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Ecological Risk Assessment of Soil Heavy Metals and Pesticide Residues in Tea Plantations

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Abstract: Tea plantations have used many synthetic chemicals to ensure performance and control of pests. This has led to increased contamination of soils and reduced tea growth. We assessed the levels of heavy metals, including Cd, Cr, Pb, Cu, Ni, Zn, Hg, As, and pesticide residues, such as HCHs, biphenyl chrysanthemum ester, methamidophos, imidacloprid, permethrin, in the soil of tea plantations of Taiwan, Tibet, Guangdong, and Fujian. The Potential Ecological Risk Index and the Nemerow comprehensive pollution index were used to analyze the data. The results showed that risk indices in Tibet, Guangdong and Fuzhou were considered as moderate ecological harm level. Ecological risk assessment index of Anxi organic and Anxi conventional tea gardens suggested a "low" risk level. The Nemerow comprehensive pollution indices for soil pesticide residues in the tea plantations of Taiwan, Tibet, Anxi organic and Anxi conventional were considered mild. Guangdong and Fuzhou had values suggesting "slight pollution" levels. According to National Soil Environmental Quality Standard (GB15618-1995), soil in tea plantations in Taiwan, Tibet, and Anxi conventional matched the national first grade of soil quality and those from Guangdong, Fuzhou, and Anxi organic tea garden matched the national second grade.

Keywords: perennial crop; heavy metals; pesticides; soils; risk management; ecological risk; pollution

1. Introduction

Tea (*Camellia sinensis* L.) has a long history as a drink and is economically important in China and several other countries across the world. Two-thirds of the world's population drink tea [1,2]. As an important export commodity, concerns have emerged regarding potential contamination due to over use of pesticides, atmospheric pollution, especially in urban areas, and other types of environmental pollution (e.g., use of wastewater for irrigation and animal manure). In conventional systems, tea is increasingly associated with prolonged and extensive use of synthetic pesticides [3,4]. Agricultural environmental pollution can lead to bioaccumulation of heavy metals and other compounds in plants, gradually affecting human health [5–7]. With the continuous development of China's tea, quality and safety are primary goals for the tea industry.

Soil has a great influence on plant growth and tea plantation, due to its low pH [8], contamination by heavy metals and pesticide residues can affect productivity. Heavy metals can also accumulate in plants and lead to toxicity [9]. Many countries and regions have strict standards for heavy metals and pesticide residue concentrations in tea and these regulations may affect China's tea exports [4,10]. This is the case in China where the Environment quality standard for soils (GB15618-1995), maximum pesticide residue limit of Food safety national standard (GB 2763-2016) and the Procedural regulations regarding the environment quality monitoring of soil (NY/T 395-2000) are important references for soil and tea quality control.

To evaluate the potential toxicity of bioaccumulation of heavy metals or pesticides may have in plants, there is a need to assess not only their concentrations in soil but also calculate their risks in plants. In our study, we used two indices that are common for such analyses: the Potential Ecological Risk Index (PERI) and the Nemerow comprehensive pollution index. The PERI has the advantage to integrate the toxic factor into the equation and has been employed in various ecosystems. For example, coal mines in various regions such as Czech Republic [11] and China [12] have been assessed through this index. PERI is versatile enough to be used in sediments as well as shown in a study of the coastal zone of Egypt on the Mediterranean where Fe and Mn have been found to have the highest risk values [13]. In a recent review [14], PERI has been considered one important index on the 18 analyzed, adding however that it is better to use more than one index. In our case, we have added the Nemerow comprehensive pollution index. This index has been calculated for different ecosystems such as on roadsides in China to examine heavy metal contamination from mining [15] and even in water sampling [16].

The southern region of China is the main tea growing region. Due to its wide distribution and differences in agricultural practices and environmental conditions within the region, tea productivity and quality are uneven [2]. Previous studies have been conducted at the local scale and show high variability among sub-regions e.g., [17,18]. To fully understand the pollution status of heavy metals and pesticide residues in the soil of Chinese tea, we conducted an ecological risk assessment in tea plantations located in Taiwan, Tibet, Guangdong and Fujian. The aim of this study was to provide a scientific basis for the remediation and control of soil heavy metals and pesticide residues in Chinese tea plantations and support the sustainable development of the industry.

