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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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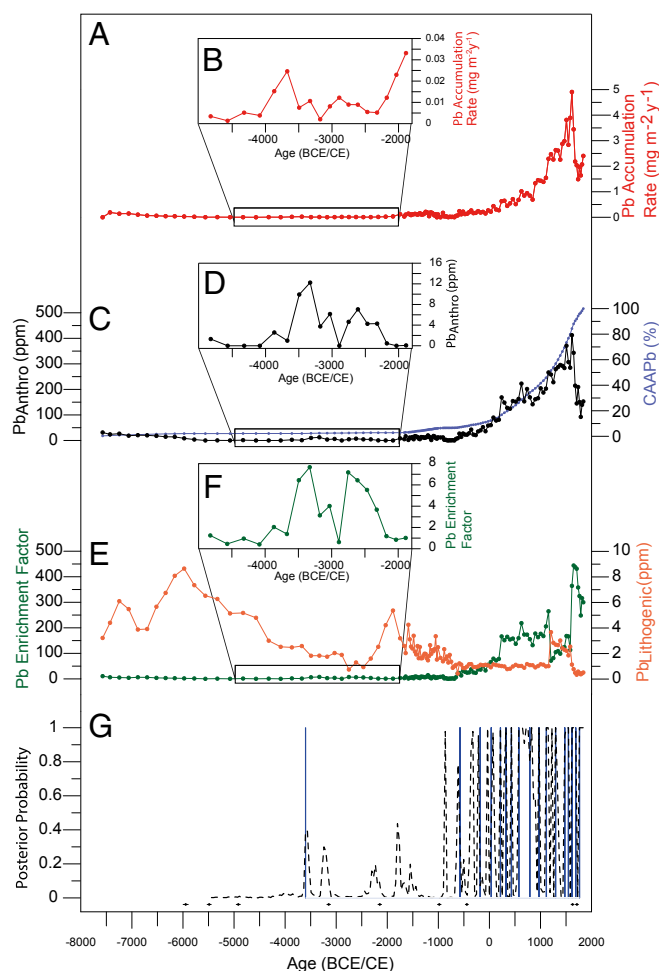


Fig. 2. Methods for elucidating the depositional history of Pb pollution at Crveni Potok. (A) The Pb AR, presented alongside the peak medieval Pb AR from Kohlühütte Moor (88). (B) Inset focusing on Pb AR between 5,000 BCE and 1,800 BCE. (C) CAAPb (blue line), alongside the anthropogenic Pb component (PbAnthro). (D) Inset focusing on PbAnthro between 5,000 BCE and 1,800 BCE. (E) The lithogenic Pb component (PbLithogenic) and Pb enrichment factor. (F) Inset focusing on Pb enrichment factor between 5,000 BCE and 1,800 BCE. (G) Change-point modeling documenting (black dashed line) posterior probability of a change point occurring at each age, calculated from PbAnthro. Blue lines document points at which change points are statistically likely to have occurred. Also displayed at the base of G are radio-carbon dates and errors used to construct the age model.

western Serbia may indeed be linked to local metallurgy at this time (53, 54), although more research is needed to verify this. The timing of the initial PbAnthro enrichment as documented in the Crveni Potok data places it as the earliest record of environmental Pb pollution observed within a paleoenvironmental record in Europe (55), and is therefore the earliest indirect geochemical evidence of the well-constrained (via archaeological finds) early development of the Bronze Age in the Balkans at this time. The geochemical evidence is supported by a concurrent rise in charcoal concentration (Fig. 4B), suggestive of an increase in biomass burning, potentially related to a broad range of economic activities, including perhaps fuel production for metal smelting.

Interestingly, PbAnthro values remain low (Fig. 3A) during the transition into the Middle Bronze Age (2,500 BCE to 1,750 BCE), confirming a postulated nonlocal supply (although possible local smelting) of metal for the numerous bronze artifacts within Serbia (56), and the neighboring Carpathian Basin (57).

The western Carpathians and eastern Alps have been proposed as the most likely metal sources during this period (57, 58).

PbAnthro displays high, but fluctuating values between 1,750 BCE and 950 BCE (Fig. 3A), a trend reflected also in the Cu, Zn, and Cr records (SI Appendix, Fig. S1). This corresponds to the rapid expansion of metal working in the Carpathian–Balkan region during the Middle and Late Bronze Age (33), and the first major forest clearances attributed to human activity both locally, in the Dinaric Alps (59) but also more regionally, over the Danube lowland basins (60). Across the Balkans, a large number of metal artifacts have been documented, many attributed to the Vatin (53) culture of the Late Bronze Age. This regional pollution may have been linked to mining and associated bronze manufacturing that presumably took place at locations around Mt. Cer (150 km north of Crveni Potok), proposed as a source for Sn found within archaeological artifacts of the Late Bronze Age (53, 56). Additional evidence for increasingly strong anthropogenic impact at this time is seen in Crveni Potok's enhanced fire activity reconstruction based on microcharcoal data, and centered around 1,550 BCE (47) (Fig. 4B). Furthermore, land-use changes, likely associated to enhanced regional human pressure and possible metal processing activities (53), may be inferred from the first appearance of coprophilous fungi (*Cercophora* and *Sporormiella*, Fig. 4D), and increasing values for the anthropic pollen indicators (*Plantago lanceolata* and *Cerealia-type*, Fig. 4C) in the Late Bronze Age at Crveni Potok.

