Heritage Science

# Copper exposure in medieval and post-medieval Denmark and northern Germany: its relationship to residence location and social position

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**Abstract**

For medieval and post-medieval Denmark and northern Germany, trace elements can potentially contribute to our understanding of diet, migration, social status, exposure to urban settings, and disease treatment. Copper, of particular interest as a marker of access to everyday metal items, can be used to clarify socioeconomic distinctions between and within communities. Postmortem alteration of bone (diagenesis), however, must be ruled out before the elements can be used to characterize life in the past. Femoral cortical bone samples of ca. 40 mg were thoroughly decontaminated, and the concentrations of Al, Ca, Mn, Fe, Cu, As, Sr, Ba, and Pb were measured using inductively coupled plasma mass spectrometry. The concentrations of these elements were quantified in bone samples from 553 skeletons from 9 rural and urban cemeteries, and 34 soil samples obtained near three burials. Copper, the primary element of interest in this work, is generally absent from the femoral cortical bone of rural people, although it occurs in high concentrations in the skeletons of the inhabitants of towns. The Cu in medieval to post-medieval bones likely originated from everyday objects, notably kitchen utensils. A rural to urban distinction in Cu concentrations, found repeatedly at two sites, likely resulted from differential access to much-desired, although still utilitarian, household items. An uneven distribution of metal objects used in domestic contexts, demonstrated through bone chemistry, was greater between rural and urban communities than it was within urban centres, at least among the socioeconomic positions sampled in this study.

**Keywords:** Bone chemistry, Copper, Lead, Medieval northern Europe, Cooking utensils

## Introduction

For several decades it has been recognized that the chemical composition of human skeletal remains can contribute much to an understanding of past societies, especially with regard to dietary composition, migration, social position, and medical practices [1–16]. Much of this work has focused on the stable isotopic composition of bone, although elemental concentrations have also played a part in this research. Among the trace elements in bone, Cu can potentially yield insights into medieval and early modern European social and economic systems through exposure to items, notably metal household utensils, that had uneven temporal, geographical, and social distributions. However, bone Cu concentrations have rarely been used for that purpose. The value of Cu for furthering understandings of life in the past is demonstrated here through an examination of Cu concentrations in 553 skeletons from nine centuries-old cemeteries from Denmark and northern Germany.

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During the medieval to early modern period, Cu exposure, hence its concentration in the skeleton, usually would have been related to an individual's access to everyday metal objects. Items such as kitchen utensils made from Cu or its alloys were irregularly distributed among and within European communities because access to trade networks and markets was uneven, and distinctions in social status had a great influence on the kinds of goods people could afford. In addition to socioeconomic reasons for differential Cu exposure, the element is a potential marker of the relatively few people who were directly involved in mining or metal working. Finally, elemental concentrations in archaeological bone, including Cu [17–23], can possibly be affected by diagenesis. In short, Cu in excavated bones might originate from the food and drink consumed, environmental exposure, or alterations in composition long after a skeleton was buried. Because the last confounds interpretations of archaeological skeletons, it is fortunate that Cu concentrations in bones from medieval to early modern Danish cemeteries are largely free of diagenetic effects as long as suitable precautions are taken when sampling thick cortical bone [24].

Denmark and adjacent portions of Germany are particularly well-suited for a study of Cu and what it can indicate about medieval and early modern societies. That is because objects fashioned from Cu and its alloys, especially bronze, were widely, but variably, used by different segments of the northern European population [25–38]. In general, the most important sources of exposure were metal kitchen utensils that were highly valued substitutes for their ceramic or wooden counterparts. When available, metal cooking utensils possessed several clear advantages for the households fortunate enough to have them: they were durable, capable of withstanding thermal shock from repeated use over open flames, and were relatively easy to clean.

Despite the potential for metal household items, including kitchen utensils, for providing insights into the nature of medieval and post-medieval societies, historical and archaeological information regarding their distribution are sparse, incomplete, and inconsistent, hence difficult to interpret [30, 32–34, 37]. Written records are scarce, and only occasionally do they provide a detailed accounting of household possessions. Archaeological materials are no better. Metal cooking vessels are likely to be underestimated in excavation samples because they are not as well preserved as pottery, and they had a longer use-life than their ceramic equivalents, hence are not as common in archaeological deposits. When broken, valuable and readily reworked metal could be reused for other purposes. In contrast, a broken ceramic vessel had no use at all, and the pieces were merely cast aside.

Because items fashioned from Cu are so poorly represented in habitation deposits relative to other debris, and the interpretation of excavated material is complicated by different depositional histories and dissimilar sampled contexts, it is difficult to evaluate the social and economic significance of an irregular distribution of metal kitchen utensils among archaeological sites.

Because of these problems with historical and archaeological information, human bones are more than just an additional source of evidence about Cu exposure. Bones are, in fact, potentially the most direct means of assessing temporal, geographical, and social variation in access to items fashioned from Cu and its alloys. That is because Cu concentrations in bone are a means of quantitatively measuring an individual's exposure to that element, as long as diagenesis does not muddy the picture.

Although this study focuses on Cu, the concentrations of several other elements are also reported. Lead has previously been shown to be an indicator of exposure attributable to where people lived and their position within society [10, 39, 40], and Sr and Ba provide information about residence location and dietary intake [4, 10, 11, 14, 41–45]. Calcium permits assessments of sample integrity, and Mn, Fe, Al, and As are useful in the evaluation of diagenesis as it pertains to Cu. Together these elements provide a level of detail about medieval and early modern life in northern Europe that cannot be obtained from other historical or archaeological sources.

## Copper in human skeletons
### A necessary element
Copper, an essential trace element, has long been regarded as having important, but as yet incompletely understood, effects on human health. Copper is involved in several metabolic processes, including the functioning of the immune system [46–51].

In modern populations, Cu intake is generally sufficient; in fact, it usually exceeds what is required [46, 52]. Dietary Cu absorption mainly occurs in the small intestine, and the liver plays a large role in its regulation through excretion via bile into the gastrointestinal tract in a form that prevents reabsorption [46, 49, 53, 54]. The absorption and excretion of Cu normally vary according to dietary intake to maintain proper levels in the body [49, 50, 54].

Copper concentrations within the body vary by age, sex, geographical region, and health status [46]. Unusually low concentrations of Cu have been associated with several pathological conditions, although it is often unclear precisely how deficiencies are related to pathological processes [46, 49, 51, 55]. From the perspective of the skeleton, Cu deficiency has been linked to osteoporosis, decreased bone strength, and femoral head necrosis

[46, 48, 52, 55]. Other pathological conditions are associated with high Cu levels [46, 47, 49, 56]. A toxic excess of Cu is rarely seen in clinical settings, but it can come about through impaired physiological functions [46, 48, 50, 53, 56] or through exposure to industrial or agricultural pollutants [57]. Such problems are usually not a consequence of surplus dietary Cu because of the effectiveness of normal regulatory mechanisms [47].

Copper in modern femoral samples varies greatly. Several studies report mean Cu concentrations below 1 μg g$^{-1}$ for femoral cortical, cancellous, both, or unspecified bone [58–60]. Maximum values, when provided, range from 1.89 (without osteoporosis) to 5.01 μg g$^{-1}$ [59, 60]. Another study found that Cu concentrations in femoral head cortical and cancellous bone had means of 3.7 and 2.6 μg g$^{-1}$ and maximum values of 17.7 and 20.4 μg g$^{-1}$, respectively [61]. The high values were from hip-replacement patients from Poland (Silesia), but these individuals were not otherwise selected for complications perhaps associated with excessive levels of Cu. Copper concentrations in the sternum, ribs, parietals, and unspecified bones are generally similar to those of the femora [62–65]. The significance of variation in the results from different studies is unclear because sampled people (age and sex), bones, parts of bones, and analytical procedures differ. For example, Cu concentrations in femoral cortical bone exceed those of cancellous bone in some studies [61, 66].

### Dietary origin

Considering the many ways people today can be exposed to Cu—through food, tap water, and industrial and agricultural contamination—it is difficult to evaluate the origin of variation in the element's concentration in biological tissues. The issue is by no means straightforward when trying to isolate what is contributed by the diet alone. Despite Cu being more concentrated in meat (muscle and organs), it only provides 15 to 20% of the dietary intake of Cu in present-day France, as opposed to cereals and vegetables that provide 40% or more [47]. The Cu content of different foods must be balanced against the amount of those same foods that are consumed. Then there is the bioavailability of Cu to consider once foods and liquids are ingested. For example, Cu adsorption was found to be greater in a vegetarian than a nonvegetarian diet; in the former, relatively less Cu was absorbed from food that had a higher Cu content [67].

When used for the reconstruction of diets in the distant past, high Cu concentrations in bone have been said to indicate a diet rich in meat from various sources, although it can be obtained from other kinds of food as well [68–75]. Other researchers regard Cu as ambiguous with respect to dietary composition [76], although high

levels could be consistent with a diet heavy in cereals and legumes [45], especially as absorption through the gastrointestinal tract is not straightforward [74]. More work is therefore needed before Cu can be effectively used as a dietary indicator [77]. Ambiguity about what the Cu content of bone signifies, coupled with a concern about diagenetic effects, is presumably why the element has received scant attention in palaeodietary research.

In addition to what is naturally present in food, Cu can be ingested as a result of either storing or cooking liquids and food in containers made from the metal and its alloys [57]. In unusual circumstances, doing so can lead to toxic levels of Cu, although in some clinically recognized conditions there is a genetic component that affects metabolism with outcomes severe enough to include death [49, 78]. Tap water is a frequent source of exposure in modern populations [47, 49, 78]. While acute or chronic Cu poisoning can occur today, it is unlikely to have been a problem for the great majority of people in the distant past because Cu pipes were not present and metal kitchen utensils, even when available, were in short supply. Nevertheless, exposure attributable to metal cooking and storage vessels, when present, will complicate dietary interpretations from archaeological bones. Depending on the nature and frequency of their use, Cu exposure from the vessels could completely mask a dietary signature.

### Environmental exposure

Environmental Cu concentrations vary from one location to another, and can be quite high in places affected by mining, industrial processes, or some agricultural practices. While commonly thought of as a feature of modern life, anthropogenic introductions of metals, including copper, to local settings, hence what people experienced on a daily basis, date back to antiquity.

