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Analyses of Heavy Metals in Sea Sediments from the İzmir Karaburun Region

İzmir Karaburun Bölgesinden Alınan Deniz Sedimentlerinin Ağır Metal Analizleri

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Abstract

The present study aimed to determine heavy metal pollution in the İzmir Karaburun region of Turkey by analyzing the marine sediments within the İzmir Karaburun peninsula. Sediment samples were taken using a drilling method from six different regions on the peninsula and analyzed using laser-induced breakdown spectroscopy (LIBS). The percentage of the elements in the samples that matched the standard elements described in the device were determined. The results showed that potassium (K) with a 97% matching percentage and iron (Fe) with a 94% matching percentage was intensive in six different regions. In the first, fourth, and sixth regions, silver (Ag), which is a frequent heavy metal, was found at a high incidence of 50% as regards that in other regions. The results of these analyses were parallel to each other in six different regions in the İzmir Karaburun

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peninsula, and amount of possibly toxic heavy metals were found. When the LIBS conclusions were compared with the conclusion found in the literature, the existence of some elements, such as mercury (Hg), lead (Pb), and arsenic (As), which are known to be toxic elements and a danger to human health, were found in only trace amount; as a consequence, we supposed that there is no heavy metal pollution that could pose a hazard to human health and marine ecosystems within that region.

Keywords: Heavy metal, LIBS, marine sediments, Karaburun

Öz

Bu çalışmada İzmir Karaburun bölgesindeki deniz sedimentleri analiz edilerek bölgedeki ağır metal kirliliğinin tespit edilmesi amaçlanmıştır. Sediment örnekleri sondaj yöntemi kullanılarak altı farklı bölgeden alınmış ve lazer indüklenmiş plazma spektroskopi (LIBS) yöntemi kullanılarak analiz edilmiştir. Cihazda önceden kalibre edilmiş tanımlı elementler ile analiz sonucunda tespit edilen element yüzdeleri karşılaştırılmıştır. Bu karşılaştırma sonucunda %97 eşleşme oranıyla potasyum (K) elementi ve %97 eşleşme oranıyla demir (Fe) elementinin altı farklı bölgede de yoğun olduğu tespit edilmiştir. Bu elementlerin yanı sıra birinci, dördüncü ve altıncı bölgelerde, yaygın ağır metaller olarak karşımıza çıkan gümüş (Ag) elementi diğer bölgelere göre %50 gibi yüksek bir oranda tespit edilmiştir. Altı farklı bölgede de tespit edilen elementler birbiriyle benzerlik göstermiş olup, her bölgede bu ağır metallere eser miktarlarda rastlanmıştır. Yapılan LIBS analizi sonucunda tespit edilen veriler literatür ile karşılaştırıldığında, toksik element oldukları bilinen ve insan sağlığı açısından tehlikeli olarak adlandırılan civa(Hg), kurşun(Pb) ve arsenik(As) gibi ağır metallerin tespit edilmediği yada eser miktarlarda tespit edildiği görülmüştür. Bu sonuçlara göre bölgede insan sağlığına ve deniz ekosistemine tehlike oluşturabilecek bir ağır metal kirliliğine rastlanmadığı belirlenmiştir.

Anahtar kelimeler: Ağır metal, LIBS, deniz sedimentleri, Karaburun

INTRODUCTION

Environmental pollution a major problem for natural ecosystems and human health. One of the biggest environmental problems is heavy metal pollution. Heavy metals cannot be degraded physically, chemically, or biologically (Duffus,2002); therefore, they accumulate in their environment and appear within a wide area as pollution in the soil, air, water, and sediment. These heavy metals can be taken into the human body through nutrition, contact, and respiration. Some of these, such as iron (Fe), nickel

(Ni), copper (Cu), and selenium (Se) are heavy metals that our bodies need; however, at specific concentrations (>1–10 ppm), they become toxic. Apart from these heavy metals, nonvital heavy metals, such as cadmium (Cd), lead (Pb), and mercury (Hg), show toxic effects from their initial concentrations and seriously threaten human health, even at low concentrations (i.e., 0.001–0.1 ppm) (Bengtson, 2017; Järup, 2003; Özbolat,15) therefore, it is of great importance that these heavy metals be detected in terms of both environmental pollution and human health. Various methods, such as X-ray fluorescence (XRF) and inductively coupled plasma–optical emission spectrometry (ICP–OES) have been used in several studies to detect heavy metals (Peralta et al., 2020; Turner & Taylor, 2018; Yumun & Kam, 2019).

