Lead concentrations in antlers of European roe deer (Capreolus capreolus) from an agricultural area in Northern Germany over a 119-year period—a historical biomonitoring study

Catharina Ludolphy & Uwe Kierdorf

Abstract
We analyzed the lead content in antlers of 90 adult European roe bucks (Capreolus capreolus) that had been culled between 1901 and 2019 in an agricultural-dominated hunting district in Lower Saxony (Northern Germany). Antler lead values ranged between 0.2 and 10.9 mg/kg dry weight. Median lead concentration was highest after World War II, during a period (1956–1984) of rapidly increasing mass motorization and use of leaded gasoline. Lead levels in antlers decreased markedly after the phase-out of leaded gasoline, but high values were still found in some recently collected antlers. This could indicate persistent lead pollution from former use of lead additives to gasoline, other traffic-related sources, or from agricultural sources (e.g., sewage sludge, fertilizers). This study highlights the suitability of analyzing roe deer antlers for the historical monitoring of changing lead levels in the environment. By collecting antlers and providing them for study, local hunters can significantly contribute to environmental surveillance and the monitoring of environmental pollution by bone-seeking contaminants.

Keywords Bioindication · Deer · Environmental pollution · Germany · Herbivores · Leaded gasoline

Introduction
Lead (Pb) is a metal that has no physiological function and is toxic even at low concentrations (Ewers and Schlipköter 1991; Pattee and Pain 2003; Ma 2011; Caiço et al. 2017; Maret 2017). Various mammalian organs and organ systems are affected by lead toxicity, the most severe impacts concerning the nervous and hematopoietic systems and the kidneys (Ma 2011; Caiço et al. 2017; Maret 2017). The developing brain is particularly susceptible to the toxic effects of lead, and therefore, lead neurotoxicity is an issue of special concern in children (Lidsky and Schneider 2003; Caiço et al. 2017).

Lead mining dates back to at least the 4th millennium BC, and Pb mining and smelting activities were widespread in ancient Greek and Roman societies (Retief and Cilliers 2005). The emissions from ancient Greek and Roman lead and silver mining and smelting activities caused widespread lead pollution in the Northern Hemisphere that has been traced both in Greenland ice cores (Hong et al. 1994) and in European bogs (Shotyk 1998).

Compared to the pre-industrial period, the production and anthropogenic discharge of lead dramatically increased during the industrial age, with a particularly steep rise in the second half of the twentieth century (Cullen and McAlister 2017). Thus, global refined lead production amounted to 11.76 million tonnes in 2019 (U.S. Geological Survey 2020). Anthropogenic lead emissions to the atmosphere during the mid-1990s, approximately 120,000 tonnes/year, by far exceeded median fluxes from natural sources, estimated at 12,000 tonnes/year (Cullen and McAlister 2017). The drastically increased discharge of lead from human activities led to widespread lead pollution of the environment on a global scale, with the highest levels of contamination near urban-industrial areas (Nriagu 1990; Hernberg 2000).

Major anthropogenic sources of lead release to the environment include the combustion of fossil fuels for electricity and heat production, the mining and smelting of lead and other metal ores, iron and steel production, cement production, the use of lead-containing products (like batteries, ammunition, and paint), waste disposal, and vehicular traffic (Stroud 2015; Cullen and McAlister 2017; Baranowska-Bosiacka...
Emissions from the latter source were the dominant cause of global lead pollution during much of the twentieth century, resulting in serious impacts on human and environmental health (Cullen and McAlister 2017; Filella and Bonet 2017). Lead emissions from vehicular traffic were largely caused by the use of alkyl-lead additives (mostly tetraethyl lead, TEL) as antiknock agents in gasoline (Stroud 2015; Filella and Bonet 2017). The inorganic lead derived from the organolead additives is highly persistent in the environment and, despite the more recent phasing out of leaded gasoline, high concentrations of legacy lead are therefore present in soils (Filella and Bonet 2017).

