npj | Clean Water

www.nature.com/npjcleanwater

ARTICLE OPEN

Check for updates

Climate change extreme and seasonal toxic metal occurrence in Romanian freshwaters in the last two decades—case study and critical review

Andreea Maria Iordache[1], Constantin Nechita[2✉], Cezara Voica[3], Tomáš Pluháček[4] and Kevin A. Schug[5]

The relationship between metal levels in the Olt River ecosystem in southern Romania (measured during 2018–2019, with 1064 sediment and water samples) and daily climate data were explored to assess the need for targeted source identification and mitigation strategies. In 2018, there was a strong relationship between the sediment Pb, As, Cd, and Hg contents and temperature ($r > 0.8$, $p < 0.001$). Mercury in sediments had a positive correlation with precipitation, and Hg in the water correlated with minimum temperature in May 2018 ($p < 0.01$). In July 2019, heavy metals were positively correlated with precipitation and negatively correlated with temperature. According to nonsymmetrical correspondence analysis, the four climate parameters analyzed were linearly correlated with the frequency of metal detection ($p < 0.001$) in both years. The statistical analysis showed strong relationships between heavy metal levels and climatic factors and attributed the discrepancies in elemental concentrations between 2018 and 2019 to climate warming.

npj Clean Water (2022)5:2 ; https://doi.org/10.1038/s41545-021-00147-w

INTRODUCTION

The IPCC Working Group II Fourth Assessment Report found that many natural systems are already affected by regional climate warming[1]. Europe experienced its warmest air temperature on record in May–October 2018. This resulted in increasing mean and maximum lake surface temperatures (increases between 1.5 and 2.4 °C for over 46,557 lakes across the continent)[2]. In June–July 2019, two record-breaking heatwaves that exceeded more than 1 °C (especially in Western Europe) were purported to be one of the deadliest climate warming-related disasters in the world[3]. The challenges of climate warming-induced increases in the frequency and intensity of hydroclimatic extremes (e.g., droughts and floods) have promoted a new framework for the consideration of environmental stressors. Given the critical importance of freshwater ecosystems under a growing global population, long-term water quality monitoring assessment is imperative to understand regional hotspots of water scarcity[4].

The global contamination of freshwater systems is one of the critical environment-related issues associated with increased industrialization, natural and mineral resource exploitation, and social practices (e.g., tourism and local population growth)[5]. Heavy metals (HMs) released into river ecosystems are unequally distributed between aqueous and riverbed sediments. Metals transfer at the sediment-water interface depends on the chemical forms and physicochemical characteristics of water and sediment[6]. HMs, which are nonbiodegradable and nonthermodegradable elements, gradually become enriched in river environments and reach toxicity levels that are transferable to the biota. The dynamic balance between HMs in sediment deposits and water flow can be observed due to their significant remobilization and transfer under hydroclimatic extremes[7]. Under climate change, river discharges become more frequent, and riverbed elements accumulate in the overlying waters. Therefore, deeply buried pollutant deposits can considerably change the water composition and quality over time.

This study evaluated the extreme climate indices that explicitly linked environmental conditions with metal levels in water and sediments in 2018 and 2019. Our main objective was to create a holistic representation of the drivers with outcomes that will become common in the following years (e.g., heatwaves, water discharges, and floods). We determined if air temperature and rainfall are responsible for changing the temporal-spatial distribution of elemental levels in the sediments and water in Olt River lakes. Additionally, we reviewed the most relevant literature from Romania to reveal all hotspots polluted with HMs in the last two decades. Furthermore, we quantified the natural and anthropogenic sources linked to their seasonality to highlight the future risks that can occur once with increasing climate extremes, especially in a hot season. Finally, we identified aspects of these dynamics that can support policymakers and future research in the area subjected to such hazards.

RESULTS AND DISCUSSION

Climatic framework

The daily climate parameters investigated emphasized atypical weather conditions for the two extreme sites, #1, Cornetu Lake (316 m altitude), and #12, the Danube River upstream of the Olt River (27 m altitude), in 2018–2019 (Fig. 1a, b). Contrary to the pattern in 2018, the combined effect of summer days (SD) > 25 intervals and increased TX mean value shifted in 2019 (Fig. 1a), which increased the variability of temperature and the occurrence of extreme events. The historical perspective of climate reconstruction for more than two centuries[8] demonstrated significant

[1]National Research and Development Institute for Cryogenics and Isotopic Technologies—ICSI, Ramnicu Vâlcea 240050, Romania. [2]National Research and Development Institute for Forestry "Marin Drăcea"—INCDS, Câmpulung Moldovenesc 725100, Romania. [3]National Institute for Research and Development of Isotopic and Molecular Technologies—INCDTIM, Cluj-Napoca 400293, Romania. [4]Department of Analytical Chemistry, Faculty of Science, Palacky University, Olomouc CZ-771 46, Czech Republic. [5]Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019, USA. ✉email: ncincds@gmail.com

Published in partnership with King Fahd University of Petroleum & Minerals

npj nature partner journals

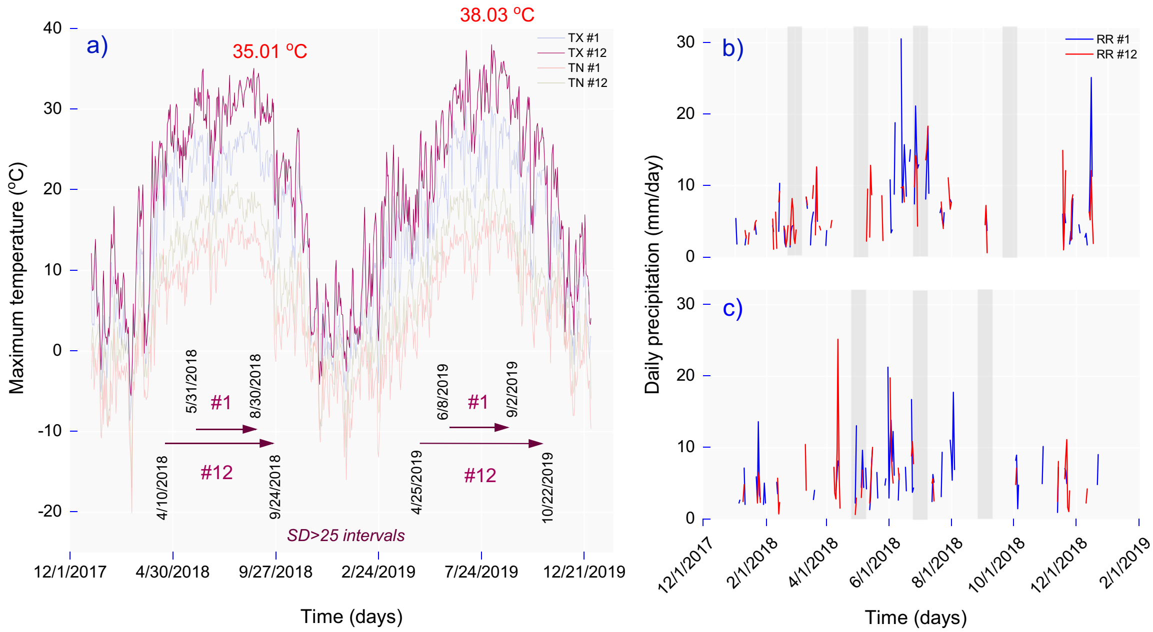

Fig. 1 Climate data for the extreme sites Cornetu Lake (#1) and Danube River—upstream of the Olt River (#12). a digital daily minimum (TN) and maximum (TX) temperature; **b** the sum of daily precipitation (RR) for sites #1 and #12 in 2018, and **c** the sum of daily precipitation (RR) for sites #1 and #12 in 2019; dark bars indicate the sampling periods; SD summer days. The climate data were extracted from European Climate Assessment and Dataset (ECA&D) database (https://www.ecad.eu/download/ensembles/download.php).

