to be about 25.4 kg C m^{-2}, with slightly higher values for Humic Andosols (29.4 kg C m^{-2}). Our data suggest, on the one hand, that the OC stocks of the undisturbed páramo ecosystem in northern Ecuador, covered by Frailejones, are about twice as high. Therefore, this ecosystem is among those with the highest OC stocks in soils worldwide (Batjes 1996; Siewert et al. 2015). On the other hand, our results show that a change in land use—specifically, from a páramo ecosystem to an agricultural ecosystem—leads to a significant decrease in the OC stock. Especially in the topsoil, where the input of OC takes place, this impact becomes visible (Table 2). Therefore, the cultivated sites can be distinguished from the sites with natural vegetation, as OC inputs differ due to the loss of natural vegetation cover at the cultivated sites. Particularly for CU2, the difference to the other sites is significant due to the long-term agricultural use. Looking at the 1 m soil profile, about half of the OC stock (≈30 kg C m^{-2} at CU2 vs. ≈55 kg C m^{-2} at the páramo sites) was lost over at least 100 years. It can be inferred that most of the lost OC

(≈25 kg C m^{-2}) was oxidized to carbon dioxide (CO_2), resulting in a total emission of ≈92 kg CO_2 m^{-2}. In contrast, emissions from mangrove forests over similar time periods are approximately twice as high (≈179 kg CO_2 m^{-2}) (Kauffmann et al. 2016).

4.3 | Cold Water Extractable OC

In this study, soil C extraction using water (both cold and hot) was chosen because it is one of the simplest chemical procedures for determining LOC (Landgraf, Leinweber, and Makeschin 2006; Sparling, Vojvodić-Vuković, and Schipper 1998). This method does not require toxic agents, as would be required for acid extraction or permanganate digestion, and it can be performed on previously air-dried samples, allowing for a more flexible testing schedule (Dodla, Wang, and DeLaune 2012; McLauchlan and Hobbie 2004; Sparling, Vojvodić-Vuković, and Schipper 1998; Weil et al. 2003). In addition, Sparling, Vojvodić-Vuković, and Schipper (1998) suggested its suitability as a tool for monitoring soil quality on a broader geographic scale.

The different land uses investigated in this study were reflected in the CWEOC values, with the cultivated soils having lower CWEOC values than the páramo soils (Table 3). Similar results from other studies support this trend, where soils under natural vegetation and forests had higher CWEOC contents compared to soils used for grazing or cultivation (Ghani, Dexter, and Perrott 2003; Hamkalo and Bedernichek 2014; Waldrip et al. 2022). Examining two levels of agricultural use (20 years and at least 100 years), we observed a significant degradation of CWEOC after only 20 years of cultivation, suggesting its potential use as an early indicator of soil degradation and C decomposition. This is consistent with the results of Sun et al. (2013). Furthermore, the ANOVA indicates that even small changes in vegetation (e.g., small fires in PA3) can lead to a decrease in the CWEOC content.

However, when evaluating the cold-water extraction method, it is important to note that CWEOC measurements were conducted on rewetted soils under laboratory conditions. This process can affect the quality and quantity of CWEOC, potentially leading to an overestimation due to C degradation of more stable organic compounds during drying or storage and subsequent microbial activity during incubation (Landgraf, Leinweber, and Makeschin 2006; Waldrip et al. 2022). This could lead to an overestimation of CWEOC values, which could affect the interpretation of positive land management effects on the soil. Conversely, factors leading to an underestimation include field-level influences excluded from the analysis, such as land cover and plants. Without new C inputs from plant litter or root exudates, the labile C pool may decrease, affecting the analysis due to surviving microorganisms depending on soil composition (Sparling, Vojvodić-Vuković, and Schipper 1998). In addition to the degradation of stable OC pools during the drying and storage process, mineralization of labile C pools can also occur (Waldrip et al. 2022).