These preferred methods have advantages and some disadvantages. Some of the disadvantages are damage to the sample and a long pretreatment process. The laser-induced breakdown spectroscopy (LIBS) method, which was the preferred technique in the present study, has many advantages over other conventional methods. Although preliminary preparation is not required for LIBS, analyzes are conducted within a very short period of time and without damaging the sample. These advantages allow the LIBS method to be used in several different fields, such as forensics, medicine, food, archeology, metallurgy, geology, and environmental studies (Abbas vd., 2021; Bengtson, 2017; Jiang vd., 2021; Lee vd., 2021). In the present study, heavy metal analyses were conducted on sediment samples taken from six different regions in the İzmir Karaburun peninsula of Turkey using the LIBS method. Heavy metal pollution within the region was determined, and its effects on the environment and human health were investigated.

MATERIAL AND METHODS

Sample collection

In the present study, sediment samples taken from six different points within the İzmir Karaburun peninsula were examined. The points where the samples were to be taken were carefully selected to analyze a large area of the peninsula. Sediment samples were obtained from a depth of ~5–15 m using the drilling method. The map and coordinate information of the sampled points are shown in Fig. 1 and Table 1.

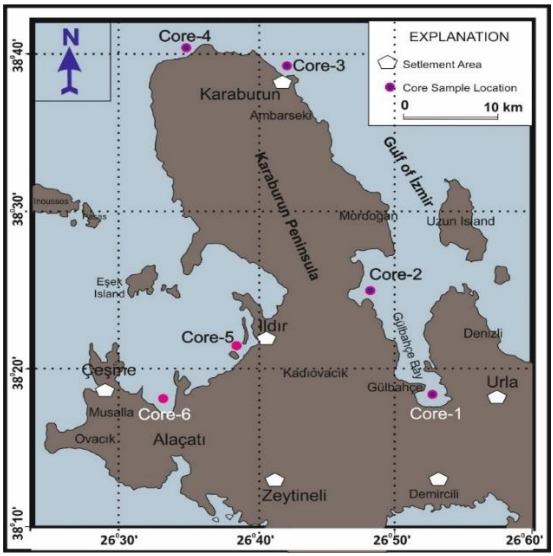
Table 1

Sample Coordinates

Sample Number	Y West	X North
Core 1	472533.00 d E	4241089.00 m N
Core 2	464609.43 d E	4253153.77 m N
Core 3	450908.18 d E	4281133.54 m N
Core 4	458971.45 d E	4275944.35 m N
Core 5	453766.15 d E	4248539.62 m N
Core 6	444920.00 d E	4241972.00 m N

***Figure* 1**

İzmir Karaburun Sediment Sample Locations



LIBS method

LIBS is a fast optical emission spectroscopy method that uses a short laser pulse to create a microplasma at the sample surface. With this method, a comprehensive element analysis can be conducted, including analysis of light elements, such as hydrogen (H), beryllium (Be), lithium (Li), carbon (C), nitrogen (N), oxygen (O), sodium (Na), and magnesium (Mg). The detection limit for heavy metal elements is within the low ppm range. LIBS can be applied to a wide variety of matrices, including metals, semiconductors, glasses, biological tissues, plastics, soils, and electronic materials (Pasquini vd., 2007; Schechter, 1997). In this analyses, the laser pulse focused on the sample and a small portion of the sample mass was removed. With this laser ablation process, the ablated mass interacted with the laser pulse to create a high-energy plasma containing excited atoms and

ions (Fogarassy vd., 1996). When the laser pulse ended, the plasma began to cool. During the plasma cooling process, the electrons of the excited atoms and ions fell into their natural ground state, causing the plasma to emit light having separate spectral peaks. The light emitted from the plasma was transmitted to the spectrometer by a collector lens. The transmitted beam was analyzed by matching atomic lines within the LIBS spectrum. Approximately 0.1 after plasma formation on the sample, the first ionic diffusion followed by atomic diffusion from the elements could be detected. Calibration curves were then drawn when determining the concentration of any element in the sample, and the slopes of these curves provided information about the sensitivity of the method (Castle vd., 1998; Kam & Önce, 2016; Rusak vd., 1997; Song vd., 1997; Yümün & Önce, 2017). In the present study, a UK origin Ecco brand LIBS device was used (Yümün at al., 2019).

Sample Preparation

Using the drilling method, the samples taken from ~5–15 m deep within the sea were dried in an oven at 50–70°C. The dried samples were then crushed and turned into powder, after which 3 g powdered sample was mixed with 0.9 g cellulose and pressed under pressure at ~1450.37 psi for 5s. These pressed samples, or "pellets" were then used for LIBS analyses.