On a global scale, measurements from Greenland ice cores indicate Cu concentrations noticeably increased from background levels during the Roman period, and from that time onward were variable but remained relatively high [79]. This period of atmospheric pollution, attributed to production in Europe and China, was followed by greatly increased Cu levels from the industrial revolution to the present day.

Specific environmental settings in Europe, often complicated by the proximity of mining operations, present a mixed picture with regard to the ice core findings, although marked increases in Cu concentrations took place over the last several hundred years, extending as far back as about a half millennium [80–84]. Not all sequences, however, conform to higher levels of Cu starting a few centuries ago, perhaps because of local environmental conditions, specific sampling locations, or inaccurate dating [82, 85, 86]. A picture of variable Cu

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concentrations in the Greenland ice cores is also apparent in European deposits dating back to the Roman period, if not before, presumably as a result of both atmospheric Cu and nearby mining and ore processing [80, 83, 87].

The Cu content of human bones from Europe likewise differed from one time and place to another. Copper was highest in Roman period skeletons from the Cartagena area in Spain when compared to earlier and later bones, including modern ones [88], although these results have been questioned because of the possibility of diagenesis [89]. Notably high concentrations have also been found in archaeological skeletons from individuals thought to have been involved in the extraction and production of items made from Cu or living in settings contaminated from such activities [20, 90, 91]. Pollution from ancient Cu production can have a lasting effect on local environments, as seen by elevated concentrations in soil, plants, and animals that have persisted to the present day [92, 93].

### Copper from diagenesis

From the perspective of assessing Cu concentrations in skeletons from archaeological contexts, it is fortunate that bone stores much of the Cu in the body [46]. That makes the skeleton a potentially good source of samples for measuring Cu exposure. Postmortem alteration of the elemental composition of bone, however, complicates any such interpretations about the life experiences of people in the past.

Postmortem alterations of the elemental concentration of archaeological specimens can come about through a replacement of elements in the bone's original crystalline matrix or as foreign material within vascular canals and microbe-produced openings that had precipitated out of solution or was introduced as particles [94–96]. Unsurprisingly, the possibility of such contamination is related to the chemical composition of the sediment and groundwater surrounding the skeletal material [97]. With regard to Cu, its adsorption in hydroxyapatite powder from finely ground bone has been found to be rapid [98]. Because of the small grain size, such experimental work is not directly applicable to skeletal material, especially intact cortical bone. More relevant for archaeological purposes are animal bones from a medieval Parisian workshop where copper-alloy objects were produced [19]. The heavily contaminated nature of soil in and around the workshop led to a green staining on some bones, and these specimens had higher Cu concentrations than others from the site. Copper-alloy particles were even detected in small cavities within the bones. In cross sections, Cu concentrations were highest near a bone's external and internal surfaces.

Although diagenetic Cu contamination has been a concern for most, but not all, studies of archaeological materials [17–23, 39, 99, 100], a recent study of centuries old Danish skeletons has shown that alterations in Cu content occur within the outer 500 μm of compact bone [24]. This work shows that suitable precautions taken when sampling thick cortical bone, starting with a mechanical removal of the outermost surface to a depth of at least 1 mm, are sufficient to obtain satisfactory samples from Danish medieval or later skeletons.

## Materials

### Human bones

Samples of femoral cortical bone were analysed from 553 medieval to post-medieval skeletons. The skeletons came from nine cemeteries in Denmark and northern Germany that held the remains of people from rural and urban communities (Fig. 1). The skeletons are stored at the Schloss Gottorf in Schleswig, Germany, and at ADBOU at the University of Southern Denmark in Odense, Denmark.

1. Ole Worms Gade was a parish cemetery for the town of Horsens, and it was used from the early Middle Ages to AD 1480 [101, 102]. The Church of Our Lady was awarded to the Knights Hospitaller by King Valdemar Atterdag in AD 1351, although the cemetery remained a burial ground for the people of Horsens until AD 1480 when the parish was transferred to the Church of Our Saviour at the town square. It even continued in use until the Reformation in AD 1536. The long and intensive use of Ole Worms Gade meant that many early graves were destroyed by later ones. Therefore, a disproportionately large number of the skeletons that were complete, or nearly so, date to the later use of the cemetery, mainly the 15th century. Like many urban populations, Horsens' inhabitants are thought to have been relatively mobile, with many coming from the surrounding countryside. Eighty-five skeletons were analysed.

2. Tirup was a rural village located 1.3 km outside of medieval Horsens. Graves surrounded a church, which was replaced once. The graveyard was used from ca. AD 1150 to 1350, based on archaeological and documentary sources [103–105]. Grave and body positions indicate that most of the deaths took place in the 13th century [106]. The people interred in this cemetery, of which 54 were analysed, did not move as frequently during their lifetimes as the inhabitants of contemporaneous urban communities [10, 107, 108].

3. A cemetery surrounding Our Lady's Church in Haderslev (it became Haderslev Cathedral in 1922) was

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**Fig. 1** The Danish and German study area showing cemetery locations

in use from the early medieval period to shortly after AD 1800. All excavated skeletons date from AD 1661 to 1810 [109]. Haderslev was a major town in south-eastern Jutland, and the cemetery holds the remains of what was probably, for its time, a relatively urban and mobile population. Nineteen individuals were analysed.

4. The Nybøl church and cemetery was situated some 12 km west of the medieval city of Haderslev. Archaeologically, the cemetery probably goes back to the 13th century, and it is mentioned as an abandoned chapel around AD 1450 in the register of Schleswig Cathedral [109]. It is likely that the cemetery went out of use after the Black Death, but it is possible that burials were made even into the 15th century. The 70 skeletons excavated were well preserved, but damaged by potato farming. The skel-

etons have never been reported in detail, although they were included in data used to characterize the general characteristics of Denmark's medieval population [110]. Twenty-two skeletons were analysed.

5. Schleswig's Rathaus Markt cemetery was 80 m east of the town's cathedral, but the graveyard most likely belonged to a church, St. Trinity, that no longer exists [111]. Oak coffins in 25 graves were dendrochronologically dated to between AD 1060 and 1205 [112]. The church and associated cemetery were abandoned early in the 13th century, perhaps when a market square, the Rathaus Markt, was established [113]. In AD 1234, a Franciscan Friary was built that partly overlapped the cemetery. The skeletal sample was large [111, 114], and 50 individuals, all of whom died before AD 1234, were analysed.

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6. St. Clements Kirche was located northeast of Schleswig's medieval centre, just outside the town's northern gate. St. Clements parish was mentioned in documents for the first, and only, time in AD 1196. The church and cemetery predated Schleswig's town gate, which was built around AD 1200, because graves have been found under the road that passed through it [115]. Previously, St. Clements has been considered an urban cemetery because it is well within the present city limits. Our analyses, however, have shown that the people buried there were in some respects similar to what would be expected of a rural population [10, 111]. Twenty skeletons were examined. It is the only sample where individuals were selected to conform to a specific age range, in this instance 20 to 40 years; that was done to meet the requirements of a separate project.

7. The Dominican Friary in Schleswig was 110 m south of the eastern end of the cathedral in Pastorenstraße 3–7 and in a garden to the south. The monastery was founded in AD 1239, its patron saint was St. Mary Magdalene, and the friary belonged to the Dominican province of Dacia. The cemetery was situated east of the friary, and graves were also found in the inner courtyard and surrounding galleries [113, 116]. Of the skeletons at the site [111], 64 were analysed.

8. Johanitter Kloster (St. John's Nunnery) in Schleswig was on the *Holm*, a small island primarily inhabited by fishermen east of the town-centre. A parish church, built around AD 1170, was taken over by the Benedictines as a nunnery, which was founded early in the 13th century. The cemetery was south of the church where monastery buildings were later erected. The first structure was made of wood, and it burned down in AD 1299. Later three wings, dating to the 14th to 15th centuries, were built of bricks [112, 115, 117]. Thirty-one skeletons from a larger skeletal collection were examined. Some of them predated the Benedictine monastery, whereas others probably were post-Reformation burials [111, 118, 119].

9. Ribe is the oldest town in present-day Denmark, and it was home to the earliest Christian community dating as far back as ca. AD 860 [120–122]. The 208 skeletons analysed here came from an area south of the cathedral that was part of a processional walk and an inner courtyard, the *Lindegaarden*. Archaeological evidence and stratigraphic positioning allow the skeletons to be separated into four periods: AD 800–1050 (Viking Age), AD 1225–1425, AD 1425–1738, and AD 1738–1805.

## Soil samples

Thirty-four soil samples were also analysed from around skeletons in Horsens' Ole Worms Gade graveyard. The soil samples were taken in increasing distance from one of the major long bones, horizontally and sometimes also vertically. That was done to determine if it was possible to identify soil with a chemical signature corresponding to soft tissue that had decayed centuries ago, and to monitor diagenesis.

## Methods

Skeletons from all nine sites were cleaned years ago, many of them before the present sampling procedures for bone chemistry were established. The general practice—then and now—is to brush bones in running tap-water to remove adhering soil. There is no written record indicating that the bones were treated with preservatives that could result in Cu contamination, and the application of consolidants has not been a common practice in the study area. Perhaps more to the point, the bones do not look as if they were treated with a material to preserve them either during excavation or afterwards in the laboratory. Generally, such material is readily apparent when applied to archaeological bones.

Sampled areas of bone did not have the distinctive green staining that occurs when Cu objects are in contact with archaeological skeletons or when the soil is saturated with Cu. In fact, such staining rarely occurs on medieval and post-medieval bones from the study area, other than occasionally on skulls from Cu-pins or parts of hairnets.

Samples were cut from femora, including samples of both cortical and trabecular bone, with a 2 mm diameter stainless steel drill bit mounted on a Dremel Multipro drill. The drill bit was washed between samples in deionized water, and subsequently dried in an ethanol flame. Surface bone was removed by drilling to avoid contamination from soil as well as from handling during excavation, initial cleaning, and storage. Only cortical bone deeper than 1 mm was used for chemical analyses. Examinations of cortical bone cross-sections have shown that 1 mm is at least twice the depth of physically and chemically degraded bone normally seen in Danish medieval skeletons [24].