2. Materials and Methods

2.1. Sample Collection and Pretreatment

Soil samples were collected in four regions of southern China where tea plantations are commercially important: Taiwan (Nantou), Tibet (Yigong), Guangdong (Zhanjiang), and Fujian. In Fujian province, three tea plantations were selected: Fuzhou, Anxi organic, and Anxi conventional plantations (Figure 1). All selected tea plantations had been under cultivation for more than 30 years. Taiwan (Nantou) was about 50 years; Tibet (Yigong), 60 years; Guangdong (Zhanjiang), 30 years; Fuzhou, 30 years; Anxi organic, 60 years; and, Anxi conventional, 60 years. Plantations varied in soze from the smallest being in Tibet and the largest in Anxi. The plantation size of Tibet (Yigong) was 16,000 ha and was located at 1900–2300 m altitude, which was the highest organic tea production base in the world, the fertilizer used was also mainly farm manure. The plantation size of Anxi was 40,000 ha with a total output of tea of 65,000 tons per year.

Figure 1. Distribution map of soil sampling points in the study area. Sampling site: Taiwan: N: 23°63′15″, E: 120°63′01″; Tibet: N: 30°10′50″, E: 94°54′12″; Guangdong: N: 20°31′10″, E: 110°14′56″; Fuzhou: N: 27°42′50″, E: 118°00′06″; Anxi organic: N: 25°00′05″, E: 117°52′19″; Anxi conventional: N: 24°59′60″, E: 117°52′21″.

In each tea plantation, soil samples were collected at a depth of 10–15 cm in September and October 2017. We used the composite soil sampling method (five random points per sample) to collect three separate soil samples of approximately 500 g (fresh weight) per plantation. Samples were brought back to the lab, air-dried and then sieved through a 20-mesh sieve to remove plant roots, gravel and other debris. All soil samples were stored in refrigerator until analyses.

2.2. Analytical Methods for Heavy Metals

Soil pH was measured with deionized water at a ratio 1:5 (soil:water) and a pH meter (PHS-3E) [19]. Heavy metals analyses were done by first digesting 1 g of soil with 15 mL of Aqua regia (HNO3 and HCl in 3:1 ratio) at 80 °C until a transparent solution was obtained. The heated samples were then allowed to cool down and were filtered by 0.45 µm filter paper and finally diluted to 50 mL in a volumetric flask. These samples were transferred to high-quality polyethylene bottles and analyzed by flame atomic absorption spectrophotometer (AAS) (Agilent 240 FS AA model) for the following heavy metals: Cd, Cr, Pb, Cu, Ni, Zn, Hg and As. The standard solutions of selected metals were obtained from Agilent (1000 mg/L) and were diluted to make solutions of various standard concentrations. All analyses were completed in three replicates. After every ten sample readings, the standards were re-used to ensure 95% accuracy [20]. All analytical methods were strictly in accordance with national standards, as follows: Cu, Zn: GB/T 17138-1997; Ni: GB/T 17139-1997; Cd: GB/T 17141-1997; Cr: HJ491-2009; Hg, As, Pb: GB/T 22105.2-2008; and, pesticide residues: EPA3540C-1996.

2.3. Ecological Risk Assessment

The Potential Ecological Risk Index (PERI) was used to analyze the data [21]. This method is the most widely used and comprehensively combines the interactions among heavy metals, their toxicity, chemistry, and ecological sensitivity [21]. The comprehensive potential ecological risk index (RI) is calculated with the following equations:

$$E_r^i = T_r^i \cdot C_f^i = T_r^i \cdot C_s^i / C_n^i \quad (1)$$

$$RI = \sum E_r^i = \sum T_r^i \cdot C_f^i = \sum T_r^i \cdot C_s^i / C_n^i \quad (2)$$

where E_r^i is the potential ecological hazard index of heavy metal i; and T_r^i is the toxicity coefficient of heavy metal i. The toxicity coefficients of Zn, Cr, Pb, Cu, Ni, As, Cd and Hg are 1, 2, 5, 5, 5, 10, 30 and 40, respectively [21,22]. C_f^i is the enrichment factor of heavy metal i. C_s^i is the measured value of heavy metal i. C_n^i is the background value of heavy metal i [23]. The grading standards for both $E^i{}_r$ and RI are shown in Table 1 [24].