RESULT AND DISCUSSION

Evaluation of LIBS results

The analyses of the heavy metals in the sediment samples were conducted using the LIBS method. As a result of the analyses, 22 different elements were detected in each of the sediment samples. Among the detected elements, K, Fe, Li, and Mg were matched at a high rate to the standards within all six regions. Low percentage of aluminum (Al), silver

(Ag), and manganese (Mn) were also detected. Element percentages for the six different regions are provided in Figs. 2– 7.

Figure 2
Core 1 Element Percentages

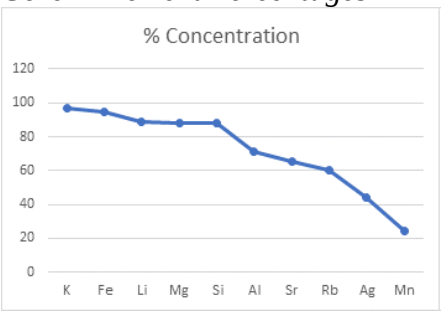


Figure 3
Core 2 Element Percentages

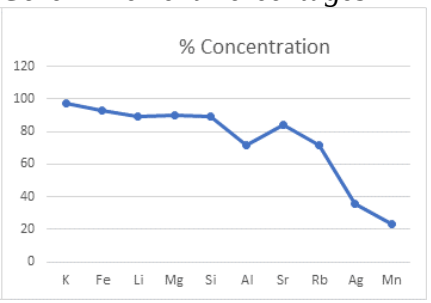


Figure 4
Core 3 Element Percentages

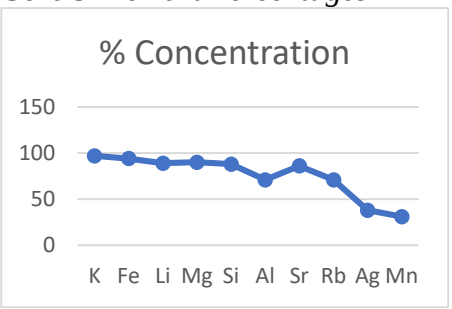


Figure 5
Core 4 Element Percentages

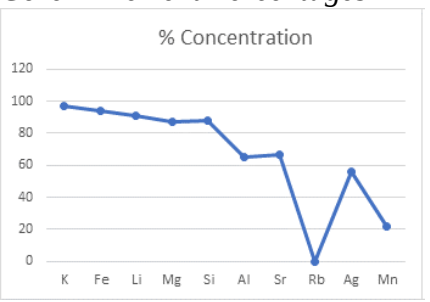


Figure 6
Core 5 Element Percentages

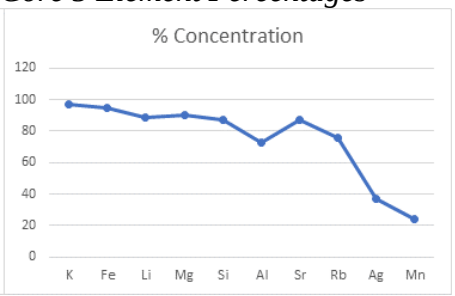
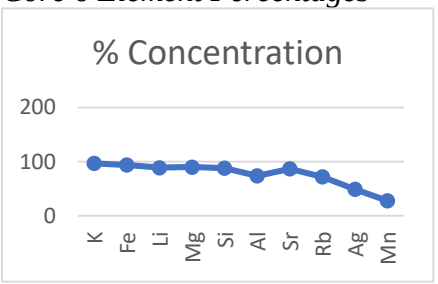


Figure 7
Core 6 Element Percentages



In the present study, the elemental distributions within the six different regions were examined, and it was determined that the element types and percentages within the regions were similar to each other. As a result of these findings, we observed that the LIBS method was successful for detecting heavy metals within the regions. The LIBS spectral analysis results are shown in Figs. 8–13.

