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ВЛИЯНИЕ ИЗМЕНЕНИЯ КЛИМАТА НА ПОДВИЖНОСТЬ МЕДИ (Cu) И СВИНЦА (Pb) В ОБРАЗЦАХ ПРИБРЕЖНЫХ ОТЛОЖЕНИЙ В ОЗЕРАХ, ПОДВЕРЖЕННЫХ ЗАСУХЕ (ОЗ. БОГАЗИЧИ)

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Изучается мобилизация меди (Cu) и свинца (Pb) в образцах осадка, собранных из оз. Богазичи (Тузла), водно-болотные угодья которого составляют площадь 562 га на юго-западе Турции. Рассматриваются переменные окружающей среды, связанные с изменением климата, в частности температура, соленость и pH, влияют на подвижность этих металлов в осадке. Образцы осадка разделялись на четыре фракции с использованием метода последовательной экстракции Бюро по стандартизации Британского сообщества (BCR), а концентрации металлов анализировались методом ICP-OES. Результаты свидетельствуют, что Cu и Pb присутствуют преимущественно в окисляемой и остаточной формах, в то же время как Pb в подвижных фракциях легко высвобождается в водную среду, Cu демонстрирует более широкий диапазон подвижности в отличие от Pb. Медь, содержащаяся в окисляемой и остаточной фракциях, также может высвобождаться в воду при изменяющихся условиях окружающей среды. Результаты изучения показали, что Pb показывает сложное поведение, зависящее как от pH, так и от солености, тогда как мобилизация Cu сильно зависит от температуры, но относительно независима от pH. Таким образом, итоги исследования позволяют предположить, что изменения окружающей среды, вызванные изменением климата, могут оказывать большее влияние на мобилизацию меди, чем свинца в отложениях оз. Богазичи.

Ключевые слова: озеро Богазичи; осадки; последовательная экстракция BCR; мобилизация металлов; воздействие изменения климата; тяжелые металлы (Cu, Pb).

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THE EFFECT OF CLIMATE CHANGE ON THE MOBILITY OF COPPER (CU) AND LEAD (Pb) METALS IN COASTAL SEDIMENT SAMPLES IN DROUGHT-AFFECTED LAKES (BOĞAZIÇI LAKE)

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This study investigates the mobilization of copper (Cu) and lead (Pb) in sediment samples collected from Boğaziçi (Tuzla) Lake, at 562-hectare wetland in southwestern Turkey. Additionally, the research explores how environmental variables associated with climate change specifically temperature, salinity, and pH influence the mobility of these metals within the sediment. Sediment samples were partitioned into four fractions using the Bureau Communautaire de Reference (BCR) sequential extraction method, with metal concentrations analysed via ICP-OES. The results indicate that Cu and Pb are primarily present in oxidizable and residual forms. While Pb in the mobile fractions is readily released into the aqueous environment, Cu demonstrates a broader range of mobility; unlike Pb, copper held in oxidizable and residual fractions can also be released into the water under changeable environmental conditions. The study further determined that Pb exhibits complex behaviour influenced by both pH and salinity, whereas Cu mobilization is highly temperature-sensitive but relatively independent of pH. Ultimately, these findings suggest that the environmental shifts driven by climate change may have a further impact on the mobilization of copper than lead in the sediments of Boğaziçi Lake.

Keywords: Boğaziçi lake; sediment; BCR sequential extraction; metal mobilization; climate change impacts; heavy metals (Cu, Pb).

Introduction

Climate change, chemical pollution, and biodiversity loss represent the most critical environmental challenges of the modern era. Climate change characterized by rising temperatures and a higher frequency of extreme weather events exacerbates the ecological and health risks posed by chemical pollutants [12]. It achieves this by altering their environmental distribution, bioavailability, and toxicity [15; 31]. Furthermore, shifting precipitation patterns and thermal increases strongly influence hydrological cycles and biogeochemical processes [26], which can significantly alter heavy metal dynamics in freshwater systems [9]. This interaction often increases the mobility and subsequent environmental risk of pollutants [10].

The mobility and bioavailability of heavy metals, such as lead (Pb) and copper (Cu), are largely dictated by the pH, redox potential (Eh), and organic matter (OM) content of the medium [10]. In drought-affected lakes, climate change influences metal mobility in coastal sediments through complex, multifactorial mechanisms. Generally, rising temperatures and altered moisture/redox cycles often resulting from drought increase the solubility and release risk of Cu and Pb [6].

While Cu and Pb typically exhibit more stable mobility than other metals due to their strong binding affinity for organic matter and Fe-Mn oxides, these protective mechanisms can weaken under conditions of increasing temperature and acidification [3; 10]. For instance, drought-induced water level declines can transform normally anoxic sediments into oxic environments [29]. This oxidation can trigger acidification, lowering the pH and increasing the solubility of toxic elements like Cd, Zn, Pb, and Cu [22].

