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Regional Geochemical Characteristics and Influence Factors of Soil Elements in the Pearl River Delta Economic Zone, China

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Abstract

Soil heavy metal pollution is one of the main environmental problems in Pearl River Delta Economic Zone of China. Based on multi-purpose regional geochemical survey, regional eco-geochemical assessment, local eco-geochemical assessment and comprehensive appraisal, the eco-geochemical survey and assessment in Pearl River Delta Economic Zone of 41,698 km^2 were completed. Samples from soils were collected in accordance with the two-layer grid method. Totally 54 elements and indicators for soils were determined. Compared to deep soils, the sampled surface soils are enriched in OrgC, N, P, Cd, S，Hg, Ag, B, Au, S and poor with As, Ni, I, Co, Cr, V, MgO, Sc, Al_2O_3, Fe_2O_3 etc. The characteristics of geochemical reference value of element in soil that inherited soil parent material and regional elements combined features reflected that the elements enriched in the soil was interrelated with acid rock, sandstone and shale. The spatial distribution characteristics of element regional geochemistry were conditional by regional environmental geological conditions, and effected by human activities. The Pearl River Delta plain is a typical geochemical landscape area with regional anomaly of multiple-elements. The north, western and eastern parts of the Pearl River Delta Economic Zone are quite different in geochemical features due to regional geological background, soil parent materials, geomorphic characteristics and human activities. Environment quality evaluation results show that the grade I and grade II soil accounted for 19.9% and 57.3% of the total area. Many samples that widely distributed in the economic developed of Pearl River Delta Plain area reached the third-grade of national soil environment standard. The soil enriched in Cd, Hg, As, and the area ratio accounting for 22.8% of the total area. It is mainly controlled by the geochemical background, the Pearl River Delta formation evolution process, especially the marine transgression process lead to Cd, Cu, Zn and Pb enrichment in Pearl River Delta plain. At the same time, under the influence of higher pressure of human activities, all kinds of exogenous input material carrying heavy metal pollutants on soil environmental quality also could not to ignore.

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Keywords

Regional Geochemical Characteristic, Soil Elements, Source of Anomalous Elements, Influence Factors, Pearl River Delta Economic Zone, China

1. Introduction

In the last three decades, the sustained and rapid socio-economic development of the Pearl River Delta region of China gained a great success, but also paid a heavy price in resources and environment, such as decline in the quantity and quality of natural resources, urban and rural environment pollution, shortage of resources, which seriously restricted the economic development [1]-[7]. In order to provide a scientific basis for socio-economic development and planning to improve the ecological environment of this region, Guangdong Provincial People's Government and China Geological Survey of the Ministry of Land and Resources signed an cooperation agreement of "Eco-geochemical Survey and Assessment in Pearl River Delta Economic Zone of Guangdong Province" in January 2006. This project is part of the multi-purpose geochemical survey program of China.

Ecological geochemistry, as part of application geochemistry, is an edge discipline on the basis of exploration geochemistry. Based on geochemical cycle theory, it deals with the relationship between element geochemical distribution and allocation of state ecological environment through multi-purpose geochemical survey methods [6]. This project includes the multi-purpose regional geochemical survey and ecological geochemical assessment [7]-[9].

Soil and sediment samples from surface and deep soils were systematically collected by means of two-layer grid sampling in the former; different methods were applied in agricultural land ecosystem, shallow water ecosystem and city ecosystem in the latter. Combined with the characteristics of the studied area, we firstly carried out the study of geochemical character of delta formation evolution, the regional radiation environment quality evaluation, the simulation of the effects of acid rain on soil quality and formulation of the local standards for soils environmental quality, and experiment of heavy metal contaminated soil remediation etc.

2. Description of the Studied Area

2.1. Location of the Studied Area

Pearl River Delta Economic Zone is located in the middle part of Guangdong Province, facing to the South China Sea in the south and is adjacent to Hong Kong and Macao. Its geographic coordinates are 112˚00′ - 115˚24′E, 21˚43′ - 23˚56′N (**Figure 1**). The land area is 41,698 km^2, accounting for about 23.2% of land area of the whole province. Pearl River Delta Plain, as the major part of the surveyed area, is surrounded by intermittent mountain land and hills in the west, north and east sides. The Pearl River system consists of Pearl River and its tributaries such as Xijiang River, Beijiang River, Dongjiang River and Tanjiang River are arranged in a crisscross pattern. This area belongs to the subtropical monsoon climate, mild and wet with plentiful rainfall. As the pioneer of reform and opening-up, the Pearl River Delta Economic Zone is the important economic central area of our country. Meanwhile, this area is also the growing area for important crops and commercial crops of Guangdong province and the breeding area of aquatic product. It is also developed in the export-oriented agriculture and aquatic product breeding industry.

2.2. Geological Overview

Varied and complete strata are widely distributed in the Pearl River Delta Economic Zone, accounting for about 70% of the whole zone (**Figure 1**). The outcrops range from Metamorphite series with stronger deformation and metamorphism of Mesoproterozoic era to loose debris sediment of Quaternary period. Quaternary strata are the primary outcrops, others are Nanhua strata, Sinian strata, Cambrian strata, Devonian strata, Carboniferous strata, Jurassic strata, Cretaceous strata etc. Magmatic rocks are mainly composed of the intrusive rock (including the gneissic complex), while the volcanic rocks are only developed in small areas. The intrusive rocks mainly consist of the granite, and then the medium acid monzonite granite, granodiorite and quartz diorite, and other rare types of rocks. Basites are seldom outcropped. The volcanic rocks can be divided into Variscan-Indosinian, Yanshanian and Himalayan according to their formation ages.