Figure 8

Core 1 LIBS Spectral Analysis

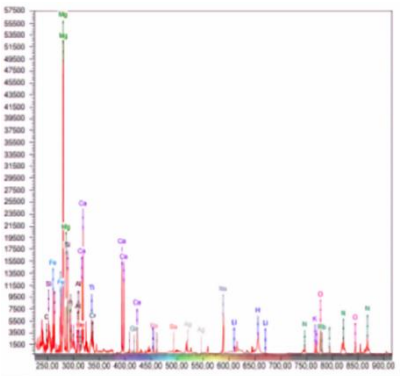


Figure 9

Core 2 LIBS Spectral Analysis

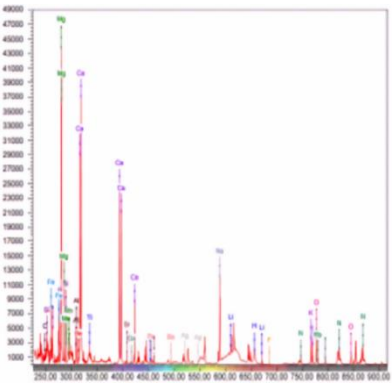


Figure 10

Core 3 LIBS Spectral Analysis

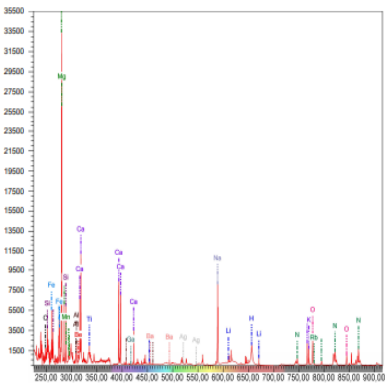


Figure 11

Core 4 LIBS Spectral Analysis

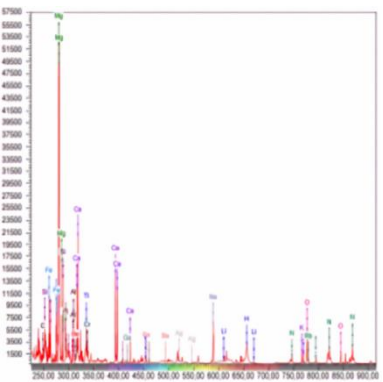


Figure 12

Core 5 LIBS Spectral Analysis

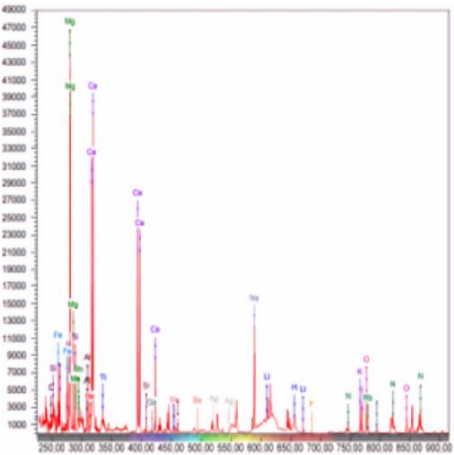
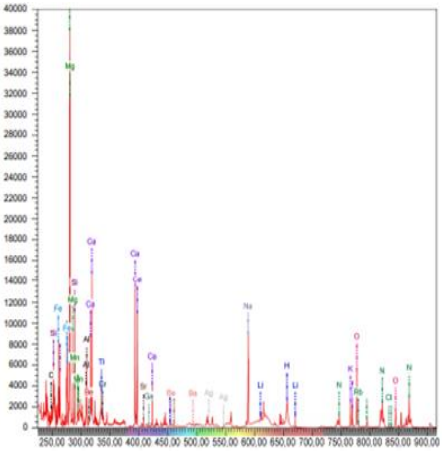


Figure 13

Core 6 LIBS Spectral Analysis



CONCLUSION

In the present study, the results of LIBS analyses performed on the sediment samples taken from six different points within İzmir Karaburun peninsula were evaluated. The results indicated that high amounts of K (97%), Fe (94%), Li (89%), and Mg (89%) were found within each region. In addition, heavy metals, such as Al (71%), Ag (36%), and Mn (25%), were detected at low concentrations. Heavy metals, such as Cd, Pb, As, and Hg, detected in aquatic environments are potentially harmful substances and are reported as priority hazardous substances by the European Commission (Directive 2013/39/EU) (El Nemr vd., 2016; Hussain & Gondal, 2008; Kontas vd., 2020; N'guessan vd. 2009; Yümün, 2017). When the results of the analyses in the present study were evaluated, we observed that Hg, Pb, and As, which are harmful to human health and marine ecosystems, were not found within the İzmir-Karaburun region; therefore, we suggest that

there is no heavy metal pollution that threatens the health of humans and other animals within that region.

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Author Contributions

All authors contributed jointly at every stage of the study.

Conflict of Interest

No conflict of interest was reported by the authors.

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Ethical Statement

Ethics committee approval is not required for the study.