Several trace element concentrations were quantified using inductively coupled plasma mass spectrometry (ICP-MS), but only Cu, Pb, Sr, Ba, Fe, Mn, Al, As, and Ca are reported here. Approximately 40 mg of bone powder were taken, 20 mg of which were used for the ICP-MS analysis. The bone samples were at all times handled by stainless-steel utensils, which were rinsed in MilliQ water and heated in an ethanol flame between

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each sample. After a sample was weighed, it was transferred to a clean 50 mL disposable polypropylene centrifuge tube. To bring the samples into solution, 2 mL of concentrated 69% ICP-MS grade $HNO_3$ (TraceSELECT® Fluka) and 1 mL of concentrated 30% ICP-MS grade $H_2O_2$ (TraceSELECT® Fluka) were added to the tube. The lid was loosely put on the tube before it was placed on a shaking table for no less than 3h. The quantity of $H_2O_2$ consumed during bone dissolution depends on how much collagen was present, and an overabundance of $H_2O_2$ was added to each sample. After this treatment, the surplus $H_2O_2$ was removed by adding 335 μL of concentrated 37% ICP-MS grade HCl (PlasmaPURE Plus® SCP Science) and then placing the tube, with its loosely fitted lid, on a shaking table overnight. The solutions were subsequently stored at +4 °C until analyses could be conducted. The day before being analysed, each sample was diluted quantitatively to 10 mL with MilliQ water, after which it was filtered through a 0.45 μm PVDF Q-Max® RR Syringe filter into a new 15 mL disposable polypropylene centrifuge tube. One-half of the solution was used for ICP-MS. Further quantitative dilution was done in 15 mL tubes according to the concentrations of specific samples, normally a 3 mL sample solution and 9 mL MilliQ water. In so doing, the diluted samples acquired an acid concentration of approximately 1%, which is suitable for ICP-MS analysis.

The ICP-MS analyses were undertaken with a Bruker ICP-MS 820 equipped with a frequency matching RF-generator and a Collision Reaction Interface (CRI) operated with either helium or hydrogen as skimmer gas. Samples were introduced through a Bruker SPS3 autosampler and an OneFast flow injection inlet system. The radiofrequency power was 1.40 kW, plasma gas flow rate was 15.50 L min⁻¹, auxiliary gas flow rate was 1.65 L min⁻¹, sheath gas flow rate was 0.12 L min⁻¹, and nebulizer gas flow rate was 1.00 L min⁻¹. Several isotopes were measured without skimmer gas: Mg24, Al27, Ca44, Mn55, Sr88, Sb121, Ba137, and Pb208. For Fe, Cu, Zn, and As, the CRI reaction system was used because of interferences with polyatomic species produced by isotopes from the argon plasma, reagents, and the bone matrix. Hydrogen was used as a skimmer gas for Fe56 and Zn66, and helium for Cu63 and As75. A mixture of Sc45, Y89, and Tb159 was added continuously to all samples as an internal standard, which was used to correct the signal for possible drift or spurious variations. It should be noted that neither Y nor Tb are unusually high in the analysed samples. The dwell time on each peak was between 5 and 20 ms. For each dissolved bone sample five replicate analyses were performed. Each replicate was measured with 30 mass scans using peak-hopping. The ICP multi-element standard solution XXI for MS
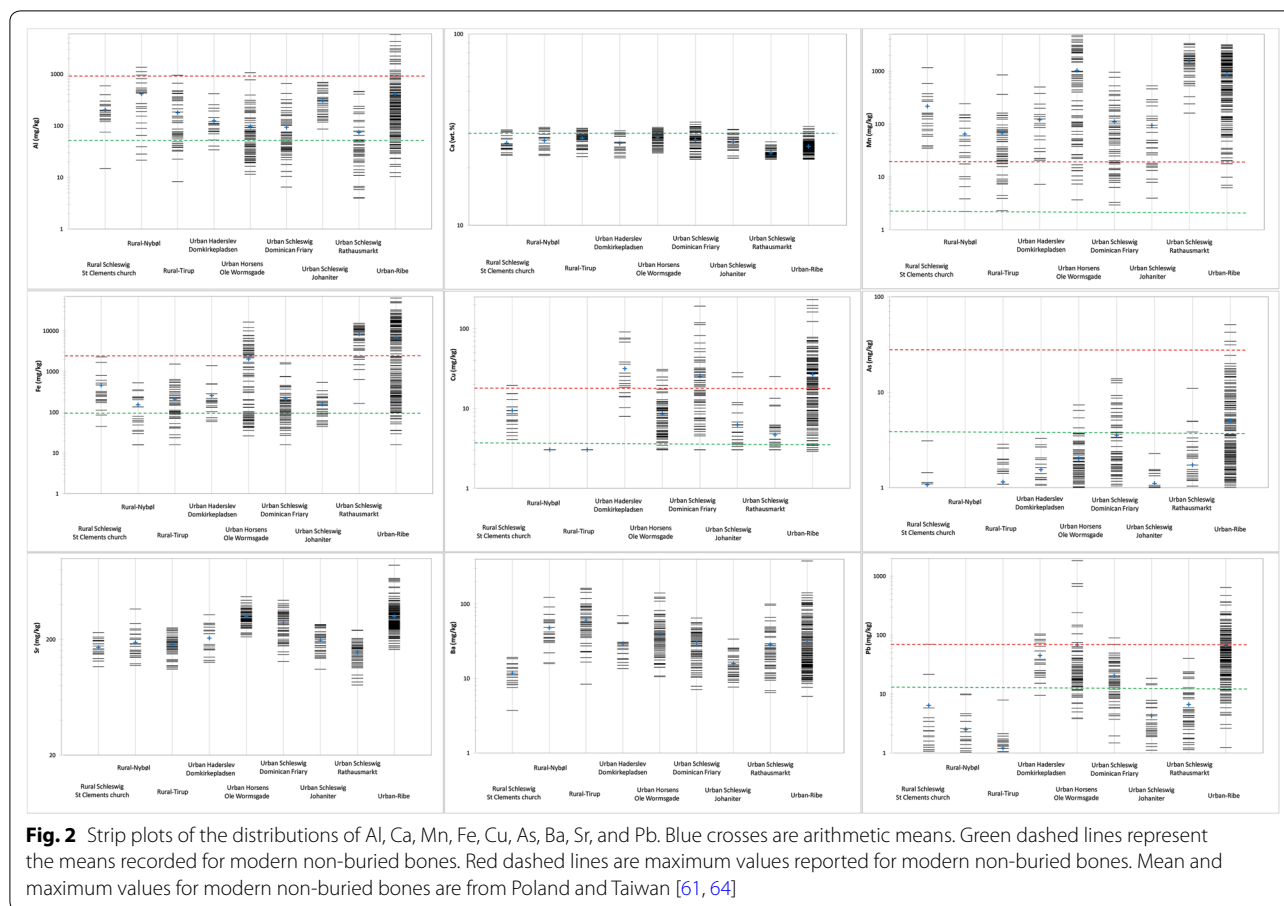
from Merck was prepared in ICP-MS grade 1% $HNO_3$ (TraceSELECT® Fluka) at five concentrations: 1, 10, 20, 100, and 200 μg L⁻¹. Three of these standard solutions were used for each element. They were chosen to fit the appropriate concentration range of the actual samples. For Ca three standards (Fluka TraceCert® ICP Standard) of concentrations 100, 200, and 250 mg L⁻¹, corresponding to 10, 20, and 25 wt % Ca in the bone, were used. Elements showing higher than expected concentrations had count rates attenuated automatically by the MS-detector. Blank samples of MilliQ water and 1% $HNO_3$ were run before the standard blank to ensure that there were no pollutants lingering in the system at start up. Between each bone sample, a blank sample of 1% $HNO_3$ was passed through the system to suppress possible memory effects. An in-house bone standard manufactured from a crushed and homogenized medieval bone was analysed each day to monitor the equipment's overall performance. Also analysed with the bone samples was an international standard of modern bone, NIST SRM-1486. For the modern samples more $H_2O_2$ was added to cope with its higher collagen content. The overall procedure has been described previously [10, 14].

Concentrations below the LOQ (limit of quantification) are reported as < LOQ. The LOQ is calculated as 10 times the standard deviation, which in turn is calculated as a mean of the uncertainties measured over a ca. half-year period with one or two weekly runs. At present, the LOQ values are as follows: Al, 3.63 μg g⁻¹; Ca, 40.7 μg g⁻¹; Mn, 2.22 μg g⁻¹; Fe, 15.9 μg g⁻¹; Cu, 3.04 μg g⁻¹; As, 0.92 μg g⁻¹; Sr, 3.06 μg g⁻¹; Ba, 3.52 μg g⁻¹; and Pb, 0.94 μg g⁻¹. The measurements reported in this publication were done over a period of several years, and the LOQs have improved somewhat over time through method optimization; therefore, the LOQs were slightly different (higher) when some of the early measurements were done.

Soil samples were handled in a manner similar to the bone samples. The analyses, therefore, reflect the content of bioavailable elements. Other than carbonates, the material analysed excludes geological components such as mineral crystals that cannot be digested.

## Results

For each sample, Cu, Pb, Sr, Ba, Ca, Mn, Fe, Al, and As concentrations are reported plus-and-minus one standard deviation of analytical uncertainty (see Additional file 1). Soil samples are similarly presented (see Additional file 2). Elemental distributions are displayed in Fig. 2. To calculate mean concentrations of Cu, Pb, and As, the values < LOQ were replaced by their respective LOQ values. These substitutions, of course, distort the true distributions, if they could be known. That said,

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**Fig. 2** Strip plots of the distributions of Al, Ca, Mn, Fe, Cu, As, Ba, Sr, and Pb. Blue crosses are arithmetic means. Green dashed lines represent the means recorded for modern non-buried bones. Red dashed lines are maximum values reported for modern non-buried bones. Mean and maximum values for modern non-buried bones are from Poland and Taiwan [61, 64]

because the same number was used for each element, comparisons between cemeteries are still relevant. A Spearman correlation coefficient matrix was calculated individually for the nine cemeteries (Table 1). The correlation of Cu, Pb, and As were only calculated based on values that were > LOQ. There were not enough data points > LOQ to calculate correlation coefficients for samples from the three rural cemeteries.