changes in precipitation anomalies for many years, but the 2018–2019 period was not found to be extreme (Fig. 2). The summer of 2018 was the third-warmest summer recorded for the studied areas (Fig. 2e) and belonged to the fourth warmest global record since 1880[9,10]. In 2018–2019, unprecedented dry conditions from spring/summer were reported all over Europe[11,12] where positive anomalies characterized northern and western Europe, while south-eastern Europe was marked by negative anomalies[13]. We observed significant differences ($p < 0.001$, two-tailed hypothesis) between mean extreme site values for daily mean temperature (TM), daily minimum temperature (TN), daily maximum temperature (TX), and total daily precipitation (RR) (t-values $= -14.50$, -15.19, -14.89, and 6.34, respectively) in the time interval between 1960 and 2019. Consecutive dry days (CDDs) have decreased in Cornetu Lake since the 1980s, but no trend was observed for the Danube River upstream of the Olt River. This indicated that climate change effects at intramountain sites are stronger than those at lower altitudes (Fig. 2f). Since 1980, the extreme temperature intensity indices (TXx, TNx, TXn, and TNn) have shown a significant positive trend, similar to those in other geographical regions[14].

The ETCCDI indices indicate changes in frequency, intensity, and duration of extreme events responsible for flash floods in the last two centuries. Thus, the percentile-based indices TN10p (cold nights) and TX10p (cold days) significantly decreased after 2000, while the frequency of warm nights (TN90p) and warm days (TX90p) increased since 1984 (Fig. 2a–d). Further climate projections indicated fewer days of below-freezing temperatures by the mid-21st century[15]. Our study area exhibited a significant increasing trend for extreme temperatures in the past, but only in summer and winter. Substantial changes were found during nights rather than daytime, comparable with research observations from other geographical areas[16]. The warm spell duration index (WSDI) showed a sharp increase starting at the beginning of the 1990s, with a maximum for the Cornetu Lake (2018 indices ranked third) and Danube River upstream of the Olt River (2019 ranked fifth) sites (Fig. 2e). The intensity of heavy precipitation events in the former five-day events (Rx5day) has been positive since 1960, with a divergent tendency for southern Europe[17]. The highly wet days (Rx5day) index increased only at intramountain sites. However, it did not exhibit a consistent statistically significant trend (within the 1 SD range), instead of showing a positive anomaly for #1 in 2018 and a negative anomaly for #1 in 2019 and negative values for #12 in both years (Fig. 2h). The incremental tendency of extreme precipitation indices is less spatially consistent and strongly correlated with elevation, indicating future risk for intramountain sites. The intensification of short-duration heavy rain is responsible for severe flash discharges, and the Rx5day increase is associated with greenhouse gas forcing regulating hydrological cycles[18].

Compared with average, few extreme values were found for precipitation in both sites in 2018–2019. In recent decades, severe positive anomalies (RR99p) (2014, 2008, 2005, and 1998) and extreme adverse events (2011–2012, 2019, 2006, 2002, and 1999) were observed for Cornetu Lake, but only partially and with lower intensity for the Danube River upstream of the Olt River (Fig. 2j). A differential change in the annual cycle shows increased summer extreme temperatures coupled with an increased winter temperature at plain sites, consistent with what has been reported in the Mediterranean Basin[19]. Based on climate parameters quantifying spring-summer conditions, in 2018, the record drought in 2019 was exceeded, especially at sites in the intramountain area (#1–9). Several models and observations on the 2018 heatwave drought indicated only a 12% probability of occurrence under our current climate and an overhead 50% chance in the future during the mid-21st century[20]. Similar drought conditions are expected to become common according to future projections. Overall, the 2018 event will be the first with synchronal spring and summer anomalies[21].

Temporal-spatial distribution of heavy metals in sediments and water

The national sediment background values, namely, 150, 100, 40, 35, 85, 29, 0.8, and 0.3 mg/kg for Zn, Cr, Cu, Ni, Pb, As, Cd, and Hg, were included for this survey due to the lack of consistent data in the study area. Extreme concentrations for analyzed elements that