Commercial production of TEL started in 1923 and worldwide increased dramatically during the following decades (Hernberg 2000). The struggle to remove lead from gasoline extended over many years (Hernberg 2000; Needleman 2000; von Storch et al. 2003) and was achieved against strong resistance from industry and industry-funded researchers that denied or tried to downplay the public health risks of using leaded gasoline (Hernberg 2000; Needleman 2000). In the Federal Republic of Germany (FRG), the production and importation of gasoline containing more than 0.4 g Pb/liter were prohibited in 1972. Up to then, the usual lead content of gasoline had been 0.6 g/liter. In 1976, the permissible concentration of lead in gasoline was further reduced to 0.15 g/liter (von Storch et al. 2003). Unleaded gasoline (tolerable lead content of 0.013 g/liter) was introduced in the FRG in October 1984, regular leaded gasoline was banned in 1988 (while leaded premium gasoline was still allowed), and since 1997, leaded gasoline is no longer sold in Germany. The lowering of the lead content of gasoline and the subsequent phase-out of leaded gasoline, along with measures reducing lead release from other sources, caused a drastic reduction of anthropogenic lead emissions to the atmosphere, from 16,446 tonnes in 1975 (values for FRG and German Democratic Republic combined, von Storch et al. 2003) to 716 tonnes in 1995 in reunified Germany (European Monitoring and Evaluation Programme (EMEP) - Centre on Emission Inventories and Projections 2021). Since then, lead emissions in Germany further declined to 207 tonnes in 2018 (EMEP. Centre on Emission Inventories and Projections 2021). Currently, industry is the main lead emission source, followed by road traffic, the latter now primarily due to tire wear and brake abrasion (McKenzie et al. 2009; Grigoratos and Martini 2015; Adamiec et al. 2016; Adamiec 2017; Bourliva et al. 2018). Recent studies on lead exposure of biota and humans demonstrate that lead contamination of the environment remains an issue of high concern (Müller-Graf et al. 2017; Stolcke et al. 2017; Gerofke et al. 2018, 2019; Martin et al. 2019; Pain et al. 2019a; Helander et al. 2019; Taggart et al. 2020; Lemen et al. 2021).

Lead uptake into the mammalian body occurs primarily via the gastrointestinal tract and the respiratory system. Upon absorption, lead rapidly enters the bloodstream and is transported to different tissues (Ma 2011; Cai et al. 2017). In the body, lead accumulates predominantly in mineralized tissues, and approximately 95% of the body burden of lead in adult humans (75% in children) is present in bones and teeth (Cai et al. 2017). Lead is taken up into the bone mineral (carbonated hydroxyapatite), where the Pb$^{2+}$ ion is incorporated at Ca$^{2+}$ sites during bone formation, while after the stop of crystal growth, it can replace Ca$^{2+}$ by ion substitution (Pemmer et al. 2013). Lead stored in the skeleton is considered a biological marker of long-term exposure; however, under certain physiological and pathological conditions associated with increased bone turnover, skeletaly stored lead can be mobilized and re-enter the bloodstream (Cai et al. 2017).

Several studies have demonstrated that antlers are well suited to monitor lead pollution of the environment (Sawicka-Kapusta 1979; Medvedev 1995; Kierdorf and Kierdorf, 1999, 2000a,b, 2002a,b, 2003, 2004, 2005, 2006; Pokorny 2000; Pokorny et al. 2009; Sobota et al. 2011; Wieczorek-Dąbrowska et al. 2013; Cappelli et al. 2020; Güzjejewska et al. 2020). Antlers are periodically replaced, bony cranial appendages of male deer (and females in the reindeer, Rangifer tarandus) that are grown and cast from permanent protuberances of the frontal bones known as pedicles (Goss 1983; Landete-Castillejos et al. 2019). The annual antler cycle of male deer is tightly coupled to their reproductive cycle and controlled by changes in androgen concentrations in blood. In deer from temperate and arctic regions, the reproductive cycle is closely linked to the photoperiod (Goss 1983; Bubenik 1990; Lincoln 1992). Antlers are the fastest forming bones in the animal kingdom and grow during a seasonally fixed timespan of a few months. After the shedding of the skin (velvet) that covers the antlers during their growth, they die off and the bare bony (“hard”) antlers are exposed (Goss 1983; Lincoln 1992; Landete-Castillejos et al. 2019).

Growing antlers can accumulate large amounts of “bone-seeking” elements like lead during their short, seasonally fixed lifespan (Sawicka-Kapusta 1979; Kierdorf and Kierdorf 1999, 2000a, 2000b, 2002a, 2004, 2005, 2006; Pokorny 2000; Pokorny et al. 2009; Sobota et al. 2011; Wieczorek-Dąbrowska et al. 2013; Cappelli et al. 2020; Güzjejewska et al. 2020). Antlers can therefore be used to monitor ambient lead levels, as they constitute “naturally standardized” environmental samples (Kierdorf and Kierdorf 1999, 2005, 2006; Tataruch and Kierdorf 2003). In contrast to other bones, the lead content of antlers constitutes a marker of exposure over a medium timescale of a few months (the antler growth period). Furthermore, contrary to other types of bone, the lead content of antlers is not markedly affected by the age of an individual (Pokorny et al. 2004). Since antlers are collected as trophies by hunters and kept in private or public collections, larger sets of antlers with known dates of collection and locality are often available for study. Such antler series constitute environmental archives whose analysis enables the reconstruction of temporal changes in ambient lead concentrations (Kierdorf and Kierdorf 2005, 2006).