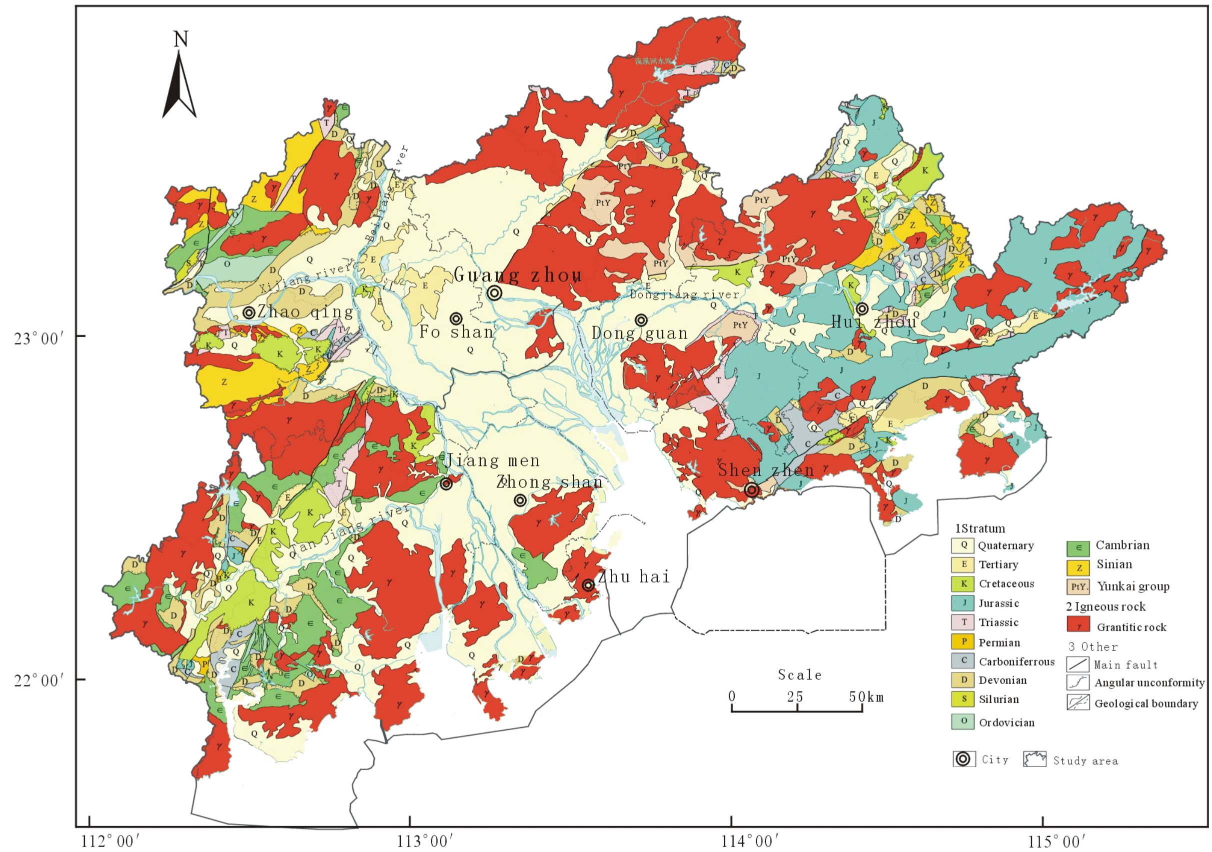


Figure 1. Geological map of the study area.

3. Materials and Methods

3.1. Multi-Purpose Regional Geochemical Survey

3.1.1. Sample Collection

Surface and deep soils were separately collected in terrestrial areas according to two-layer grid sampling. Normally, surface soils were collected at a sampling density of 1 or 2 samples/km^2. Samples from the urban areas of Guangzhou, Foshan, Shenzhen and so on were collected at a sampling density of 2 samples/km^2. All samples were from 0 - 20 cm in depth. Four surface soil samples from adjacent grids of land area were combined into one sample for chemical analysis, and single sample of intertidal zone was taken for chemical analysis. Samples from the deep soil of land area at 150 - 200 cm depth were collected at a sampling density of 1 sample/4 km^2. Sixteen deep soil samples from adjacent grids of land area were combined into one sample for chemical analysis, and single sample of intertidal zone was taken for chemical analysis.

Each sample weighed no less than 1000 g. After air-dried, the samples were sieved with 20 mesh screen (<0.84 mm) and further processed with –200 mesh (<0.074 mm) for analysis. PH values of soils were measured after sieving with 10 mesh screen (<2 mm). During the process of sample collecting, transportation, processing and compositing, anti-pollution measures are required.

A total of 43,499 surface soil samples and 10,741 deep soil samples have been collected with 10,908 composite topsoil samples and 2798 composite deep soil samples for analysis.

3.1.2. Sample Analysis

Totally 54 elements and indicators, including Ag, As, Au, B, Ba, Be, Bi, Br, Cd, Ce, Cl, Co, Cr, Cu, F, Ga, Ge, Hg, I, La, Li, Mn, Mo, N, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Th, Ti, Tl, U, V, W, Y, Zn, Zr, SiO_2, Al_2O_3, TFe_2O_3, MgO, CaO, Na_2O, K_2O, TC, Corg and pH for soils (including the intertidal zone) and samples of sediments from offshore marine area were determined. All the samples were analyzed by the Analytical Center of the Institute of Geophysical and Geochemical Exploration (IGGE). The analysis method is based on XRF, ICP-MS and ICP-OES test, combined with other advanced sensitive analysis instruments.