The onset of the Iron Age is characterized by very low values for all metals investigated (Fig. 3 and SI Appendix, Fig. S2), clearly indicative of the disruptive socioeconomic impact the well-known Late Bronze Age Collapse has had in the wider Balkan region as inferred from archaeological and paleoenvironmental data (61, 62). This period represents the last interval of peat deposition without significant evidence of PbAnthro (Fig. 3A) as, remarkably, from roughly 600 BCE onward the Crveni Potok record shows a near-constant increase in the level of PbAnthro deposited through time, until ~1,700 CE. The increased PbAnthro between 600 BCE and 200 BCE is likely reflective of the ability of the local La Tène material cultures, including the Celtic Scordisci who occupied much of the western Balkans at this time, and the Dacians, Thracians, Illyrians, and Greeks throughout the remainder of the region, to mine and smelt metals. Indeed, the Scordisci were known for their metallurgical proficiency and are considered the craftsmen behind a major Pb ingot discovery at Valle Ponti (northeastern Italy) (63), and several silver hoards (64). The source of the Pb ingot is thought to be Sirmium (located 200 km north of Crveni Potok) (Fig. 1), an important smelting center, before the Roman conquest of the area, and exploiting Ag–Pb sources in the Dinaric Alps (63). The Crveni Potok record likely reflects contribution from regional metal smelting activities, with rapid, stepwise increases in PbAnthro throughout Classical Antiquity and into the Roman period paralleling the historical socioeconomic development in the wider region (600–150 BCE, Fig. 3). This economic activity is also reflected in the extent of regional forest clearance, as observed in Bosnia, 100 km west of Sirmium (65), coincident with the increase in PbAnthro at Crveni Potok throughout Roman times, and into the subsequent medieval period. At Crveni Potok, no major decrease in forest cover is inferred from the pollen data in the Iron Age (47) (Fig. 4C and D).

The Romans conquered much of the Balkans between 200 and 100 BCE. As in other regions with rich mineral deposits (e.g., Hispania and later Dacia), the Romans systematically cataloged and mined ores (66). In the Crveni Potok record, PbAnthro increases dramatically to a peak at ~240 CE, with particularly sharp increases around 50 CE and 150 CE. The second pulse is clearly identified via change-point modeling at ~181 CE (Fig. 2F), reflecting the extent of Roman mining and smelting throughout the Balkans (Fig. 1). Further evidence of intense

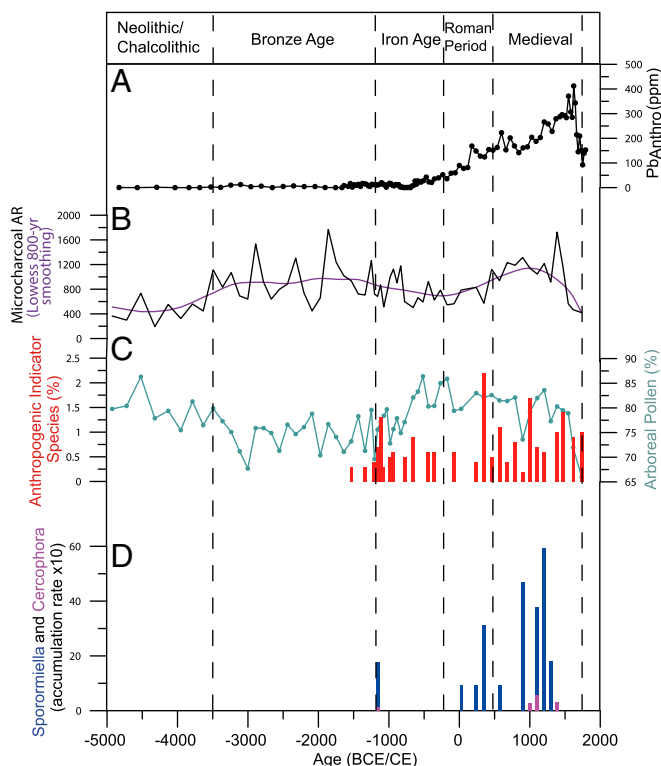


Fig. 4. Comparison of Pb_{Anthro} with other proxies of human activity from Crveni Potok for the past 7,000 y. (A) Pb_{Anthro} data as displayed in Fig. 2B. (B) Microcharcoal AR, with both raw values (black line) and a smoothed curve (purple line), produced using a Lowess 800-y smoothing window (41). (C) Percentage values of anthropogenic indicator pollen species (*Plantago lanceolata* and *Cerealia*-type), alongside arboreal pollen percentages. (D) Stacked bar chart of ARs for two coprophilous fungi species: *Cercophora* and *Sporomella*.

throughout the early medieval period (41) to satisfy demand for silver in Europe and the Middle East (41). The Pb_{Anthro} reaches a high level at ~1,500 CE (Fig. 3B), and just after the Ottoman conquest of Serbia in 1,459 CE (76). This was a period of rapid growth in mining output throughout the Balkans, as most other European mining centers were in decline at the time (41, 77). Under Ottoman rule, metal resource exploitation continued to be productive, even after the introduction of the Kanun-name (Ottoman law) regulating and restricting mining in 1,536–1,537 CE (76), until Pb pollution peaked in ~1,620 CE (Fig. 3B), by which time mines in the region were producing over 24.9 tons of Ag a year (77, 78).