Among European cervid species, the European roe deer (Capreolus capreolus) is for several reasons particularly...
suited as a bioindicator. Firstly, it is by far the most abundant deer species, with a harvest (including deaths from other causes than hunting) of 1,226,169 individuals in the hunting year 2019/2020 in Germany, and an annual harvest of more than 1 million animals over the last 20 years (DJV. Deutscher Jagdverband 2021). Secondly, the species is highly adaptable and therefore inhabits a wide range of habitats (Andersen et al. 1998). Thirdly, it has a relatively small home range, enabling a monitoring with rather high spatial resolution (von Raesfeld et al. 1978; Danilkin 1995; Stubbe 1997).

The present paper reports lead concentrations in the antlers of European roe deer that had been culled in a hunting district in Northern Germany over a period of 119 years (1901–2019). This time span covers the period from before the era of mass motorization and the use of leaded gasoline to after the phase-out of leaded gasoline and reduced anthropogenic lead emissions from other sources. We hypothesized that these changes would be reflected by variation in antler lead levels over the study period.

Materials and methods

Specimens and study area

We analyzed the antlers of 90 adult roe bucks that had been culled in the hunting district Harsum between 1901 and 2019. All antlers were regenerated ones. Adult roe bucks in Germany cast their old antlers between October and December, followed by antler regrowth during winter. The

Fig. 1 Study area. Localization of the hunting district Harsum in the northern part of the county of Hildesheim, federal state of Lower Saxony, Germany (upper left). Aerial photo of the hunting district Harsum (boundaries are indicated by the red line) (right). The orange lines mark the three major traffic infrastructures, and the blue line indicates the branch canal. Diagram showing the current land use in the study area (lower left)
velvet is shed from the antlers in March/April, and the rutting period extends from mid-July to mid-August (von Raesfeld et al. 1978; Stubbe 1997). Antlers were assigned to the years in which the respective bucks had been taken. For thirteen antlers from the period 1958–1981, the exact year of collection was not known. No antlers from the period 1940–1955 were available, as no hunting was performed in the study area during most of World War II, and private ownership of firearms was not allowed after the end of the war until 1955.

The hunting district Harsum (altitude about 82 m above sea level) lies in the northern part of the county of Hildesheim (federal state of Lower Saxony, Germany) (Fig. 1). The area has a temperate climate, with annual mean temperature of 8.7°C, an annual precipitation of 676 mm (climate-data.org 2020), and prevailing westerly winds (DWD CDC. Deutscher Wetterdienst Climate Data Center 2018). The hunting district is bordered by a branch canal of the Mittelland canal in the west that started operations in 1928 (Hafenbetriebsgesellschaft mbH Hildesheim n.d.). Less than 500 meters to the west of the hunting district, a north-south oriented section of the motorway A7/E45 is located that was completed in 1962. Further larger traffic infrastructures are the federal highway B494, a section of which is located in the east of the hunting district, and a railway line (electrified in 1965) that divides the district into a larger western and a smaller eastern part. The hunting district has a size of about 1120 hectares and consists mainly of arable farmland (74%) and few patches of deciduous forest (9%). Urban settlements and industrial/commercial areas account for 13% and 4%, respectively (EEA. European Environment Agency 2020). Based on the pattern of land use, the roe deer inhabiting the study area are considered to be of the “field” ecotype (Kahziński 1982; Demesko et al. 2018). There are nine covered contaminated sites (slurry ponds, dredge material dumps, pond fillings, and a former clay pit) within the hunting district, which add up to an area of approx. 21 ha (2% of the study area; NIBIS Kartenserver 2020). No further information was available about a possible hazardous potential of these areas.

**Bone sampling and analysis**

Antler bone samples were obtained as described by Kierdorf and Kierdorf (2000b, 2002b). Prior to sampling, the antlers were thoroughly cleaned with a nylon brush to prevent contamination of the bone samples by dust or dirt. Subsequently, a hole was drilled into the back of the main beam of each antler approximately 1.5 cm above the antler-pedicle junction using a hand-held electric drill with a tungsten carbide cutter (Fig. 2). The bone powder obtained from each pair of antlers was collected, thoroughly mixed by stirring, individually stored in a small plastic container, and labeled with a consecutive number for each buck sampled.

Precisely weighed samples (approximately 0.2 g for each double determination) of antler bone powder were digested with 5 ml of 65% (w/v) nitric acid (HNO₃; Suprapur®) and filtered into glass vials. The digestion vessels were rinsed with high-purity water (AnalaR® NORMAPUR® ISO 3696 Grade 3), and the content was also filtered into the glass vials, which were made up to 25-ml volume with the high-purity water. Subsequently, each sample was decanted into a 50-ml polyethylene container and stored in a fridge at 4°C until analysis.