External quality control was carried out by analyzing 4 pieces (50 pieces per lot) of blind control samples (BCS), 1327 pieces in total along with the collected samples. Several parameters were then calculated, including qualification rate (%), correlative coefficients (r) and two-sample variance (F) between the measured value and standard value of BCS 10] (China Geological Survey, 2011). The average qualification rate and detected rate of the BCS analysis quality are 99.81% and 99.69% respectively. Internal quality control was performed by analyzing 4 pieces (50 pieces per lot) of BCS. 1723 pieces in total along with the collected samples, re-analyzing 743 blind duplicate samples, accounting for 5.49% of total samples and checking 36,884 anomalous data. Based on the standard values of certified reference samples, qualification rate (%) of accuracy and precision (λ) were calculated to monitor the accuracy and precision of the analytical methods. According to the results of repeatability checking and anomalous data random-inspection, the qualification rates of relative deviation were calculated to control the analytical accuracy. The average qualification rate of internal inspection is above 99.8% (**Table 1**).

Table 1. Analysis method and detection limits for samples.

Elements	Analysis Method	Method Detection Limit[a]	Elements	Analysis Method	Method Detection Limit[a]
Ag	ES	0.02	Pb	XRF	2
As	HG-AFS	1	Rb	XRF	5
Au	GF-AAS	0.0003	S	XRF	50
B	ES	1	Sb	HG-AFS	0.05
Ba	XRF	5	Sc	ICP-MS	1
Be	ICP-OES	0.5	Se	HG-AFS	0.01
Bi	ICP-MS	0.05	Sn	ES	1
Br	XRF	1.5	Sr	XRF	5
Cd	ICP-MS	0.02	Th	ICP-MS	1
Ce	ICP-MS	1	Ti	XRF	10
Cl	XRF	20	Tl	ICP-MS	0.1
Co	ICP-MS	1	U	ICP-MS	0.1
Cr	XRF	5	V	XRF	5
Cu	XRF	1	W	ICP-MS	0.3
F	ISE	100	Y	ICP-MS	1
Ga	XRF	2	Zn	XRF	2
Ge	HG-AFS	0.1	Zr	XRF	2
Hg	CV-AFS	0.0005	SiO_2	XRF	0.1
I	COL	0.5	Al_2O_3	XRF	0.05
La	ICP-MS	1	TFe_2O_3	XRF	0.05
Li	ICP-OES	1	MgO	ICP-OES	0.05
Mn	XRF	10	CaO	XRF	0.05
Mo	ICP-MS	0.3	Na_2O	ICP-OES	0.02
N	Combustion-Gas Chromatography	20	K_2O	XRF	0.05
Nb	XRF	2	TC	Combustion-Gas Chromatography	0.1
Ni	XRF	2	Corg	Oxidative Pyrolysis-Potentiometry	0.1
P	XRF	10	pH	Potentiometry	0.1

[a]Unit for the content of SiO_2, Al_2O_3, MgO, CaO, Na_2O, K_2O, C and Corg is %; pH is dimensionless; other measurement unit is $\mu g \cdot g^{-1}$.

3.2. Eco-Geochemical Assessment

Ecological geochemical assessment mainly study on the distribution characteristics, origin of sources, migration and transformation and impact mechanism of toxic elements and beneficial elements in the important regional distribution region or local geochemical anomaly area. Rural and urban ecological environment, safety evaluation of agricultural geological suitability and agricultural cultivation had also been studied. A total of 16,514 rock, soil, sediment column, water, suspended solids, chemical fertilizers and pesticides, biological, human hair, wet and dry sedimentation and dust from all types of samples were collected and full-effective volume, shape, composition, physical and chemical indicators were tested, finally 532,100 data were obtained.

4. Results and Discussion

4.1. Regional Geochemical Characteristics

4.1.1. Elements Content Characteristics in Soil

Geochemical parameters of the surface and deep soil samples are shown in **Table 2**. Content of elements in deep soil and crustal abundance comparative results showed that the soil was enriched in Bi, N, I, Cs, Se, B, Hf, As, Sn, Th, W, Pb, U, Tl, Zr, Ce, Tm, Be, Rb, Li, Pr, C, Ta, Al_2O_3, Ga, Nd, Dy and Ge, poor with CaO, Na_2O, Sr, Te, MgO, Ni, Mn, Co, Cl, P, Cu, Cd, Au, S, Cr, Lu, Fe_2O_3, V, Sc, Ti, Br, Ho, Ag, Gd, Eu, Tb, Hg, Ba, In, Zn, etc.

Table 2. Geochemical background and reference value of elements in soil[b].