Table 1. Grading standards of potential ecological risk assessment, source: [21].

$E^i{}_r$ Grade	Pollution Grade	RI Grade	Comprehensive Ecological Risk Grade
$E^i{}_r < 40$	Slight (Low)	RI < 135	Slight (Low)
$40 \le E^i{}_r < 80$	Mid (Medium)	135 ≤ RI < 265	Mid (Medium)
$80 \le E^i{}_r < 160$	Strong (Heavy)	265 ≤ RI < 525	Strong (Heavy)
$160 \le E^i{}_r < 320$	Stronger (Heavier)	525 ≤ RI	Stronger (Serious)
$320 \le E^i{}_r$	Strongest (Serious)		

2.4. Analytical Methods for Pesticide Residues in Soil

Soxhlet extraction (EPA3540C-1996) was used to determine the concentrations of HCHs (hexachlorocyclohexane), bifenthrin (2-methyl -1,1′-biphenyl-3-yl-methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate), methamidophos (O,S-dimethyl phosphoramidothioate), imidacloprid (1-[(6-chloro-3-pyridinyl)methyl]-N-nitro-2-imidazolidinimine), and permethrin [3-phenoxybenzyl(1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] in soil samples. To do so, 15 g of soil were digested with 150 mL dichloromethane, followed by Soxhlet extraction for 24 h. The solution was then spin evaporated to 1–2 mL and replaced by n-hexane. The resulting solution was then passed through a solid phase extraction column (the fillers were secondary amine and carbon black) for purification and then diluted with n-hexane to 1 mL. Pesticide residues were analyzed by GCMS-QP2010 gas chromatography-mass spectrometry (GC-MS).

Single factor pollution index and comprehensive pollution index were calculated for pesticide residues. Nemerow multi-factor index considers both the mean pollution value of single factor and the effects of high concentrations of pollutants on environmental quality [25,26]. The Nemerow pollution index was calculated as follows:

$$P_i = \frac{C_i}{S_i} \quad (3)$$

$$P = \sqrt{\frac{\overline{P_i}^2 + P_{imax}^2}{2}} \quad (4)$$

In the Equation (3): P_i refers to the environmental quality index of pollutant i, C_i is the measured value of the pollutant i (mg/kg), S_i is the evaluation criterion of pollutant i (mg/kg). In the Equation (4): P is the soil comprehensive pollution index, P_{imax} is the maximum value of the mean value of single pollution index, $\overline{P_i}$ is the mean of the average value of single pollution index. Soil environmental quality assessment using I class standard values of Environment quality standard for soils (GB15618-1995) and maximum pesticide residue limit of Food safety national standard (GB 2763-2016). Soil rating adopts Procedural regulations regarding the environment quality monitoring of soil (NY/T 395-2000).

The grading standards of which are as follows: $p \leq 0.7$, non-pollution; $0.7 < p \leq 1$, slight pollution; $1 < p \leq 2$, mild pollution; $2 < p \leq 3$, middle pollution; and $p > 3$, heavy pollution.

2.5. Statistical Analyses

Heavy metal and pesticide residue concentrations were first checked for normality and homogeneity of variance. Values that did not meet the assumptions were ln-transformed and listed on Table 2. One-way analysis of variance was used to compare concentrations among sites (SPSS v. 21).

Table 2. Descriptive statistics (means ± (sd)) of pH, heavy metals (mg/kg) and pesticide residue contents (μg/kg) in soil samples (n = 3 samples/sites). Significant differences among sites (within a row) are marked by letters in superscripts according to Duncan's LSD multiple range test following a one-way analysis of variance (Bonferroni, $p \leq 0.006$). Note that statistical analyses were not performed for HCHs, Imidacloprid and Permethrin due to undetectable values in many sites.