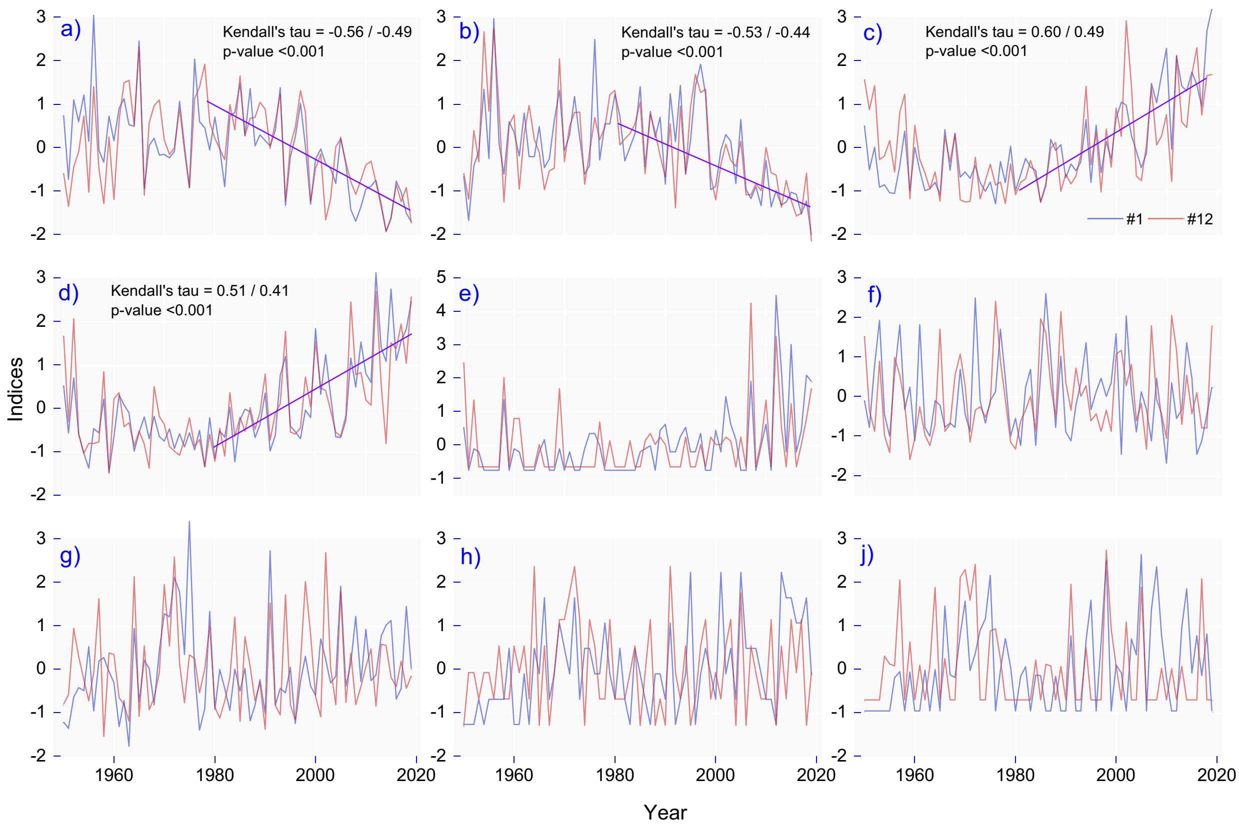

Fig. 2 Normalized values for extreme climate indices in extreme sites Cornetu Lake (#1—blue line) and Danube River—upstream the Olt River (#12—red line). **a** TN10p—the annual percentage of days when TN < 10th percentile; **b**TX10p—the annual percentage of days when TX < 10th percentile; **c** TN90p—the annual percentage of days when TN > 90th percentile; **d** TX90p—the annual percentage of days when TN > 90th percentile; **e** WSDI—the annual number of days contributing to events where six or more consecutive days experience TX > 90th percentile; **f** CDD—the maximum annual number of consecutive dry days (when precipitation < 1.0 mm); **g** RRX5day—maximum 5-day precipitation total; **h** RR20mm—annual number of days when precipitation ≥ 20 mm, and **j** RR90p—the annual percentage of days when TX > 90th percentile. The climate data were extracted from European Climate Assessment and Dataset (ECA&D) database (https://www.ecad.eu/download/ensembles/download.php).

exceeded the national standards[22] varied between sites and investigated periods. The river section water was alkaline with mean pH values of 8.1 ± 0.37 (2018) and 8.6 ± 0.77 (2019) and maximum pH values of 9.1 (2018) and 11.99 (2019). A faster HM release rate from sediments is expected at lower pH values[23]. The temporal-spatial distribution of Cd, Hg, As, and Pb in the water and sediments of the mainstream Olt River lakes showed variability linked to water volume and the rate of evapotranspiration during summer days (Fig. 3). The mean contents of Zn, Cr, Cu, Ni, Pb, As, Cd and Hg were (in mg/kg) 69 ± 5.1, 23 ± 1.8, 21 ± 2.0, 37 ± 2.1, 26 ± 2.1, 94 ± 8.5, 0.36 ± 0.02, and 0.12 ± 0.01, respectively (Supplementary Table 1). Representative studies performed in various Romanian environments indicated that Olt River lakes are highly polluted with HMs[24–26]. The measurements performed in the present study corroborate this view.

Except for the two extreme values measured, the 2019 average contents of Zn and Ni in the sediments were 2.8 ± 1.9 and 2.12 ± 1.7 mg/kg (Fig. 3). The extreme metal contents of Cr, Cu, Pb, As, Cd, and Hg were significantly higher in 2018 (100, 176, 94, 240, 1.23, and 0.23 mg/kg, respectively) than in 2019 (4.4, 17, 12, 7.7, 0.38, and 0.02 mg/kg, respectively). Temporal assessment could be accomplished only for sediments from site #8 (Băbeni Lake), which represents the area highly contaminated with Hg (44 mg/kg)[24]. The two-sample test for variance demonstrated that the differences in Zn, Cu, As, Cd, and Hg contents for all sampling sites in 2018 and 2019 were statistically significant ($F = 0.28$, 3.7, 18, 1095, 4.8, and 73; $p < 0.001$). The two-sample t-test for the mean ($p < 0.001$) showed a significant difference between yearly concentration levels only for Pb, As, Cd, and Hg ($t = 8.3$, 15, 7.2, and 4.3) when equal variance was assumed. Even so, the lowest amounts of As, Cd, Pb, and Hg were located downstream of river and lakes sediments; they were highest in the intramountain area. Except for sites #3, #8, #12, and #19, the soluble metal concentration was over eight times higher in 2018 than in the 2019 seasonal profile.

In lake water, the concentrations of HMs and trace elements usually do not exceed the national threshold values. In 2018–2019, the maximum HM concentrations in water were in the range of 6.9–94 µg/L As, 0.84–15.75 µg/L Pb, 1.3–6.5 µg/L Cd, and 3.3–1.56 µg/L Hg. In the case of Hg, a very high level up to 47 µg/L was found for site #8 (Băbeni Lake) in 2014–2016, indicating large metal deposits downstream of the Râmnicu Vâlcea Chemical Industrial Platform[25]. The two-sample test for variance showed significant differences ($p < 0.001$) between samples collected in 2018 and 2019 for As, Pb, Cd, and Hg ($F = 98$, 544, 0.01, and 2.86, respectively). The two-sample t-test (with equal variances assumed) demonstrated a significant difference between the means only for As and Pb ($t = 3.6$ and 4.0; $p < 0.001$). Exceptional concentrations were measured for As in March 2018, when they reached nine times the national threshold for surface water (94 µg/L). For Pb, Cd, and Hg, the results indicated enriched levels in both investigated years exceeding the first degree of pollution. The mean concentration (µg/L) and the standard deviation were 12 ± 1 (As), 2.6 ± 4 (Pb), 0.48 ± 0.1 (Cd), and 0.97 ± 0.9 (Hg) in 2018 and 2.6 ± 1.9 (As), 0.18 ± 0.1 (Pb), 0.8 ± 1.4 (Cd), and 0.94 ± 0.5 (Hg) in 2019. The combined analysis of Fig. 3 indicates that for Cd, Hg,

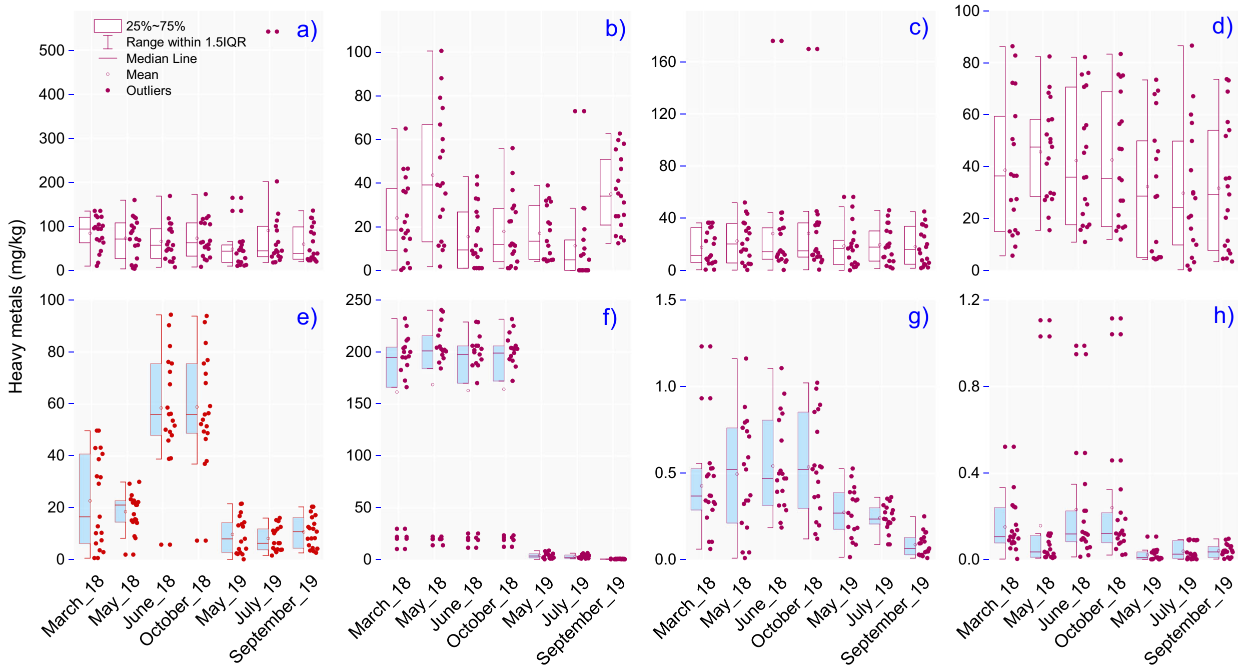

Fig. 3 Distribution of heavy metal sediment content collected during seven periods in 2018−2019 and 19 sites along middle and lower Olt River riches. a Zn, **b** Cr, **c** Cu, **d** Ni, **e** Pb, **f** As, **g** Cd, **h** Hg.