Our study revealed a steep depth gradient of CWEOC concentrations (Table 3), consistent with numerous other experiments (Cheng et al. 1996). The availability of the LOC pool is highest in the topsoil and rhizosphere (De Feudis et al. 2017; Hamkalo and Bedernichek 2014; Uchida, Nishimura, and Akiyama 2012; Waldrip et al. 2022) due to root exudates, excreta, and plant litter as prominent sources (Cao et al. 2017; Mganga et al. 2023). The concentration of the labile C pools in the upper soil layers is sensitive to land-use change, as the destruction of natural vegetation as a labile C source disrupts the former soil nutrient cycle and may even deplete nutrients essential for plant growth in cultivated scenarios (Buytaert et al. 2006; Pesántez et al., 2018; Poulenard et al. 2001). Hamkalo and Bedernichek (2014) and Podwojewski et al. (2002) highlighted the sensitivity of the upper soil layer to stress and its role in the mineralization of the labile C pool.

4.4 | Hot-Water Extractable OC

HWEOC serves as an indicator of readily mineralizable C potentially available in soils (Ahn et al. 2009; Breulmann et al. 2012). In different soils—wetland, forest, and volcanic soils—HWEOC content consistently exceeds the CWEOC content (e.g., Cao et al. 2017; Dodla, Wang, and DeLaune 2012; Ghani, Dexter, and Perrott 2003; Landgraf, Leinweber, and Makeschin 2006), a trend also observed in Andosols (Uchida, Nishimura, and Akiyama 2012), which our results confirm. The amount of OC extracted by hot water surpasses that of cold water due to the extraction of root exudates, amino acids, C bound to soil enzymes, and microbial biomass C (Leinweber, Schulten, and Körschens 1995; Ghani, Dexter, and Perrott 2003; Sparling, Vojvodić-Vuković, and Schipper 1998).

Considering the HWEOC:SOC ratio, Ghani, Dexter, and Perrott (2003) found that volcanic soils contain about 3%–6% HWEOC of their soil organic matter, slightly lower than the OC content of our soils (30.9–170 g kg^{-1}). In contrast, páramo sites had ≤2.9% HWEOC. For CU2, the proportion was ≤3.9%, indicating a possible shift from stable to LOC fractions due to long-term cultivation. Other studies on different soils reported even higher HWEOC proportions, varying with land use (forest, arable land, grassland). Arable land (up to 28%) generally showed higher HWEOC proportions than grassland (Hamkalo and Bedernichek 2014; Landgraf, Leinweber, and Makeschin 2006; Ukalska-Jaruga, Klimkowicz-Pawlas, and Smreczak 2019). However, in the study by Hamkalo and Bedernichek (2014), the proportion of HWEOC in forest soils (Gleyic Albeluvisol) exceeded that in neighboring arable soils.

According to Haynes and Francis (1993), the HWEOC content is significantly influenced by soil aggregate stability, as the C extracted by hot water consists mainly of microbial C stabilized by the root mass. Andosols exhibit high aggregate stability compared to nonvolcanic soils due to stable complexes formed between C and Fe and Al (Buytaert et al. 2006; Shoji, Nanzyo, and Dahlgren 1993), resulting in increased water retention and strong binding of OC compounds (Poulenard et al. 2001). However, Shirato, Hakamata, and Taniyama (2004) argue that the greater aggregate stability and availability of strong binding partners or potential MOAs (metal-organic associations) in Andosols such as allophane, Al, and Fe could hinder the dissolution of OC by hot water. This suggests that hot water extraction may not be directly comparable when evaluating Andosols against other soils, especially Fluvisols (Uchida, Nishimura, and Akiyama 2012; Wada and Higashi 1976). Nevertheless, Ghani, Dexter, and Perrott (2003) found a positive correlation ($R^2 = 0.84$) between microbial biomass C and HWEOC in allophanic soils, which contradicts the assumption of Shirato, Hakamata, and Taniyama (2004) and supports the results of our study.

Ghani, Dexter, and Perrott (2003) specifically highlighted the influence of cultivation on HWEOC, where values were lowest in cultivated sites, similar to the trend observed in CWEOC values. However, in the case of HWEOC, only the oldest site (CU2) was significantly different from all others, suggesting that HWEOC reflects long-term effects of land use change on the soil. Hamkalo and Bedernichek (2014) argue that because HWEOC represents a larger OC proportion, it may provide greater insight into the OC state of soils. Several studies suggest that HWEOC may serve as an indicator of soil quality parameters such as LOC availability, long-term soil OC changes, and current soil conditions (Breulmann et al. 2012; Ghani, Dexter, and Perrott 2003; Leinweber, Schulten, and Körschens 1995; Waldrip et al. 2022). Our results, with a positive correlation between soil OC and HWEOC ($r_s \leq 0.886$; Tables 4 and 5), support this notion.

