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Research Article

Silivri (İstanbul) ve Çanakkale Boğazı Arasındaki Denizel Sedimanların Element Konsantrasyonlarının ICP-OES ve LIBS Yöntemleri İle Analizi ve Korelasyonu

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Öz

Bu çalışmada Marmara Denizi deniz sedimanlarının toksik element (Fe, Zn, Al, Mn, Co, Cr, Cu, Ni, Na, Mg, K, Ca) konsantrasyonları LIBS (Lazer İndüklenmiş Plazma Spektroskopisi) ve ICP-OES (İndüktif Eşleşmiş Plazma-Optik Emisyon Spektrometresi) teknikleri ile belirlenmiştir. LIBS tekniği ile elde edilen sonuçların desteklenmesi için aynı sediman örnekleri ICP-OES yöntemi ile de analiz edilmiştir. İki yöntemden de elde edilen sonuçlar karşılaştırıldığında LIBS yönteminin sediman örnekleri üzerinde kullanılabilirliği görülmüştür. Çünkü ICP-OES ile elde edilen sonuçlar ile LIBS ile elde edilen sonuçlar birbirleri ile paralellik göstermektedir. Geleneksel diğer tüm yöntemlerden hızlı sonuç vermesi, taşınabilir olması, analiz maliyetlerinin düşük olması, kullanılan örneğin analiz sırasında zarar görmemesi ve tekrar kullanılabilmesi ve ön hazırlık sürecinin kısa olması gibi avantajları vardır. Bununla birlikte LIBS yöntemi, doğal ve antropojenik kökenli elementlerin belirlenmesi için önemli ve pratik bir tekniktir. Bu metot günümüzde gıda, çevre, sağlık ve tekstil alanlarında kullaılan yeni bir yöntemdir. ICP-OES yöntemiyle yapılan analiz sonuçlarında elementlerin miktarları ppm cinsinden, LIBS yöntemiyle elde edilen analiz sonuçları ise sadece % cinsinden verilmektedir. Bu çalışmada ICP-OES analizi sonucuna göre Zn (42.2-111.7 ppm), Mn (163.2-581.1 ppm), Co (37.14-65.87 ppm), Cr (42.5-112.6 ppm), Cu (5.71-24.33 ppm), Ni (98.20-175.55 ppm), Al (16568.8-24850.9 ppm), Fe (20936.9-37397.9 ppm), Na (5223.4-12384.7), Mg (4800.4-7385.3 ppm), K (3290.8-5582.0), Ca (42405.2-154577.0 ppm) olarak elde edilmiştir. LIBS analiz sonuçlarıda; Zn (% 0-22), Mn (%0-28), Co (%0-21), Cr (%0-23), Cu (%0-19), Ni (%0-2), Al (%67-78), Fe (%94-95), Na (%70-87), Mg (%82-90), K (%85-94), Ca (%66-80) olarak elde edilmiştir. Sonuçlar incelendiğinde LIBS yönteminin; Antropojenik faktörlerle deniz sedimentinde artan Mn, Cr, Co ve Cu gibi toksik elementlerin belirlenmesinde önemli sonuçlar verdiği görülmüştür. Denizel veya karasal ortamlardaki elementlerin kaynağını belirlemek için LIBS metodu, ICP-OES metodu ile paralellik gösterdiği için kullanılabilir.

Anahtar Kelimeler: LIBS, ICP-OES, Toksik Element, Marmara Denizi, Çanakkale Boğazı

Analysis and Correlatıon of Element Concentratıons of Marine Sediments between Silivri (İstanbul) and Dardanelles by ICP-OES and LIBS Methods

Abstract

In this work, the LIBS (Laser Induced Breakdown Spectroscopy) and ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometer) technique applied to the determination of total concentration of some elements (Fe, Zn, Al, Mn, Co, Cr, Cu, Ni, Na, Mg, K, Ca) derived from soil samples of Marmara Sea. To support to the technique, LIBS data were compared with data have been obtained on the same soil samples by application of Conventional Inductively Coupled Plasma Spectroscopy (ICP-OES). The similarity of results obtained between the two sets of data suggested the potential applicability of the LIBS technique to the