Variable	Sites							
	Taiwan	Tibet	Guangdong	Fuzhou	Anxi Organic	Anxi Conven	*F* Value	*p*
Cd	0.037 ^{a} (0.014)	0.076 ^{a} (0.062)	0.084 ^{a} (0.003)	0.158 ^{b} (0.010)	0.037 ^{a} (0.016)	0.015 ^{a} (0.006)	36.89	<0.001
Cr[1]	75.0 ^{c} (4.2)	51.4 ^{bc} (29.9)	216.7 ^{d} (15.1)	31.7 ^{ab} (1.7)	15.8 ^{a} (2.0)	15.7 ^{a} (0.7)	35.95	<0.001
Pb	33.2 ^{b} (4.6)	30.6 ^{b} (14.0)	11.0 ^{a} (7.0)	73.5 ^{c} (4.1)	49.2 ^{b} (4.4)	35.3 ^{b} (3.5)	25.09	<0.001
Cu[1]	20 ^{b} (1.9)	17.1 ^{b} (5.9)	70.7 ^{c} (3.6)	86.0 ^{c} (9.1)	15.7 ^{b} (2.0)	5.7 ^{a} (1.0)	100.24	<0.001
Ni[1]	21.9 ^{b} (4.8)	21.5 ^{b} (10.4)	106 ^{c} (5.0)	17.8 ^{b} (0.4)	6.5 ^{a} (1.3)	5.8 ^{a} (0.4)	51.38	<0.001
Zn[1]	66.7 ^{b} (4.8)	76.3 ^{bc} (13.5)	89.9 ^{c} (0.6	151.3 ^{d} (2.6)	76.9 ^{bc} (1.2)	40.4 ^{a} (1.3)	53.67	<0.001
Hg	0.06 (0.01)	0.07 (0.05)	0.074 (0.007)	0.073 (0.009)	0.069 (0.003)	0.054 (0.004)	0.351	0.872
As	8.1 (0.6)	14.1 (10.3)	10.6 (0.3)	5.66 (0.340)	3.99 (0.05)	4.01 (0.63)	2.71	0.073
pH	4.01 ^{b} (0.08)	5.56 ^{d} (0.30)	5.15 ^{c} (0.08)	6.82 ^{e} (0.05)	3.33 ^{a} (0.05)	3.63 ^{a} (0.19)	223.94	<0.001
Methamidophos	93.4 (16.4)	94.9 (41.8)	64.3 (14.4)	60.5 (30.3)	91.1 (33.3)	111.4 (29.3)	1.358	0.306
Imidacloprid	32.0 ^{a} (10.1)	41.8^{a} (34.3)	101.6 ^{b} (49.6)	14.1^{a} (1.6)	22.5^{a} (17.8)	6.5^{a} (1.5)	5.208	0.009
HCHs	-	1.1 (1.1)	-	-	-	0.4 (0.4)	-	
Bifenthrin	3.3 (1.0)	-	-	1.0 (1.8)	-	0.3 (0.5)	-	
Permethrin	18.7 (14.9)	-	76.0 (131.6)	10.1 (17.4)	-	-	-	

[1] These variables were ln-transformed to satisfy normality. Different letters beside the means in a same row indicate significant differences, using a post hoc LSD test ($p < 0.05$).

3. Results

3.1. Heavy Metals in Soil of Tea Plantations

Descriptive statistics of the concentrations of heavy metals in soil samples from the sampled tea plantations are shown in Table 2. The concentrations of all heavy metals, except Hg and As, significantly varied among sites (Table 2). The concentrations in Anxi organic and conventional soils were relatively similar, despite having different types of soil management. Their values were among the lowest in terms of heavy metals. Interestingly, pH also was the lowest among all the sites. Fuzhou and Guangdong tended to have higher concentrations of heavy metals despite having higher pH (Table 2).

In general, the potential ecological hazard index $E^{i}{}_{r}$ varied among heavy metals and sampling sites (Table 3). Tibet (118.9 mg/kg) and Guangdong (54.8 mg/kg) had the highest indices for Hg and these values were considered as high and medium potential ecological risk (Table 1). In Fuzhou, Cd was considered a strong risk. The rest of the $E^{i}{}_{r}$ values were lower than 40, suggesting a low ecological risk. The soil PERI values for Tibet, Guangdong and Fuzhou were 169.08, 142.48 and 173.69, considered to be "medium" in terms of risk. Both Anxi organic and Anxi conventional tea plantations exhibited low PERI levels (Table 3).

Table 3. Potential ecological hazard index (E_r^i) of each heavy metal and PERI (*RI*) values in soils of tea plantations in China.