Comparing the responses of CWEOC and HWEOC to land use changes, it is apparent that CWEOC decreases more rapidly than HWEOC after such changes. This suggests that CWEOC acts as an indicator of short-term soil changes (Sun et al. 2013), reflecting land use changes at an early stage of soil degradation. On the contrary, HWEOC functions as a long-term indicator of soil quality, which is supported by other authors (Breulmann et al. 2012; Ghani, Dexter, and Perrott 2003; Leinweber, Schulten, and Körschens 1995; Waldrip et al. 2022).

4.5 | Molar Absorptivity of LOC

The molar absorptivity values, in both the cold and hot water extracts, strongly reflect the different land uses at the sites. In particular, site CU2 had values up to 10 times higher than the other sites at all sampling depths for both labile C pools. As aromaticity indicates the stability of labile C compounds (Guigue et al. 2015), our results suggest a depletion of readily degradable labile C, leaving behind compounds with higher aromaticity. A comparison with Waldrip et al. (2022) reveals striking differences between native vegetation and cultivated land. Waldrip et al. (2022) found significant effects on the aromaticity of a soil sample due to different land management practices, which mirrors our findings in the cultivated site CU2 (Table 3), where aromaticity levels were similar to those observed in the continuous cultivation sites observed in their study (up to 334 L mol^{-1} cm^{-1}). This suggests a more rapid utilization of available labile C, whereas more complex structures such as aromatic and lignin compounds persist longer in the soil (Jiang et al. 2017; Mganga et al. 2023). The negative correlation (r_s MA-CWEOC = −0.621; r_s MA-HWEOC = −0.594) between the molar absorptivity of both labile C pools and OC further emphasizes this trend (Table 4).

Beyond responses to long-term agricultural use, anthropogenic fire clearance in PA3 may be reflected in a higher molar absorptivity in the soil samples. Fires induce SOC degradation, resulting in higher aromaticity of the remaining C compounds (Gerschlauer et al. 2019; Kalbitz et al. 2003), which consequently increases the molar absorptivity of soils (Bu et al. 2010; Maizel and Remucal 2017; Rodríguez, Schlenger, and García-Valverde 2016; Weishaar et al. 2003).

The trend in the molar absorptivity of CWEOC and HWEOC in the soil profiles of the páramo sites and CU1 is similar to the findings of Corvasce et al. (2006) and Bu et al. (2010). The highest values are found in the topsoil, where production and utilization rates of easily mineralizable C compounds are highest. Less soluble C compounds persist longer and contribute to higher C levels (Jandl and Sollins 1997). However, CU2 showed an inverse trend throughout the soil profile (Table 3). Ghani, Dexter, and Perrott (2003) found that in soils under pasture or agricultural use, C decomposition exceeds the C compounds accumulation, resulting in TC loss. When correlated with the molar absorptivity of labile C pools, this suggests a long-term reflection of soil degradation, especially when the entire soil profile is affected (Waldrip et al. 2022).

5 | Conclusions

OC stocks and LOC fractions serve as key indicators for the assessment of soil health. The study of the impact of land-use change on Ecuadorian Andosols revealed an overall negative effect on both indicators. Transforming natural páramo vegetation into agricultural land resulted in an early decrease of CWEOC contents and an increased molar absorptivity. We thus agree that the water extractable OC fractions and their molar absorptivity can be a useful tool in predicting soil degradation. As burgeoning population growth drives the conversion of areas covered with natural páramo vegetation into agricultural land, the environmental situation is expected to worsen. These shifts signal a noticeable decline in soil health soon after land use changes. In the future, this is expected to result in the release of climate-relevant CO_2 into the atmosphere, exacerbating the course of climate change. This underscores the urgent need for proactive measures and sustainable land management practices to counteract the negative effects of rapid land-use change on soil health and its far-reaching effects on our climate.

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References

Ahn, M. Y., A. R. Zimmerman, N. B. Comerford, J. O. Sickman, and S. Grunwald. 2009. "Carbon Mineralization and Labile Organic Carbon Pools in the Sandy Soils of a North Florida Watershed." *Ecosystems* 12: 672–685. https://doi.org/10.1007/s10021-009-9250-8.