Temperature increases can accelerate heavy metal bioaccumulation by speeding up metal uptake rates and metabolic activities [22]. Research has shown that high temperatures specifically increase Cu solubility in aquatic environments [35] and raise the risk of Pb and Zn release from sediments [22].

For environmental risk assessments, the bioavailability and mobility of Cu and Pb are more significant than their total concentrations. Their fate within the sediment matrix depends heavily on the sediment's physicochemical properties [12].

Copper has a higher binding affinity for organic matter than other metals like zinc [31]. Consequently, Cu is mainly associated with oxidizable (organic-bound) and residual fractions [15]. Studies have shown that Cu can account for up to 60 % of the total metal content in organically bound fractions [26]. Pb generally exhibits a high affinity for both organic matter and Fe-Mn oxides (the reducible fraction). Its mobility is typically lower than that of Cd, Zn, or Ni because it adheres strongly to specific sorption sites with high energy. Furthermore, Pb mobility remains low at pH values above 6.0 [9; 26].

High temperatures accelerate metal release by enhancing geochemical processes and adsorption/desorption kinetics. Interestingly, Cu adsorption on silty soil has been observed to increase as temperatures rise from 20 to 60 °C, indicating an endothermic reaction where increased heat improves adsorption performance [23].

Salinity also plays a crucial role by increasing the concentration of anions, particularly chloride (Cl^-). Chloro-complexation promotes the mobilization of weakly bound metals through desorption, as (Cl^-) ions form soluble complexes (e. g., $CdCl^+$, $CdCl_2^0$). However, research in the Yangtze River estuary suggests that while salinity promotes the mobility of Cd and Manganese (Mn), Cu and Pb behave more conservatively due to their high affinity for Fe-Mn oxides and organic matter [14; 30; 35].

Previous reports indicate that Cu release is significantly correlated with Fe-Mn oxides (F3) and Total Organic Carbon (TOC) content, while Pb release correlates with Fe-Mn oxides, the organic fraction (F4), and TOC [29]. This suggests that mobility is influenced by both sediment properties and chemical speciation [27; 28].

This study determines the chemical fractions of Cu and Pb in coastal sediment samples from *lake Boğaziçi,* which is currently under drought stress. By evaluating the effects of temperature, salinity, and pH, this research aims to clarify how climate-driven variables influence metal mobilization and to understand the ecological risks these metals may pose under various future climate scenarios.

Materials and Methods

Study Area. The sediment samples for this study were collected from Boğaziçi (Tuzla) Lake, located in southwestern Turkey (37.12’ N, 28.21’ E). This 562-hectare wetland is currently under significant climate stress (Fig. 1).



Fig. 1. The map of the study area map

According to the National Wetland Inventory Management Information System (General Directorate of Nature Conservation and National Parks, Ministry of Agriculture and Forestry), the lake was officially registered as a wetland of national importance on July 31, 2019 [Milas Municipality, 2024].

Sample Collection and Preparation. Surface sediment samples were collected from eight distinct points along the lake’s shoreline using an Ekman grab sampler. The samples were stored in 1 L plastic containers and transported to the laboratory. After air-drying and homogenization, the eight samples were pooled into three composite samples.

For total metal and chemical fraction analysis of Pb and Cu, the composite samples were placed in glass petri dishes and oven-dried at 80 °C for 24 hours. The dried sediments were then ground using a mortar and pestle, passed through a 200-mesh sieve, and prepared for subsequent analysis.

Experimental Setup and Artificial Seawater Preparation. Artificial seawater was prepared following the protocol by [13], which was defined as 100 % seawater. To simulate varying salinity levels, this stock was diluted with ultrapure water at ratios of 1:2 and 1:4. Pure water was used to represent the freshwater control.

For the mobilization experiments, 25 g of sediment was placed in 50 mL plastic flasks, to which 50 mL of the respective liquid (pure water, 1/4 seawater, 1/2 seawater, or 100 % seawater) was added. The experimental intervals were set at 6, 12, 24, 48, 72, and 96 hours. The samples were placed in a shaker incubator and maintained at four temperature setpoints: 25 °C, 40, 45, and 50 °C.

To evaluate the effect of pH, samples were adjusted to two specific values pH 5.5 and 6.5 using acetate and phosphate buffers. The reason the lowest pH value of 5.5 was chosen is that it is the pH value of pure water in equilibrium with the global atmospheric CO_2 concentration (330 ppm), and this pH value of 5.6 was used as the boundary line for acidic precipitation [Demirak, A., 2007]. All pH, conductivity, and temperature measurements were recorded using a Hanna HI9828 Multiparameter probe. Each experimental condition was performed in triplicate to ensure statistical reliability.