Sampling Site	E^i_r								*RI*
	Cd	Cr	Pb	Cu	Ni	Zn	Hg	As	
Tibet	28.17	1.34	5.25	3.90	3.34	1.03	118.89	7.16	169.08
Guangdong	25.32	7.06	0.94	19.37	23.86	1.25	54.81	9.85	142.48
Fuzhou	87.59	1.53	10.53	19.92	6.60	1.83	35.88	9.80	173.69
Anxi organic	20.28	0.76	7.05	3.63	2.40	0.93	34.07	6.91	76.03
Anxi conventional	8.28	0.76	5.05	1.32	2.13	0.49	26.83	6.94	51.80

Note: Due to the undetermined soil background values, the ecological risk index could not be calculated for Taiwan samples.

Correlation analyses of heavy metals in soil can help to understand the similarity in geochemical behavior of soil elements (positive correction) [11]. Our correlations showed that pH values were significantly correlated with Cd and Zn (Table 4). Cd and Zn were also positively correlated (0.962) as well as Cr and Ni (0.987), Cu and Zn (0.867), and Cd and Cu (0.885). As and Pb were not significantly correlated with any elements (Table 4).

Table 4. Correlation coefficients between heavy metals in tea garden soil.

	Cd	Cr	Pb	Cu	Ni	Zn	Hg	As	pH
Cd	1								
Cr	0.16	1							
Pb	0.493	−0.706	1						
Cu	0.885 *	0.482	0.258	1					
Ni	0.236	0.987 **	−0.649	0.553	1				
Zn	0.962 **	0.077	0.62	0.876 *	0.15	1			
Hg	0.74	0.429	0.098	0.693	0.496	0.734	1		
As	0.208	0.512	−0.55	0.086	0.477	0.014	0.453	1	
pH	0.952 **	0.193	0.338	0.787	0.255	0.837 *	0.658	0.417	1

Note: * indicates significant correlation at the level of 0.05; ** indicates significant correlation at 0.01 level.

3.2. Pesticide Residue Contents and Pollution Index in Tea Garden Soils

Among the pesticides analyzed in this study, methamidophos and imidacloprid were detected in all sites and comparison showed no significant differences among sites (Table 2). Imidacloprid concentration in Guangdong was significantly higher than other sites. HCHs was only detected at low concentrations in Tibet and Anxi conventional tea plantations while bifenthrin was found in Taiwan, Fuzhou, and Anxi conventional tea plantations (Table 2).

The resulting single pollution index values varied from 0.0005 for Permethrin in Fuzhou to 2.23 for methamidophos in soil coming from Anxi conventional tea plantation (Table 5). While these values would be considered medium in terms of risk, other values were all considered low to non-pollution risk levels. The comprehensive pollution index values of soil pesticide residues in the tea plantations of Taiwan, Tibet, Anxi organic and Anxi conventional were considered mild pollution ($p \leq 3$). According to the standards, soils from Guangdong and Fuzhou were classified as slight pollution ($p \leq 2$).

Table 5. Pesticide residue pollution indices for each soil pesticide residue in the soil samples of tea plantations in China.

Sampling Site	Single Pollution Index P_i					Comprehensive Pollution Index P
	HCHs	Bifenthrin	Methamidophos	Imidacloprid	Permethrin	
Taiwan	-	0.007	1.87	0.06	0.0009	1.375
Tibet	0.02	-	1.90	0.08	-	1.399
Guangdong	-	-	1.29	0.20	0.0038	0.943
Fuzhou	-	0.002	1.21	0.03	0.0005	0.877
Anxi organic	-	-	1.82	0.04	-	1.334
Anxi conventional	0.01	0.001	2.23	0.01	-	1.647

4. Discussion

The present study showed that heavy metal contamination among sites varied with Fuzhou and Guangdong having the highest concentrations. Fuzhou had high levels for Cd, Pb, Cu, and Zn, despite having the highest pH while Guangdong, the highest values of Cr and Ni. These high concentrations may be related to the locations, as both places are more urbanized (both having a population of approximate 7 million) than other sites. Jia et al. [27] report that in rapidly urbanized areas such as Chongqing in the upper Yangtze Basin, heavy metals in soils tend to increase due to anthropogenic activities including heavy industry and transportation. It is therefore possible that high levels of heavy metals maybe related to several factors including urbanization, industrialization, fertilizers (synthetic or organic), and management practices [18]. In another study, Cd has been linked to P fertilizers as the main source of contamination [17].