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measurement of elements in soils. According to the study, it has been seen that the elements determined by ICP-OES analysis also determined by LIBS method. It has the advantages of being faster than other traditional methods, being portable, having low analysis costs, not being damaged and re-used during the analysis and short preparation period. However, the LIBS method is an important and practical technique for the determination of elements of natural and anthropogenic origin. In the analysis made by ICP-OES method, the amounts of the elements in ppm are determined, while the results of LIBS analysis show the presence of the element only in %. According to LIBS method, Zn, Mn, Co, Cr and Cu concentrations vary according to each region. In this study, according to ICP-OES analysis, Zn (42.2-111.7 ppm), Mn (163.2-581.1 ppm), Co (37.14-65.87 ppm), Cr (42.5-112.6 ppm), Cu (5.71-24.33 ppm), Ni (98.20-175.55 ppm), Al (16568.8-24850.9 ppm), Fe (20936.9-37397.9 ppm), Na (5223.4-12384.7), Mg (4800.4-7385.3 ppm), K (3290.8-5582.0) and Ca (42405.2-154577.0 ppm)). LIBS analysis results showed that parallels Zn (0-22%), Mn (0-28%), Co (0-21%), Cr (0-23%), Cu (0-19%), Ni (%) 0-2), Al (67-78%), Fe (94-95%), Na (70-87%), Mg (82-90%), K (85-94%), Ca (66-%) 80). The LIBS method is an important technique for identifying elements enriched with anthropogenic factors and elements originating from natural processes. The LIBS method can be used to determine the source of elements in marine or terrestrial environments. In addition, the LIBS method; It has also shown important results in the determination of toxic elements such as Mn, Cr, Co and Cu which increase in marine sediment by anthropogenic factors.

Keywords: LIBS, ICP-OES, Toxic Element, Marmara Sea, Çanakkale Strait

1. Introduction

With the development of industry in recent years, all seas are highly polluted due to anthropogenic and natural waste. The main accumulation point of marine pollution is sediments at the sea floor. Since the toxic elements coming from terrestrial environments to marine environments cannot be biodegraded, they precipitate and accumulate in the sediment. Specifically, living things in the sediment suffer the greatest damage from this pollution. Since toxic elements are not biodegradable, it is one of the most damaging pollutant parameters.

Toxic elements that are mixed into the marine environment can be mixed in different ways such as agricultural activities (fertilizers and pesticides), industrial liquid and solid wastes, municipal wastes and ship wastes [1]. Determination and monitoring of sediment quality is very important for public health and environmental quality. The determination of toxic elements in the sediment content is important for determining the types of protective measures to be taken in the receiving environment. Conventional methods such as ICP-OES, ICP-MS and XRF are the most commonly used methods for the analysis of sediment quality in terms of toxic elements. These are very reliable methods that give quantitative results. However, the main disadvantages of these methods are the preparation process, measurement time, measurement costs, contamination of the solutions used and the inability of the measuring device to be portable. In recent years, new measurement methods have been started to be investigated by considering these disadvantages. In particular, the portable devices are the most important advantage. With the development of technology, LIBS (Laserinduced breakdown spectroscopy) method has gained importance instead of traditional methods.

The LIBS method has been used in the determination of the elements on the surface of Mars and has attracted attention in scientific researches. The most important advantages of the method are that the LIBS device is portable, there is no sample preparation process, it does not damage the sample surface during the measurement process and it gives fast measurement results [2 and 3]. Due to these advantages, LIBS is used in many different fields such as environment, industry, biology, chemistry, medicine and geology [4, 5, 6, 7, 8, 9 and 10].

2. Material and Method

2.1. Sample Collection

In this work, seventeen core sediments samples have been examined. Samples were taken from between Silivri (İstanbul) and Çanakkale Strait. The soil samples were selected on the basis of their representativity of investigation area. The coordinates of the samples are given in Table 1 and the location map are shown in Figure 1.