Analysis of Cu and Pb in Sediment. Sediment samples were initially digested using aqua regia via a microwave digestion system. The resulting solutions were filtered through a 0.45 µm membrane filter into 50 mL volumetric flasks and diluted with ultrapure water.

The BCR sequential extraction procedure was applied to 1 g sediment samples to determine the chemical speciation of Cu and Pb across four fractions (Table 1). Concentrations of Cu and Pb in both the extracts and the total digested sediment were quantified using an Agilent Technologies 5100 ICP-OES.

Table 1

The steps of the chemical sequential extraction BCR procedure (Nemati et al., 2011;Demirak et al., 2021)

Step	Processes	Target fraction
1	0.11 M CH_3COOH (40 mL) 22 ± 5 °C, 16 h shaking.	Carbonates/exchangeable fraction (F1)
2	Residue + 0.5 M $NH_2OH.HCI$ (40 mL), pH = 2, 22 ± 5 °C, 16 h shaking	Oxides Fe/Mn /reducible fraction (F2)
3	Residue + 8.8 M H_2O_2 (10 mL), pH = 2, 22 ± 5 °C, 1 h Shaking; + 8.8 M H_2O_2 (10 mL), pH = 2, 85 ± 5 °C, 1 h Shaking; 1 M NH_4CH_3COO, pH = 2, 22 ± 5 °C, 16 h shaking	Organic matter and sulfides/oxidizable fraction (F3)
4	Residue + 6 mL HNO_3 + 2 mL HCl + 2 mL HF Microwave digestion	Residual fraction (F4)

Quality Assurance and Quality Control (QA/QC). To verify the accuracy and reliability of the analytical method, a recovery study was performed using Analytika AN9118(MN) certified reference material (CRM). The results, detailed in Table 2, show recovery rates between 90 and 110 %, confirming the high degree of analytical precision for this study. Furthermore, since the data did not show a statistically significant distribution, the Kruskal-Wallis test, a non-parametric test, was applied.

Table 2

Results of the recovery study with Analytika AN9118(MN) CRM

Metals	Certificate Value (mg/kg)	Value Obtained (mg/kg)	Recovery (%)
Bakır (Cu)	5.00	5.28	106
Kurşun (Pb)	5.00	5.24	105

Result and Discussion

The analysis of Cu and Pb concentrations and their respective chemical fractions in the sediment samples is summarized in Table 3.

Table 3

Analysis results of Cu and Pb in sediment

Metals	F1	F2	F3	F4	Total
Pb (mg/kg)	0.25 ± 0.005	4.60 ± 0.019	7.00 ± 0.029	44.87 ± 0.016	56.72
Cu (mg/kg)	2.00 ± 0.000	2.75 ± 0.005	2.35 ± 0.004	48.94 ± 0.008	56.04

The vast majority of Pb (91.4 %) was associated with the F3 and F4 fractions, indicating that the metal exists primarily in relatively stable forms. The total mobile fraction (F1 + F2) accounted for only 8.6 % of the total content. These findings suggest that the environmental risk posed by Pb in these sediment samples is moderate-to-low. However, a potential risk remains due to the possible mobilization of the F2 fraction particularly under anoxic (oxygen-free) conditions or the F3 fraction under oxidizing conditions [27].

Consistent with the behavior of Pb, Cu was found predominantly in stable forms, with the combined F3 and F4 fractions accounting for 91.5 % of the total concentration. Correspondingly low concentrations of Cu were detected in the mobile fractions (F1 and F2). These results indicate that the primary carrier phases for Cu in the sediment are organic matter and residual fractions. Nevertheless, significant shifts in environmental parameters, such as acidic conditions or intense redox (oxidation/reduction) fluctuations, could potentially mobilize a portion of these metals into the water column.

Pb Mobility in Sediment Samples. To investigate the influence of salinity and temperature on lead (Pb) mobility, sediment-water mixtures (1:2 w/v) were incubated in various aqueous media seawater, freshwater, and two seawater dilutions (50 and 25 %) across a temperature range of 25 to 50 °C.

As shown in Table 4, no statistically significant increase or decrease in Pb concentrations was observed over time across the different temperatures and water types. Measured values typically fluctuated between 0.01 and 0.06 mg/L, with average concentrations across the four temperatures remaining remarkably consistent (0.0317–0.0342 mg/L). These results suggest that within the studied range, Pb solubility is not significantly temperature-dependent. Interestingly, the highest average concentrations occurred at 40 °C (0.0342 mg/L) and 25 °C (0.0333 mg/L), while the lowest was recorded at 50 °C (0.0317 mg/L). This lack of a linear correlation suggests that thermal effects are negligible or are overshadowed by other dominant factors, such as sediment composition or internal experimental variation.

The low and fluctuating values observed likely stem from the analytical sensitivity of the instrumentation. The detection limits (LOD) for the Agilent 5100 ICP-OES were 5.5 µg/L for Pb and 1.5 µg/L for Cu, while the quantification limits (LOQ) were 16.5 µg/L and 3.5 µg/L, respectively. Consequently, the observed fluctuations may reflect experimental noise rather than a physical trend.