Element	Surface		Deep		Element	Surface		Deep	
	n[c]	Background	n[c]	n[c]		n[c]	Background	n[c]	Reference
Ag	9941	77	2567	57	N	10,266	995	2602	441
As	9775	9	2431	10.4	Nb	9787	18.4	2476	19
Au	9528	1.67	2614	1.34	Ni	9515	9.5	2529	12.9
B	10,067	46.9	2541	47.4	P	10,098	413	2585	260
Ba	10,356	293	2614	304	Pb	10,062	37	2526	38
Be	10,120	2.12	2562	2.34	Rb	10,011	117	2543	124
Bi	9530	0.77	2405	0.83	S	9911	233	2387	162
Br	9985	3.8	2508	2.9	Sb	9827	0.68	2516	0.68
Cd	8442	69	1992	45	Sc	10,415	8.7	2625	10.6
Ce	10,150	85	2530	89	Se	10,256	0.51	2600	0.52
Cl	9376	62	2294	57	Sn	9731	7.9	2556	7.8
Co	9235	3.8	2413	5	Sr	10,365	35	2611	34
Cr	10,425	40	2634	47	Th	9783	19.6	2501	23.1
Cs	10,246	8.3	2567	9.8	Ti	10,366	3848	2610	4149
Cu	9435	12.9	2482	13.7	V	10,433	66	2634	80
F	10,275	413	2580	443	W	9720	3.34	2541	3.78
Ga	10,393	18.4	2619	21.6	Y	10,117	26.3	2523	26.7
Ge	10,203	1.51	2599	1.62	Zn	10,206	50	2617	51
Hg	9420	84	2511	62	Zr	10,210	305	2588	272
I	10,062	3.48	2583	4.72	SiO_2	10,467	71.07	2642	65.36
La	10,148	38.2	2551	40.4	Al_2O_3	10,414	15.1	2642	18.71
Li	10,266	28	2596	32	TFe_2O_3	10,436	3.73	2627	4.69
Mn	9163	213	2421	221	OrgC	10,318	1.65	2492	0.69
Mo	9600	1.11	2380	1.26	pH	10,404	5.28	2299	5.26
N	10,266	995	2602	441					

[b]Unit for Ag, Au, Cd and Hg is $ng \cdot g^{-1}$; the unit for SiO_2, Al_2O_3, TFe_2O_3 and OrgC is %; for the other elements is $\mu g \cdot g^{-1}$; pH is dimensionless. [c]n is the statistical data that eliminated abnormities.

The results also indicated that the geochemical reference value of soil element was originated from the soil parents' and regional elements combined features reflected that the elements enriched in the soil was interrelated with acid rock, sandstone and shale.

The results indicated that geochemical reference values and background values of the element were inherited from source rocks. Compared with the soil background value, the surface soil of Quaternary sediments relatively enriched in Au, Ag, Cu, Zn, Cr, Ni, Cd, Hg, F, As, Sb, Co, P, Mn, B, Ba, V, Ti, Li, Be, Sr, Te, CaO, Na_2O, MgO, Fe_2O_3, Pr, Nd, Sm, Eu, Gd, Dy, Er, Y, etc.; nearly half of the element background value of the sedimentary source material reached the lowest, including W, Sn, Mo, Pb, Zn, Hg, Mn, Be, Rb, Ta, U, Th, Ga, In, Tl, TC, K_2O, Na_2O, Al_2O_3, Ce, Pr, Nd, Sm, etc.; background value of U, Th, Sn, Bi, Ta, I, Tl and Tb were significantly higher, while the background of Au, Ag, Cu, Cr, Ni, As, Sb, Co, V, Ti, B, Ba, MgO were significantly lower; the soil originated from volcanic rocks had a high background value of Mo, Mn, Br, I, Zr, Hf, Nb, Ta, Th and low background value of Sn, Bi, Au, Cu, Cr, Ni, Cd, As, Co, V, B, P, Ba, CaO, Na_2O.

4.1.2. Distribution Characteristics of Elements in Soil

The Pearl River Delta Plain is a typical geochemical landscape area with spatial distribution of elements. The middle, western and eastern parts of the Pearl River Delta Economic Zone are quite different in geochemical features due to regional geological settings, soil parent materials, geomorphic characteristics and human activities (**Figure 2**).

Multi-cycle marine deposition and alluviation with a variety of material sources resulted in high content of N, P, K_2O, MgO, CaO, Na_2O, Ba, Mo, B, TFe_2O_3, Mn, Co, Ni, Ti, V, Cr, Sc, Y, REE, Hg, Cd, Pb, As, Cu and Zn in the middle part of the surveyed area [10].

Originating from weathered granite and sandshale ourcropped in the west, there occour many anomalous belts with complex elements combinations, such as the low content area of P, F, Mn, Fe, W, Sn, Zn, K_2O, Na_2O, Co