Lead concentrations were determined with a graphite furnace atomic absorption spectrometer (ContrAA 800D, Analytik Jena), using a 5-point calibration with 10, 30, 50, 80, and 100 μg Pb/l. After every tenth sample, a certified reference material (NIST Standard Reference Material (SRM)® 1486 Bone Meal) was measured. Recovery rate of the SRM was 96.2 ± 13.4% (mean ± SD), and the nominal concentrations in the antler bone samples were corrected for the recovery rate. The limit of detection (LOD) of the analytical method calculated using the calibration curve method was 0.2 mg Pb/kg. All determined lead concentrations in antler bone, given as milligrams per kilogram on an air-dry weight (d.w.) basis, were ≥ LOD. Individual lead values

| Period | N  | Range | Median (IQR) | Mean (SD) | CV (%) |
|--------|----|-------|--------------|-----------|--------|
| 1 (1901–1939) | 39 | 0.7–10.3 | 1.6 (1.3–2.0) | 1.9 (1.5) | 80.2   |
| 2 (1956–1984) | 19 | 0.3–8.0 | 3.2 (2.4–4.6) | 3.5 (2.0) | 115.9  |
| 3 (1985–2019) | 32 | 0.2–10.9 | 1.3 (0.7–2.4) | 2.0 (2.2) | 132.0  |

IQR, interquartile range; SD, standard deviation; CV, coefficient of variation.
reported and used for calculation are means of two determinations per bone sample.

Statistics

All statistics were performed using R version 4.0.3 (R Core Team 2020). Based on the culling years of the roe bucks, antlers were grouped in three sampling periods (period 1: 1901–1939; period 2: 1956–1984; period 3: 1985–2019). Period 1 was a time of rather low motor traffic, with the number of registered motor vehicles in Germany increasing rather slowly from approximately 10,000 in 1906 to 715,000 in 1938 (Hoffmann 2000). Period 2, starting with the permission to again use private firearms for hunting after World War II, was a time of increasing lead emissions due to rapid mass motorization (from 8,003,654 vehicles registered in the FRG in 1960 to 30,617,641 in 1985; KBA. Kraftfahrtbundesamt 2021) and industrial growth. Period 3 started after the introduction of unleaded regular gasoline in October 1984 and covered the time following the ban of leaded gasoline. Differences between the three periods were analyzed by a Kruskal-Wallis H test, followed by pairwise post hoc comparisons using the Wilcoxon-Mann-Whitney U test (two-sided), with Bonferroni adjustments of P-values. For all pairwise post hoc comparisons, adjusted P-values are reported, and for all statistical tests P-values < 0.05 were considered statistically significant.

Results

The lead content of the analyzed antlers ranged between 0.2 and 10.9 mg/kg. Minimum lead values decreased from period 1 over period 2 to period 3, while the coefficients of variation increased (Table 1).

Antler lead content differed significantly among the three sampling periods (Kruskal-Wallis H test: chi-squared = 15.184, df = 2, P < 0.001). Concentrations significantly (P < 0.001) increased from period 1 (median: 1.6 mg Pb/kg) to period 2 (median: 3.2 mg Pb/kg), and significantly (P < 0.01) decreased from the latter to period 3 (median: 1.3 mg Pb/kg, Fig. 3). The difference between periods 1 and 3 was not significant (P = 0.549). Before World War II, the clustering of the individual values is rather dense, with only one antler showing a markedly increased lead content of 10.3 mg/kg. In period 2, the scatter of the data points is still rather small, with two outlying low values (0.3 and 0.6 mg Pb/kg) of antlers collected, respectively, in 1982 and 1984. Period 3 shows the highest intra-sample variation, as well as the highest individual value (10.9 mg Pb/kg) for an antler collected in 2018.
Discussion

Our study revealed a marked drop in overall lead concentration in roe deer antlers from the study area following the introduction of unleaded gasoline in the FRG in October 1984. These findings are consistent with the results of other studies that focus on the trend of lead concentrations in antlers of European roe deer over time (Table 2), as well as in antlers of red deer (Cervus elaphus) (e.g., Giżejewska et al. 2020) and in other terrestrial biota (e.g., Schnyder et al. 2018; Helander et al. 2019). This indicates the overall success of the phase-out of leaded gasoline and additional measures taken to reduce lead release to the environment from anthropogenic sources.

While all other European deer species grow their antlers during spring and summer, antler growth in the European roe deer occurs in autumn and winter. This is an important difference, as lead concentrations in plants browsed by deer are markedly higher in autumn/winter than in spring (Reuter et al. 1996; Pattee and Pain 2003) and therefore roe bucks are exposed to higher lead levels than males of other deer species during the period of antler growth, which is a phase of high mineral demand.