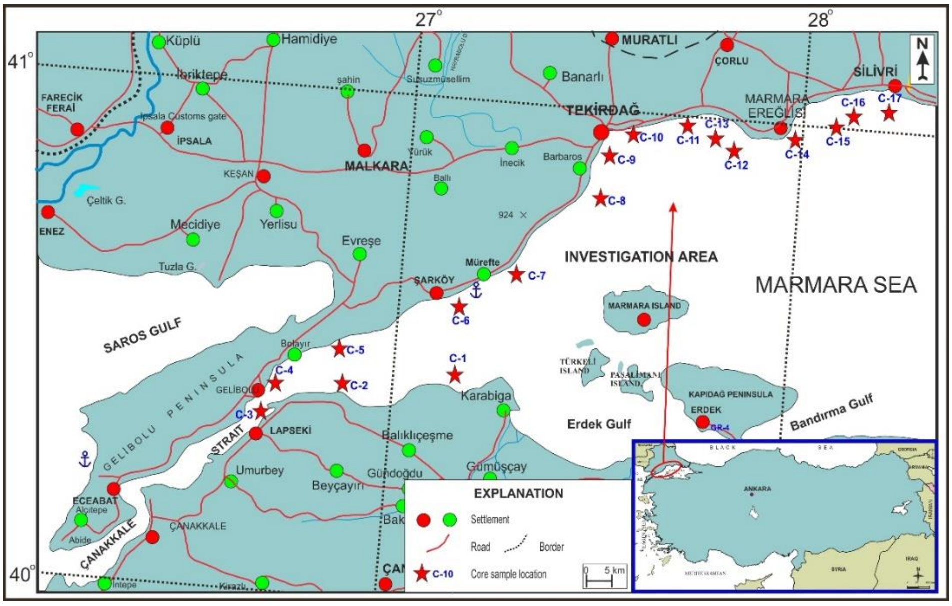

Figure 1. *Location map of investigation area and sample locations*

Table 1. *Sample coordinates of the work area*

CORE SAMPLE NO	DEPTH (m)	GEOGRAPHIC POSITION (WGS-84)	
		Y	**X**
Core 1	46	051 44 52	447 87 84
Core 2	29	049 02 82	447 33 47
Core 3	36	047 39 14	446 99 71
Core 4	43	047 29 08	447 24 87
Core 5	26	048 80 99	448 10 25
Core 6	41	051 10 08	449 48 09
Core 7	30	540197	4522435
Core 8	33	542591	4530386
Core 9	32	546815	4533986
Core 10	30	560139	4536953
Core 11	32	569767	4535792
Core 12	33	580368	4533824
Core 13	33	588549	4541739
Core 14	32	596782	4544493
Core 15	30	603222	4545684
Core 16	31	540197	4522435
Core 17	35	542591	4530386

2.2. Performing the Analysis

Two different methods were used to determine the elemental composition of sediment samples. For ICP-OES analysis, we divided the toxic elements into groups 1 and 2. First of al, element analysis of (Fe, Zn, Al, Mn, Co, Cr, Cu, Ni, Na, Mg, K, Ca) the samples taken from the sediment samples obtained from the study area was carried out in the Scientific and Technological Research and Application Center of Namık Kemal University using the ICP-OES device [11]. For these analyzes, firstly sediment samples have been dried and pounded using mortar. These samples have been separated as 0,5 gr. The collected samples are placed in incineration tubes and burned for 1 hour at 98^0C and 1.5 hours at 200^0C by adding 12 ml HNO_3 and 4 mL HCl.

After the lids of the cooling tubes have been pulled out in the furnace, it has been completed to 50 ml with ultrapure water and filtered using filter papers. Elemental analysis was performed using the ICP-OES device. The samples have been placed in the measurement unit of the ICP-OES device and readings made [11, 12, 13 and 17].

The other method of analysis is LIBS. Laser Induced Plasma Spectroscopy (LIBS) is an optical emission spectroscopy method used for multi-elemental analysis of materials. LIBS is an alloy identification tool which can also deliver a good chemistry when required. The technique involves short, high-intensity laser pulses capable of ablating a small amount of material, thereby creating a momentary plasma. It's one of the fastest analytical technologies available today to analysis sediments. Laser-induced breakdown spectroscopy (LIBS) technique offers many advantages for in sediment elements analysis. In the last years, It has gained a great popularity in elemental analysis because of its portability, lightning speed, low cost, nonrequirement for chemicals, minimal or no sample preparation, simultaneous determination of multiple elements, and capability to perform express identification [14] . The optimum instrumental parameters for soil analysis have been obtained when repetition rate, td, and tw equaled 10 Hz, 1 μs, and 10 μs, respectively. Standard reference material (SRM-2586) has been used to prepare pellets for the parameter analysis (Yang, 2009). Samples taken from the same levels have been placed into the pellet container which is 20-25 gr and pressed for 5 seconds in the press machine under a pressure of approximately 100 bar. This form of samples is called the pellet. The pelletized samples have been placed in locked pouches and sent to the LİBS analysis [10,15,18].

