

# Exceptionally high levels of lead pollution in the Balkans from the Early Bronze Age to the Industrial Revolution

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The Balkans are considered the birthplace of mineral resource exploitation and metalworking in Europe. However, since knowledge of the timing and extent of metallurgy in southeastern Europe is largely constrained by discontinuous archaeological findings, the long-term environmental impact of past mineral resource exploitation is not fully understood. Here, we present a high-resolution and continuous geochemical record from a peat bog in western Serbia, providing a clear indication of the extent and magnitude of environmental pollution in this region, and a context in which to place archaeological findings. We observe initial evidence of anthropogenic lead (Pb) pollution during the earliest part of the Bronze Age [ $\sim 3,600$  years before Common Era (BCE)], the earliest such evidence documented in European environmental records. A steady, almost linear increase in Pb concentration after 600 BCE, until  $\sim 1,600$  CE is observed, documenting the development in both sophistication and extent of southeastern European metallurgical activity throughout Antiquity and the medieval period. This provides an alternative view on the history of mineral exploitation in Europe, with metal-related pollution not ceasing at the fall of the western Roman Empire, as was the case in western Europe. Further comparison with other Pb pollution records indicates the amount of Pb deposited in the Balkans during the medieval period was, if not greater, at least similar to records located close to western European mining regions, suggestive of the key role the Balkans have played in mineral resource exploitation in Europe over the last 5,600 years.

peat bog | metal resources | Balkans | lead pollution | medieval

The discovery of metals and refinement of alloys has been fundamental to the development of modern industrialized society (1). The earliest use of metals in the form of native copper in Anatolia roughly 9,000 y before common era (BCE) (2) preceded the invention of extractive metallurgy and alloying at around 5,000 BCE (3). Evidence of intentional thermal treatment of ores to produce metals, and complex metalworking around this time has been uncovered in several places throughout the Balkans (3–6) as well as in the Middle East (7). Building on the discoveries of these early metalworking pioneers, humans have continuously employed metals in a wide range of applications. However, the exploitation of mineral resources has a broad range of environmental impacts, including metal-contaminated wastewater and the release of chemical particulates to the atmosphere (8), from mining (9) and smelting (10), and the use of toxic metals in tools and artifacts [e.g., Pb in Roman water pipes (11)]. As a result, the effects of highly toxic Pb poisoning on the broader ecosystem (12) and on human health during the past two millennia are well documented, particularly for the Roman Empire, where Pb was a highly sought-after metal commodity (13).

Trends and amplitudes of mineral resource exploitation have been documented in central-western Europe primarily via the geochemical composition of peat, building on earlier work on

polar ice cores (14, 15) and lake sediments (16–18). Released to the atmosphere through mining and smelting, once deposited within peat or lake sediments, Pb is effectively immobile (19), resulting in its reliability as a proxy for reconstructing past pollution directly related to such anthropogenic activities (20). Due in part to its biogeochemical immobility, and after the early detection (21) of a clear environmental Pb pollution peak from Roman times in British peat records, much of the focus has been on this metal (20). To date, traces of Roman period Pb pollution have been found in records spanning most of Europe (20), including Spain (22–24), Switzerland (25), and even areas outside Rome's reach such as Sweden (26) and Central Europe (27). Typically, such reconstructions focus on ombrotrophic peat fed only by direct atmospheric fallout (25), but the applicability of minerogenic bogs and even lake sediments in recording a reliable geochemical signal of past pollution has also been proven (28). As a result, the development, impact, and scale of mineral resource exploitation through time in central and western Europe has been well assessed, providing an improved understanding of both socioeconomic development, and of our impact on the environment through time.

## Significance

A detailed record of historical lead (Pb) pollution from a peat bog in Serbia provides a unique view on the extent and timing of Balkan mining and metallurgy. Evidence of the earliest European environmental pollution is followed by large-scale and sustained increases in the amount of anthropogenically derived Pb after 600 BCE, through the Roman/Byzantine periods, and into the medieval period. Occasional evidence of drops in pollution output reflects the disruptive socioeconomic impact of periods of turmoil. Our data show a trend significantly different to records in western Europe, where Pb pollution decreases dramatically after the collapse of the Roman Empire. These results suggest metal-rich southeastern Europe should be considered a more major player in environmental metal pollution through time.