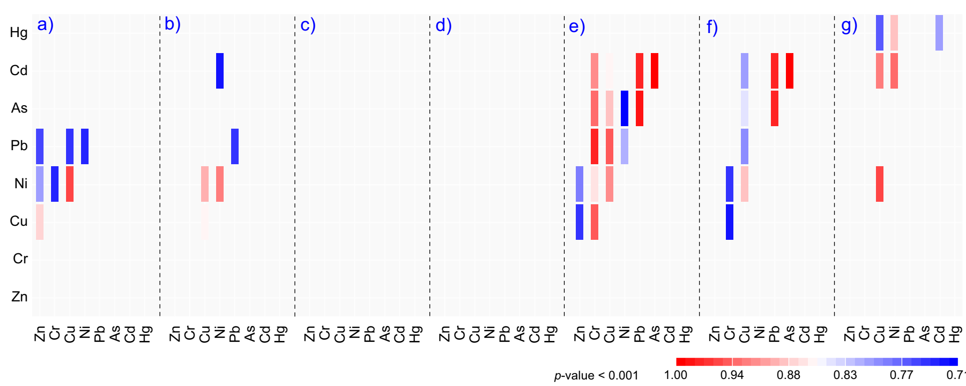

Fig. 4 Significant Pearson's correlation diagram ($p < 0.001$) of heavy metal concentration from the Olt River basin in the 19 sites investigated. a 2018 March, **b** 2018 May, **c** 2018 June, **d** 2018 October, **e** 2019 May, **f** 2019 July, and **g** 2019 September.

Pb, and As, the seasonal and interannual variability in trace element contents was significant.

Climate-trace element relationships

Until the mid-century, projected variability in south-eastern Europe revealed a sustained warming process with decreasing precipitation amounts and increasing evapotranspiration in the investigated study area[27]. Climate change interacts with the hydrological cycle on global and regional scales. Low river discharge (limited dilution of the chemical load from point sources) and high temperature during summer/autumn increased metal levels. In March/June 2018 and July/September 2019, the highest correlation between trace elements and daily climate data were calculated (Supplementary Table 2). The correlation was negative with temperature and positive with rainfall in spring (March). In June 2018 and July/September 2019, the correlation indices were positive with temperature and negative with precipitation. In water, temperature represents the main factor that controls multiple chemical reactions. Significant differences appear during the daily and diurnal conditions and, associated factors, such as thermal mass, restrict the seasonal oscillation in spreading temperature heatwaves in water. The exchanges in water (vertical, lateral, and longitudinal flow)[28] are fundamental in the interaction between various chemical elements in the river body, such as the intake and reduction of physicochemical compounds in water and vertical redox gradients in sediments. Dammed reservoir traps are responsible for the sedimentation of HMs and concordance with water fluxes. The most polluted deposits materialize in the bottom layers[29], reaching up to 90% in the case of Pb, Cd, and Cu. Differences in sediment texture, pH, redox potential, salinity, moisture, organic matter and electrical conductivity in 2018–2019 compared to 2014–2015 in the Viridi Channel (Côte d'Ivoire, West Africa) were also found[30]. Thus, the scale of climate change effects on water ecosystems has been evident worldwide since the recent 2018–2019 heatwaves.

The correlation matrix emphasized a weak but significant relationship between trace elements in 2018 (narrow in June and October) and a robust correlation in 2019, especially in May (Fig. 4). The relationships between Zn–Cu–Ni–Pb in 2018 indicated similar effects of anthropogenic activities. At $p < 0.01$, Hg (sediments) had a positive relationship with RR ($r = 0.58$) in May

Published in partnership with King Fahd University of Petroleum & Minerals

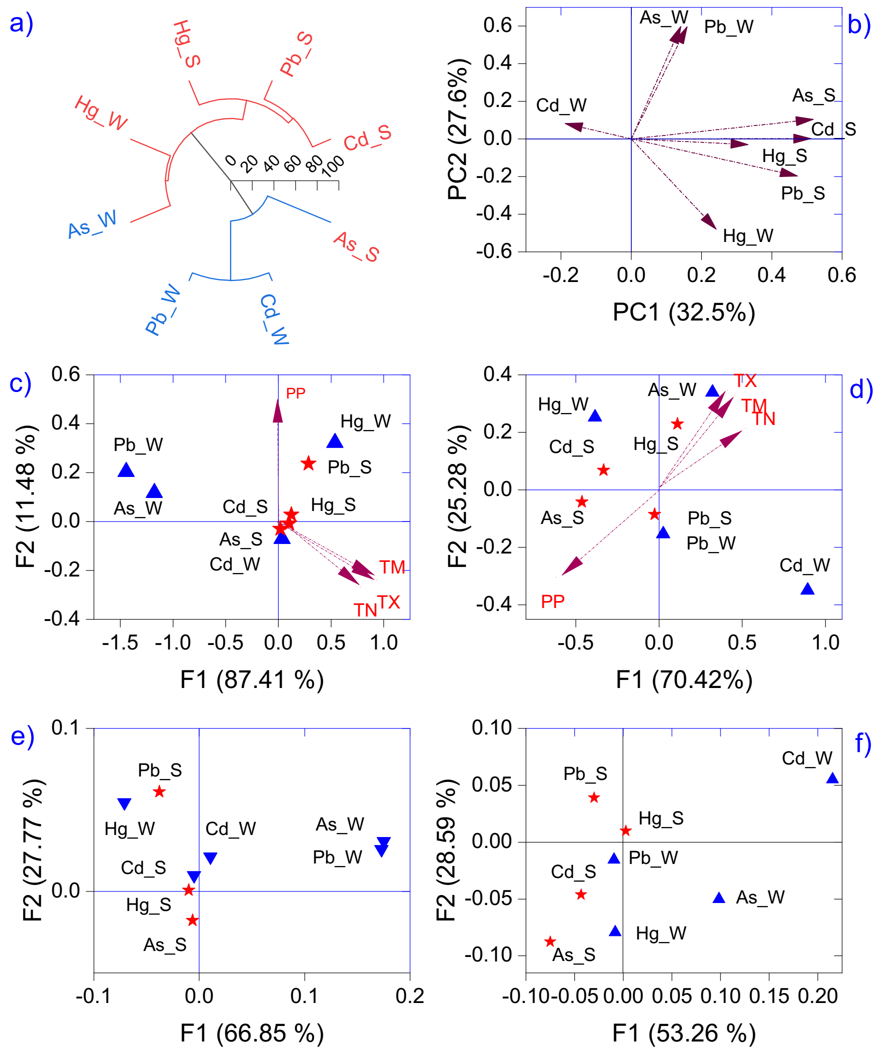

Fig. 5 The multivariate statistical results for heavy metals and climate data. a Dendrogram of hierarchical cluster analysis (HCA) based on similarities; **b** principal component analysis (PCA) to provide a grouping of variables; **c** canonical correspondence analysis (CCA) for 2018 datasets; **d** CCA analysis for 2019 datasets; **e** non-symmetrical correspondence analysis (NSCA) demonstrated high variability of data in 2018; **f** NSCA indicated insignificant variability of data for ($p < 0.001$) in 2019.