3. Findings

The results of ICP-OES analysis of the study area have been given in Table 2 and the results of LIBS method also given in Table 3. Toxic elements are classified as group 1 and group 2.

Tablo 2. *ICP-OES analysis results of core samples (Yümün, 2017)*

CORE SAMPLE NO	ZN (PPM)	MN (PPM)	CO (PPM)	CR (PPM)	CU (PPM)	NI (PPM)	AL (PPM)	FE (PPM)	NA (PPM)	MG (PPM)	K (PPM)	CA (PPM)
CORE-1	111.7	414.0	61.75	66.4	22.52	117.30	24850.9	34352.0	9376.1	5660.6	5582.0	61444.0
CORE-2	79.6	308.1	53.09	44.0	22.00	87.00	21585.3	29663.9	8260.7	6053.7	4340.7	116603.0
CORE-3	98.5	359.0	63.27	69.1	24.33	121.31	24322.1	34764.6	8744.5	5593.9	4781.1	42405.2
CORE-4	83.8	464.6	60.90	78.9	22.21	154.47	23652.5	31169.2	8758.8	7160.5	5536.8	65945.2
CORE-5	59.2	320.9	45.95	61.9	15.94	121.23	20963.3	25975.4	12384.7	9569.1	5283.4	194094.0
CORE-6	92.6	581.1	78.56	112.6	22.50	217.15	24235.6	37397.9	7614.5	8993.3	5652.5	66031.9
CORE-7	94.7	508.3	77.74	106.3	21.62	214.77	23723.4	36989.0	8129.7	8579.0	5652.7	54287.2
CORE-8	87.4	332.3	61.70	81.0	21.16	171.72	23367.9	33354.8	7892.8	6351.6	5171.6	49661.0
CORE-9	76.4	416.4	65.87	79.2	18.38	175.55	21550.8	31759.4	6606.2	6907.8	4406.8	51710.9
CORE-10	74.7	386.8	64.19	81.5	17.05	168.15	21896	31733.3	6604.9	6617.1	4755.4	55814.9
CORE-11	54.1	229.4	41.06	52.1	11.39	113.25	20515.2	24098.0	8513.4	6869.3	4534.1	154577.0
CORE-12	69.2	303.6	54.07	67.8	14.52	146.84	22556.8	29657.9	10340.0	6680.6	5003.5	68214.4
CORE-13	51.8	222.8	42.98	51.5	11.22	107.05	20182.9	23867.4	7062.5	5032.8	4045.7	84885.1
CORE-14	42.2	319.9	43.52	45.9	5.71	98.20	16568.8	22484.8	5223.4	4387.1	2874.9	50987.6
CORE-15	77.3	326.5	55.49	80.6	18.22	157.22	25265.9	31778.0	15359.4	7385.3	6892.6	77610.1
CORE-16	46.9	194.3	37.14	42.5	10.33	98.58	18610.3	21508.8	8902.1	6010.4	4041.8	157686.0
CORE-17	42.3	163.2	38.69	46.1	9.35	106.40	17768.2	20936.9	6046.8	4800.4	3290.8	80924.2

When the LIBS analysis results were examined, it was observed that the elements such as Fe, Al, Ca, K, Mg and Na which are in the natural structure of the soil, had a higher percentage. The LIBS results of the same elements have been compared with the ICP-OES results, it has been observed that the elements with high percentage in the LIBS analysis are high concentration values in the ICP-OES results (Figure 2 and 3).