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Such work also indicates the reality of atmospheric long-distance transport of Pb, although differences between records hint at strong regional and temporal variability (8), necessitating further investigations of pollution loading in regions (both sources and sinks) with a rich ore endowment and a documented long history of metal use. Pertinently, long-term Pb pollution records for southeastern Europe have not yet been investigated (Fig. 1), thereby limiting the inference of past metal use, the associated environmental pollution, and the likely impact on human health in this region and beyond. However, the rich archaeological heritage of the Carpathian-Balkan region includes the earliest known sites of mining and extractive metallurgy in Europe (29), with exploitation centers at Rudna Glava in Serbia (30) and Ai Bunar in Bulgaria (31), and workshops in Pločnik and Belovode in Serbia (4, 32) all dating broadly to ~5,500–4,500 BCE (Fig. 1). These early activities ushered in significant metalworking activities for several millennia related mainly to the Vinča and other contemporaneous or successive material cultures (3, 30), extending from the Carpathians in the north throughout most of the Balkans. Metal production in the area further bloomed during the Copper Age and especially during the Bronze Age, with metallic artifacts reaching exceptional quantities and sophistication in design (33, 34) after 3,000–2,800 BCE (35). Further significant metal exploitation was undertaken by the Romans and their Byzantine successors, with evidence of exploration and large-scale mining in the area at the time (36, 37). Despite this apparent understanding of Balkan metal use history, metallurgical activities during significant periods of time are still inferred from a scarce and at times ambiguous archaeological record. Periods such as the Early Bronze Age are represented by only a handful of artifacts of uncertain age and provenance (34, 38). Additionally, little reference is made to medieval mining activity (39), although it has been suggested that silver (Ag)-rich ores in modern-day Serbia were likely exploited since the medieval period (40, 41). As such, the exact scale and impact of such activity in the broader region are unclear in many respects, especially after modern-scale exploitation of mineral resources, which has largely destroyed many old

vestiges. It may be that such finds are indeed representative of a rich metallurgical history, but that has yet to be proven unequivocally.

The ~7,500-y-long history of mining and metallurgy in the Balkans was likely facilitated by the significant endowment in polymetallic ores, very rich in base and precious metals (Fig. 1). For instance, the Apuseni Mountains (western Romania) host the Metaliferi mining district, home to Europe's largest gold and silver (Au–Ag) deposits (42, 43). In addition, other mining fields have been or are still being exploited on the 1,500-km-long Banatitic Magmatic and Metallogenic Belt, which runs from Romania, through Serbia, and into Bulgaria, and is the most important ore-bearing (particularly Cu, Au, and Pb–Zn) belt of the Alpine–Balkan–Carpathian realm (44, 45), itself a section of the Thethyan Eurasian Metallogenic Belt (46).

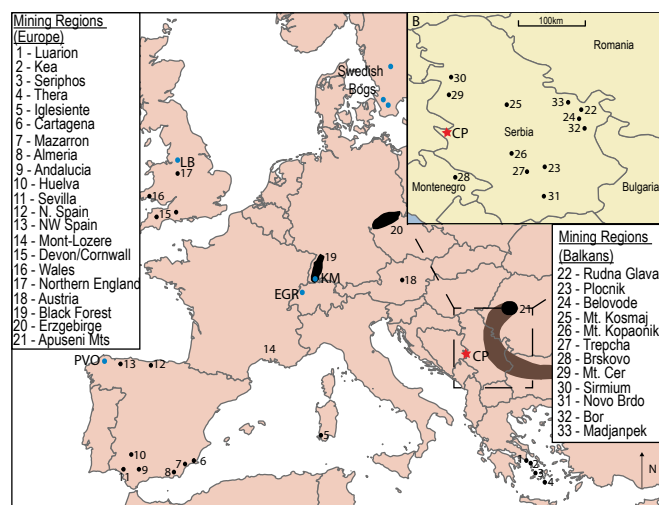
Here, we present a high-resolution record of past anthropogenic pollution based on the geochemical data from Crveni Potok peat bog (Fig. 1), reconstructing past metal-related environmental pollution linked to mineral resource exploitation in the Balkans. The approach delivers a view on the chronology of past mineral resource exploitation and related pollution load in southeastern Europe. It allows for the gap between indirect geochemical inferences and direct archaeological evidence to be bridged in a region that has likely been crucial from the first steps of metal exploitation at the onset of human technological development, and through all of European metallurgical history (3–6, 29).