No significant kinetic trends were identified within the first 96 hours of measurement. At all temperatures, Pb concentrations reached an immediate steady state between the sediment and the aqueous phase. This suggests that Pb mobilization exists in a state of dynamic equilibrium within this timeframe. Furthermore, the low concentrations released into the water phase indicate that Pb is either released very slowly or is strongly sequestered by the sediment matrix [Geng, et al., 2024; Frang, et al., 2025].

Table 4

The amount of Pb extracted from the sediment-water mixture due to the effect of temperature

		6. Hour	12. Hour	24. Hour	48. Hour	72. Hour	96. Hour
SW	25 °C	0.05 ± 0.005	0.02 ± 0.005	0.04 ± 0.005	0.04 ± 0.010	0.05 ± 0.010	0.02 ± 0.005
	40 °C	0.02 ± 0.005	0.05 ± 0.015	0.04 ± 0.010	0.04 ± 0.005	0.04 ± 0.005	0.03 ± 0.035
	45 °C	0.02 ± 0.005	0.04 ± 0.005	0.05 ± 0.015	0.03 ± 0.350	0.04 ± 0.020	0.04 ± 0.005
	50 °C	0.05 ± 0.005	0.03 ± 0.005	0.04 ± 0.060	0.05 ± 0.020	0.02 ± 0.002	0.03 ± 0.005
FW	25 °C	0.02 ± 0.005	0.03 ± 0.015	0.02 ± 0.005	0.03 ± 0.050	0.03 ± 0.005	0.01 ± 0.005
	40 °C	0.03 ± 0.005	0.01 ± 0.005	0.02 ± 0.005	0.02 ± 0.005	0.04 ± 0.005	0.04 ± 0.020
	45 °C	0.03 ± 0.005	0.02 ± 0.015	0.02 ± 0.025	0.02 ± 0.005	0.02 ± 0.005	0.03 ± 0.005
	50 °C	0.02 ± 0.005	0.04 ± 0.020	0.02 ± 0.005	0.01 ± 0.020	0.03 ± 0.005	0.02 ± 0.240
1/2SW	25 °C	0.03 ± 0.010	0.05 ± 0.005	0.04 ± 0.005	0.02 ± 0.350	0.06 ± 0.020	0.04 ± 0.010
	40 °C	0.04 ± 0.005	0.02 ± 0.005	0.03 ± 0.005	0.04 ± 0.015	0.02 ± 0.020	0.02 ± 0.005
	45 °C	0.03 ± 0.015	0.03 ± 0.005	0.04 ± 0.010	0.04 ± 0.005	0.02 ± 0.045	0.05 ± 0.010
	50 °C	0.03 ± 0.005	0.02 ± 0.005	0.03 ± 0.015	0.03 ± 0.005	0.04 ± 0.015	0.04 ± 0.020
1/4SW	25 °C	0.03 ± 0.010	0.04 ± 0.025	0.03 ± 0.005	0.03 ± 0.005	0.03 ± 0.035	0.03 ± 0.015
	40 °C	0.03 ± 0.005	0.04 ± 0.005	0.03 ± 0.005	0.03 ± 0.015	0.03 ± 0.005	0.03 ± 0.005
	45 °C	0.02 ± 0.005	0.03 ± 0.200	0.03 ± 0.005	0.04 ± 0.005	0.03 ± 0.005	0.04 ± 0.030
	50 °C	0.03 ± 0.025	0.04 ± 0.005	0.03 ± 0.005	0.03 ± 0.005	0.04 ± 0.005	0.03 ± 0.005

SW: Sea water, FW: Fresh Water.

Contrary to the general expectation that increased temperature promotes desorption and solubility, this study found no such trend. For example, the average Pb concentration in freshwater remained constant at 0.023 mg/L at both 25 and 50 °C; similarly, seawater values remained stable at 0.037 mg/L at both temperature extremes.

Furthermore, salinity appeared to have no significant impact on Pb migration. While high ionic strength in seawater typically facilitates complexation or precipitation, the data did not reflect a clear shift in Pb behavior between freshwater and seawater environments. These findings indicate that Pb in these sediments is largely immobile. The sediment matrix likely composed of clay minerals, metal oxides, or organic matter binds Pb so effectively that fluctuations in salinity are insufficient to disrupt these bonds [4]. Ultimately, this study confirms that the sediment acts as a robust natural barrier, effectively trapping Pb and mitigating its impact on water quality [6].

In general, the solubility of lead (Pb) in aquatic systems is inversely proportional to pH; as pH increases, solubility typically decreases due to the formation of insoluble hydroxides or other stable complexes [7; 35]. Consequently, higher pH levels typically lead to reduced Pb migration into the aqueous phase. However, the mobilization of Pb from sediment to solution is highly sensitive to the interplay between pH, salinity, and the presence of specific complexing agents [35].