2018, whereas Hg (water) was correlated with TN ($r = 0.68$), RR ($r = 0.71$), TM ($r = -0.84$), TX ($r = -0.79$), and TN ($r = -0.88$) in July 2019. (Supplementary Table 2). Our results demonstrated strong relationships of As with Cr, Cu, Ni, and Pb ($r = 0.94$, 0.89, 0.71, and 0.99, respectively) and of Cd with Cr, Cu, Pb, and As ($r = 0.91$, 0.85, 0.97, and 0.99) in May 2019. Fewer associations were noted in July (Pb vs. As and Cd; $r = 0.97$) and September (As vs. Cd, $r = 0.99$ and Hg vs. Cu, Ni, and Cd, $r = 0.76$, 0.88, and 0.80). The metals originated from anthropogenic activities, including mining, waste plant discharge, and industrial plants[26]; these sources explain the strong-significant correlations revealed in the data analysis.

The Pearson product-moment correlation coefficients indicated that in March, there were negative, robust relationships ($p < 0.001$) of lead in sediments with the mean and maximum air temperatures (Supplementary Table 2). The positive correlation between lead in water and precipitation ($r = 0.91$) found only in May 2018 can explain the significant differences in elemental trends during 2018–2019. Furthermore, arsenic in May 2018 for $p < 0.001$ correlated negatively with maximum temperature ($r = -0.70$) and positive with precipitation ($r = 0.72$). A divergent relationship was noted in June 2018 and July 2019 for TX ($r = 0.71/0.72$) and RR ($r = -0.72/-0.79$). The influence of extreme temperature on Pb and As (from water and sediments) was strongly negative in spring (Supplementary Table 2).

Lead reductive oxide dissolution could be increased 36 times at 20 °C relative to a lower temperature of 4 °C[31]. A significant increase in the As level at 25 °C was observed compared to a reference of 11 °C[32]. The postdepositional As mobility in lacustrine environments were found to be correlated with the dissolution of iron-(oxy) hydroxides and coprecipitation with sulfides. Labile organic C is expected to increase under projected climate warming via a redox-mediated mechanism and organic loading, which interacts with As instability in the river system.

Intermetal relationships and factor loadings

Various multivariate techniques were used to identify and explore HM sources and the ecological status of the Olt River ecosystem. The hierarchical dendrogram resulting from the HCA approach shows that trace elements were categorized into two distinct clusters. The first homogeneous group consisted of As, Cd, Pb, and Hg in sediments and Hg in water. The second formed a single branch consisting of As, Pb, and Cd in water, indicating anthropogenic drivers of the HM and trace elements analyzed. In the plot, the *y*-axis shows similarity with a circular orientation (Fig. 5a). PCA was applied, and the high Kaiser-Meyer-Olkin value (0.68) ($p < 0.001$) from Bartlett's test indicated that the results were representative. Two eigenvectors were superior to one, and their components explained 60% of the total variance. Thus, the trace elements formed three groups, with the first containing those from sediments and Hg in water, the second containing Pb, and the third containing the Cd in water, indicating different origins of these elements (Fig. 5b).

NSCA revealed a linear dependence between trace elements related to site and period data in 2018 ($p < 0.001$) compared to 2019 when the results were nonsignificant for the same statistical significance test. The Goodman–Kruskal tau index is a measure of asymmetry for two-way contingency tables. In our case, one-way correspondence between variables had a value of 0.004 (2018) and 0.01 (2019). The cumulative percentage of inertia presented by the first two factorial axes explained 94% of the variance in 2018 (Fig. 5c) and 81% in 2019 (Fig. 5d). Trace elements with a significant contribution to the orientation of the two primary factorial axes were Pb in sediments and As in water in 2018 (Fig. 5e, f). The contribution of those elements explained the trend in both years. The organic forms of As typically occur in waters highly affected by industrial activities at a pH of 6.5–8.5. The overall conclusion is that human-derived sources are dominant in trace element origins. The first two axes of the CCA analysis explained 98–95% of the trace element variance based on climate (TM, TN, TX, and RR daily data) in 2018–2019, corresponding to 55–75% of the inertia. According to the permutation test (1000 random permutations), the significant ($p < 0.001$) effects of the four climate parameters on the observed frequency of trace element concentrations were assessed, and it was concluded that the data were linearly related to site variables for both years.

Climate-induced elemental increasing trend in the last two decades

Impressive HMs concentration in lake sediments (quasi-static environments with a low flow velocity that progressively accumulated deposits and pollution) were noted in the last two decades. Investigations in eastern Romania (Prut River) revealed concentrations of Cu (67 mg/kg), Cd (0.7 mg/kg), Pb (30 mg/kg), and Zn (98 mg/kg) in 2001–2010 and indicated that this water body was without pollution risk[33,34]. In contrast, most studies on western and southern Romanian rivers have shown increased metal levels in recent decades[35–37]. Extreme HM concentrations were noted in 2000[38–40], 2006[24], 2008[41], 2012[42–44], 2014[45], 2015[46], 2017[47], and 2019[26,48].

In 2000, a dam containing toxic waste was damaged[27] and released into the Lăpuș and Someș Rivers (a tributary of the Tisza River) more than 120 tons of cyanide and 20,000 tons of sediments containing HMs, representing over 100,000 cubic meters of waste. The investigations revealed unusual meteorological conditions induced by heating never recorded before during the last century, which caused an abundance of precipitation in December 1999. The abruptly reduced temperatures and snowfall from the beginning until mid-January was followed by increasing the temperature and abrupt snowmelt, causing braking dam[49]. The contaminated waves affected the Tisza and Szamos Rivers, and sediments collected in June 2000 and February 2001 showed very high pollution, with Cu, Cd, Pb, Cr, Ni, and Zn in sediments reaching 664, 23, 374, 159, 85, and 3095 mg/kg, respectively. Furthermore, the summer of 2006 was exceptionally hot, with the maximum temperature at the end of June causing it to be recorded as the warmest month since official instrumental measurements began[50]. In January 2008, a freezing snap occurred, and during July, dry climatic conditions were affected by floods and drought in northern Europe[51].

In lake sediments, during 2008–2016 as much as 593 mg/kg Pb, 82 mg/kg Cd, 1784 mg/kg Zn, 143 mg/kg Ni, 725 mg/kg Cr, and 277 mg/kg Cu were found[35,52,53] (Supplementary Table 4). In south-eastern Romania (near the Black Sea, Tasaul Lake), sediments were investigated for HMs from 2011 to 2013, showing values of 34, 133, 57, 103, 0.14, 17, and 83 mg/kg for Pb, Zn, Ni, Cr, Hg, As, and Cu, respectively[48]. In central Transylvania, the Gilău dam on the Someș River was reported during 2008–2011 to be sediment enriched with Pb, Cd, Zn, Cr, Hg, As, and Cu (40, 2.97, 193, 192, 0.28, 172, and 85 mg/kg, respectively)[54]. In river sediment from Baiaga stream (also Transylvania) located near two sterile mining dumps in Hunedoara County, extensive contents of Cu, Cd, Pb, Cr, Ni, As, and Hg (298, 106, 467, 274, 386, 1197, and 1.21 mg/kg, respectively)[36] were noted in April 2014, the year characterized by the warmest yearly average temperature in Europe.