**Copper and lead**
Copper concentrations were highly variable among the nine cemeteries, but some trends stand out. Copper was virtually absent from the femoral cortices of people from rural Nybøl and Tirup (Additional file: 1). Contrasts between nearby urban and rural settings were most striking in paired settlements, each consisting of a town and village. Copper concentrations are plotted as a function of those for Pb for Haderslev, an urban site, and rural Nybøl (Fig. 3a), as well as for urban Horsens and rural Tirup (Fig. 3b). Copper concentrations for all individuals from the Tirup and Nybøl villages were below LOQ (< 3.04 μg g$^{-1}$). Lead was also lower in skeletons from the rural sites.

Beyond the rural–urban distinction, there was a noticeable difference between Cu concentrations in skeletons from the towns of Horsens and Haderslev (Fig. 3a, b). Individuals from Haderslev's Cathedral graveyard generally had somewhat higher Cu concentrations (ca. 10–100 μg g$^{-1}$) than those from Horsens' Ole Worms Gade (mostly between 3 and 30 μg g$^{-1}$, with a few below LOQ).

By way of comparison, Cu and Pb concentrations reported by Grattan et al. [20] for individuals from a community of copper smelters in southern Jordan during the 4th to 7th centuries ACE are shown (Fig. 3c). These data are generally consistent with Cu-exposed people from towns in medieval and early modern Denmark.

Data from the four Schleswig cemeteries underscore the variation that can occur in urban settings (Fig. 4). Skeletons from the parish cemetery Rathaus Markt tended to have low Cu concentrations; in fact, 28 of 50 individuals were < LOQ. This finding might have to do with the age of the cemetery because it predated the establishment of a Franciscan Friary built on the site in AD 1234. The Johanitter Kloster skeletons also had rather low Cu concentrations, although fewer of them

**Table 1 Spearman correlation coefficient matrix. The correlation coefficients for Al, Ca, Mn, Fe, Ba, and Sr are calculated on the entire population (553 samples)**

| Cemeteries | Variables | Al | Ca | Mn | Fe | Sr | Ba | Cu | As | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| | Al | 1 | | | | | | | | |
| | Ca | − 0.547 | 1 | | | | | | | |
| | Mn | 0.323 | − 0.636 | 1 | | | | | | |
| Rural Schleswig-St Clements | Fe | 0.668 | − 0.466 | 0.657 | 1 | | | | | |
| | Sr | − 0.135 | 0.188 | 0.195 | 0.329 | 1 | | | | |
| | Ba | 0.514 | − 0.367 | 0.325 | 0.564 | 0.014 | 1 | | | |
| | Cu | NA | NA | NA | NA | NA | NA | NA | | |
| | As | NA | NA | NA | NA | NA | NA | NA | NA | |
| | Pb | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | Al | 1 | | | | | | | | |
| | Ca | − 0.290 | 1 | | | | | | | |
| | Mn | 0.689 | − 0.092 | 1 | | | | | | |
| Rural-Nybøl | Fe | 0.727 | − 0.225 | 0.613 | 1 | | | | | |
| | Sr | − 0.046 | 0.735 | − 0.197 | − 0.038 | 1 | | | | |
| | Ba | − 0.085 | − 0.011 | − 0.119 | − 0.048 | 0.084 | 1 | | | |
| | Cu | NA | NA | NA | NA | NA | NA | NA | | |
| | As | NA | NA | NA | NA | NA | NA | NA | NA | |
| | Pb | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | Al | 1 | | | | | | | | |
| | Ca | − 0.361 | 1 | | | | | | | |
| | Mn | 0.338 | − 0.299 | 1 | | | | | | |
| Rural-Tirup | Fe | 0.857 | − 0.331 | 0.311 | 1 | | | | | |
| | Sr | 0.064 | 0.365 | − 0.328 | 0.142 | 1 | | | | |
| | Ba | 0.461 | 0.088 | − 0.047 | 0.496 | 0.582 | 1 | | | |
| | Cu | NA | NA | NA | NA | NA | NA | NA | | |
| | As | NA | NA | NA | NA | NA | NA | NA | NA | |
| | Pb | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| | Al | 1 | | | | | | | | |
| | Ca | − 0.242 | 1 | | | | | | | |
| | Mn | 0.596 | − 0.588 | 1 | | | | | | |
| Urban Haderslev-Our Lady's Church | Fe | 0.677 | − 0.163 | 0.402 | 1 | | | | | |
| | Sr | − 0.247 | 0.811 | − 0.514 | − 0.040 | 1 | | | | |
| | Ba | − 0.388 | 0.061 | − 0.470 | − 0.004 | 0.398 | 1 | | | |
| | Cu | 0.380 | 0.500 | 0.230 | 0.294 | 0.297 | − 0.642 | 1 | | |
| | As | − 0.081 | 0.125 | − 0.076 | 0.194 | 0.449 | 0.564 | − 0.245 | 1 | |
| | Pb | 0.368 | − 0.353 | 0.392 | 0.047 | − 0.341 | − 0.304 | − 0.083 | − 0.051 | 1 |
| | Al | 1 | | | | | | | | |
| | Ca | − 0.334 | 1 | | | | | | | |
| | Mn | 0.131 | − 0.308 | 1 | | | | | | |
| Urban Horsens-Ole Wormsgade | Fe | 0.372 | − 0.329 | 0.827 | 1 | | | | | |
| | Sr | − 0.197 | 0.287 | 0.200 | 0.138 | 1 | | | | |
| | Ba | 0.309 | − 0.219 | 0.580 | 0.669 | 0.247 | 1 | | | |
| | Cu | 0.238 | 0.032 | − 0.040 | − 0.067 | 0.130 | 0.120 | 1 | | |
| | As | 0.032 | 0.053 | 0.352 | 0.462 | 0.197 | 0.456 | 0.193 | 1 | |
| | Pb | − 0.054 | − 0.089 | 0.022 | − 0.056 | − 0.160 | − 0.033 | 0.211 | − 0.160 | 1 |
| | Al | 1 | | | | | | | | |
| | Ca | − 0.274 | 1 | | | | | | | |
| | Mn | 0.567 | − 0.367 | 1 | | | | | | |

**Table 1 (continued)**

| Cemeteries | Variables | Al | Ca | Mn | Fe | Sr | Ba | Cu | As | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| Urban Schleswig-Dominican Friary | Fe | *0.462* | *0.275* | 0.072 | *1* | | | | | |
| | Sr | 0.140 | *0.640* | 0.016 | *0.437* | *1* | | | | |
| | Ba | 0.159 | *0.462* | − 0.035 | *0.466* | *0.582* | *1* | | | |
| | Cu | *0.481* | 0.028 | *0.312* | *0.311* | *0.303* | 0.204 | *1* | | |
| | As | 0.110 | *0.526* | − 0.027 | *0.410* | *0.404* | *0.468* | *0.325* | *1* | |
| | Pb | *0.296* | 0.052 | 0.150 | *0.311* | 0.123 | − 0.034 | − 0.030 | 0.095 | *1* |
| | Al | *1* | | | | | | | | |
| | Ca | − 0.114 | *1* | | | | | | | |
| | Mn | *0.481* | 0.104 | *1* | | | | | | |
| Urban Schleswig-Johaniter Kloster | Fe | *0.735* | − 0.016 | *0.476* | *1* | | | | | |
| | Sr | 0.083 | *0.356* | 0.106 | − 0.159 | *1* | | | | |
| | Ba | 0.238 | − 0.078 | − 0.090 | 0.103 | 0.196 | *1* | | | |
| | Cu | − 0.119 | 0.595 | 0.357 | 0.000 | 0.476 | − 0.381 | *1* | | |
| | As | 0.357 | − 0.619 | − 0.238 | 0.190 | − 0.500 | 0.548 | − *0.857* | *1* | |
| | Pb | 0.357 | − 0.167 | − 0.357 | 0.119 | − 0.190 | 0.333 | − 0.167 | 0.500 | *1* |
| | Al | *1* | | | | | | | | |
| | Ca | − 0.267 | *1* | | | | | | | |
| | Mn | *0.699* | − 0.252 | *1* | | | | | | |
| Urban Schleswig-Rathaus Markt | Fe | *0.610* | − *0.353* | *0.703* | *1* | | | | | |
| | Sr | *0.508* | 0.080 | *0.606* | *0.386* | *1* | | | | |
| | Ba | *0.303* | 0.019 | *0.569* | *0.394* | 0.275 | *1* | | | |
| | Cu | 0.037 | 0.191 | 0.516 | 0.103 | 0.297 | 0.244 | *1* | | |
| | As | *0.442* | − 0.024 | 0.160 | *0.415* | 0.270 | 0.244 | − 0.130 | *1* | |
| | Pb | − 0.037 | 0.508 | − 0.125 | − 0.209 | − 0.024 | 0.182 | − 0.130 | − 0.442 | *1* |
| | Al | *1* | | | | | | | | |
| | Ca | − 0.052 | *1* | | | | | | | |
| | Mn | *0.356* | − *0.171* | *1* | | | | | | |
| Urban-Ribe | Fe | *0.679* | − *0.141* | *0.771* | *1* | | | | | |
| | Sr | *0.303* | *0.201* | *0.293* | *0.373* | *1* | | | | |
| | Ba | *0.601* | − 0.126 | *0.671* | *0.853* | *0.365* | *1* | | | |
| | Cu | *0.219* | 0.096 | 0.131 | *0.152* | *0.192* | *0.264* | *1* | | |
| | As | *0.518* | − 0.118 | *0.648* | *0.830* | *0.356* | *0.757* | *0.157* | *1* | |
| | Pb | *0.275* | − 0.148 | 0.032 | 0.113 | − 0.116 | 0.126 | *0.159* | 0.010 | *1* |