***Tablo 3**. LIBS analysis results of core samples*

CORE SAMPLE NO	ZN (%)	MN (%)	CO (%)	CR (%)	CU (%)	NI (%)	AL (%)	FE (%)	NA (%)	MG (%)	K (%)	CA (%)
CORE-1	16	22	20	19	15	2	78	95	75	82	89	75
CORE-2	0	24	21	23	0	0	70	94	74	83	88	73
CORE-3	5	20	18	20	15	2	75	95	75	80	85	70
CORE-4	0	19	16	17	19	0	74	95	70	90	89	80
CORE-5	5	16	15	14	18	2	75	95	70	90	85	80
CORE-6	2	15	15	10	18	2	75	95	70	85	92	80
CORE-7	0	20	16	0	0	0	73	95	71	88	91	76
CORE-8	0	28	0	0	0	0	67	95	72	82	87	66
CORE-9	0	18	15	0	0	0	71	94	72	89	90	79
CORE-10	5	16	13	12	15	1	70	95	70	85	85	80
CORE-11	8	18	15	10	7	2	74	95	73	84	97	80
CORE-12	22	0	0	0	0	0	72	94	87	90	94	81
CORE-13	15	27	18	13	11	0	73	95	71	80	94	73
CORE-14	10	22	15	10	8	2	75	95	70	75	93	75
CORE-15	6	20	16	25	9	3	74	95	70	84	79	81
CORE-16	22	20	16	25	5	1	74	95	83	77	93	71
CORE-17	16	18	15	22	3	1	75	90	85	76	92	70