In this study, the observed Pb mobility in seawater did not strictly align with standard solubility trends. Values ranged from 0.01–0.04 mg/L at pH 5.5 and 0.02–0.05 mg/L at pH 6.5, with a slightly higher average at the higher pH (Table 5). This deviation may be attributed to the high ionic strength of seawater, where Pb can form soluble chloro-complexes (e. g., $PbCl^+$ and $PbCl_2^0$) that are highly pH-dependent [Acosta et al., 2011]. Furthermore, at higher pH levels within this specific marine matrix, the precipitation of insoluble hydroxides may be less favored than in lower-salinity environments [16].

Table 5

The amount of Pb extracted from the sediment-water mixture due to the effect of pH

	pH	6. Hour	12. Hour	24. Hour	48. Hour	72. Hour	96. Hour
SW	5.5	0.03 ± 0.001	0.04 ± 0.015	0.03 ± 0.005	0.01 ± 0.005	0.04 ± 0.250	0.03 ± 0.005
	6.5	0.05 ± 0.015	0.04 ± 0.005	0.03 ± 0.005	0.02 ± 0.055	0.04 ± 0.005	0.04 ± 0.250
FW	5.5	0.02 ± 0.005	0.02 ± 0.405	0.04 ± 0.015	0.03 ± 0.005	0.02 ± 0.005	0.04 ± 0.010
	6.5	0.01 ± 0.005	0.01 ± 0.005	0.02 ± 0.005	0.02 ± 0.060	0.02 ± 0.005	0.01 ± 0.005
1/2SW	5.5	0.03 ± 0.002	0.04 ± 0.005	0.02 ± 0.095	0.01 ± 0.005	0.01 ± 0.955	0.02 ± 0.050
	6.5	0.04 ± 0.005	0.03 ± 0.005	0.03 ± 0.015	0.03 ± 0.045	0.03 ± 0.005	0.04 ± 0.010
1/4SW	5.5	0.04 ± 0.001	0.04 ± 0.030	0.05 ± 0.015	0.03 ± 0.015	0.05 ± 0.040	0.02 ± 0.005
	6.5	0.03 ± 0.002	0.02 ± 0.005	0.02 ± 0.005	0.03 ± 0.200	0.04 ± 0.015	0.03 ± 0.080

Conversely, the results for freshwater were consistent with established literature. The average Pb concentration was 0.0283 mg/L at pH 5.5, dropping to 0.015 mg/L at pH 6.5. This decrease confirms that at low ionic strength, Pb solubility is limited by the precipitation of $Pb(OH)_2$ or other solid phases as pH rises. It should be noted, however, that the narrow pH range selected for this study makes a definitive characterization of mobilization trends challenging.

Lead concentrations did not exhibit a clear temporal trend but rather fluctuated throughout the study period. For instance, in seawater at pH 5.5, the concentration dropped to 0.01 mg/L at 48 hours before rising to 0.04 mg/L at 72 hours. In freshwater, the concentration remained at 0.04 mg/L at both the 24-hour and 96-hour marks. These fluctuations suggest that a state of rapid dynamic equilibrium was reached early in the experiment, or that the results reflect inherent experimental and analytical variations. Overall, the release of Pb into the water column appears to exhibit unstable behavior over time under these specific conditions.

Cu Mobility in Sediment Samples. To evaluate the influence of salinity and temperature on copper (Cu) mobility, sediment-water mixtures (1:2 w/v) were incubated across a range of thermal and saline conditions. As detailed in Table 6, a consistent kinetic trend was observed across all temperatures (25 °C, 40, 45, and 50 °C) and water types (seawater, freshwater, and various dilutions).

Table 6

The amount of Cu extracted from the sediment-water mixture due to the effect of temperature