For Cu, As, and Pb the coefficients are calculated on the samples, excluding those less than LOQ (351 samples)
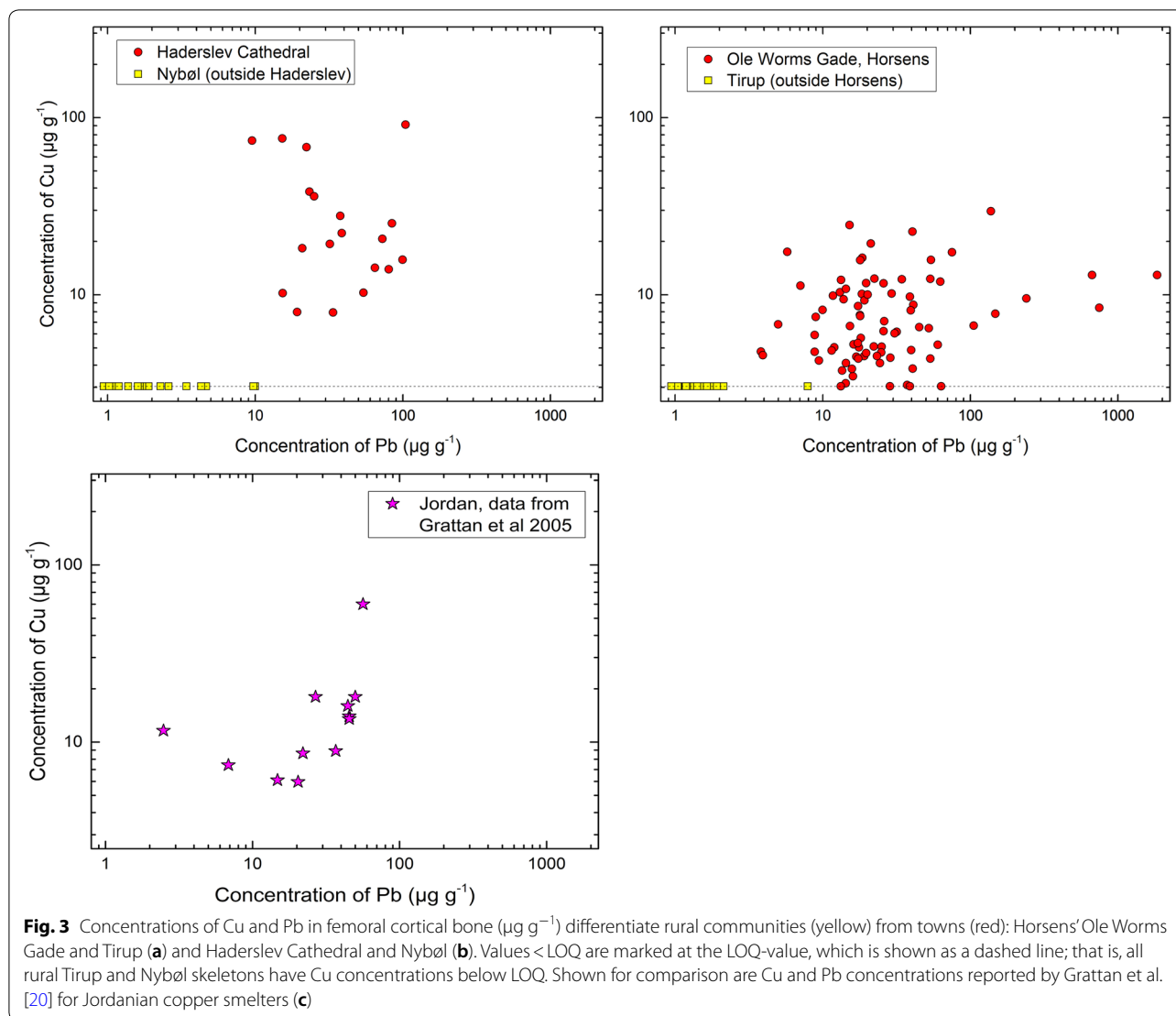
Italic = significative value with p value < 0.05

*NA* Not applicable because of small sample size

were below LOQ. The Johanitter Kloster graveyard was initially attached to a Benedictine Nunnery, but many of the people interred there likely dated to the post-Reformation period. At that time, they would have been part of an urban community that encompassed residents of the small island *Holm* and nearby Schleswig proper. Moderately low Cu concentrations were found in skeletons from St. Clements Kirche, located next to the town. The highest Cu concentrations in Schleswig were found in skeletons from the cloister walk of the Dominican Friary, established near the cathedral in AD 1239. Some of these individuals were probably Dominican friars, but many

were not because graves for women and children were scattered among those for men. The Dominican Friary skeletons also tended to have higher Pb concentrations than those from the three other Schleswig cemeteries.

An extensive graveyard around the cathedral in Ribe, one of the largest medieval Danish communities, provides a perspective on change over time in Cu and Pb exposure within urban settings (Fig. 5). The range of Cu values for the Viking Age (AD 800–1050) skeletons was every bit as large as it was later in time, although in aggregate the concentrations were lower than in individuals who died during the AD 1225–1425 period. Copper

**Fig. 3** Concentrations of Cu and Pb in femoral cortical bone (µg g$^{-1}$) differentiate rural communities (yellow) from towns (red): Horsens' Ole Worms Gade and Tirup (**a**) and Haderslev Cathedral and Nybøl (**b**). Values < LOQ are marked at the LOQ-value, which is shown as a dashed line; that is, all rural Tirup and Nybøl skeletons have Cu concentrations below LOQ. Shown for comparison are Cu and Pb concentrations reported by Grattan et al. [20] for Jordanian copper smelters (**c**)

concentrations then seemed to decrease in the AD 1425–1738 and AD 1738–1805 periods. Some Viking Age bones had low Pb concentrations relative to later ones from the Middle Ages. In the latest time interval, AD 1738–1805, there was a slight upward shift in Pb concentrations from what they were centuries earlier. Yet despite those temporal differences in Cu and Pb concentrations at Ribe, they were in aggregate never as low as those from rural Tirup and Nybøl (Figs. 3a, b, and 5).

### Copper, strontium, and barium

The distributions of Sr and Ba in the two urban–rural cemetery pairs, Horsens-Tirup and Haderslev-Nybøl, were dissimilar. The Sr and Ba distributions from Haderslev and Nybøl overlapped (Fig. 6a). In contrast, people buried in Horsens' Ole Worms Gade, as a whole, were distinguishable from those in Tirup (Fig. 6b). While there

was some difference in Ba concentration values, there was a clear distinction in the Sr concentrations between the Horsens and Tirup skeletons.

In Schleswig, skeletons from the Dominican Friary were enriched in Sr relative to other community members, although the Ba distributions were similar (Fig. 7). In Ribe, there was little change over time in the Sr and Ba values (Fig. 8). The overall Cu and Pb distributions do not covary with those in the Sr–Ba plots for these particular sites (Figs. 5, 8).

### Copper versus diagenesis indicators

Copper concentrations at Ole Worms Gade in Horsens were not related in any predictable way to Fe, Mn, Al, or As (Fig. 9). With regard to the relationship between Cu in bones and soil, there is no systematic relationship of Cu concentrations in cortical bone (CO) and trabecular bone

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**Fig. 4** Concentrations of Cu and Pb in femoral cortical bone ($\mu g\ g^{-1}$) from skeletons in four Schleswig cemeteries: Rathaus Markt (**a**), St. Clements Kirche (**b**), Johanitter Kloster (**c**), and the Dominican Friary (**d**). Values below LOQ—Cu at 3.04 $\mu g\ g^{-1}$ and Pb at 0.94 $\mu g\ g^{-1}$—are shown on dashed lines
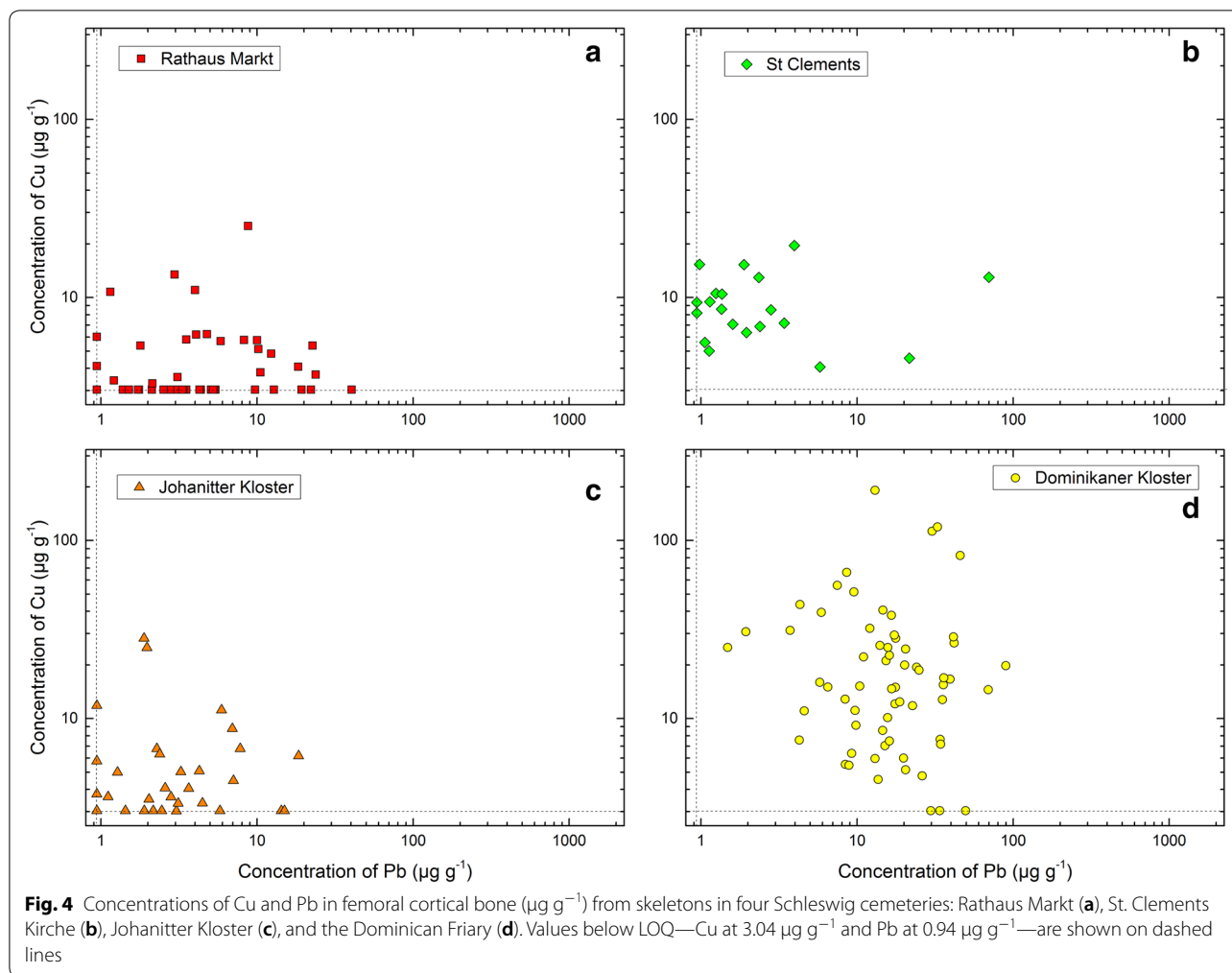
(TR) from three Horsens skeletons and the surrounding soil up to ca. 10 cm away from the bone (Fig. 10). The distributions of Cu and Pb concentrations in soil samples near each of the three skeletons are different (Fig. 11). The concentrations probably reflect local differences in soil composition as well as the contributions of now-decayed soft tissue.