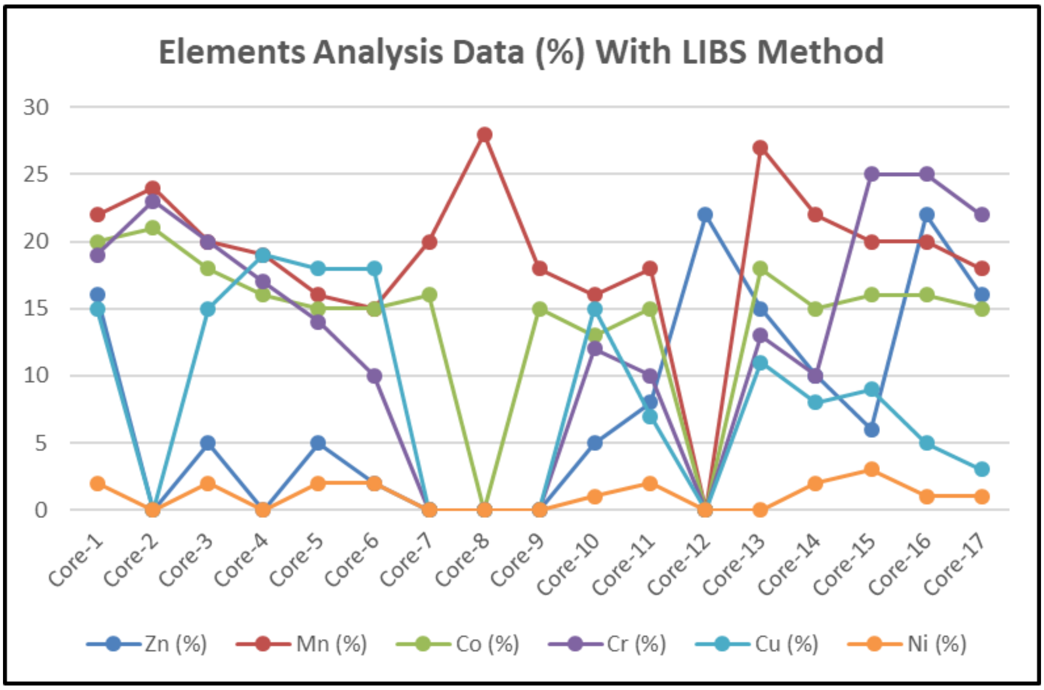

***Figure 2.** LIBS analysis results of core samples*

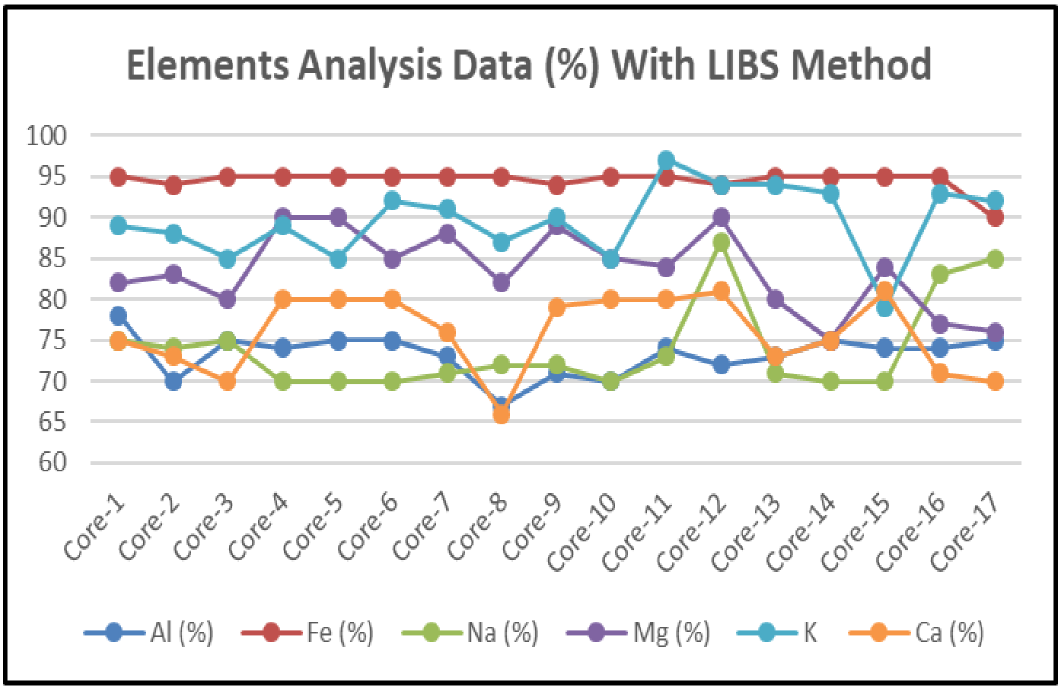

Figure 3. *LIBS analysis results of core samples (Al, Fe, Na, Mg, K, Ca)*

In addition, the LIBS method; It has also shown important results in the determination of toxic elements such as Mn, Cr, Co and Cu which increased in sea sediment with anthropogenic factors (Figure 2 and 3).