The pronounced variation in antler lead concentration observed in period 3 is of special interest. While the overall decline in lead levels compared to the preceding period can be attributed to a reduction of emission from motor traffic, the

Table 2  Lead concentrations reported for antlers of European roe deer

| Country/region | Period/year | N | Mean | Median | Minimum | Maximum | Ref. |
|---------------|-------------|---|------|--------|---------|---------|------|
| Germany/Harsum area | 1901–2019 | 90 | 2.3 | 1.6 | 0.2 (1994) | 10.9 (2018) | This study |
| Germany/Cologne area | 1932–1998 | 39 | 4.2 | 4.3 | 0.4 (1996) | 12.0 (1972) | [1], [2] |
| Germany/Siegen area | 1948–2000 | 116 | 7.0 | 4.1 | 0.3 (1995) | 166.3 (1967) | [1], [3] |
| Germany/Ruhr area | 1951–1999 | 132 | 5.4 | 3.4 | 0.6 (1999) | 19.0 (1960) | [1], [4] |
| Germany/Märkischer Kreis | 1961–1999 | 32 | 8.0 | 3.8 | 0.7 (1995/1998) | 58.1 (1964) | [1], [5] |
| Germany/13 regions (North Rhine-Westphalia) | 1990–1999 | 172 | 1.6 | 1.2 | 0.3 | 14.0 | [1], [6] |
| Germany/Northern Hesse (Knüll) | 1971–1990 | 148 | 8.6–30.4 | - | - | - | [1], [7] |
| Poland/Białowieża Forest | 1961–1974 | 14 | 3.8 | - | - | - | [1], [8] |
| Poland/Niepolomice Forest | 1972–1975 | 18 | 4.5 | - | - | - | [1], [9] |
| Poland/Ojów National Park | 1968–1973 | 6 | 7.6 | - | - | - | [1], [8] |
| Poland/Silesian Forest | 1938–1950 | 17 | 6.4 | - | - | - | [1], [8] |
| Poland/Silesian Forest | 1951–1973 | 30 | 14.8 | - | 3.8 | 33.3 | [1], [8] |
| Poland/Lower Silesia | 1993–1994 | 23 | 1.7–2.3 | - | 0.6 | 2.9 | [1], [9] |
| Poland/Rogów | 1985 | 32 | 1.5 | - | 0.2 | 3.2 | [1], [10] |
| Poland/Wrocław | 1982–1986 | 27 | 20.4 | - | - | - | [1], [11] |
| Poland/Szczecin | 2000–2006 | 11 | 0.8 | - | 0.03 | 2.1 | [12] |
| Poland/Drawsko Pomorskie | 2000–2006 | 9 | 1.1 | - | 0.3 | 1.8 | [12] |
| Slovakia/Sitno | 1881–1918 | 14 | 25.0 | 20.7 | 5.9 | 75.0 | [1], [13] |
| Slovakia/Sitno | 1980–1990 | 18 | 3.0 | 2.2 | 1.4 | 9.6 | [1], [13] |
| Slovenia/Šalek Valley, | 1961–2002 | 116 | 1.3 | 1.1 | 0.2 (2000–2002) | 7.3 (1960–1969) | [14] |
| Slovenia/Upper Meža Valley | 1925–2003 | 45 | 54.7 | 18.1 | 2.7 (2000–2003) | 554 (1980–1989) | [15] |
| Sweden/Bogesund and Garpenberg | 1968–1983 | 28 | 2.7 | - | 0.2 | 8.5 | [16] |
| United Kingdom/Cumbria | 1985–1986 | 10 | 3.0 | - | - | - | [1], [17] |

References: [1] Kierdorf and Kierdorf (2005), [2] Kierdorf and Kierdorf (2000b), [3] Kierdorf and Kierdorf (2004), [4] Kierdorf and Kierdorf (2002a), [5] Kierdorf and Kierdorf (2001), [6] Kierdorf and Kierdorf (2000a), [7] Volmer and Herzog (1995), [8] Sawicka-Kapusta (1979), [9] Chyla et al. (1996), [10] Sawicka-Kapusta et al. (1991), [11] Lorenz et al. (1991), [12] Sobota et al. (2011), [13] Tataruch and Schönhöfer (1993), [14] Pokorny et al. (2004), [15] Pokorny et al. (2009), [16] Kardell and Källmann (1986), [17] Samiullah and Jones (1991)
increased variation in lead concentrations in period 3 compared to periods 1 and 2 points to an increased variability in exposure conditions of the roe deer from our study area in more recent times. Some bucks apparently took up larger amounts of lead, including the individual with the highest antler lead concentration of the entire sample. Further studies are needed to elucidate the sources and pathways of the underlying high but apparently locally restricted exposure. In previous studies, local point sources could be identified as the cause of an increased pollutant exposure of roe deer (e.g., Kierdorf and Kierdorf 2002b; Pokorny et al. 2009).