Various accidental discharges or constant HM contamination from distinct sources have reached water bodies, where they have been deposited in sediments or transported by floods downstream into the Danube River. Therefore, severe pollution of the Danube River and the Black Sea has been recently reported[55]. The HM contents measured in Danube River sediments were comparable in 2011–2013 for Cu, Zn, Cr, Ni, Cd, and Pb (86, 206, 68, 93, 1.33, and 77 mg/kg, respectively)[56] with those in 2012–2014 (42, 106, 46, and 38 mg/kg, with Cd and Pb not included in this study)[57]. Climatic records described the year 2012 as the hottest and driest summer in south-eastern Europe[58]. In 2017, called the "Lucifer" plague year in Europe, showed the most sustained extreme heat event from January to October worldwide[59], and the contamination levels of the Danube River increased to 1570, 1049, 488, 61, 2.9, and 1315 mg/kg, respectively[57]. Consistent with these reports, the Olt River is not Romania's most polluted water body, but it has contributed significantly to maximizing HM pollution in Danube River sediments[24,26,60,61].

Water pollution in Romanian lakes appears to be less impressive than that in sediments. The maximum metal concentration in the Danube River water in 2011–2014 fluctuated significantly for Cu (9.1–147 μg/L), Zn (79–15 772 μg/L), Cd (0.19–32 μg/L), and Pb (3.18–15.5 μg/L)[44,56,57]. Industrial activity and mining decreased significantly after 1990 in Romania. Even so, various studies have indicated considerable ecological disaster-level contamination by metals and trace elements that have affected water ecosystems in recent years. The mentioned reports portray the increasing vulnerability of freshwater environments to HM contamination due to extreme weather conditions that have advanced over the past 20 years. Additionally, the results highlight the predisposition of the western and southern regions of the country to the occurrence of exceptional HM pollution events; these regions are also expected to be exposed to increasing climate extremes according to future projections.

Policy themes for water conservation

National long-term policy themes for clean freshwater require the commitment of society and decision-makers to strengthen and apply strategies. They need to promote water recovery and reduce the factors that deteriorate the quantity and quality of water resources. Romania is poor in freshwater resources (ranked 13th in Europe) and is dependent on precipitation. Climate warming leads to decreased river runoff due to increasing air temperature, which, in turn, accelerates evapotranspiration. Changing maximum monthly mean discharges from spring to winter have already been demonstrated in the studied area[62], which will affect the insufficient water supply and increase the need for agricultural practices. In addition, the stress on the water will increase pollution frequency, reduce dissolved oxygen, and lead to eutrophication. Far from the end, floods and flash floods will shift from spring and summer to winter (e.g., the dam break in Maramureș County in January 2000).

With all examples presented in this analysis, critical thematic areas for transboundary policymakers, environmentalists, and decision-makers are highlighted for possible discussion concerning future management practices and endorsement strategies. The modern society acts through various engines to disrupt natural ecosystems. The most evident are sediment exploitation from the riverbed, sometimes until bedrock, or river regularization constructions. Also, population pressure is a paramount driver of society's needs for wood exploitation and processing facilities and the production of industrial waste. Organic pollution resulting from untreated domestic waste discharges, composites from sawdust and recycled plastics, environmental pollution, and fertilizer runoff accentuate the river ecosystem's stress. Population pressure (a complex of socio-economic dimensions), corruption, and poverty negatively impact the sustainable use of water resources. Therefore, mitigating these drivers' effects will be an alternative for complex policy regulations with long-term positive impacts. The government needs to cooperate through financial support development programs with water and forest management institutions to motivate and involve skill transfer at the national level. In addition, the policies can implement long-term monitoring programs that can offer support in understanding future implications of climate change on aquatic ecosystems and facilitate transparency.

METHODS

Field sampling and climate

The sampled sites were distributed along the middle and lower courses of the Olt River. They were selected to correspond to different hydrostratigraphic units with varying typologies of the water drainage system. Our model of HMs pollution in the area was based on 16 representative lakes with different environments and geomorphologic-hydrodynamic regimes in which HMs accumulate. The other three sampled sites were along the riverbed, one in the Olt River before the point at which it discharges into the Danube River and two in the Danube River upstream and downstream of the Olt River discharge point (Supplementary Table 3). Samples were collected during four periods in 2018 (March, May, June, and October) and three periods in 2019 (May, July, and September) to cover the various thermal and hydrological conditions that occur in the Olt River. Climate data derived from the European Climate Assessment and Dataset (ECA&D) archive were extracted for each sample site from 1950–2019. Four parameters, including the daily mean temperature (TM), daily minimum temperature (TN), daily maximum temperature (TX), and total daily precipitation (RR), were used to investigate differences in 2018–2019 climate extremes. The Expert Team on Climate Change Detection and Indices (ETCCDI) defined a set of indices for evaluating multidecadal changes in the extreme climate of the mid-20th century and the beginning of the 21st century. The indices included a definition for heatwaves; they are defined as the number of days in a year exceeding a specific threshold with a fixed value or relative to a base period or day-count index. The selected subset of extreme climate event indices was calculated to describe the frequency, intensity, and duration of such events. The higher precipitation over 5 days (Rx5day) index can indicate significant floods, and the maximum length of a dry spell (CDD) highlights intense drought seasons. The warm spell duration index (WSDI) calculated using a percentile-based threshold was used to investigate the impact of heatwaves. The closed vessel microwave acid digestion, atomic absorption spectroscopy, and inductively coupled plasma mass spectrometry instruments were used to determine total levels of HMs in environmental samples (details are summarized in Supplementary Methods).

Data analysis

The differences between climate data from the two extreme sites (#1 and #12) were assessed using two-sample t-tests for the difference of means. The Shapiro-Wilk normality test was used to check the normality of the data. The two-sample t-test and two-sample test for a variance were applied to compare the central values of the underlying distributions of the concentration levels between 2018 and 2019, respectively. HMs were visualized using boxplots to identify outliers, and extreme values were plotted as individual points. The values are presented as the mean ± standard deviation (SD). The relationships between HMs from sediments were investigated using Pearson correlation coefficients at a significance of $p < 0.001$. Hierarchical clustering analysis (HCA) and principal component analysis (PCA) were used to analyze the possible contamination sources of HMs in sediments and water. The HCA approach used the squared Euclidian distance, following the Wards method, to approximate the distance between pollutant clusters. Principal components (PCs) were extracted using Varimax with the Kaiser normalization and rotation method. The accuracy of the PCA was assessed prior to using Bartlett's sphericity test and the Kaiser-Meyer-Olkin (KMO) adequacy test. Canonical correspondence analysis (CCA) was applied to analyze the interaction between the trace element distribution and daily climate data. The nonsymmetrical correspondence analysis (NSCA) unconstrained ordination method was used to explore variability in a dataset associated with metal concentration using the Goodman-Kruskal tau index for two-way tables to decompose associations. We reviewed systematic literature following the PRISMA protocol to compare our results with those from similar studies in Romania conducted in the last twenty years. The literature search was performed on Web of Science, Google Scholar, and Scopus using keywords containing "Olt River" or "Romania heavy metal pollution" or "heavy metal", or "trace elements", or "freshwater metal contamination" or "water and sediments heavy metal pollution." Initially, no constraint was placed on the year of the publication. The first search returned 17,700 documents; thus, we restricted the analysis to 2000–2021. We excluded references marked as duplicates, erroneous records from studies with other geographical regions, and conference abstracts and books without quantitative data, resulting in a database with 65 studies selected for detailed review (Supplementary Table 4).