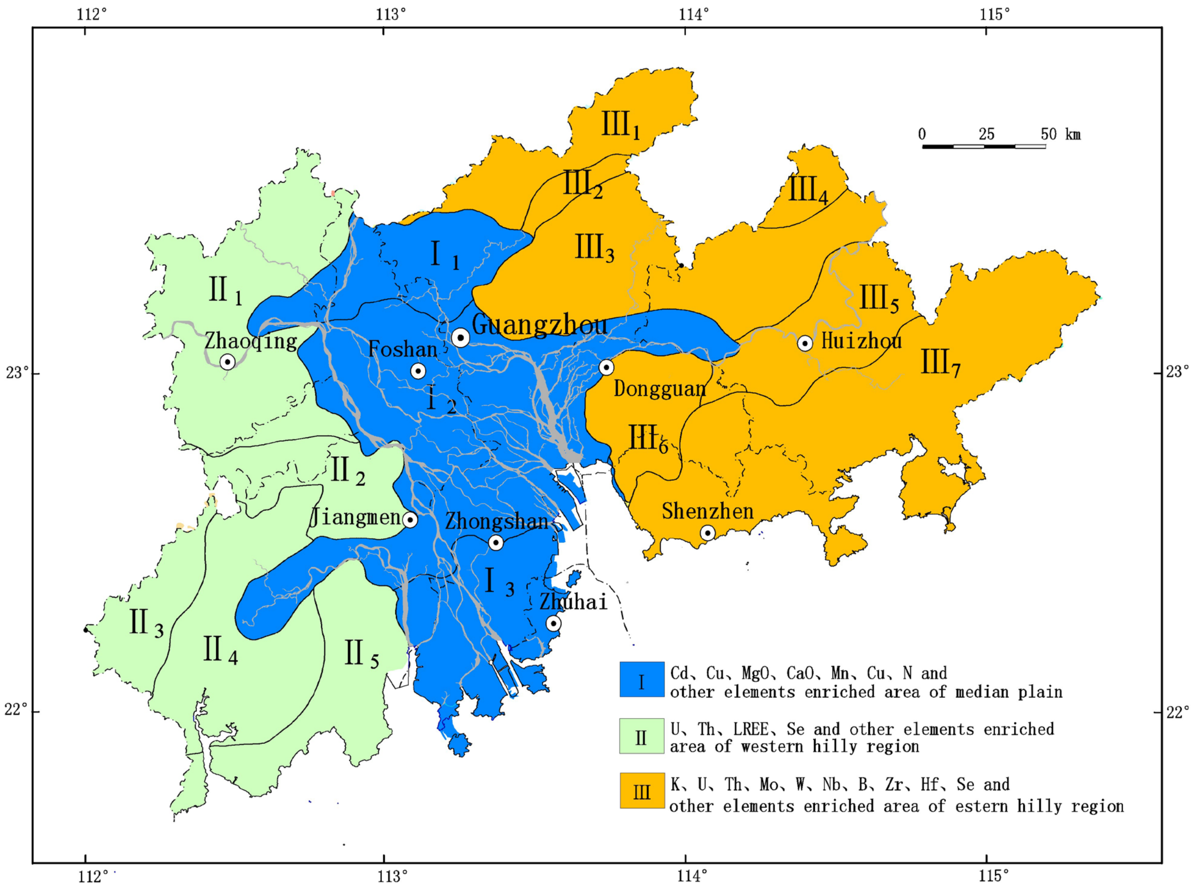


Figure 2. Geochemical zoning map of soil.

and Mo etc. Along Taishan-Enping, the enriched areas of U, Th and REE in Tianlu Mountains and Gudou Mountains. And selenium-rich soils are widely distributed here, for instance the selenium-rich belts along Taishan-Kaiping-Enping and Zhaoqing-Sihui [10].

The east area features lack of microelements and low background resulted from well-developed old strata such as gneiss and migmatite and volcanic rocks in the south to Dongjiang River [10]. A few high anomalies occur due to mineralization of acid intrusive and extrusive rocks.

4.2. Geochemical Characteristics of Different Evolution Stage of Pearl River Delta

Because of the sedimentary dynamic complexity, lateral facies variation and sea level drops erosion during the formation of the Pearl River Delta, many basic problems are still in debate [11]-[14], for example, how many sedimentary cycles took place since the Late Pleistocene. Were there one or two ocean transgressions since Holocene. Were there the last glacial deposits in the studied area. On the basis of the multipurpose regional geochemical analysis, we studied the distribution characteristics of elements in main tectonic framework and sedimentary cycles, through the borehole profiles of Pearl River Delta.

Four sedimentary cycles could be recognizes in the Pearl River Delta of Late Quaternary, on the basis of sedimentology analysis, combined with heavy minerals, grain size, and B, Ba, Sr and other trace element characteristics. Geochemical evolution characteristics of the elements showed that there were three marine transgression events in the Pearl River Delta since Late Quaternary (**Table 3**, **Figure 3**), which provided important information for quaternary Environmental Evolution. This study firstly revealed three-dimensional evolution characteristic and the concentration of the elements in sediments of different areas, so as to fill in the gaps of geochemical characteristics texts study in the region, and enhanced the Quaternary research in Pearl River Delta.