Vehicular traffic is today still an important source of lead release to the environment. After the phase-out of leaded gasoline, current lead release from traffic is, however, mainly due to wear of brakes and tires (De Silva et al. 2021). However, due to the persistence and low mobility of inorganic lead, deposition from the previous use of leaded gasoline still contributes to current high lead concentrations in roadside soils (MacKinnon et al. 2011). These authors suggest that previously deposited lead is continuously redistributed, maintaining a more or less constant transfer into the biosphere along roads. In line with this view, also other studies found high concentrations of lead in roadside dust, and in soils and biota along roads (Walraven et al. 2014; Adamiec et al. 2016; Adamiec 2017; De Silva et al. 2021). We assume that roe bucks from our study area were exposed to traffic-related lead near the motorway (A7) and the federal highway (B494). Especially lead bound to the particulate matter fraction of < 2.5 \( \mu \text{m} \) in diameter is readily distributed via atmospheric transport and has a high bioavailability (Padoan et al. 2017; De Silva et al. 2021).

It has been stated that deposition on surfaces of preferred feeding plants is a main exposure route of lead for browsing mammals (Tataruch and Kierdorf 2003). According to Demesko et al. (2018), field roe deer exhibit higher lead burdens than conspecifics from forest habitats, as dry deposition of lead on forest floor vegetation is relatively low compared to open fields (Grönholm et al. 2009; Schaubroeck et al. 2014). Regarding the lead exposure of field roe deer, also the contribution of lead from manure, sewage sludge, and mineral fertilizers must be considered (Knappe et al. 2008). It can further be assumed that lead bound to soil particles is mobilized by wind erosion on agricultural fields after harvest, which is also intensified by agricultural tillage, and deposited on grazing plants. In Northern Germany, this is particularly the case in late autumn/winter (Willand et al. 2014), i.e., during the antler growth phase of European roe bucks.

**Conclusion**

The present study revealed marked variation in antler lead concentration of roe deer in an agricultural-dominated area of Northern Germany over a period of 119 years. The findings underscore that the analysis of antlers, which constitute “naturally standardized” monitoring samples, provides a suitable tool for assessing temporal variation in environmental lead levels. The widespread, abundant, and highly adaptable European roe deer is particularly suited as a monitoring species in cultural landscapes. A main advantage of using roe deer antlers as monitoring units is that large samples spanning longer periods of time are readily available, thereby allowing the reconstruction of time trends of the level of bone-seeking pollutants in roe deer habitats. As the antlers can be obtained from individuals harvested in the course of regular management operations for population control, there is no need to kill animals only for providing samples. Since antlers are collected and kept as trophies, local hunting communities can provide the necessary material for studies on changing levels of bone-seeking contaminants in their neighborhood. In this way, hunters are able to significantly contribute to environmental surveillance and monitoring in an interesting example of citizen science (Cretois et al. 2020).

**Acknowledgements** We would like to thank Dr. J. Algermissen for allowing us to sample the roe deer antlers of his private collection. We further gratefully acknowledge the expert technical assistance of T. Fischer.

**Author contribution** CL, UK, and HK contributed to the conception and design of the study. CL and HK performed the sampling. Sample preparation, data collection, and analysis were performed by CL. CL, UK, and HK participated in the writing and revision of the draft manuscript and approved the final version.

**Funding** Open Access funding enabled and organized by Projekt DEAL.

**Data availability** The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Declarations**

**Ethics approval and consent to participate** Not applicable.

**Consent for publication** Not applicable.

**Competing interests** The authors declare no competing interests.

**Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.
References

Adamiec E (2017) Chemical fractionation and mobility of traffic-related elements in road environments. Environ Geochem Health 39:1457–1468. https://doi.org/10.1007/s10653-017-9983-9

Adamiec E, Jarosz-Krzemińska E, Wieszala R (2016) Heavy metals from non-exhaust vehicle emissions in urban and motorway road dusts. Environ Monit Assess 188:369. https://doi.org/10.1007/s10661-016-5377-1

Andersen R, Duncan P, Linnell JDC (eds) (1998) The European roe deer: the biology of success. Scandinavian University Press, Oslo

Baranowska-Bosiacka I, Korb Chek J, Marlewicz M (2019) Lead, Pb. In: Kaliszewska E (ed) Mammals and birds as bioindicators of trace element concentrations in terrestrial environments. An ecotoxicological assessment of the Northern hemisphere. Springer, Cham, pp 563–592

Bouritua EA, Kantira N, Papadopoulou L, Aidona E, Christophoridis C, Bourliva A, Kantiranis N, Papadopoulou L, Aidona E, Christophoridis C, Cappelli J, Frasca I, García A, Landete-Castillejos T, Luccarini S, Caito S, Almeida Lopes ACB, Paoliello MMB, Aschner M (2017) Climate-data.org (2020) Klima Harsum. https://de.climate-data.org/