## Discussion

### Diagenesis indicators—Fe, Mn, Al, As

Before inferences are drawn about past conditions from archaeological bones, it must be established that the element(s) of interest is indicative of what took place during the lives of the sampled individuals rather than what happened after they had died and were buried. The elements Fe, Mn, Al, and As have consistently been reported as being strongly affected by diagenesis [24, 123–125].

The correlation coefficient matrix shows a strong correlation (> 0.7) between Fe and Mn in the urban cemeteries of Ribe, Horsens, and Rathaus Markt (Additional file: 1).

The same (correlation between 0.6 and 0.7) can be said about Fe and Mn in skeletons from the rural cemeteries of Schleswig's St. Clements Kirche and Nybøl. The mean values of Fe from the rural cemeteries of Tirup and Nybøl and the urban Dominican Friary and Johanitter Kloster cemeteries in Schleswig and the Haderslev Cathedral were close to values recorded for non-buried modern bones [61] (Fig. 2). Iron values were slightly higher in the St. Clements Kirche sample. In the urban cemeteries of Ribe, Horsens, and Schleswig's Rathaus Markt, the Fe and Mn means exceeded those of the other sites and modern populations (Fig. 2). Furthermore, many samples were above the maximum values recorded in modern non-buried samples by a factor of 10 to 100. The Mn values followed a pattern similar to Fe. Most of the Mn concentrations were greater than the maximum recorded for modern non-buried bones.

Iron and Mn were positively correlated with Ba in some cemeteries, but rarely with Sr (Additional file: 1). There were moderate correlations (between 0.5 and 0.6)
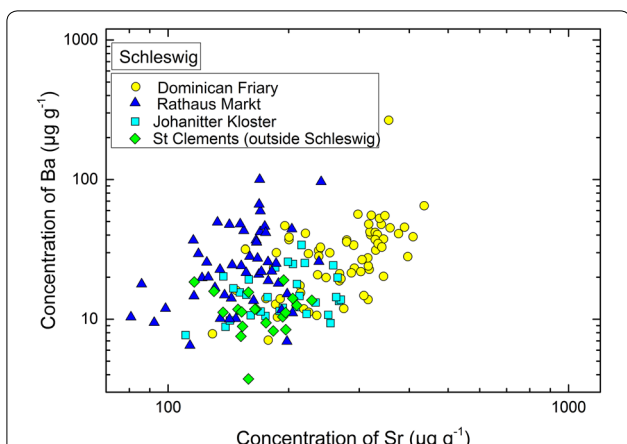
**Fig. 5** Concentrations of Cu and Pb in femoral cortical bone (μg g$^{-1}$) from Ribe Cathedral graveyard skeletons dating to AD 800–1050 (**a**), AD 1225-1425 (**b**), AD 1425–1738 (**c**), and AD 1738–1805 (**d**). Values below LOQ—Cu at 3.04 μg g$^{-1}$ and Pb at 0.94 μg g$^{-1}$—are shown on dashed lines



**Fig. 6** Concentrations of Sr and Ba in femoral cortical bone (μg g$^{-1}$) in skeletons from rural communities (yellow) from towns (red): Haderslev Cathedral and Nybøl (**a**) and Horsens' Ole Worms Gade and Tirup (**b**). Differences in local environmental settings or diet are pronounced for Ole Worms Gade and Tirup, but not for Haderslev Cathedral and Nybøl

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**Fig. 7** Concentrations of Sr and Ba in femoral cortical bone (µg g$^{-1}$) in skeletons from four Schleswig cemeteries. The distribution of the Dominican Friary sample, which contained many churchmen, is different from those consisting of skeletons from other contexts

between Mn and Ba in urban Horsens and Schleswig's Rathaus Markt, and a stronger correlation in Ribe (0.67). Moderate to strong correlations between Fe and Ba were also observed in samples from Horsens (0.67) and St. Clements Kirche (0.56). In Ribe the association was even stronger (0.85). For Sr, the only correlation above 0.5 for Mn-Sr was found in Rathaus Markt (0.61).

The As distribution was less variable than those of Mn and Fe (Additional file: 1). Mean values of As for five cemeteries were between 1 and 2 µg g$^{-1}$, which is close to those for modern non-buried bones. A significant As enrichment was observed in samples from Ribe, Schleswig's Dominican Friary, and Horsens' ole worms gade. In Ribe, As was positively correlated (> 0.5) with Al, Fe, Mn, and Ba, and in the Haderslev sample with Ba.

The distributions of Al in the nine cemeteries showed considerable variation, with mean concentrations ranging from 90 to 400 µg g$^{-1}$. The mean values were
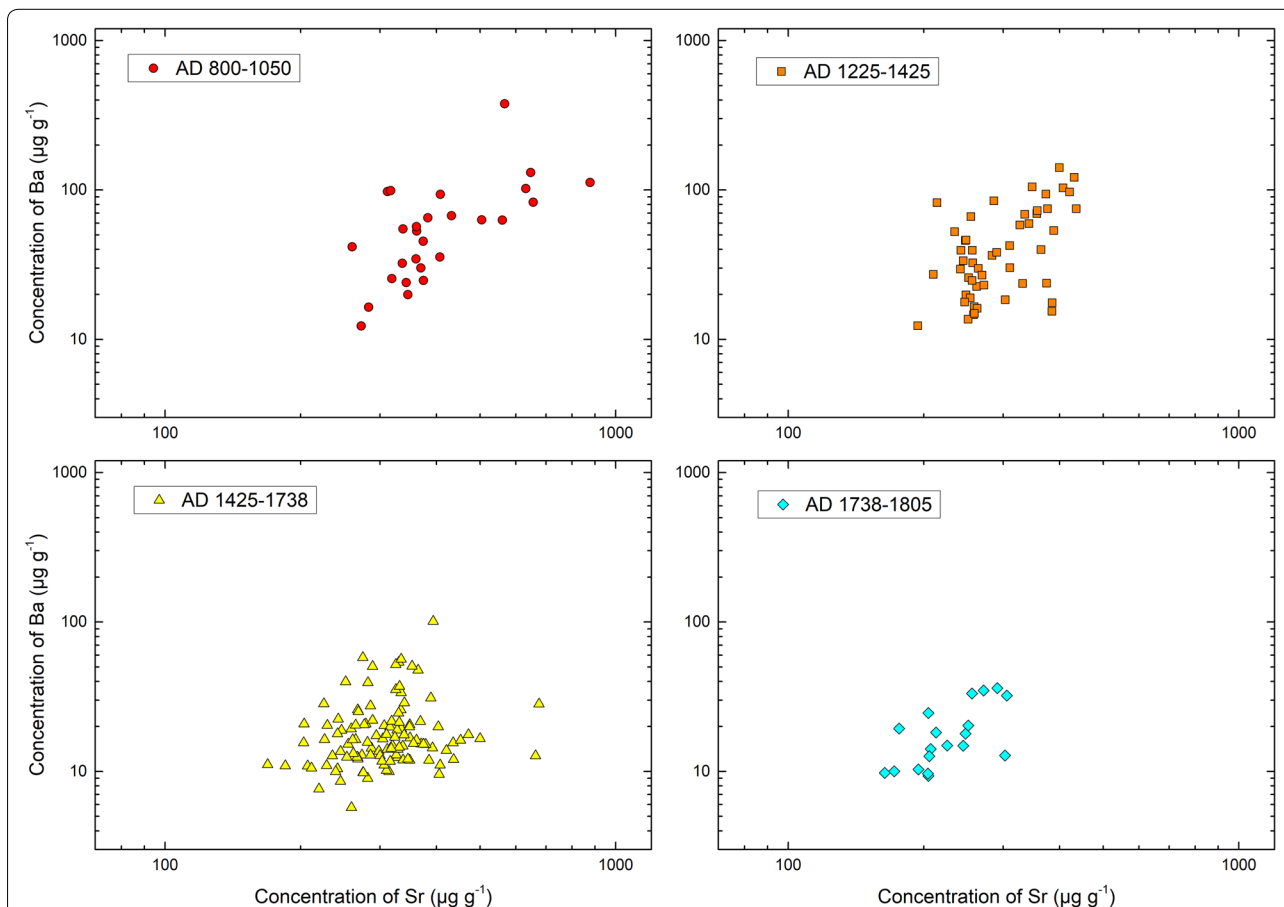


**Fig. 8** Concentrations of Sr and Ba in femoral cortical bone (µg g$^{-1}$) from early to late Ribe Cathedral graveyard skeletons: AD 800–1050 (**a**), AD 1225-1425 (**b**), AD 1425–1738 (c), and AD 1738–1805 (**d**)