According to National Soil Environmental Quality Standard (GB15618-1995), Taiwan, Tibet and Anxi conventional tea garden soils could be considered as excellent (first standard level). Guangdong, Fuzhou, and Anxi organic tea garden soil samples would be classified in the second standard level of environment quality standards for soils. All the soil samples of tea plantations except Guangdong were in line with the Soil Environmental Quality of Pollution-Free Tea Garden (NY 5020-2001). Contrary to Wen et al. [12], we found that pH was positively correlated with Cd and Zn suggesting that their concentrations increased with pH. Differences may be due to variation in management or the locations and soil types where the studies were carried out. Comparisons with other studies may be difficult due to the variation in analytical techniques, environmental standards, and individual plantation management practices. As Wen et al. [18] stated, there is a need for improved consistency among countries for soil analysis that can consider these various factors.

The limited differences between Anxi organic and conventional suggest that the time period for the organic plantation without synthetic chemicals might have been too short for heavy metals to be removed from the soil. Heavy metals in soil cannot be disintegrated like organic contaminants, but only be slowly relocated from one place to another [28].

The concentration of methamidophos in the soil of Anxi conventional plantation was the highest and this might be closely related to the local farmers' spraying habits. In Vietnam, it has been shown that farmers often ignore the risks of pesticides and their overuse leads to soil contamination and human health issues [29]. Relevant agricultural and health departments should attach greater importance in informing farmers of the risks of pesticides and strengthening the market regulations to promote a more sustainable and safer use of synthetic agrochemicals and development of the local tea industry. HCHs are of great health concerns due to their persistence in soils and the food chain and have been banned in China for over 25 years [30]. Despite this, HCHs were found in Fuzhou and Anxi conventional plantations. The values detected here were similar to those of Yi et al. [30]. They report a correlation between HCHs concentrations in soil and plants, which is of great concern for health reasons. Imidacloprid, which is a neonicotinoid, was found in all plantations, with high amounts in Guangdong. This can become an issue considering that many countries, especially the European countries have banned neonicotinoids [31].

Permethrin is a synthetic pyrethroid insecticide commonly used in agriculture. While its concentration might not have been detected or at low amount in the study sites, Das et al. [32] report that such insecticides tend to reduce ammonifying and nitrifying bacteria and increase non-symbiotic N-fixing bacteria in the soil thus resulting in negative effects on total N and organic C. Bifenthrin is also a pyrethroid pesticide widely used in agriculture. Its half-life can be up to 345 d and has become an environmental concern [33]. Such issues should be considered, especially for sustainable tea plantations where soil management can be quite complex and site-specific.

The use of pesticides on this cash crop has principally been guided by the Maximum Residue Limits (MRLs) and tolerance limits prescribed by the Commission of European Communities (CEC), the Environmental Protection Agency (EPA), the Food and Agricultural Organization (FAO), the Food Control (FC) and the Codex Alimentarius Commission (CAC). There is an increasing interest among these regulating bodies in alternative control strategies to replace or reduce the use of costly pesticides and to avoid the health problems potentially caused by residues.

Understanding the levels of contamination in soil is quite important as plants may uptake some of these heavy metals or contaminants and increase risks to human health. Wen et al. [18] report that the concentrations of Pb, Ni, Zn, and Cu in soil do not relate to concentrations in leaves but there is a significant correlation for Cr. Further studies are needed to better understand these mechanisms and whether this is the case in our studied plantations.

5. Conclusions

Our study showed that heavy metal contamination in tea plantations was present and Hg and Cd might be the most important heavy metals to be monitored. The PERI showed that Fuzhou and Guangdong plantations were more at risk globally than the other sites due to greater contamination. In terms of pesticides, methamidophos and Imidacloprid were present in all plantations. This was especially disconcerting considering that even the organic plantation had high levels of both pesticides. Further studies will be required to assess the possibility of long-term accumulation of these pesticides in the soil, limiting the capacity of these organic plantations to be certified.

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