Batjes, N. H. 1996. "Total Carbon and Nitrogen in the Soils of the World." *European Journal of Soil Science* 47, no. 2: 151–163. https://doi.org/10.1111/j.1365-2389.1996.tb01386.x.

Baveye, P. C. 2021. "Soil Health at a Crossroad." *Soil Use & Management* 37, no. 2: 215–219. https://doi.org/10.1111/sum.12703.

Becker, J. N., M. A. Dippold, A. Hemp, and Y. Kuzyakov. 2019. "Ashes to Ashes: Characterization of Organic Matter in Andosols Along a 3400 M Elevation Transect at Mount Kilimanjaro Using Analytical Pyrolysis." *Catena* 180: 271–281. https://doi.org/10.1016/j.catena.2019.04.033.

Berendse, F. 1998. "Effects of Dominant Plant Species on Soils During Succession in Nutrient-Poor Ecosystems." *Biogeochemistry* 42: 73–88. https://doi.org/10.1023/A:1005935823525.

Breulmann, M., E. Schulz, K. Weißhuhn, and F. Buscot. 2012. "Impact of the Plant Community Composition on Labile Soil Organic Carbon, Soil Microbial Activity and Community Structure in Semi-Natural Grassland Ecosystems of Different Productivity." *Plant and Soil* 352: 253–265. https://doi.org/10.1007/s11104-011-0993-6.

Bu, X., L. Wang, W. Ma, X. Yu, W. H. McDowell, and H. Ruan. 2010. "Spectroscopic Characterization of Hot-Water Extractable Organic Matter From Soils Under Four Different Vegetation Types Along an Elevation Gradient in the Wuyi Mountains." *Geoderma* 159, no. 1–2: 139–146. https://doi.org/10.1016/j.geoderma.2010.07.005.

Buytaert, W., R. Célleri, B. De Bièvre, et al. 2006. "Human Impact on the Hydrology of the Andean Páramos." *Earth-Science Reviews* 79, no. 1–2: 53–72. https://doi.org/10.1016/j.earscirev.2006.06.002.

Buytaert, W., J. Sevink, B. De Leeuw, and J. Deckers. 2005. "Clay Mineralogy of the Soils in the South Ecuadorian Páramo Region." *Geoderma* 127, no. 1–2: 114–129. https://doi.org/10.1016/j.geoderma.2004.11.021.

Cai, G., M. Shahbaz, T. Ge, et al. 2022. "Root Exudates With Low C/N Ratios Accelerate CO_2 Emissions From Paddy Soil." *Land Degradation & Development* 33, no. 8: 1193–1203. https://doi.org/10.1002/ldr.4198.

Calispa, M., F. J. Vasconez, S. Santamaria, and P. Samaniego. 2023. "Los suelos de los páramos del Ecuador." In *Los Páramos del Ecuador: Pasado, Presente y Futuro*, edited by R. Hofstede, P. Mena-Vásconez, and E. Suarez, 40–75. Gurgaon: USFQ Press. https://doi.org/10.18272/USFQPRESS.71.

Cao, L., J. Song, Q. Wang, et al. 2017. "Characterization of Labile Organic Carbon in Different Coastal Wetland Soils of Laizhou Bay, Bohai Sea." *Wetlands* 37: 163–175. https://doi.org/10.1007/s13157-016-0858-0.

Cheng, W., Q. Zhang, D. C. Coleman, C. R. Carroll, and C. A. Hoffman. 1996. "Is Available Carbon Limiting Microbial Respiration in the Rhizosphere?" *Soil Biology and Biochemistry* 28, no. 10–11: 1283–1288. https://doi.org/10.1016/S0038-0717(96)00138-1.

Corvasce, M., A. Zsolnay, V. D'Orazio, R. Lopez, and T. M. Miano. 2006. "Characterization of Water Extractable Organic Matter in a Deep Soil Profile." *Chemosphere* 62, no. 10: 1583–1590. https://doi.org/10.1016/j.chemosphere.2005.07.065.

Cross, S. K. 2001. "Adaptation of the giant rosette plant, Espeletia pycnophylla subsp. angelensis, to ultraviolet radiation over an elevation gradient on Volcán Chiles." In *The Ecology of Volcán Chiles: high-altitude ecosystems on the Ecuador-Colombia border*, edited by P.M. Ramsay, pp 81–90. Plymouth: Pebble & Shell.