**Fig. 9** For the skeletons from Horsens' Ole Worms Gade, Cu concentrations are plotted against elements known to be prone to diagenetic processes: Fe (**a**), Mn (**b**), Al (**c**), and As (**d**), all in µg g$^{-1}$. No correlations are observed
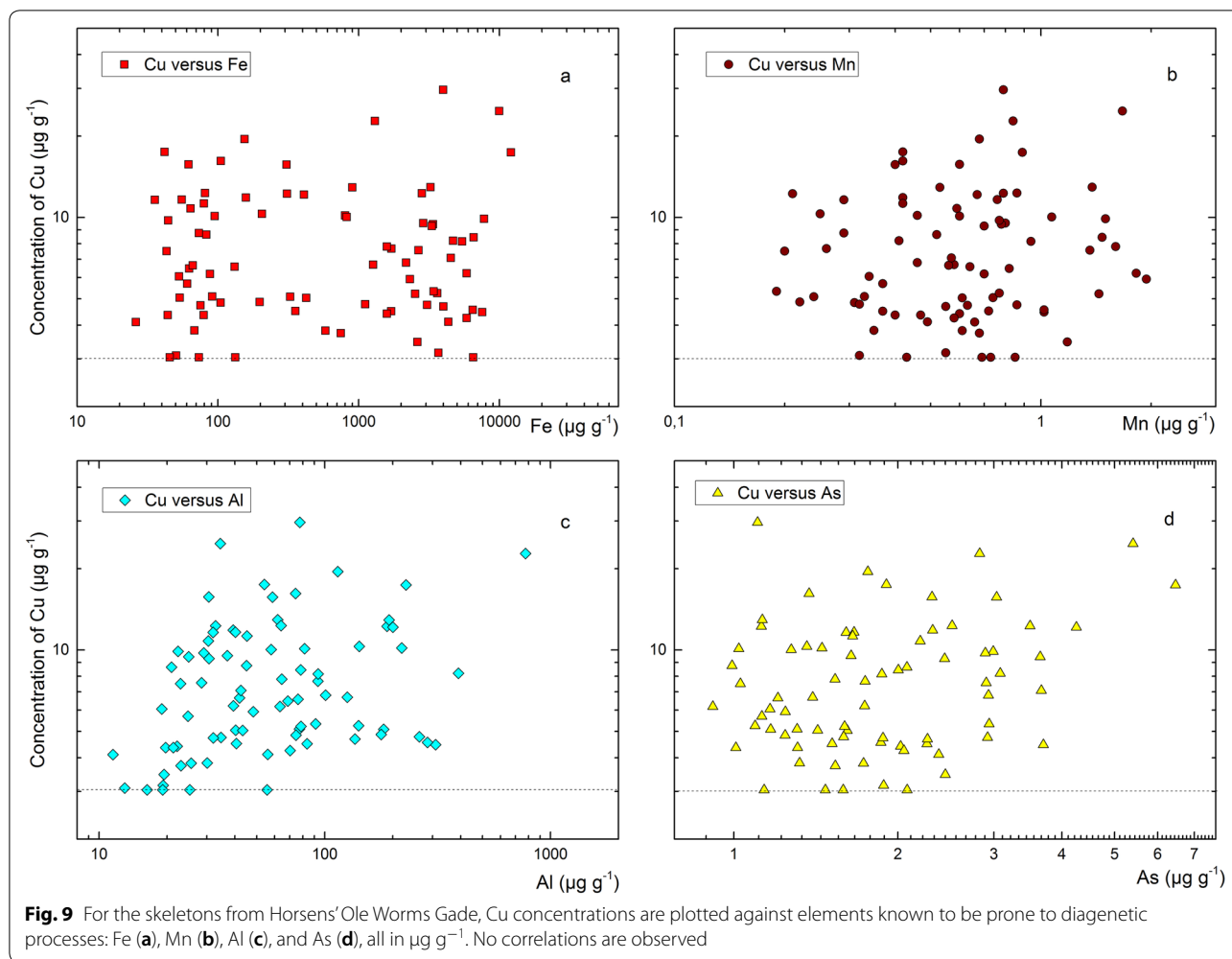
somewhat higher than those reported for present-day populations [24, 61, 64] (Fig. 2), but they were not above the upper bounds of ranges for modern non-buried bones, except for Ribe. The diagenetic origin of Al is supported by the strong correlation found with Fe and Mn. The association between Al and Fe is especially clear in Tirup (0.85) and above 0.6 in other cemeteries except for Horsens' Ole Worms Gade and Schleswig's Dominican Friary. Correlations between Al and Ba in Ribe (0.60) and Schleswig's St. Clements Kirche (0.51) were noteworthy, but not for the other cemeteries.

In short, there is a demonstrable diagenetic signal for Fe, Mn, and Al in many cemetery samples, and to a lesser degree for As.

With regard to the present study, neither Cu nor Pb appear to be systematically affected by the postmortem alteration of bone. Few Cu or Pb concentration values were higher than the upper limits reported for modern non-buried bones. Furthermore, the only significant correlation coefficients ($p < 0.05$) show weak associations of

Cu and Pb with Fe, Mn and Al, all three of which have a strong diagenetic signal in these samples.

### Diagenesis—other studies

Previous studies based on smaller and less diverse archaeological bone samples have not viewed the antemortem versus postmortem significance of Cu the same, although the tendency has been to emphasize the role of diagenesis [17–20, 22, 75, 88, 90, 93]. Some of this research, however, has focused on heavily contaminated deposits and included specimens with the distinctive green stain that results from direct contact with Cu.

High-resolution imagery of bone microstructure in archaeological bones from Denmark has shown that postmortem changes tend to be of little consequence for Cu—as well as the other elements indicative of life histories selected for this study, Pb, Sr, and, less clearly, Ba—as long as appropriate procedures are part of the sample acquisition process [24]. It is worth repeating in this context that none of the Danish bones were stained

**Fig. 10** Concentrations of Cu ($\mu g\ g^{-1}$) in soil samples associated with three skeletons from Old Worms Gade in Horsens, as measured in centimetres outward from femora (positive numbers, with 0 being immediately adjacent to the bone). Copper concentrations ($\mu g\ g^{-1}$) for cortical and trabecular bone are plotted as well. No soil concentration profile is consistent with diffusion from soil to bone



**Fig. 11** Concentrations of Pb and Cu ($\mu g\ g^{-1}$) in soil samples surrounding three skeletons from old worms gade in Horsens. The soil samples were taken close to skeletons, and probably partly reflect the composition of now-decayed soft tissue. They are the same samples as plotted in Fig. 9

green from Cu. As expected, other research has detected elevated Cu concentrations near exposed surfaces in non-human bones, including those with the distinctive green stain, from a medieval workshop that yielded abundant Cu alloy scraps [19]. Moreover, in the present study no reasonably high correlations (r values above 0.5) were observed between Cu and two elements, Fe and Mn, thought to be indicative of diagenesis. Bone Fe and Mn concentrations are usually considered to be altered by a precipitation of $Fe^{3+}$ and $Mn^{4+}$ that originated in soil and groundwater surrounding the skeletons [8, 126].

It remains true, however, that postmortem changes in bone Cu content cannot be entirely ruled out, despite precautions taken to obtain clean samples. Yet based on the present data and earlier work [24], there is no reason to believe that diagenetic processes were sufficient to alter the overall, and rather coherent, picture of regional, temporal, and socioeconomic variation in the Danish and German skeletons. To have a general effect,

Cu contamination would have to affect all skeletons from a particular cemetery, shifting sample concentrations upward relative to those from other cemeteries. Moreover, diagenetic changes, if they were indeed present, would have had to occur in a manner that makes temporal, residential location, and sociopolitical sense. The parsimonious inference is that the variation in Cu content indeed reflects differences in the life histories of the people who were sampled.

### Kitchen utensils and food

There are two pathways from kitchen utensils to Cu ingestion, hence to bones. One is mechanical, which can occur when an abrasive or sharp object, such as a metal knife, is scraped across a pot's interior, removing minute metal particles. That material is later brought into solution by the hydrochloric acid in the stomach. The other is a dissolution of Cu when acidic foods are cooked or stored in metal vessels. When looking at bones alone, one cannot distinguish between the two sources of Cu exposure. From a life history perspective, it is a distinction without a difference. The mere use of kitchen utensils containing Cu is of concern, not precisely how the contaminant got into the food or liquids that were consumed. That is, the availability of valued and limited distribution metal objects is of interest. These items were mostly restricted to commercial centres, the towns, where people enjoyed preferential access to metal utensils through local production and markets that, like Horsens, Haderslev and Ribe, were often connected by shipborne trade with distant parts of Europe.

The possibility that variation in Cu exposure was related to access to particular kinds of kitchen utensils, not food, is consistent with a lack of correspondence with the Sr and Ba concentrations. The latter have been shown to be good dietary and provenance indicators in Danish archaeological samples [11, 14]. For Cu, the skeletons from towns and villages were clearly separable in the two pairs of geographically and socially proximate sites (Fig. 3). That was not the pattern for Ba and Sr. In both urban–rural pairs, Ba values overlap considerably. For Sr, there is a good separation of values for only one of the site pairs, Horsens' Ole Worms Gade and Tirup (Fig. 6b). In these two cemeteries, no positive correlation was found between Sr and the diagenetic indicators Mn, Fe, Al, and As. For the other site pair, Haderslev and Nybøl, the Sr distributions are similar (Fig. 6a). It is reasonable to conclude that Cu is not derived directly from food because differences in its concentration in bone do not vary consistently with those of Sr and Ba.

Much the same can be said about Cu and Sr, and to a lesser extent Ba, in the Schleswig and Ribe skeletons. Higher Sr concentrations for some individuals from Schleswig's Dominican Friary presumably resulted from a diet that was different from the food consumed by most of their contemporaries in the town (Fig. 8). Nevertheless, there was still considerable overlap in the Sr distributions from Schleswig's various cemeteries, including the Dominican friary graveyard. That is probably because not all of the people buried in the Dominican cemetery were friars, as indicated by the skeletal sample's mixed sex and age composition. In Ribe, changes over time in Cu, Ba, and Sr distributions, although they were not great, did not covary. That is consistent with the concentrations of these three elements not being all attributable to the same underlying cause, such as the food people ate.