4.3. Ecological Geochemical Assessment

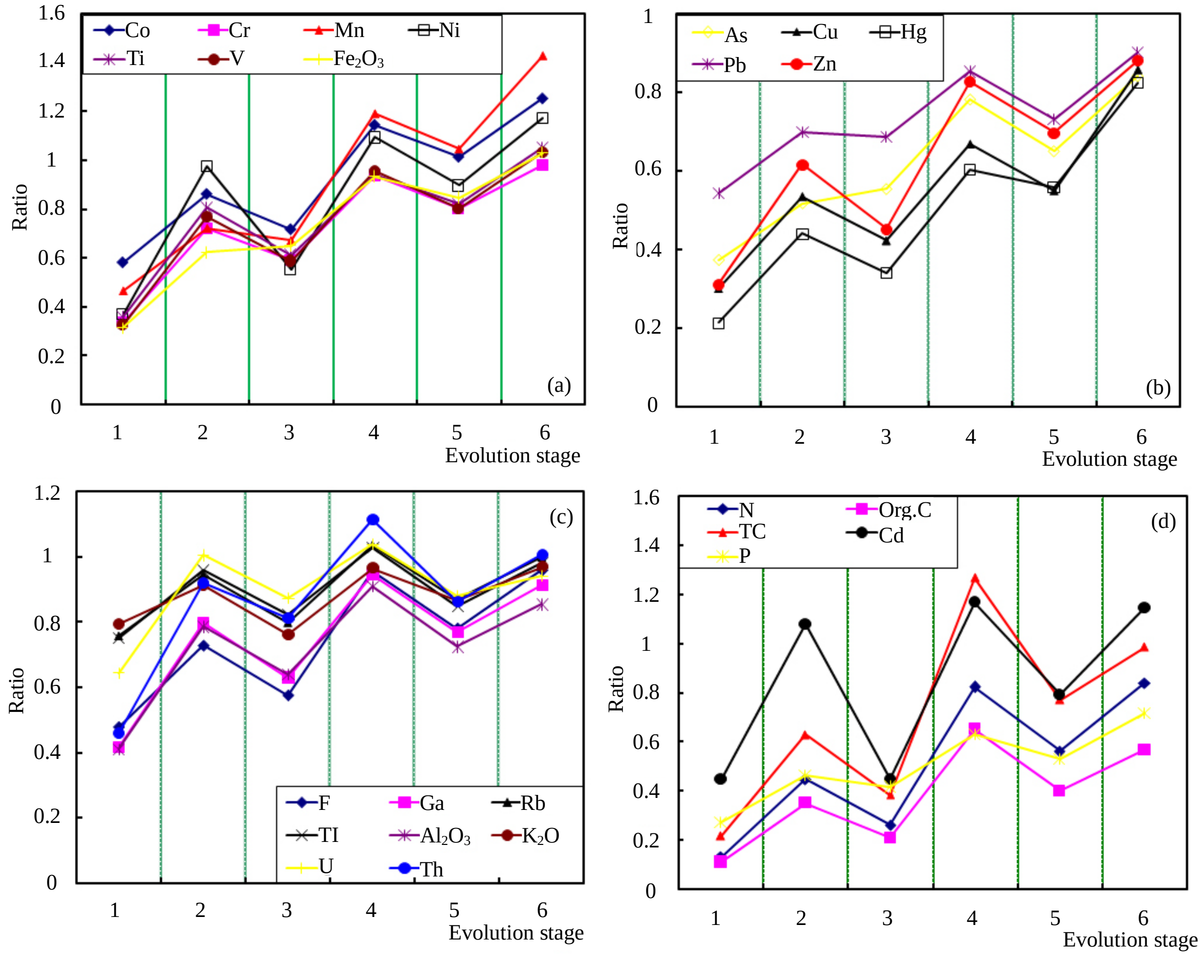
4.3.1. Soil Environmental Quality Assessment

The variation range of pH was 3.28 - 9.42 and the vast majority of soils are with low pH values. According to the classification standard of soil acidity and alkaline from the Second Soil Survey (**Table 4**), the specific land occupation lays on 24544 km^2 of strong acidic and acidic soil (pH ≤ 5.5), accounting for 60.1% of the total area; the specific land occupation lays on 11814 km^2 of weak acidic soil (pH 5.5 - 6.5), accounting for 28.9% of the total area; the specific land occupation lays on 3937 km^2 of neutral soil (pH range of 6.5 to 7.5) accounting for 9.7% of the total area and the specific land occupation lays on 514 km^2 of alkaline soil (pH > 7.5), accounting for 1.3% of the total area. Statistics found that the acidic soil was mainly composed of the parent materials of diluvial, volcaniclastic rocks, volcanic rocks, granitoids and metamorphic rocks. Parent materials of most neutral soil are marine sediments and paralic sediments. The weak alkaline soils are distributed near the river estuary, which soil parent materials are almost marine sediments. According to geomorphological types, strong acidic and acidic soils are almost distributed in the hill area, while weak acidic soils and neutral soils are distributed in the delta plain. Because of the sub-tropical climate and environment weathering, soils with low pH values were distributed widely.

According to the soil environmental quality standards [15], the green food production and environmental

Table 3. Characteristics of element content in Vertical deposition system of the Pearl River Delta.

Sedimentary system	Depositional sequence		Element content	Transgression/Regression	Sedimentary subfacies
	First cycle	Secondary cycle			
Holocene	II	2	High	Transgression	Delta plain facies/Delta-front facies
			Low	Local regression	Delta plain facies
		1	High	Transgression	Prodelta/Delta-front facies
			Low	Regression	Fluvial facies/Weathering period
Late Pleistocene	I	2	High	Transgression	Delta plain facies
		1	Low	Regression	Fluvial facies



note: Ration is the element content of each evolution stage to surface soil;
The number of 1, 3 and 5 denotes transgression, 2, 4 and 6 denotes regression.

Figure 3. Changes of the typical element contents in transgressive and regressive process of the Pearl River Delta.

Table 4. Soil pH classing standards and classification results.

Class	Alkaline	Neutral	Weak acid	Acid	Strong acid
pH	>7.5	6.5 - 7.5	5.5 - 6.5	4.5 - 5.5	≤4.5
Proportion (%)	1.26	9.73	28.92	60.06	0.04
Area (km^2)	514	3973	11814	24529	15

quality standards and other relevant standards [16], the results of soil environmental quality evaluation showed that the soil environmental problem of the region was serious (**Figure 4**). Many samples that widely distributed in the economic developed Pearl River Delta Plain area reached the third-class national soil Environment standard. The soil enriched in Cd, Hg, As, and the area ratio accounting for 22.8% of the total area. First-class soil and second-class soil that suitable for agricultural cultivation land account for 19.9% and 57.3% of the total area of 41,698 km^2. Environmental quality green agricultural area is 21,847 km^2, accounting for 52.4% of the total area.