Davidson, E. A., and I. A. Janssens. 2006. "Temperature Sensitivity of Soil Carbon Decomposition and Feedbacks to Climate Change." *Nature* 440, no. 7081: 165–173. https://doi.org/10.1038/nature04514.

De Feudis, M., V. Cardelli, L. Massaccesi, et al. 2017. "Altitude Affects the Quality of the Water-Extractable Organic Matter (WEOM) From Rhizosphere and Bulk Soil in European Beech Forests." *Geoderma* 302: 6–13. https://doi.org/10.1016/j.geoderma.2017.04.015.

Dodla, S. K., J. J. Wang, and R. D. DeLaune. 2012. "Characterization of Labile Organic Carbon in Coastal Wetland Soils of the Mississippi River Deltaic Plain: Relationships to Carbon Functionalities." *Science of the Total Environment* 435: 151–158. https://doi.org/10.1016/j.scitotenv.2012.06.090.

Don, A., J. Schumacher, and A. Freibauer. 2011. "Impact of Tropical Land-Use Change on Soil Organic Carbon Stocks–A Meta-Analysis." *Global Change Biology* 17, no. 4: 1658–1670. https://doi.org/10.1111/j.1365-2486.2010.02336.x.

Eswaran, H., E. Van Den Berg, and P. Reich. 1993. "Organic Carbon in Soils of the World." *Soil Science Society of America Journal* 57, no. 1: 192–194. https://doi.org/10.2136/sssaj1993.03615995005700010034x.

Farley, K. A., E. F. Kelly, and R. G. Hofstede. 2004. "Soil Organic Carbon and Water Retention After Conversion of Grasslands to Pine Plantations in the Ecuadorian Andes." *Ecosystems* 7: 729–739. https://doi.org/10.1007/s10021-004-0047-5.

Gerschlauer, F., G. Saiz, D. Schellenberger Costa, M. Kleyer, M. Dannenmann, and R. Kiese. 2019. "Stable Carbon and Nitrogen Isotopic Composition of Leaves, Litter, and Soils of Various Ecosystems Along an Elevational and Land-Use Gradient at Mount Kilimanjaro, Tanzania." *Biogeosciences* 16, no. 2: 409–424. https://doi.org/10.5194/bg-16-409-2019.

Ghani, A., M. Dexter, and K. W. Perrott. 2003. "Hot-Water Extractable Carbon in Soils: A Sensitive Measurement for Determining Impacts of Fertilisation, Grazing and Cultivation." *Soil Biology and Biochemistry* 35, no. 9: 1231–1243. https://doi.org/10.1016/S0038-0717(03)00186-X.

Graves, S., H.-P. Piepho, L. Selzer, and S. Dorai-Raj. 2023. *Multcompview: Visualizations of Paired Comparisons*. R package version 0. 1–9. https://cran.r-project.org/package=multcompView.

Guigue, J., J. Lévêque, O. Mathieu, et al. 2015. "Water-Extractable Organic Matter Linked to Soil Physico-Chemistry and Microbiology at the Regional Scale." *Soil Biology and Biochemistry* 84: 158–167. https://doi.org/10.1016/j.soilbio.2015.02.016.

Hamkalo, Z., and T. Bedernichek. 2014. "Total, Cold and Hot Water Extractable Organic Carbon in Soil Profile: Impact of Land-Use Change." *Zemdirbyste-Agriculture* 101, no. 2: 125–132. https://doi.org/10.13080/Z-A.2014.101.016.

Haynes, R. J., and G. S. Francis. 1993. "Changes in Microbial Biomass C, Soil Carbohydrate Composition and Aggregate Stability Induced by Growth of Selected Crop and Forage Species Under Field Conditions." *Journal of Soil Science* 44, no. 4: 665–675. https://doi.org/10.1111/j.1365-2389.1993.tb02331.x.

IUSS Working Group WRB. 2022. *World Reference Base for Soil Resources. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*. 4th edition. Vienna, Austria: International Union of Soil Sciences (IUSS).

Jandl, R., and P. Sollins. 1997. "Water-Extractable Soil Carbon in Relation to the Belowground Carbon Cycle." *Biology and Fertility of Soils* 25: 196–201. https://doi.org/10.1007/s003740050303.