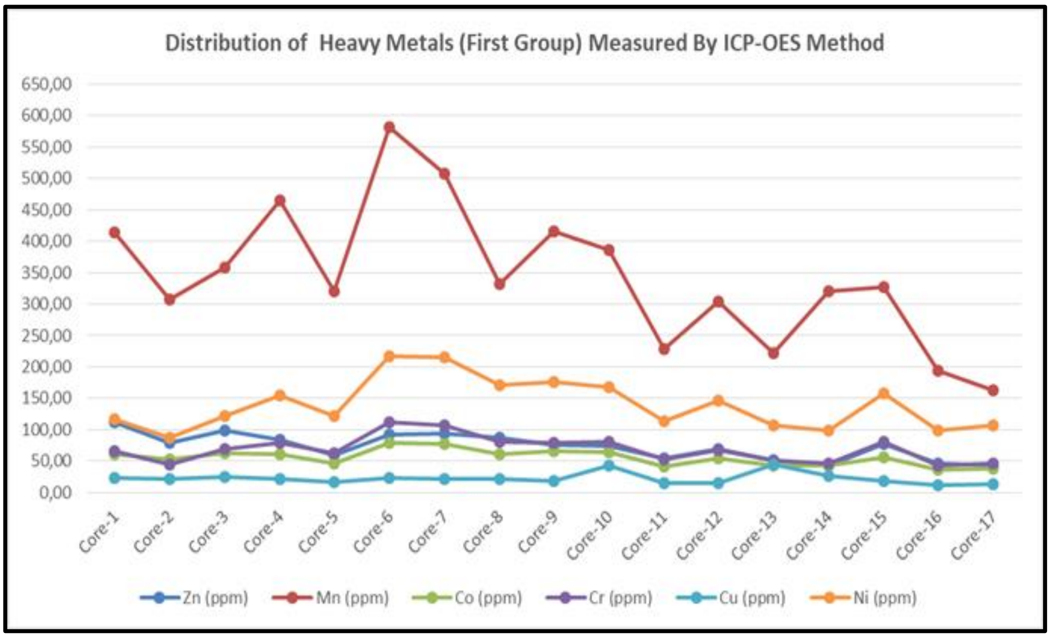

Figure 4. *ICP-OES analysis results first group elements of core samples*

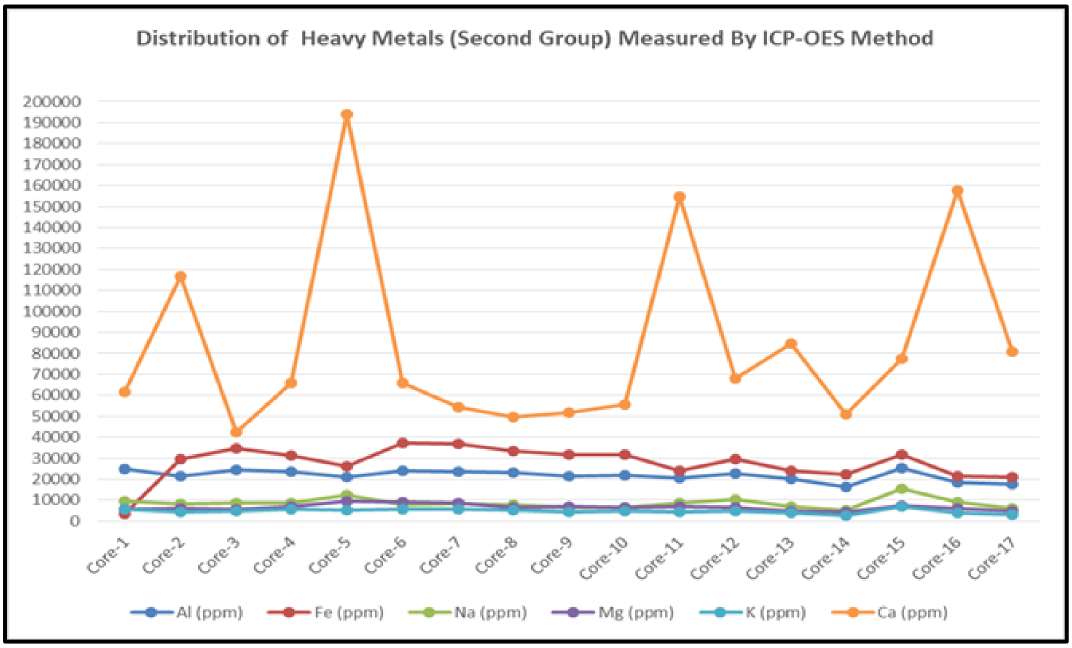

Figure 5. *ICP-OES analysis results second group elements of core samples*

4. Conclusions

This study demonstrates that the LIBS technique used in the determination of many heavy metals in soil is successful in qualitative recognition of metal species. However, when metal concentration values need to be measured, they are considered semi-quantitative. The LIBS method proved its usefulness compared to conventional methods such as ICP-OES. Despite its some disadvantages, LIBS method can be considered as a usefull analytical technique for its intrinsic advantages.

The existence of the elements present in the sample by the LIBS method is determined by a probability defined by %. In contrast, the analysis does not give the amounts of elements in the sample. Although this is seen as a disadvantage, this method gives very useful results for practical and preliminary investigations. According to ICP-OES analysis are Zn (42.2-111.7 ppm), Mn (163.2-581.1 ppm), Co (37.14-65.87 ppm), Cr (42.5-112.6 ppm), Cu (5.71-24.33 ppm), Ni (98.20-175.55 ppm), Al (16568.8-24850.9 ppm), Fe (20936.9-37397.9 ppm), Na (5223.4-12384.7), Mg (4800.4-7385.3 ppm), K (3290.8-5582.0) and Ca (42405.2-154577.0 ppm)). LIBS analysis results showed that parallels Zn (0-22%), Mn (0-28%), Co (0-21%), Cr (0-23%), Cu (0-19%), Ni (%) 0-2), Al (67-78%), Fe (94-95%), Na (70-87%), Mg (82-90%), K (85-94%), Ca (66-%) 80). In this study, when the analysis results were examined, it has been seen that the elements (Fe, Zn, Al, Mn, Co, Cr, Cu, Ni, Na, Mg, K, Ca) determined by ICP-OES analysis were also determined by LIBS method. In the analysis made by ICP-OES method, the amounts of the elements in ppm are determined, while the results of LIBS analysis show the presence of the element only in %. According to LIBS method, Zn, Mn, Co, Cr and Cu concentrations vary according to each location. This result obtained by LIBS method gave similar results with ICP-OES method. If analyzes are performed to determine the origin of elements in the medium, the LIBS method is an important technique for identifying elements enriched with anthropogenic factors and elements originating from natural processes.

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