Crveni Potok (43°54'49.63" N; 19°25'11.08" E) is a small bog (<3 ha) located in the Tara Mountains National Park, on Serbia's western border with Montenegro, at 1,090 m above sea level (a.s.l.), within the Dinaric Alps (Fig. 1). Today, the mire is surrounded by forest, with the majority of the tree cover consisting of conifers (*Abies alba*, *Picea abies*) and *Fagus sylvatica* (47) and a small population of the endemic Serbian spruce (*Picea omorika*). The mean annual temperature is 7 °C, with the bog receiving ~970 mm of precipitation per year (48). The bedrock consists of Triassic limestone, with Cretaceous marbles and ultrabasic (and extremely Pb-poor) igneous bedrock located to the southwest of the site (47).

## Results and Discussion

### Reconstructing the History of Metal Pollution in the Central Balkans.

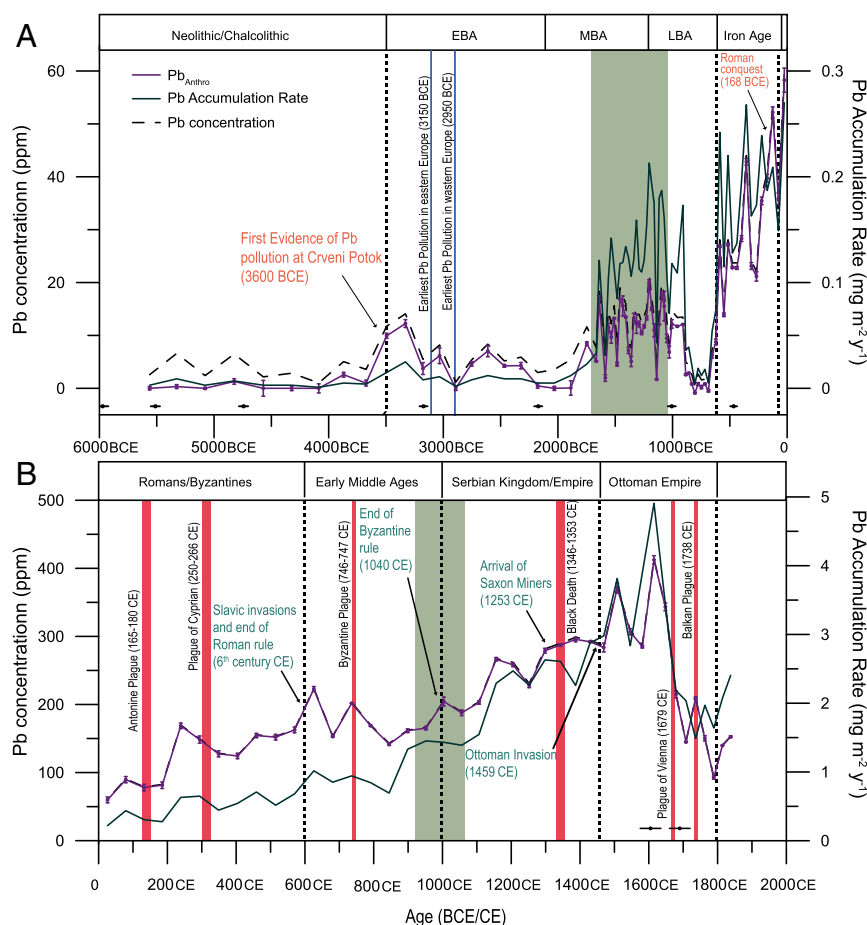
Although the Crveni Potok peat record covers the last 9,500 y, the shift from a minerogenic sediment to peat occurred at around 5,600 BCE (*SI Appendix, Supplementary Text*), and therefore discussion of the geochemical record of this early section in terms of human activity is avoided. After 5,600 BCE (Figs. 2B and 3A), the Pb<sub>Anthro</sub> record, a measure of the Pb originating from anthropogenic activities (*Materials and Methods*), remains at low levels until ~3,900 BCE. We found clear evidence of Pb<sub>Anthro</sub> enrichment, and a modeled change point in the dataset (Fig. 2G), at  $3,600 \pm 122$  BCE and peaking by  $3,490 \pm 128$  BCE (Fig. 3A). This finding strengthens the limited archaeometallurgical evidence of the inception of the Bronze Age in the Carpathian–Balkan region, with evidence for arsenical bronze use at this time (6) especially close to the Cu-rich deposits south of Danube. This finding strengthens the limited archaeological indications of the southeastern European Bronze Age onset a millennium earlier compared with similar developments in central and western Europe (49). Such activity may be linked with several regionally representative cultures (e.g., Baden, Tiszapolgar), although archaeological evidence is scarce (29, 30, 50). Copper may have been sourced from documented centers of metallurgy in central Serbia such as Rudnik in the Early Bronze Age (51), although evidence points to a wide trading network at this time in Europe (52). In terms of tin (Sn), the other main constituent of bronze, a more local origin may be possible. Uncertain archaeological evidence for Sn mining in