Jiang, L., X. Han, N. Dong, Y. Wang, and P. Kardol. 2011. "Plant Species Effects on Soil Carbon and Nitrogen Dynamics in a Temperate Steppe of Northern China." *Plant and Soil* 346: 331–347. https://doi.org/10.1007/s11104-011-0822-y.

Jiang, T., J. Kaal, J. Liang, et al. 2017. "Composition of Dissolved Organic Matter (DOM) From Periodically Submerged Soils in the Three Gorges Reservoir Areas as Determined by Elemental and Optical Analysis, Infrared Spectroscopy, Pyrolysis-GC–MS and Thermally Assisted Hydrolysis and Methylation." *Science of the Total Environment* 603: 461–471. https://doi.org/10.1016/j.scitotenv.2017.06.114.

Kalbitz, K., D. Schwesig, J. Schmerwitz, et al. 2003. "Changes in Properties of Soil-Derived Dissolved Organic Matter Induced by Biodegradation." *Soil Biology and Biochemistry* 35, no. 8: 1129–1142. https://doi.org/10.1016/S0038-0717(03)00165-2.

Kauffman, J. B., H. Hernandez Trejo, C. J. del, M. Garcia, C. Heider, and W. M. Contreras. 2016. "Carbon Stocks of Mangroves and Losses Arising From Their Conversion to Cattle Pastures in the Pantanos de Centla, Mexico." *Wetlands Ecology and Management* 24, no. 2: 203–216. https://doi.org/10.1007/s11273-015-9453-z.

Kottek, M., J. Grieser, C. Beck, B. Rudolf, and F. Rubel. 2006. "World Map of the Köppen-Geiger Climate Classification Updated." *Meteorologische Zeitschrift* 15, no. 3: 259–263. https://doi.org/10.1127/0941-2948/2006/0130.

Landgraf, D., P. Leinweber, and F. Makeschin. 2006. "Cold and Hot Water–Extractable Organic Matter as Indicators of Litter Decomposition in Forest Soils." *Journal of Plant Nutrition and Soil Science* 169, no. 1: 76–82. https://doi.org/10.1002/jpln.200521711.

Lehmann, J., D. A. Bossio, I. Kögel-Knabner, and M. C. Rillig. 2020. "The Concept and Future Prospects of Soil Health." *Nature Reviews Earth & Environment* 1, no. 10: 544–553. https://doi.org/10.1038/s43017-020-0080-8.

Leinweber, P., H. R. Schulten, and M. Körschens. 1995. "Hot Water Extracted Organic Matter: Chemical Composition and Temporal Variations in a Long-Term Field Experiment." *Biology and Fertility of Soils* 20: 17–23. https://doi.org/10.1007/BF00307836.

Li, Q., X. Cheng, Y. Luo, et al. 2017. "Consistent Temperature Sensitivity of Labile Soil Organic Carbon Mineralization Along an Elevation Gradient in the Wuyi Mountains, China." *Applied Soil Ecology* 117–118: 32–37. https://doi.org/10.1016/j.apsoil.2017.04.018.

López-Sandoval, M. F. 2004. "Agricultural and Settlement Frontiers in the Tropical Andes." PhD thesis, University of Regensburg.

Maizel, A. C., and C. K. Remucal. 2017. "Molecular Composition and Photochemical Reactivity of Size-Fractionated Dissolved Organic Matter." *Environmental Science & Technology* 51, no. 4: 2113–2123. https://doi.org/10.1021/acs.est.6b05140.

McLauchlan, K. K., and S. E. Hobbie. 2004. "Comparison of Labile Soil Organic Matter Fractionation Techniques." *Soil Science Society of America Journal* 68, no. 5: 1616–1625. https://doi.org/10.2136/sssaj2004.1616.

Mganga, K. Z., J. L. Rolando, S. Kalu, C. Biasi, and K. Karhu. 2023. "Priming Effect Depending on Land Use and Soil Types in a Typical Semi-Arid Landscape in Kenya." *Biogeochemistry* 163: 49–63. https://doi.org/10.1007/s10533-023-01016-z.

Minaya, V., G. Corzo, H. Romero-Saltos, et al. 2015. "Altitudinal Analysis of Carbon Stocks in the Antisana páramo, Ecuadorian Andes." *Journal of Plant Ecology* 9, no. 5: 553–563. https://doi.org/10.1093/jpe/rtv073.