The rapid decrease in Pb_{Anthro} at Crveni Potok at 1,649 CE, clearly identified as change point (Fig. 2F), appears linked with the restrictive impact of Ottoman laws and taxation system, which became progressively more convoluted and inefficient through the 17th century (41). The onerous laws and taxes, combined with the appearance of cheap and plentiful sources of Ag in the New World, particularly South America (79, 80), meant that by 1,690 CE Ag production in the region had all but ceased and did not recover until the end of Ottoman rule (41, 77). This is strongly reflected in the Pb_{Anthro} record, with progressive decreases until ~1,790 CE (Fig. 3B), a trend echoed also in the reduction in microcharcoal, and anthropogenic indicator taxa at Crveni Potok (Fig. 4), pointing to region-wide economic stagnation as stated in historical records (41).

The uppermost section of the Crveni Potok record (1,700–1,820 CE, Fig. 4) indicates that the low mining output that characterized later Ottoman Serbia was reversed in the early

19th century, around the time of the two uprisings (1,804–13 and 1,815–17 CE), which eventually led to the establishment of the Serbian state (81, 82). This Pb_{Anthro} upturn likely indicates the first impact of the Industrial Revolution in the Balkan area (Fig. 3B).

Comparison with Central-Western European Pollution Records. There are several similarities between Crveni Potok and western European pollution records, suggestive of comparable continent-wide metal production trends at times. Pb enrichment in the Bronze Age has previously been observed in Spain (22, 55), France (83), and Great Britain (84), although not as early as indicated in Crveni Potok (between 3,900 and 2,500 BCE). Furthermore, Roman-related pollution (as observed at Crveni Potok from 150 BCE onward) has previously been documented continent-wide (Fig. 5), from Spain (85, 86) through central Europe (87–89) and as far from centers of occupation as the Faroe Islands (90) and Greenland (91, 92). Finally, the impact of medieval pollution, which is so well expressed in the Crveni Potok record, has been observed previously but primarily close to known mining areas in southern Germany (88, 89) and northern England (21). Further away from such metallurgically active areas, only small-scale pollution is typically observed during the medieval period (Fig. 5) (90).

It is not the similarities with western European records that are the most interesting, however, but the differences. For example, clearly, the Romans had a major influence on the pollution history of the Balkans, echoing a Roman Pb pollution peak observed across much of Europe (Fig. 5) (20). However, as we show in this study, the end of the Roman period in central-western Europe did not bring a cessation of the mining activities in the Balkans (Figs. 3B and 5). This is in contrast to western

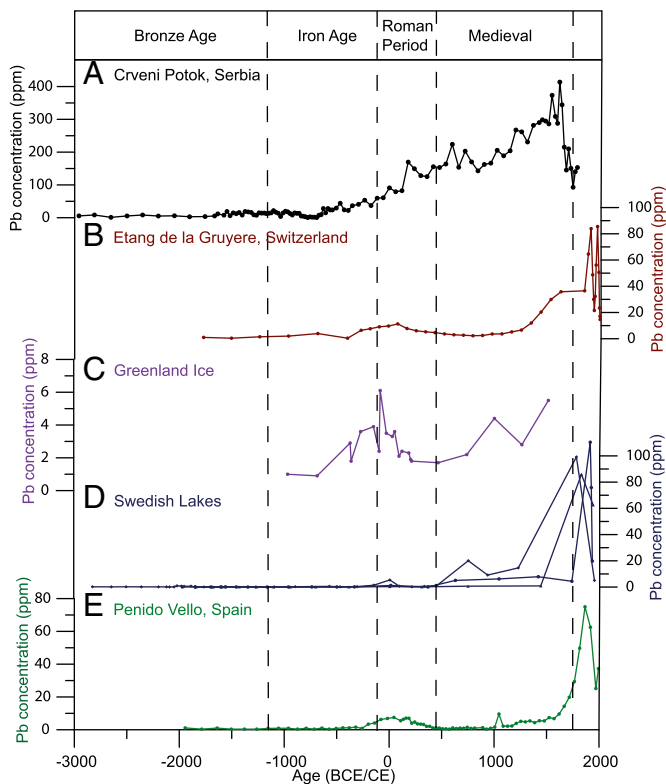


Fig. 5. Comparison of Pb_{Anthro} from Crveni Potok (A) with Pb records from western and northern Europe, (B) northern Switzerland (86), (C) Greenland ice (13), (D) southern Sweden (25), and (E) northwestern Spain (82).

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. 3*B*) (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}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 cm³ 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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