DATA AVAILABILITY

The data that support the findings of this study are available from the National Research and Development Institute for Cryogenics and Isotopic Technologies. Still, restrictions apply to the availability of these data, which were used under license for the current study and are not publicly available. Data are, however, available from the authors upon reasonable request and with permission from the National Research and Development Institute for Cryogenics and Isotopic Technologies.

Received: 10 August 2021; Accepted: 1 December 2021;
Published online: 13 January 2022

REFERENCES

1. Parry, M. et al. (eds.). *Climate change 2007-impacts, adaptation and vulnerability: Working group II contribution to the fourth assessment report of the IPCC*. (Cambridge University Press, 2007).
2. Woolway, R. I., Jennings, E. & Carrea, L. Impact of the 2018 European heatwave on lake surface water temperature. *Inland Waters* **10**, 322–332 (2020).
3. CRED. *Disaster year in review 2019*. https://www.emdat.be/cred-crunch-58-disaster-year-review-2019-0. (2020).
4. Mekonnen, M. M. & Hoekstra, A. Y. Four billion people facing severe water scarcity. *Sci. Adv.* **2**, e1500323 (2016).
5. Hembrom, S., Singh, B., Gupta, S. K. & Nema, A. K. In *Contemporary Environmental Issues and Challenges in Era of Climate Change* 33–63 (Springer, 2020).
6. Wijesiri, B. et al. Behaviour of metals in an urban river and the pollution of estuarine environment. *Water Res.* **164**, 114911 (2019).
7. Le Gall, M. et al. Investigating the metal contamination of sediment transported by the 2016 Seine River flood (Paris, France). *Environ. Pollut.* **240**, 125–139 (2018).
8. Harris, I. P. D. J., Jones, P. D., Osborn, T. J. & Lister, D. H. Updated high-resolution grids of monthly climatic observations–the CRU TS3. 10 Dataset. *Int. J. Climatol.* **34**, 623–642 (2014).
9. Blunden, J. & Arndt, D. S. A look at 2018: Takeaway points from the State of the Climate supplement. *Bull. Am. Meteorol. Soc.* **100**, 1625–1636 (2019).
10. Cheng, L. et al. 2018 continues record global ocean warming. *Adv. Atmos. Sci.* **66**, 249–252 (2019).
11. Rao, J., Garfinkel, C. I. & White, I. P. Predicting the downward and surface influence of the February 2018 and January 2019 sudden stratospheric warming events in subseasonal to seasonal (S2S) models. *J. Geophys. Res. Atmos.* **125**, e2019JD031919 (2020).
12. Li, M. et al. Collaborative Impact of the NAO and atmospheric blocking on European heatwaves, with a focus on the hot summer of 2018. *Environ. Res. Lett.* **15**, 114003 (2020).
13. Hari, V., Rakovec, O., Markonis, Y., Hanel, M. & Kumar, R. Increased future occurrences of the exceptional 2018–2019 Central European drought under global warming. *Sci. Rep.* **10**, 1–10 (2020).