**Fig. 1.** (A) Map of Europe indicating location of Crveni Potok (red star) and of other studies referenced in text; Lindow Bog (LB) (21), Penido Vello (PVO) (85), Etang de la Gruyere (EGR) (25), Kohlthütte Moor (KM) (88), and three Swedish bog records (26). Also presented are locations of major metallogenic mining regions exploited before 1,800 CE (85) and the Banatitic Magmatic and Metallogenic Belt (highlighted in brown). (B) Serbia and surrounding countries, indicating the location of Crveni Potok with respect to the locations of mining and metal production sites as mentioned in text.





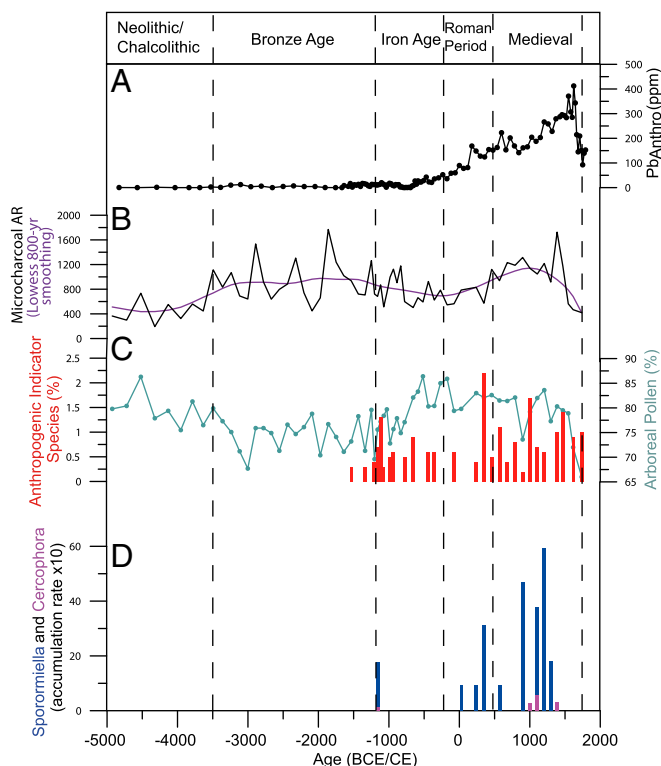


**Fig. 3.** Pb concentration (dashed black line), calculated anthropogenic contribution (Pb<sub>Anthro</sub>, purple line), and PbAR (green line) for Crveni Potok core. *Upper panel* shows the earliest section of core, from 6,000 BCE to 0 CE, while the *Lower panel* indicates the period from 0 CE to 2,000 CE. Also indicated are major periods of change in the region (green labels), and the timing of major European plagues (red bars). Changes in cultural development are indicated by black dashed lines. Green rectangles display periods of increased fire activity (47). Blue vertical lines in *A* denote the earliest appearance of Pb pollution in previous European paleoenvironmental records, from western (55) and eastern (104) Europe. Also displayed at the base of each panel are radiocarbon dates and errors used to construct the age model. Note *A* displays a smaller scale to *B*, to allow for variations in the older section to be observed.

metallurgy may be seen in the cumulative atmospheric anthropogenic Pb (CAAPb) percentage (relative to the entire Pb deposited within the core) deposited over this period at Crveni Potok, nearly 20% (Fig. 2B), a significant fraction, especially once the large Pb enrichment of the Medieval period is considered. Under the Roman influence, south of the Danube, Illyricum and Moesia became typical mining provinces, with a particular focus on gold (Au) and Pb deposits (67). Moesia hosted two major mining regions, in the south (Dardania) and in the north (*ripa Danuvii*; along the Danube including the mineral-rich Timok valley) (66). In Dardania, examples of Roman mining have been excavated at *Municipium Dardanorum (Ulpiana)* (68), while numerous traces of Roman metallurgy exist throughout the Balkans (37). Closer to Crveni Potok, it appears mineral resources within the Dinaric Alps were also exploited, particularly at Mt. Cer (150 km north of Crveni Potok), and in particular the area around Rumska (66). Other major mining areas included Mt. Kosmaj near Belgrade (69, 70) and Mt. Kopaonik (68) (Fig. 1). From Kosmaj alone, the significant quantities of ancient slag (~1,000,000 tons) are testament to the scale of Roman metal exploitation and environmental pollution in the region, primarily from the processing of Ag–Pb ores (70).