Nierop, K. G. J., F. H. Tonneijck, B. Jansen, and J. M. Verstraten. 2007. "Organic Matter in Volcanic Ash Soils Under Forest and Páramo Along an Ecuadorian Altitudinal Transect." *Soil Science Society of America Journal* 71, no. 4: 1119–1127. https://doi.org/10.2136/sssaj2006.0322.

Páez-Bimos, S., M. Villacís, O. Morales, et al. 2022. "Vegetation Effects on Soil Pore Structure and Hydraulic Properties in Volcanic Ash Soils of the High Andes." *Hydrological Processes* 36, no. 9: e14678. https://doi.org/10.1002/hyp.14678.

Pesántez, J., G. M. Mosquera, P. Crespo, L. Breuer, and D. Windhorst. 2018. "Effect of Land Cover and Hydro-Meteorological Controls on Soil Water DOC Concentrations in a High-Elevation Tropical Environment." *Hydrological Processes* 32, no. 17: 2624–2635. https://doi.org/10.1002/hyp.13224.

Posit Team. 2023. *RStudio: Integrated Development Environment for R*. Posit Software, Boston, MA: PBC. URL http://www.posit.co/.

Podwojewski, P., J. Poulenard, T. Zambrana, and R. Hofstede. 2002. "Overgrazing Effects on Vegetation Cover and Properties of Volcanic Ash Soil in the Páramo of Llangahua and La Esperanza (Tungurahua, Ecuador)." *Soil Use and Management* 18: 45–55. https://doi.org/10.1111/j.1475-2743.2002.tb00049.x.

Poulenard, J., P. Podwojewski, and A. J. Herbillon. 2003. "Characteristics of Non-Allophanic Andisols With Hydric Properties From the Ecuadorian Páramos." *Geoderma* 117, no. 3–4: 267–281. https://doi.org/10.1016/S0016-7061(03)00128-9.

Poulenard, J., P. Podwojewski, J. L. Janeau, and J. Collinet. 2001. "Runoff and Soil Erosion Under Rainfall Simulation of Andisols From the Ecuadorian Páramo: Effect of Tillage and Burning." *Catena* 45, no. 3: 185–207. https://doi.org/10.1016/S0341-8162(01)00148-5.

R Core Team. 2023. *R: A Language and Environment for Statistical Computing*. Vienna, Austria: R Foundation for Statistical Computing. https://www.R-project.org/.

Rodríguez, F. J., P. Schlenger, and M. García-Valverde. 2016. "Monitoring Changes in the Structure and Properties of Humic Substances Following Ozonation Using UV-Vis, FTIR and ^{1}H NMR Techniques." *Science of the Total Environment* 541: 623–637. https://doi.org/10.1016/j.scitotenv.2015.09.127.

Siewert, M. B., J. Hanisch, N. Weiss, P. Kuhry, T. C. Maximov, and G. Hugelius. 2015. "Comparing Carbon Storage of Siberian Tundra and Taiga Permafrost Ecosystems at Very High Spatial Resolution." *Journal of Geophysical Research: Biogeosciences* 120, no. 10: 1973–1994. https://doi.org/10.1002/2015JG002999.

Shete, M., M. Rutten, G. C. Schoneveld, and E. Zewude. 2016. "Land-Use Changes by Large-Scale Plantations and Their Effects on Soil Organic Carbon, Micronutrients and Bulk Density: Empirical Evidence From Ethiopia." *Agriculture and Human Values* 33: 689–704. https://doi.org/10.1007/s10460-015-9664-1.

Shirato, Y., T. Hakamata, and I. Taniyama. 2004. "Modified Rothamsted Carbon Model for Andosols and Its Validation: Changing Humus Decomposition Rate Constant With Pyrophosphate-Extractable Al." *Soil Science and Plant Nutrition* 50, no. 1: 149–158. https://doi.org/10.1080/00380768.2004.10408463.

Sollins, P., P. Homann, and B. A. Caldwell. 1996. "Stabilization and Destabilization of Soil Organic Matter: Mechanisms and Controls." *Geoderma* 74, no. 1–2: 65–105. https://doi.org/10.1016/S0016-7061(96)00036-5.