4.3.2. Ecological Effect

Element test on As, Cd, Hg, Pb, Cr, F, Cu, Zn, Ni and Se have been carried out, based on 805 samples, including vegetables, rice and fruit from agriculture growing area. Statistic result revealed that the association and composition of these elements from different kinds of crops were quite different (**Figure 5**). Rice was the most prominent, which had an average content of Cr, As, Cd, Pb, Cu, Zn of 0.67 mg·kg^{-1}, 0.15 mg·kg^{-1}, 0.13 mg·kg^{-1}, 0.23 mg·kg^{-1}, 4.25 mg·kg^{-1} and 9.75 mg·kg^{-1}.

Based on "Maximum levels of contaminants in foods" [17], "Tolerance limit of copper in foods" [18], "Tolerance limit of zinc in foods" [19] and "Tolerance limit of arsenic in foods" [20], various types of crops edible part of safety had been studied in this survey. The results showed that 87 samples were over standard with a total rate of 10.42%. The over standard rate of Cd and Pb were 5.75% and 5.39%, which are the mainly polluted elements. The over standard rate of Cr, Zn, Cu, Hg were 1.80%, 1.80%, 0.72% and 0.36% in small amount of samples. As didn't exceed the standard. From the results of the classification and evaluation of different types of crops, the exceeding standard rate of heavy metals such as Cd and Pb were high in rice and vegetables. The over standard of Cd, Pb and Zn were lower in beans and cucurbits.

4.4. Source of Typical Anomalous Elements in Soil

Heavy metal elements anomalies along the Yangtze River is an major ecological environmental issue discovered by the multi-purpose geochemical survey that is being carried out in China [21] made systematical studies on methodology of the source tracking and quantitative estimation of the elements anomalies along Yangtze River. Heavy metal elements anomalies along the Pearl River is similar to Yangtze River [22]. The result shows, high content elements such as Cd, Cu, Pb, Zn, Cr, F were regional distributed. The distribution range was in accordance with those of Guizhou Formation and Lile Formation, which typically controlled by geologic background. Studies on the typical strata, rock and mine, element distribution characteristics of binding rock and ore mineral assemblages of the middle and upper reaches of the Pearl River Basin, Pb isotopic composition and the evolution geochemical characteristics of delta formation showed that sediments were mainly from the upstream parent rock debris material. Material source, sediment grain size and depositional environment affected the distribution characteristics of the Pearl River Delta Quaternary sediments in Cd, Pb, Zn, other heavy metals and high content sources and migration enrichment patterns. Among all the factors, material source played an important role in

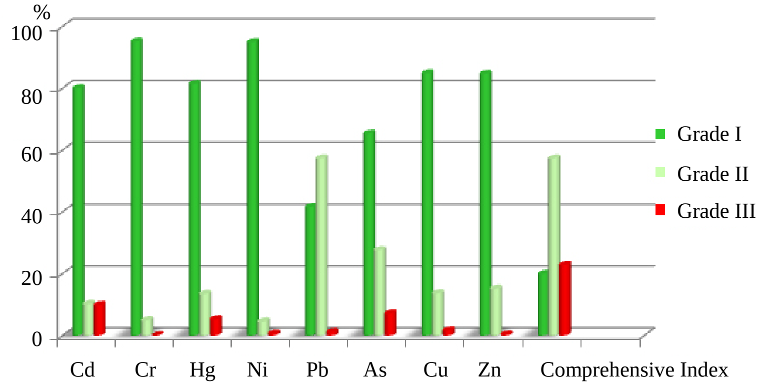


Figure 4. The ratio of each graded soil distribution to the surveyed area.

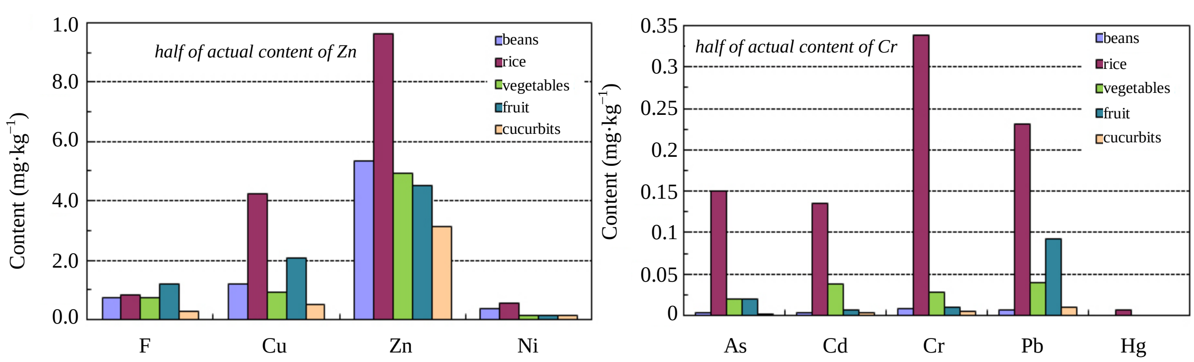


Figure 5. The average content of heavy metals in different varieties of crops.

the concentration of the elements. Materials from the upstream catchment area of the Pearl River system affected the geochemical characteristics of the delta plain soil elements [22].