After the peak at ~240 CE, the levels of Pb<sub>Anthro</sub> decline (Fig. 3B), possibly indicative of a regional slowdown in mining output, relating to repeated invasions and upheavals that affected the

Balkan area, including the abandonment by the Romans of the mineral-rich provinces north of Danube (71). However, subsequent increases after 400 CE indicate mineral exploitation in the region recovered during the Byzantine Empire, which, contrary to developments in the rest of Europe, reached its peak in economic and cultural development at this time (72). Subsequently, the decrease in Pb<sub>Anthro</sub> evident after ~740 CE and lasting up to 1,000 CE echoes the gradual decrease in influence of the Byzantine Empire in the northern Balkans as documented in historical sources (72). After 1,100 CE, and with the arrival of Saxon miners from 1,253 CE onward (73), the Serbian statehood developed into one of Europe's leading Ag producers (41, 74), reflected also in significant Pb<sub>Anthro</sub> increases in the Crveni Potok record (Fig. 3B). The major Balkan medieval mining centers all opened between 1,250 and 1,300 CE, with Rudnik (1,293 CE), Trepcha (1,303 CE), and most pertinently to the Crveni Potok record, the Brskovo mines, which opened on the Tara Mountains in 1,254 CE, 150 km to the south (41, 75) (Fig. 1). This development in mineral resource exploitation is emphasized by the percentage of Pb deposited at Crveni Potok after 1,000 CE, nearly 60% of the total Pb accumulated in the core (Fig. 2B). The ongoing increase in Pb<sub>Anthro</sub> from 1,100 CE, with the clearest change highlighted by the change-point modeling at 1,141 CE (Fig. 2F), at Crveni Potok clearly reflects the continued regional opening of new mines and development of this industry



European records, which indicate major disruptions in metal exploitation and related Pb pollution after 300 CE in both Spain and Switzerland (Fig. 5). The contrast between western and southeastern Europe is evidence for the continued exploitation of Balkan metal ores under the Byzantines, validating previous archaeological indications (71), and confirming the so-called “Dark Ages” of western Europe coincide with significant economic development in southeastern Europe. High levels of metal environmental pollution in the Balkans throughout the medieval period, and after the fall of the Byzantine Empire, indicate that this industry was firmly established in the region (Fig. 3B) (41). Thus, we demonstrate here that the Carpathian–Balkans acted as a major source for European metal pollution not only during Antiquity, but also during the early medieval period and later. The timing of the medieval increase in  $Pb_{Anthro}$  is in line with the development in Ag mining in Germany (27, 93) and increased Pb pollution in a number of peat records across Europe (20). However, in no other studies does the level of Pb pollution exceed that of the Roman period until after 1,800 CE, with major pollution associated with the inception of the industrial revolution (21, 89). This further confirms the large extent and size of the metalworking industry in the Balkans during the late medieval period.

To allow for direct comparison of the Crveni Potok pollution record with other sites, and to remove intercomparison issues relating to sedimentation rates, Pb accumulation rates (ARs) have also been calculated (Fig. 24). Despite the low sedimentation rates (*SI Appendix, Fig. S2*), and the near-pristine natural local environment at Crveni Potok today (47), Pb ARs are high for the past 2,000 y, peaking during the late medieval period, generally reflecting the  $Pb_{Anthro}$  values.