Cretois B, Linnell JDC, Grainger M, Nilsen EB, Rød JK (2020) Hunters and their compounds in the environment. Occurrence, analysis, and biological relevance. VCH, Weinheim, pp 971–1014

Demosko J, Markowski J, Demesko E, Sławińska K (2015) Brake wear particle emissions: a review. Environ Sci Pollut Res 22:2491–2504. https://doi.org/10.1007/s11356-014-3696-8

Grönholm T, Launiainen S, Ahlum L, Mårtensson EM, Kulmala M, Vesala T, Nilsson ED (2009) Aerosol particle dry deposition to canopy and forest floor measured by two-layer eddy covariance system. J Geophys Res 114:D04202. https://doi.org/10.1029/2008JD010663

Hafenbetriebsgesellschaft mbH Hildesheim Port of Hildesheim - History (in German).n.d. http://www.hafen-hildesheim.de/historic.html. Accessed 21 Dec 2020

Helander B, Sundhomb M, Runkel AA, Bignert A (2019) Temporal changes in concentrations of lead and other trace metals in free-ranging Eurasian eagle owls (Bubo bubo) in Sweden. Arch Environ Contam Toxicol 77:377–389. https://doi.org/10.1007/s00244-019-00654-5

Hernberg S (2000) Lead poisoning in a historical perspective. Am J Ind Med 38:244–254. https://doi.org/10.1002/1097-0274(200009)38:3<244::AID-AJIM3>3.0.CO;2-F

Hoffmann WG (2000) Historical number of motor vehicles and passenger kilometers by motor vehicle type in Germany from 1906 to 1959 (in German). https://de.statista.com/statistik/daten/studie/249900/umfrage/geschichte-entwicklung-von-kraftfahrzeugen-in-deutschland/. Accessed 2 Mar 2021

Hong S, Candelone J-P, Patterson CC, Boutron CF (1994) Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations. Science 265:1841–1843. https://doi.org/10.1126/science.265.5180.1841

DWD CDC. Deutscher Wetterdienst Climate Data Center (2018) Historical hourly station measurements of wind speed and wind direction for Germany, Version 006 (in German). https://opendata.dwd.de/climate_environment/CDC/observations Germany/climate/hourly/ wind/historical/. Accessed 11 Jan 2021

EAA. European Environment Agency (2020) Copernicus Land Monitoring Service. https://land.copernicus.eu/. Accessed 21 Dec 2020

EMEP. European Monitoring and Evaluation Programme - Centre on Emission Inventories and Projections (2021) Emissions of Pb (tonnes). In: Data viewer – Rep. Emiss. data. https://public.tableau.com/shared/FPQ2YMRTD/:display_count=y&:origin=viz_share_link&:embed=y. Accessed 27 Jan 2021

Ewers U, Schildkötter H-W (1991) Lead in: Merian E (ed) Metals and their compounds in the environment. Occurrence, analysis, and biological relevance. VCH, Weinheim, pp 971–1014

Filella M, Bonet J (2017) Environmental impact of alkyl lead (IV) derivatives: perspectives after their phase-out. In: Sigel A, Sigel H, Sigel RKO (eds) Lead: its effects on environment and health. Metal ions in life sciences, vol 17. DeGruyter, Berlin, pp 585–609

Gizyjewska A, Fattebert J, Nawrocka A, Szkoda J, Zmudzki J, Jaroszewski J, Gizyjewska Z (2020) Temporal trends (1953–2012) of toxic and essential elements in red deer antlers from northeastern Poland. Chemosphere 261:128055. https://doi.org/10.1016/j.chemosphere.2020.128055

Goss RJ (1983) Deer antlers: regeneration, function, and evolution. Academic Press, New York

Grigonatos T, Martini G (2015) Brake wear particle emissions: a review. Environ Sci Pollut Res 22:2491–2504. https://doi.org/10.1007/s11356-014-3696-8

Jaroszewski J, Gifford J, Gijsbers M, Flesch-Janys D, Newnham R, Munitz S, Legrand D, Burton M, Armstrong P, Martin A, Thomson M, van Vliet M, Collier C, Egerton J, Martin R, Trayer S (2012) Environmental impact of alkyl lead (IV) derivatives: perspectives after their phase-out. In: Sigel A, Sigel H, Sigel RKO (eds) Lead: its effects on environment and health. Metal ions in life sciences, vol 17. DeGruyter, Berlin, pp 585–609

Grigoratos T, Martini G (2015) Brake wear particle emissions: a review. Environ Sci Pollut Res 22:2491–2504. https://doi.org/10.1007/s11356-014-3696-8

Wageningen Academic Publishers, Wageningen, pp 585–609
distribution of the trace elements zinc, strontium and lead in human bone tissue. Bone 57:184–193. https://doi.org/10.1016/j.bone.2013.07.038