14. Lobell, D. B., Schlenker, W. & Costa-Roberts, J. Climate trends and global crop production since 1980. *Science* **333**, 616–620 (2011).
15. Lewis, S. C. & King, A. D. Evolution of mean, variance and extremes in 21st century temperatures. *Weather. Clim. Extremes.* **15**, 1–10 (2017).
16. Donat, M. G. et al. Updated analyses of temperature and precipitation extreme indices since the beginning of the twentieth century: The HadEX2 dataset. *J. Geophys. Res. Atmos.* **118**, 2098–2118 (2013).
17. Croitoru, A. E., Piticar, A. & Burada, D. C. Changes in precipitation extremes in Romania. *Quat. Int.* **415**, 325–335 (2016).
18. Frich, P. et al. Observed coherent changes in climatic extremes during the second half of the twentieth century. *Clim. Res.* **19**, 193–212 (2002).
19. Ziv, B., Saaroni, H., Baharad, A., Yekutieli, D. & Alpert, P. Indications for aggravation in summer heat conditions over the Mediterranean Basin. *Geophys. Res. Lett.* **32**, 1–4 (2005).
20. McCarthy, M. et al. Drivers of the UK summer heatwave of 2018. *Weather* **74**, 390–396 (2019).
21. Mohr, S. et al. The role of large-scale dynamics in an exceptional sequence of severe thunderstorms in Europe May–June 2018. *WCD* **1**, 325–348 (2020).
22. MESDR. *Order of Ministry (Ministry of Environment and Sustainable Development of Romania) no. 161/2006, for the approval of the Norms regarding the classification of surface water quality to establish the ecological status of the water body* http://legislatie.just.ro/Public/DetaliiDocumentAfis/74255 (2006).
23. Li, H., Shi, A., Li, M. & Zhang, X. Effect of pH, temperature, dissolved oxygen, and flow rate of overlying water on heavy metals release from storm sewer sediments. *J. Chem.* **2013**, 1–11 https://doi.org/10.1155/2013/434012 (2013).
24. Bravo, A. G., Loizeau, J. L., Ancey, L., Ungureanu, V. G. & Dominik, J. Historical record of mercury contamination in sediments from the Babeni Reservoir in the Olt River, Romania. *ESPR* **16**, 66–75 (2009).
25. Vasile, G., Gheorghe, S., Ene, C., Serban, E. A. & Stoica, C. Total mercury in fish and benthic invertebrates collected from Olt River, Romania. *J. Chem.* **70**, 263–268 (2019).
26. Iordache, A. M. et al. Past and present anthropic environmental stress reflect high susceptibility of natural freshwater ecosystems in Romania. *Environ. Pollut.* **267**, 115505 (2020).
27. Cheval, S., Dumitrescu, A. & Birsan, M. V. Variability of the aridity in the South-Eastern Europe over 1961–2050. *Catena* **151**, 74–86 (2017).
28. Byrne, P. et al. Control of river stage on the reactive chemistry of the hyporheic zone. *Hydrol. Process.* **28**, 4766–4779 (2014).
29. Frémion, F. et al. Influence of dams on sediment continuity: a study case of a natural metallic contamination. *Sci. Total Environ.* **547**, 282–294 (2016).
30. N'da, S., Yao, M. K. & Trokourey, A. Simultaneous effects of the climate change and the recent hydromorphological modification of Vridi Channel (Côte d'Ivoire) on some its hydrochemical characteristics. *Curr. J. Appl. Sci. Technol.* **39**, 82–97 (2020).
31. Masters, S., Welter, G. J. & Edwards, M. Seasonal variations in lead release to potable water. *Environ. Sci. Technol.* **50**, 5269–5277 (2016).
32. Bonte, M., van Breukelen, B. M. & Stuyfzand, P. J. Temperature-induced impacts on groundwater quality and arsenic mobility in anoxic aquifer sediments used for both drinking water and shallow geothermal energy production. *Water Res.* **47**, 5088–5100 (2013).
33. Rusu, V., Lupaşcu, T., Revenco, M. & Postolachi, L. Dynamics of heavy metals in sediments from River Prut. *Environ. Eng. Manag. J.* **3**, 305–312 (2004).
34. Matache, M. L., David, I. G., Dinu, C. & Radu, L. G. Trace metals in water and sediments of the Prut River, Romania. *Environ. Eng. Manag. J.* **17**, 1363–1371 (2018).
35. Radulescu, C. et al. Assessment of heavy metals content in water and mud of several salt lakes from Romania by atomic absorption spectrometry. *Rom. J. Phys.* **60**, 246–256 (2015).
36. Kim, L., Vasile, G., Stanescu, B., Dinu, C. & Ene, C. Distribution of trace metals in surface water and streambed sediments in the vicinity of an abandoned gold mine from Hunedoara County, Romania. *J. Chem.* **67**, 1441–1446 (2016).
37. Neamtiu, I. A. et al. Metal contamination in environmental media in residential areas around Romanian mining sites. *Rev. Environ. Health* **32**, 215–220 (2017).
38. Michnea, A. & Gherhes, I. Impact of metals on the environment due to technical accident at Aurul Baia Mare, Romania. *Int. J. Occup. Med. Environ. Health* **14**, 255–259 (2001).
39. Fleit, E. & Lakatos, G. Accumulative heavy metal patterns in the sediment and biotic compartments of the Tisza watershed. *Toxicol. Lett.* **140**, 323–332 (2003).
40. Kraft, C., Von Tuempling, W. Jr & Zachmann, D. W. The effects of mining in Northern Romania on the heavy metal distribution in sediments of the rivers Szamos and Tisza (Hungary). *Acta Hydrochim. Hydrobiol.* **34**, 257–264 (2006).
41. Levei, E. et al. Influence of Rosia Poieni and Rosia Montana mining areas on the water quality of the Aries River. *Environ. Eng. Manag. J.* **10**, 23–29 (2011).
42. Lazăr, A. L. et al. Impact of the past mining activity in Roşia Montană (Romania) on soil and vegetation. *Environ. Earth Sci.* **72**, 4653–4666 (2014).
43. Modoi, O. C., Roba, C., Török, Z. & Ozunu, A. Environmental risks due to heavy metal pollution of water resulted from mining wastes in NW Romania. *Environ. Eng. Manag. J.* **13**, 2325–2336 (2014).
44. Anghel, A. M. et al. Statistical analysis of heavy metals concentration in water and sediments in the lower part of the Danube River–Romanian section. *J. Chem.* **67**, 2151–2155 (2016).
45. Miclăuşu, C., Pop, C., Vâlcan, B., Radu, A. & Roşu, C. Study of soil pollution with heavy metals in the town of Copşa Mică. *Stud. Universitatis Babes-Bolyai, Geographia* **64**, 37–54 (2019).
46. Iordache, M., Popescu, L. R., Pascu, L. F. & Iordache, I. Assessment of the potential ecological risk with heavy metals in surface s sediments from accumulation lakes on the sector inferior of the Olt River. in *INCD ECOIND—International Symposium —SIMI 2015 "The Environment and the Industry"*, 175–184 (National Research and Development Institute for Industrial Ecology, INCD-ECOIND, 2015).
47. Barhoumi, B. et al. Occurrence, distribution and ecological risk of trace metals and organic pollutants in surface sediments from a South-eastern European river (Someşu Mic River, Romania). *Sci. Total Environ.* **660**, 660–676 (2019).
48. Vasiliu, D. et al. Assessment of the metal pollution in surface sediments of coastal Tasaul Lake (Romania). *Environ. Monit. Assess.* **192**, 1–16 (2020).
49. UNEP. *Spill of liquid and suspended waste at the aurul S.A. retreatment plant in Baia Mare*. (United Nations Environment Programme, United Nations, Office for the Co-ordination of Humanitarian Affairs, OCHA, Assessment Mission Romania, Hungary, Federal Republic of Yugoslavia, 2020).
50. Rebetez, M., Dupont, O. & Giroud, M. An analysis of the July 2006 heatwave extent in Europe compared to the record year of 2003. *Theor. Appl. Climatol.* **95**, 1–7 (2009).
51. Peterson, T. C. & Baringer, M. O. State of the climate in 2008. *Bull. Am. Meteorol. Soc.* **90**, S1–S196 (2009).
52. Kim, L. et al. In *Sedimentation Engineering* https://doi.org/10.5772/intechopen.70749 (IntechOpen, 2017).
53. Dubovina, M. et al. Distribution and ecological risk assessment of organic and inorganic pollutants in the sediments of the transnational Begej canal (Serbia-Romania). *Environ. Pollut.* **236**, 773–784 (2018).
54. Voica, C., Iordache, A. M., Ionete, R. E. & Ştefănescu, I. Aspects on the accumulation of trace metals in various environmental matrices (water, soil, plant and sediments): case study on catchment area of the Somes River, Romania. *Water Qual*. 269–291 https://doi.org/10.5772/65700 (2017).
55. Radu, V. M. et al. Overall assessment of surface water quality in the Lower Danube River. *Environ. Monit. Assess.* **192**, 1–15 (2020).
56. Ilie, M. et al. Assessment of heavy metal in water and sediments of the Danube River. *J. Environ. Prot. Ecol.* **15**, 825–833 (2014).
57. Anghel, A. M. et al. Danube River Basin Waters on Romanian Territory: Chemical Status Assessment Based on Priority Substances Data Analysis. *J. Chem.* **70**, 3292–3298 (2019).
58. Wilcox, L. J. et al. Multiple perspectives on the attribution of the extreme European summer of 2012 to climate change. *Clim. Dyn.* **50**, 3537–3555 (2018).
59. Sánchez-Benítez, A., García-Herrera, R., Barriopedro, D., Sousa, P. M. & Trigo, R. M. June 2017: the earliest European summer mega-heatwave of Reanalysis Period. *Geophys. Res. Lett.* **45**, 1955–1962 (2018).
60. Bravo, A. G. et al. Persistent Hg contamination and occurrence of Hg-methylating transcript (hgcA) downstream of a chlor-alkali plant in the Olt River (Romania). *ESPR* **23**, 10529–10541 (2016).
61. Dranguet, P. et al. Biofilm composition in the Olt River (Romania) reservoirs impacted by a chlor-alkali production plant. *Environ. Sci. Process. Impacts* **19**, 687–695 (2017).
62. Nechita, C., Čufar, K., Macovei, I., Popa, I. & Badea, O. N. Testing three climate datasets for dendroclimatological studies of oaks in the South Carpathians. *Sci. Total Environ.* **694**, 133730 (2019).

ACKNOWLEDGEMENTS

This work was supported by the Romanian National Authority for Scientific Research and Innovation, Contract No. 12N/2019, PN 19070502, Contract No. 9N/2019, PN 19110303 and 36N/2019, PN 19350202.

AUTHOR CONTRIBUTIONS

A.M.I.: Conceptualization, Methodology, Formal analysis, Investigation, Graphic illustration, Writing—initial draft, review and editing, Project administration, Resources. C.N.: Conceptualization, Methodology, Statistical analysis, Graphic illustration, Writing—initial draft, review and editing, Project administration, Resources. C.V.: Data curation, Investigation, Project administration, Resources. T.P.: Writing—review and editing. K.A.S.: Supervision, Writing—review and editing.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41545-021-00147-w.

Correspondence and requests for materials should be addressed to Constantin Nechita.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.