Sparling, G., M. Vojvodić-Vuković, and L. Schipper. 1998. "Hot-Water-Soluble C as a Simple Measure of Labile Soil Organic Matter: The Relationship With Microbial Biomass C." *Soil Biology and Biochemistry* 30, no. 10–11: 1469–1472. https://doi.org/10.1016/s0038-0717(98)00040–6.

Stadel, C. 2005. "Agricultural and Settlement Frontiers in the Tropical Andes: The Páramo Belt of Northern Ecuador, 1960–1990." *Mountain Research and Development* 25, no. 4: 386–387. https://doi.org/10.1659/0276-4741(2005)025[0386:AASFIT]2.0.CO;2.

Stadel, C. 1991. Altitudinal Belts in the Tropical Andes: Their Ecology and Human Utilization. Yearbook. Conference of Latin Americanist Geographers, 17/18, 45–60. http://www.jstor.org/stable/2576573.

Shoji, S., M. Nanzyo, and R. Dahlgren. 1993. *Volcanic Ash Soils: Genesis, Properties, and Utilization*. Amsterdam: Elsevier.

Soil Survey Staff. 2015. *Illustrated Guide to Soil Taxonomy*. Lincoln, NE, USA: US Department of Agriculture, Natural Resources Conservation Service, National Soil Survey Center.

Sun, S., J. Liu, Y. Li, P. Jiang, and S. X. Chang. 2013. "Similar Quality and Quantity of Dissolved Organic Carbon Under Different Land Use Systems in Two Canadian and Chinese Soils." *Journal of Soils and Sediments* 13: 34–42. https://doi.org/10.1007/s11368-012-0604-z.

Tonneijck, F. H., B. Jansen, K. G. J. Nierop, J. M. Verstraten, J. Sevink, and L. De Lange. 2010. "Towards Understanding of Carbon Stocks and Stabilization in Volcanic Ash Soils in Natural Andean Ecosystems of northern Ecuador." *European Journal of Soil Science* 61, no. 3: 392–405. https://doi.org/10.1111/j.1365-2389.2010.01241.x.

Uchida, Y., S. Nishimura, and H. Akiyama. 2012. "The Relationship of Water-Soluble Carbon and Hot-Water-Soluble Carbon With Soil Respiration in Agricultural Fields." *Agriculture, Ecosystems & Environment* 156: 116–122. https://doi.org/10.1016/j.agee.2012.05.012.

Ukalska-Jaruga, A., A. Klimkowicz-Pawlas, and B. Smreczak. 2019. "Characterization of Organic Matter Fractions in the Top Layer of Soils Under Different Land Uses in Central-Eastern Europe." *Soil Use and Management* 35, no. 4: 595–606. https://doi.org/10.1111/sum.12514.

United Nations. 2024. *World Population Prospects: The 2024 Revision*. New York: UN, Department of Economic and Social Affairs, Population Division. https://population.un.org/dataportal/data/indicators/49/locations/218/start/1950/end/2050/table/pivotbylocation?df=b6eb409b-3a96-4866-9529-f80ee43e4a44.

Wada, K., and T. Higashi. 1976. "The Categories of Aluminium-and Iron-Humus Complexes in Ando Soils Determined by Selective Dissolution." *Journal of Soil Science* 27, no. 3: 357–368. https://doi.org/10.1111/j.1365-2389.1976.tb02007.x.

Waldrip, H., R. C. Schwartz, Z. He, et al. 2022. "Soil Water Extractable Organic Matter Under Long-Term Dryland Cropping Systems on the Texas High Plains." *Soil Science Society of America Journal* 86, no. 5: 1249–1263. https://doi.org/10.1002/saj2.20432.

Weil, R. R., K. R. Islam, M. A. Stine, J. B. Gruver, and S. E. Samson-Liebig. 2003. "Estimating Active Carbon for Soil Quality Assessment:

A Simplified Method for Laboratory and Field Use." *American Journal of Alternative Agriculture* 18, no. 1: 3–17. https://doi.org/10.1079/AJAA200228.

Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper. 2003. "Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon." *Environmental Science & Technology* 37, no. 20: 4702–4708. https://doi.org/10.1021/es030360x.

Wickham, H. 2016. *ggplot2: Elegant Graphics for Data Analysis*. New York: Springer-Verlag.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.