		6. Hour	12. Hour	24. Hour	48. Hour	72. Hour	96. Hour
SW	25 °C	0.17 ± 0.005	0.15 ± 0.052	0.15 ± 0.320	0.15 ± 0.225	0.15 ± 0.005	0.14 ± 0.155
	40 °C	0.16 ± 0.005	0.15 ± 0.005	0.15 ± 0.150	0.15 ± 0.055	0.14 ± 0.040	0.15 ± 0.005
	45 °C	0.17 ± 0.005	0.15 ± 0.040	0.15 ± 0.005	0.17 ± 0.005	0.17 ± 0.040	0.15 ± 0.015
	50 °C	0.21 ± 0.015	0.16 ± 0.005	0.17 ± 0.025	0.19 ± 0.015	0.16 ± 0.025	0.16 ± 0.010
FW	25 °C	0.18 ± 0.005	0.15 ± 0.005	0.14 ± 0.005	0.14 ± 0.005	0.14 ± 0.020	0.14 ± 0.005
	40 °C	0.16 ± 0.005	0.14 ± 0.015	0.15 ± 0.250	0.15 ± 0.035	0.14 ± 0.020	0.14 ± 0.005
	45 °C	0.16 ± 0.001	0.14 ± 0.045	0.16 ± 0.005	0.18 ± 0.005	0.17 ± 0.002	0.14 ± 0.010
	50 °C	0.18 ± 0.150	0.18 ± 0.005	0.17 ± 0.005	0.17 ± 0.005	0.16 ± 0.030	0.16 ± 0.015
1/2SW	25 °C	0.16 ± 0.002	0.14 ± 0.050	0.14 ± 0.005	0.14 ± 0.005	0.14 ± 0.350	0.14 ± 0.050
	40 °C	0.15 ± 0.002	0.15 ± 0.005	0.15 ± 0.005	0.14 ± 0.005	0.14 ± 0.015	0.14 ± 0.005
	45 °C	0.16 ± 0.020	0.14 ± 0.020	0.14 ± 0.035	0.16 ± 0.045	0.19 ± 0.020	0.15 ± 0.005
	50 °C	0.17 ± 0.005	0.17 ± 0.025	0.16 ± 0.005	0.16 ± 0.005	0.17 ± 0.005	0.16 ± 0.005
1/4SW	25 °C	0.16 ± 0.120	0.14 ± 0.255	0.14 ± 0.015	0.14 ± 0.015	0.14 ± 0.025	0.14 ± 0.010
	40 °C	0.15 ± 0.005	0.14 ± 0.020	0.14 ± 0.005	0.14 ± 0.425	0.14 ± 0.005	0.15 ± 0.005
	45 °C	0.16 ± 0.002	0.15 ± 0.005	0.14 ± 0.002	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005
	50 °C	0.18 ± 0.005	0.17 ± 0.002	0.16 ± 0.005	0.17 ± 0.002	0.16 ± 0.005	0.16 ± 0.005

The highest Cu concentrations were generally recorded at the 6-hour mark, indicating a rapid initial mobilization from the sediment phase. Following this initial pulse, concentrations decreased significantly from the 12th hour onwards, eventually reaching a steady state between 24 and 96 hours. This plateau, characterized by relatively constant values or minor fluctuations, suggests that Cu undergoes rapid desorption followed by the establishment of a dynamic equilibrium between the sediment and the aqueous phase.

Temperature exerted a pronounced net effect on the transition of Cu from the sediment to the water column. Specifically, elevated temperatures influenced both the initial mobilization rate (at 6 hours) and the subsequent equilibrium concentration. The most substantial increase in Cu mobility was detected at 50 °C where both the rate of release and the final dissolved concentrations rose significantly.

These findings suggest that higher thermal energy facilitates the desorption of copper from sediment binding sites. From an environmental management perspective, these results demonstrate that temperature fluctuations whether driven by industrial thermal discharges, climate change, or seasonal shifts can substantially enhance the bioavailability of sequestered copper. Consequently, under elevated thermal conditions, sediments may transition from a «pollutant sink» to a «pollutant source», increasing the ecotoxicological risk to the overlying water column [23; 35]. Indeed, a check was performed to see if the data were significantly distributed. Since some data did not show a significant distribution, the Kruskal-Wallis test, a non-parametric test, was used to determine whether there was a significant difference. Temperature values showed a significant difference, especially in Cu SW and SW(1/4) ($p < 0.05$), while Pb distributions did not show a significant difference.

In contrast to the trends observed for lead (Pb), salinity appeared to have a secondary effect on Cu release. While Cu concentrations remained relatively comparable across the different aqueous media, values in seawater tended to be marginally higher, particularly at the 50 °C threshold. This suggests that while ionic strength plays a role in Cu solubility, thermal forcing remains the dominant driver of mobilization in these samples.

As demonstrated in Table 7, the pH range of 5.5 to 6.5 did not exert a significant or systematic influence on the mobilization of copper (Cu) from the sediment to the aqueous phase. Cu exhibits a highly complex chemical profile in aquatic environments; unlike lead (Pb), Cu^{2+} ions possess a notably higher affinity for sediment constituents, particularly organic matter, iron/manganese oxides, and clay minerals.