Comparison with the Pb AR records from Etang de la Gruère (25) record in Switzerland’s Jura Mountains, and that of Kohlthütte Moor (88) in southwestern Germany provide the most pertinent evaluations (Fig. 1) because similarly to Crveni Potok, these are located in remote mountain areas with relatively low local human pressure during most of the Holocene. Furthermore, geographically they are located close to pollution sources derived from centers of metallurgy: Black Forest medieval mining centers for Kohlthütte Moor, and southeastern France and the eastern Alps, regions with active mining from the Bronze Age onward, for Etang de la Gruère (Fig. 1). The comparison reveals the similarity in the Crveni Potok and Kohlthütte Moor records throughout the Roman period, with both sites indicating Pb AR between 0.5 and 1.5  $mg \cdot m^{-2} \cdot y^{-1}$ , suggesting regional smelting activities were similarly extensive. However, in both Kohlthütte Moor and Etang de la Gruère, the Pb ARs do not exceed 2  $mg \cdot m^{-2} \cdot y^{-1}$  until the Industrial Revolution. In contrast, in the Crveni Potok record, this threshold is reached eight centuries earlier (by ~1,100 CE), rising to a peak of nearly 5  $mg \cdot m^{-2} \cdot y^{-1}$  by ~1,620 CE (Fig. 24). The latter Pb AR peak is comparable to Pb pollution flux levels reached three to four centuries later in the two central European bogs, which only reach this Pb contamination level by the early 20th century CE (25, 88). Another valid comparison may be made with Lindow Bog near Manchester in northwestern England (21). Here, at a site located within a region of rich mining heritage, Pb ARs comparable to Crveni Potok are observed at roughly similar times, particularly during the medieval period; at Lindow Bog, Pb ARs reach 1.24  $mg \cdot m^{-2} \cdot y^{-1}$  in the period 1,100–1,500 CE, before a peak of roughly 4  $mg \cdot m^{-2} \cdot y^{-1}$  by the 1,450 CE.

The Pb pollution history inferred from the Crveni Potok record is reflective of major mining and smelting activity in the wider Balkan region for the last 5,600 y, which peaks in the 17th century CE. By this time, the mining activity was producing Pb pollution comparable to other known medieval mining centers such as southern Germany and northern England. A major difference, however, is the fact that there is no evidence of proximal

mining at Crveni Potok, other than rather uncertain evidence for exploitation along the Drina Valley and at Srebrenica in Bosnia (41). This suggests the high Pb output recorded by this bog is reflective of significant pollution region-wide, and noteworthy underestimation of the extent of Balkan metallurgy and its contribution to the European pollution budget through time.

The Crveni Potok record, therefore, provides evidence that the reconstructed impact of past metal smelting throughout Europe is not robust without considering the Balkans as a major source of metals. Our record shows that overall estimations of historical metal pollution (including Pb production) need improvement, to take into account the varied nature of development across Europe, and to incorporate the previously less considered contribution of Balkan metallurgical history. The fact that southeastern Europe is seldom mentioned as a metal source area in geochemical investigations of past Pb pollution contrasts markedly with the rich base and precious metal ore endowment of the Balkans, and significant field and archaeological evidence of past mining works and metal use.

**Disruption of Balkan Metallurgy by Plagues.** It has been suggested (8) that economic activities including metal production have been majorly perturbed throughout Europe by the occurrence of deadly plagues such as the Black Death of 1,346–1,354 CE (94). Albeit testing such hypothesis would require a larger number of records from the area, we found evidence to suggest such a linkage is possible with a number of major pestilences that afflicted eastern and southern Europe (Fig. 3). These include the Cyprian Plague (95), believed to be smallpox related, which had a major impact (>5,000 deaths per day in Rome at its height) on the Roman world between 250 and 266 CE, and may be reflected in the decrease in  $Pb_{Anthro}$  deposited at this time at Crveni Potok. Other major epidemics that may be reflected in our record include the plagues of Antonine (165–180 CE), Byzantine (746–747), and Vienna (1,679 CE) (96). All are associated with downturns in  $Pb_{Anthro}$  at Crveni Potok (Fig. 3). Notable, however, is the lack of apparent influence of the Black Death (1,346–1,354 CE), possibly evidence for its reduced impact in eastern Europe, thus paralleling historical accounts.

## Conclusions

The Crveni Potok peat sequence provides an unprecedented continuous record documenting the impact of mining- and smelting-related Pb pollution in the wider Balkan region from the Early Bronze Age to the Industrial Revolution. The first clear signs of anthropogenic Pb enrichment are detected during the Bronze Age, with two main periods of increased Pb pollution (3,900–2,500 BCE and 1,750–950 BCE), corroborating poorly constrained archaeological evidence of regional metal use. The first of these anthropogenic Pb enrichment phases is the earliest such evidence for European Pb pollution in an environmental record.