Pearl River system not only provided materials for the formation of Pearl River Delta in geological history, but also continued to carry a large number of debris particles and dissolved substances into the delta plain. It became an important source of the water elements in the plain rivers. The element fluxes were calculated according to the survey of suspended solids and filtered water element content of the Pearl River Delta, the Dongjiang River, the Beijiang River, Xijiang River, Tanjiang River, Liuxihe River. The results were showed in **Table 5**. Seen from **Table 5**, Ca, Mg, Na were maximally transported to the delta plain by Pearl River system, about million tons every year; K, Al, Sr, P, Tl, Mn went secondly, more than ten thousand tons every year; K, Al, Sr, P, Tl, Mn went thirdly, thousands of tons every year; Ni, REE, As, Pb were about hundreds of tons every year; Co, Cd, Hg, In were relatively less, about several to tens of tons every year. Generally, influx of the main heavy metal elements, including As, Cd, Cu, Hg, Pb, Zn, in different rivers arranged as Xijiang River > Beijiang River > Dongjiang River. Xijiang River was an important source of heavy metals to the Pearl River delta.

But under the influence of the high intensity of human activities, a variety of exogenous input materials carried by heavy metal pollutants on soil environmental quality can not be ignored. The total input flux for external source pollution pathway such as atmospheric deposition, fertilization, irrigation, pesicides was shown in **Table 6**. Atmospheric deposition and irrigation were the main input pathways for Cr, Cd, Zn, Ni, Pb, Hg, Cu, while fertilization might serve as the important pathway for F input.

Table 5. Major element flux carried into the pearl river delta plain by the pearl river system[d].

Element	Dongjiang River	Beijiang River	Xijiang River	Liuxihe River	Tanjiang River	Total
As	80.7	136.2	454.3	10.8	7.1	689.1
Ca	263,284	1,250,796	11,433,872	98,364	91,018	13,137,334
Cd	1343.6	5596.6	21912.6	455.3	306.9	29,615
Co	11.9	9.2	63.7	4.0	2.1	90.9
Cu	217.1	153.9	606.2	55.6	27.8	1060.6
Hg	166.0	270.5	2053	62.2	39.0	2590.7
In	203.2	267.8	1124.1	70.8	35.6	1701.4
K	73309	99,459	415,838	23,716	34,726	647,048
Mg	46774	154,052	1,502,493	11,351	33,301	1,747,971
Mn	1966.2	1673.4	8995.7	557.1	372.2	13564.6
Na	166,091	272,058	896,219	121,843	253,882	1,710,093
Ni	192.6	140.4	557.2	68.5	29.9	988.7
P	3718	1738	20,504	1234	791	27,985
Pb	64.6	70.2	253.2	19.6	9.2	416.9
REE	228.3	122.6	456.1	39.7	31.3	878
Sb	6.4	50.3	937.6	4.8	3.0	1002.1
Sr	821.3	2744.8	30,620	266.4	367.7	34820.8
Tl	2068	9094	15,436	253	633	27,483
Zn	445.5	976.4	3706.7	125.5	102.5	5356.6

[d]Unit for Be, Bi, Cd, Hg, In, Tl is $kg \cdot a^{-1}$, for the other elements is $t \cdot a^{-1}$.

Table 6. The ratio of elements from different sources to the total exogenous input elements.

Proportion (%)	Cr	Cd	Zn	Ni	Pb	As	Hg	Cu	F
Rainfall and fallen dust	80.76	85.76	67.55	22.66	22.86	66.44	67.04	57.22	31.19
Irrigation	13.17	12.28	29.97	75.39	72.30	26.02	23.09	38.87	18.80
fertilization	5.93	1.95	2.47	1.95	4.72	7.59	8.81	3.90	50.01
Pesticides	0.15	0.003	0.001	0.006	0.003	0.015	0.010	0.011	0.02

5. Conclusions

This project carried out the most systematic and comprehensive survey in the Pearl River Delta economic zone. Multi medium, multiple indexes of high precision for geochemical data have been obtained and detailed land quality of the Pearl River Delta economic zone also have been systematically investigated, through regional eco-geochemistry assessment, and studying the elementary composition, distribution, origin, transport process and impact mechanism of the regionally distributed toxic and beneficial elements.

Compared to deep soils, the sampled surface soils are enriched in OrgC, N, P, Cd, S, Hg, Ag, B, Au, S and poor with As, Ni, I, Co, Cr, V, MgO, Sc, Al_2O_3, Fe_2O_3, etc. The characteristics of geochemical reference value of element in soil that inherited soil parent material and regional elements combined features reflected that the elements enriched in the soil was interrelated with acid rock, sandstone and shale. The spatial distribution characteristics of element regional geochemistry were conditional by regional environmental geological conditions, and effected by human activities. The Pearl River Delta plain is a typical geochemical landscape area with regional anomaly of multiple-element. The north, western and eastern parts of the Pearl River Delta Economic Zone are quite different in geochemical features due to regional geological background, soil parent materials, geomorphic characteristics and human activities.

Environment quality evaluation results show that the first-class and second-class soil in the area accounted for 19.9% and 57.3% of the total area. Many samples that widely distributed in the economic developed Pearl River Delta Plain area reached the third-class national soil environment standard. The soil enriched in Cd, Hg, As, and the area ratio accounting for 22.8% of the total area. It is mainly controlled by the geochemical background, the Pearl River Delta formation evolution process, especially the marine transgression process lead to Cd, Cu, Zn and Pb enrichment in Pearl River Delta. At the same time, under the influence of higher pressure of human activities, all kinds of exogenous input material carrying heavy metal pollutants on soil environmental quality also cannot to ignore.

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