Table 7

The amount of Cu extracted from the sediment-water mixture due to the effect of pH

	pH	6. Hour	12. Hour	24. Hour	48. Hour	72. Hour	96. Hour
SW	5.5	0.18 ± 0.010	0.16 ± 0.015	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.001	0.18 ± 0.015
	6.5	0.17 ± 0.005	0.15 ± 0.005	0.15 ± 0.025	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005
FW	5.5	0.16 ± 0.005	0.15 ± 0.020	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005
	6.5	0.16 ± 0.250	0.15 ± 0.005	0.15 ± 0.002	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005
1/2SW	5.5	0.16 ± 0.025	0.16 ± 0.005	0.15 ± 0.015	0.15 ± 0.005	0.15 ± 0.030	0.15 ± 0.005
	6.5	0.16 ± 0.025	0.15 ± 0.005	0.15 ± 0.010	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005
1/4SW	5.5	0.17 ± 0.005	0.16 ± 0.005	0.15 ± 0.125	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.002
	6.5	0.17 ± 0.005	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005	0.15 ± 0.005

This strong thermodynamic binding suggests that the relatively minor shift in proton concentration between pH 5.5 and 6.5 is insufficient to overcome the high desorption energy required to release Cu into solution [11; 21; 34].

The pH range employed in this study (5.5–6.5) is relatively narrow, encompassing only slightly acidic to near-neutral conditions. It is likely that this interval does not span the critical pH threshold necessary to trigger significant copper desorption. While more pronounced mobilization might be expected under more extreme conditions (e. g., pH 4.0 or lower), these results indicate that variations between slightly acidic and neutral states are not a decisive factor in Cu mobilization for these specific sediment samples.

In marine environments, high chloride (Cl^-) concentrations typically facilitate the formation of soluble chloro-complexes such as $CuCl^+$ and $CuCl_2^0$ [8; 10; 11]. However, the lack of a statistically significant difference between freshwater and seawater in this study suggests that the influence of chloro-complexation remains secondary to the strong sequestering capacity of the sediment matrix under the current experimental parameters.

Comparative Mobility of Pb and Cu in Sediment-Water Systems. The average Pb concentrations released from the sediment into the aqueous phase across all time intervals (6, 12, 24, 48, 72, and 96 hours) were 0.037 mg/L for seawater, 0.023 mg/L for freshwater, 0.034 mg/L for 50 % diluted seawater, and 0.032 mg/L for 25 % diluted seawater. When expressed as a percentage of total Pb content, these values represent a mobilization rate of 4% to 6 % (Fig. 2).

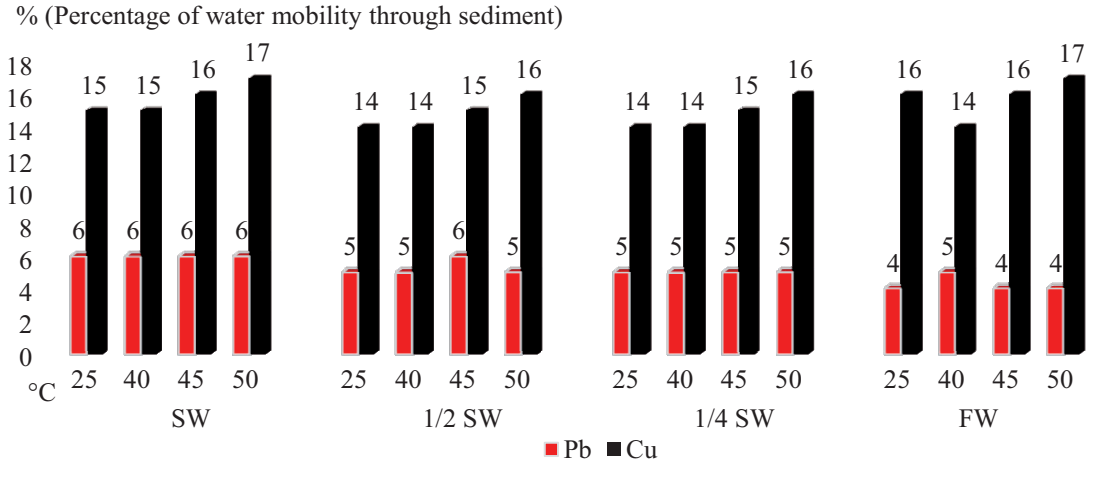


Fig. 2. Mobility rate of Cu and Pb into water

According to the BCR sequential extraction results, the combined exchangeable and acid-reducible fractions (F1 + F2) which represent the most mobile phases accounted for approximately 8.5 % of the total Pb (Figure 3). The experimental data indicates that Pb associated with the F1 fraction was entirely mobilized into the water column regardless of temperature, while a significant portion of the F2 fraction was also released. High concentrations of Pb in the F1 fraction typically signify recent anthropogenic pollution, which is characterized by rapid mobilization [17; 18; 32]. However, in this study, the relatively low proportion of Pb in the F1 fraction suggests a more stable, long-term sequestration within the sediment.

For copper (Cu), average concentration values in the aqueous phase were temperature-dependent, ranging from 0.143 to 0.175 mg/L (Figure 2). These values correspond to a mobilization percentage of 14 to 17 %. Notably, the proportion of Cu in the mobile BCR fractions (F1 and F2) was calculated at only 8.5 % (Fig. 3).