Pb enrichments correspond to increases in fire activity and early deforestation, pointing to a causal link between mineral resource exploitation and land-use changes. Major Pb pollution is recorded from 600 BCE onward, with gradually increasing values in anthropogenic Pb until a peak at ~1,620 CE. The record of gradually but continuously increasing levels of environmental pollution is indicative of a long and varied history of exploitation of metals in the area.

The Crveni Potok record highlights a significantly different pollution history in comparison with central-western European records, suggesting that the picture of European environmental impact through such activities is not complete without considering developments in the Balkans, a region very rich in metal ores and a documented long history of mineral resource and land exploitation. No previous studies have displayed constant Pb enrichment increases throughout the medieval period, with most



central-western European records peaking only during Roman and later during industrial times. Comparisons of Pb ARs in similar records corroborate the scale of metallurgical activity in the region throughout the medieval period, with values comparable only to sites located close to centers of mining and smelting today, indicative of the size and long-term persistence of the Pb pollution in the Balkans, for several millennia.

## Materials and Methods

In total, 270 cm of peat was recovered from Crveni Potok in overlapping cores using a Russian peat corer. The age–depth model was developed using nine AMS  $^{14}\text{C}$  dates calibrated using the IntCal 13 dataset (97), and Clam age–depth modeling software (98) (*SI Appendix, Fig. S2 and Table S2*). Subsamples were taken and trace metal analysis was performed on exactly 0.5 cm<sup>3</sup> of peat to allow for density calculations. Each subsample was dried overnight before homogenization and digestion via a mixed acid ( $\text{HNO}_3\text{--HCl--HF}$ ) microwave-assisted method (99) (*SI Appendix, Supplementary Text*). These solutions were analyzed via a Perkin-Elmer Optima 8000 ICP-OES system at Northumbria University. Analytical blanks were determined via analysis of a preprepared calibration solution, and all data presented have had this blank subtracted from it. Procedural blanks (digestions carried out with no sample), run at regular intervals, indicate negligible contamination, with the vast majority of analyses being below the detection limit of the instrument. To ensure accuracy, two reference materials were run alongside the samples and indicate reliable recoveries (within 10% of the expected values in the majority of runs) (*SI Appendix, Table S1*). Precision was monitored via measurement of an internal standard (either 1 ppm Sc or In; *Dataset S2*), and by triplicate measurement of each sample. SDs of each measurement are reported in *Dataset S2*. To further ensure accuracy, every 10 samples, repeats were run (*Dataset S3*).

Despite apparently low input from nonatmospheric metal sources including dust and runoff (*SI Appendix, Supplementary Text and Fig. S1*), to derive a reliable picture of past metal loading related to anthropogenic

activities it is necessary to extract the pollution-related Pb from the natural background. An approach that distinguishes the lithogenic (natural) heavy-metal component from the anthropogenic component (100) was used. This first calculates the lithogenic component (by comparison with expected values in the upper continental crust) of the heavy-metal contribution, before removal of this signal from the overall metal concentration. The remainder may be considered the anthropogenically related Pb component ( $\text{Pb}_{\text{Anthro}}$ ). In addition to calculation of  $\text{Pb}_{\text{Anthro}}$ , we also present the enrichment factor (Fig. 2C) (101) and CAAPb (Fig. 2B) (100) to better illustrate which periods dominate the Pb depositional history. Finally, to allow for direct comparison with other records (88), the Pb AR (Fig. 2A) has been calculated (85) (*SI Appendix, Supplementary Text*). In each case, we use Zr as the conservative lithogenic element.

To robustly determine where statistically significant changes occurred in the Pb data, we have performed change-point analysis. This approach marks each point where the Pb data changes abruptly and shows our findings are not method dependent (see *SI Appendix, Supplementary Text* for details). Three approaches (binary segmentation, Bayesian change-point analysis, and breakpoints analysis) were used to perform change-point modeling performed on the  $\text{Pb}_{\text{Anthro}}$  (Fig. 2F), PbAR (*SI Appendix, Fig. S4*), and raw Pb concentration (*SI Appendix, Fig. S5*). Such approaches rigorously investigate the nature of the time series and, via a selection of methods (*SI Appendix, Supplementary Text*), determine where significant shifts exist. These methods may reliably detect changes in trends (102, 103), circumventing possible overinterpretation of noisy datasets.

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