The inconsistent picture for the three elements, especially Cu and Sr, indicates that choices about food or its availability were not tied to social position, as indicated by valued objects, in a straightforward and entirely predictable manner. That means the specific nature of burial contexts must be examined to identify the groups being sampled before drawing inferences about the lives of these people. It is not sufficient to assume, for example, that all town dwellers had the same experiences. When looking at complex sociopolitical systems, such as medieval Europe, multiple sites representative of different segments of society are needed to provide culturally nuanced views of life in the past.

### Copper exposure and settlement type

The most striking result of this study is the near, if not total, absence of skeletal evidence for Cu exposure in rural villages (Tirup and Nybøl) in contrast to the situation in towns (Horsens, Haderslev, Ribe, and Schleswig). Villager Cu concentrations did not exceed the LOQ level, whereas townsfolk experienced a greater exposure to Cu, regardless of their station in life. What makes this distinction particularly remarkable is the fact that two village-and-town pairs—Tirup-Horsens and Nybøl-Haderslev—consisted of communities that were closely associated with one another geographically, economically, and politically. Differences in exposure presumably came about mostly through cooking utensils and, perhaps to a lesser extent, through jewellery, coins, or proximity to copper workshops [127]. The consistent patterning in multiple sites lends support to the inference that there truly were differences in Cu exposure for the inhabitants of towns and the surrounding countryside. The Cu findings underscore the necessity of looking at multiple well-characterized samples before drawing inferences about the life experiences of members of past societies. This is highlighted by the St. Clements cemetery, which was previously been seen as a rural community based on Hg and Pb concentrations [10]. However, for Cu the St. Clements graveyard seems as urban as the rest of the Schleswig

cemeteries (Fig. 4). Balancing the results for Pb and Cu, it appears that St. Clements should be categorized as intermediate rather than strictly rural or urban.

Differential Cu exposure was not limited to a contrast between rural and urban settings. There could also have been socioeconomic or environmental dimensions to Cu exposure within the towns, as indicated by the separate cemeteries in Schleswig. The same could be said about Pb concentrations, especially for individuals from Schleswig's Dominican Friary. Those particular skeletons included the remains of people who were not friars, and their burial location indicates they were from economically prosperous and socially well-connected families. Although a relatively high Pb exposure can be considered a marker of medieval socioeconomic success, for the people involved it entailed a biological cost to the extent they experienced Pb poisoning. These findings are broadly similar to those of Rasmussen et al. [10] where Pb concentrations were found to be greater in urban than in rural settings.

The overall picture for Pb, however, is more complex than it is for Cu. Perhaps that is because Pb exposure occurred in a wider array of contexts than it did for Cu. Whatever the reason, variation in Cu exposure yields patterns that are easier to interpret than those for Pb. In Denmark and northern Germany, therefore, Cu is superior to Pb as an indicator of socioeconomic distinctions in medieval to early modern ways of life, although it is best to examine both elements in tandem because they have somewhat different stories to tell.

The data of the present study are consistent with socioeconomic factors being the reason for differences between rural and urban sites. In the early modern period where there are reasonably good records, there was differential access to highly valued items used on an everyday basis. The well-off inhabitants of Ribe from AD 1520 to 1850, for example, possessed pots, pans, and beer-brewing pots, among other containers, made of Cu or its alloys [26]. There are no similar detailed records for the other parts of the population, although it is likely they had wooden or ceramic pots, pans, and cups, which were commonly used at the time.

A lack of appreciable Cu exposure in the rural skeletons contrasts with documentary records from medieval Denmark and England where Cu utensils were said to have been present [30, 34]. The difference between the historical documents and archaeological skeletons could be more apparent than real. The bone data shows only exposure sufficient to be measured, whereas an occasional metal cooking vessel, the possession of which was so noteworthy it was recorded, might not have been used often enough to leave a detectable Cu signature in the bones of household members. The rural and urban

difference in Cu exposure, so evident in Denmark and northern Germany in the present study, should be examined elsewhere because it provides a different, but complementary, perspective on past life than what can be gleaned from documents or archaeological debris.

### Copper exposure over time

By the 17th century, Cu objects were relatively common in Denmark and Norway, which was where many of these items available to Danes originated [128]. Although their use had increased in the previous centuries, much remains to be learned about precisely when that occurred and what segments of society first experienced greater access to items manufactured from Cu and its alloys.

It is difficult to obtain a clear picture from the present study about how Cu exposure changed across many centuries because only one sequence of graves from a single site, Ribe, covers an entire millennium (ca. AD 800–1800). Differences among samples from separate time intervals are not great (Fig. 5). During the Viking Age, Cu exposure was somewhat less than what it was in the Middle Ages, and it dropped again during the 15th century onward in the final two periods. The overall temporal trend is consistent with an increase in wealth and regional prominence until the mid-15th century, after which Ribe gradually declined in importance to the point of becoming only a rather small and insignificant provincial town by the start of the 19th century.

The nature of the Ribe sample, however, is a weakness of this study. The problem does not stem from the number of skeletons examined—a sample of 208 individuals is large by archaeological standards—but from the sample's composition. Throughout the period spanned by the graveyard, Ribe was a trading centre easily accessible by sea. Presumably many people, perhaps even the majority of them, had spent much of their life in Ribe. But some of the people attracted to the thriving market might have died when visiting the town. In the Viking cemetery, there might even have been people whose bodies were carried there for burial, as it was likely the only 9th century Christian graveyard in Jutland.

By the 12th century, Ribe had developed into a prominent harbour for agricultural products exported to markets in northwestern Europe. Horses, for example, were commonly traded from the 13th century, followed by oxen in the late Middle Ages. All medieval towns experienced an ebb and flow of people. Ribe's economic history as an important market that attracted a diverse array of people from near and far is consistent with the observed dispersion of Cu values. It appears to exceed the dispersion of Cu concentrations in the bones from ordinary people buried in Schleswig's roughly contemporaneous graveyards. Ribe's later loss of regional prominence is

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consistent with a general decline in Cu concentrations, especially an abundance of low values, in the skeletons of its inhabitants. Such an interpretation—a connection between Cu exposure and a community's economic and political fortunes—requires further evaluation with additional well-characterized skeletal samples.

If the Ribe data are taken at face value, despite the questionable nature of the skeletal sample's composition, an absence of major change over time makes Cu exposure especially useful for examining the nature of medieval and early modern northern European social and economic relations. That is because differences in Cu exposure during Ribe's development over a millennium are much smaller than those that existed between geographically proximate and socially connected medieval towns and villages. Temporal differences in Ribe's Cu values are dwarfed by those related to social and economic distinctions elsewhere in Denmark. That means Cu has a considerable potential for documenting the variation that existed in different places and social contexts, community access to a wider world through trading networks, and the movement of people between urban settings and the surrounding countryside.

The Ribe findings are of some relevance when disentangling temporal from social reasons for differences in the Cu content of skeletons from different towns, as shown by Horsens and Haderslev (Fig. 3a, b). A tendency for higher Cu values at Haderslev could be related to a shift from medieval to post-medieval economies. Greater exposure to Cu might have simply come about because more metal items, especially kitchen utensils, were in circulation later in time. Alternatively, the difference could have mostly resulted from social distinctions among the individuals buried in the two graveyards that were sampled. The two possibilities can only be adequately addressed by examining additional cemeteries, underscoring the necessity of examining multiple skeletal samples from different sites when identifying what took place in the past.

## Conclusion

Variation in bone Cu concentrations highlights the central role of skeletons in developing more nuanced views of life during the medieval to early modern periods in northern Europe. By looking at several sites, analyses of archaeological bones provide a means of assessing differences in Cu exposure and what it could indicate about the lives of people in different settings. Although individual skeletons, or even a group of them from a single site, are difficult to interpret, general patterns of cultural behaviour can be detected when samples are sufficiently large, and a diverse group of sites are examined.

In Denmark and northern Germany, the observed variation in Cu exposure is presumably related to differential access to everyday items fashioned from metal containing Cu. Almost certainly that sort of exposure was related to utensils that were habitually used when cooking food. Such objects were apparently rare or absent in outlying villages. The inhabitants of nearby towns, however, enjoyed greater, but still variable, access to them. During the Middle Ages, being able to obtain kitchen utensils fashioned from Cu and its alloys was more a matter of where people lived—rural versus urban settings—than their social position. Differences in Cu exposure had little to do with dietary intake or the geological setting. That makes the Cu concentrations of human skeletons a useful tool that enhances our understanding of medieval northern European societies.

## Supplementary information

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**Additional file 1.** Results of the chemical analysis of the bone samples. Concentrations are given in µg g$^{-1}$ except for Ca which is given in wt%. The uncertainty quoted is ± 1 standard deviation. When below LOQ, the result is designated < LOQ. Blank entries indicate that the analysis has failed or not been done. Also given are laboratory numbers (KLR-no.); field grave numbers; sex; estimated age interval at death; the bone sampled for analysis. All samples are cortical tissue.

**Additional file 2** Results of the chemical analysis of the soil samples procured in proximity to the three different skeletons. Concentrations are given in µg g$^{-1}$. The uncertainty quoted is ± 1 standard deviation. Analyses of cortical (CO) and trabecular (TR) tissue of the skeletons are also listed. Vertical profiles are coloured green, horizontal soil profiles are coloured orange.

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### Abbreviations
CRI: Collision reaction interface; ICP-MS: Inductively coupled plasma mass spectrometry; LOQ: Limit of quantification.

### Authors' contributions
Conceived and designed the experiments: KLR. Performed the experiments: KLR and LS. Analyzed the data: KLR, LS, and TD. Contributed as leading field archaeologists and with historical references FC and MS. Contributed to the anthropological and laboratory components of the work, including the interpretation of results and acquisition of references: KLR, LS, TD, JLB, and GRM. Wrote the paper, with comments from other participants: KLR, GRM and TD. The paper was approved by all authors. All authors read and approved the final manuscript.

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## Availability of data and materials
Data are available upon request from the authors.

## Ethics approval and consent to participate
No permission was required as all sample material was acquired through archaeological excavations.

## Competing interests
The authors declare that they have no competing interests.

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