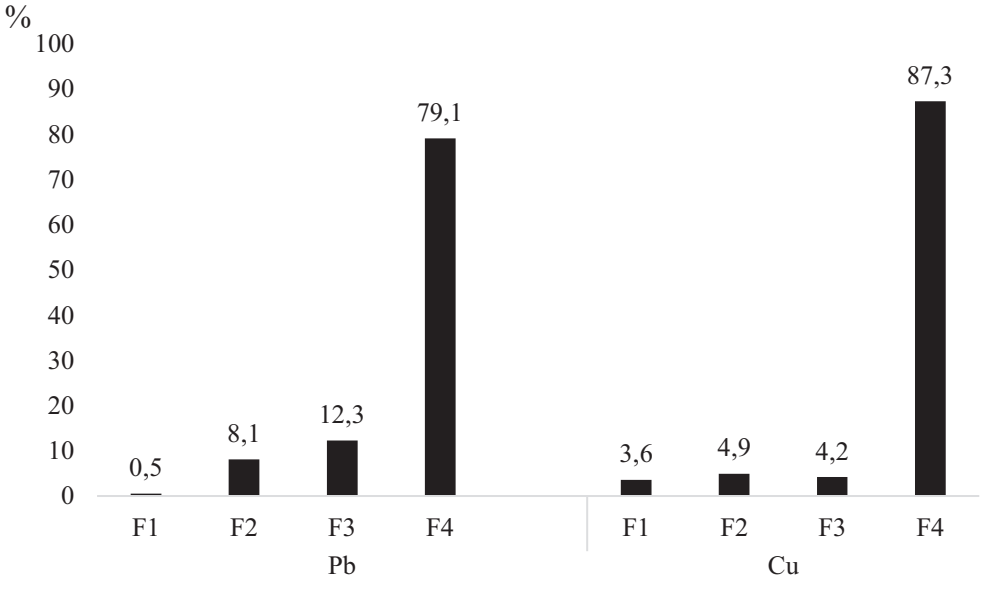


Fig. 3. Percentage distribution of fractional concentrations of Pb and Cu in sediment

This discrepancy indicates that, unlike Pb, the mobilization of Cu was not restricted to the exchangeable and acid-reducible fractions. While the Cu in F1 and F2 completely transitioned into the aquatic environment, the data suggest that additional Cu was released from the oxidizable (F3) and potentially even the residual (F4) fractions.

Several factors likely contribute to this enhanced mobilization:

– Thermal Effects: Increasing temperatures accelerate the microbial decomposition of organic matter, thereby facilitating the release of Cu into the water column [20].

– pH and Salinity: Under acidic conditions, the stability of soluble organic complexes decreases, promoting the formation of free Cu^{2+} ions [5; 33]. Furthermore, increased salinity can promote Cu transfer via the formation of soluble chloro-complexes [6; 19].

These results confirm that Cu is significantly more prone to mobilization than Pb under the studied environmental stressors, drawing from fractions previously considered «stable.»

Conclusion

Climate change is a critical driver that enhances the mobility and ecological risk of toxic metals in sediments by altering the salinity, pH, and thermal profiles of aquatic systems. This study investigated the release dynamics of Pb and Cu under various climate-simulated scenarios to provide robust environmental predictions. Furthermore, these findings underscore the necessity of integrating climate-metal interactions into future water quality policies and contamination mitigation strategies.

The primary conclusions of this study are as follows:

– Lead (Pb) Stability and Mobility: In the study area, Pb mobilization was found to be statistically independent of temperature and salinity fluctuations. The metal remains predominantly sequestered in stable forms within the sediment matrix. However, the fraction of Pb associated with the exchangeable and acid-reducible phases (F1 and F2) demonstrates a high capacity for rapid migration into both seawater and freshwater environments, regardless of external conditions.

– Copper (Cu) Sensitivity to Climate Variables: Unlike Pb, Cu mobility is significantly influenced by environmental temperature changes, which may elevate the ecotoxicological risk of the region. While Cu in the mobile phases (F1 and F2) readily transitions into the water column, climatic shifts in temperature, salinity, and pH also trigger the mobilization of Cu from previously «stable» phases, including the oxidizable (F3) and residual (F4) fractions. This suggests that Cu is highly susceptible to climate-induced desorption.

– Sediment Characterization of Lake Tuzla: The sediments of Lake Tuzla (Bosphorus) generally exhibit a stable geochemical structure regarding the studied metals. Nevertheless, the metals present in the mobile fractions are capable of complete migration into the aqueous phase. Notably, Cu demonstrates a significantly

higher overall tendency for mobilization compared to Pb, making it a more volatile contaminant under changing environmental parameters.

Ultimately, this study confirms that while the sediment acts as a natural barrier under current conditions, it may transition into a secondary source of pollution particularly for copper as climatic stressors intensify.

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