Pokorny B (2000) Roe deer (Capreolus capreolus) as an accumulative bioindicator of heavy metals in Slovenia. Web Ecol 1:54–62. https://doi.org/10.5194/we-1-54-2000

Pokorny B, Glinšek A, Ribarič-Lasnik C (2004) Roe deer antlers as a historical bioindicator of lead pollution in the Šalek Valley, Slovenia. J Atmos Chem 49:175–189. https://doi.org/10.1007/s10874-004-1223-x

Pokorny B, Jelenko I, Kierdorf U, Kierdorf H (2009) Roe deer antlers as historical bioindicators of lead pollution in the vicinity of a lead smelter, Slovenia. Water Air Soil Poll 203:317–324. https://doi.org/10.1007/s11270-009-0014-z

R Core Team (2020) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna

Retief FP, Cilliers L (2005) Lead poisoning in ancient Rome. Acta Theol 26(Suppl 7):147–164. https://doi.org/10.4314/actat.v26i2.52570

Reuter F, Kohl H, Wienhaus O (1996) Pollutant load of grazing plants in Saxonian low mountain ranges (in German). Allg Forstzeitschrift 51:252–255

Samuiliah Y, Jones KC (1991) Deer antlers as pollution monitors in the United Kingdom. In: Trans 18th IUGB Congr. Swiat Press, Krakow, Warszawa, pp 415–420

Sawicka-Kapusta K (1979) Roe deer antlers as bioindicators of environmental pollution in southern Poland. Environ Pollut 19:283–293. https://doi.org/10.1016/0013-9327(79)90120-4

Sawicka-Kapusta K, Dudzinski W, Cichonska M (1991) Heavy metals concentrations in roe deer antlers from Rogów (central Poland). In: Trans 18th IUGB Congr. Swiat Press, Krakow, Warszawa, pp 421–424

Schaubroeck T, Deckmyn G, Neirynck J, Staelens J, Adriaenssens S, Dewulf J, Muys B, Verheyen K (2014) Multilayered modeling of particulate matter removal by a growing forest over time, from plant surface deposition to washoff via rainfall. Environ Sci Technol 48:10785–10794. https://doi.org/10.1021/es5019724

Schnyder E, Strok M, Kosonen Z, Skudnik M, Masej D, Jeran Z, Thöni L (2018) Lead concentrations and stable lead isotope ratios in moss in Slovenia and Switzerland. Ecol Indic 95:250–259. https://doi.org/10.1016/j.ecolind.2018.06.072

Shotyk W (1998) History of atmospheric lead deposition since 12,370 14C yr BP from a peat bog, Jura mountains, Switzerland. Science 281:1635–1640. https://doi.org/10.1126/science.281.5383.1635

Sobotka S, Baranowska-Bosiacka I, Gutowska I, Kupiec M, Duszka E, Machoy Z, Chlubek D (2011) Biomonitoring of lead and fluoride contamination in forests using chemical analysis of hard tissues of roe deer (Capreolus capreolus L.). Pol J Environ Stud 20:435–443. https://doi.org/10.1016/S0014-4886(03)00028-1

Stokke S, Braitner S, Arnemo JM (2017) Metal deposition of copper and lead bullets in moose harvested in Fennoscandia. Wildl Soc Bull 41:98–106. https://doi.org/10.1002/wsb.731

Stroud D (2015) Regulation of some sources of lead poisoning: a brief review. In: Delajay R, Spray C (eds) Proceedings of the Oxford Lead Symposium. Lead ammunition: understanding and minimizing the risks to human and environmental health. Edward Grey Institute, The University of Oxford, Oxford, pp 8–26

Stubbe C (1997) Roe deer. Biol Ecol Manag, 4th edn (in German). Parey, Berlin,

Taggart MA, Shore RF, Pain DJ, Peniche G, Martinez-Haro M, Mateo R, Homann J, Raab A, Feldmann J, Lawlor AJ, Potter ED, Walker LA, Braidwood DW, French AS, Parry-Jones J, Swift JA, Green RE (2020) Concentration and origin of lead (Pb) in liver and bone of Eurasian buzzards (Buteo buteo) in the United Kingdom. Environ Pollut 267:115629. https://doi.org/10.1016/j.envpol.2020.115629

Tataruch F, Kierdorf H (2003) Mammals as biomonitors. In: Markett BA, Breure AM, Zehmeister HG (eds) Bioindicators and biomonitors: principles, concepts, and applications. Elsevier, Amsterdam, pp 737–772

Tataruch F, Schönhofer F (1993) Reconstruction of environmental contamination of past decades by chemical analysis of red and roe deer antlers. In: Proc 21st IUGB Congr. Halíř, pp 23–28

U.S. Geological Survey (2020) Mineral commodity summaries 2020. https://doi.org/10.3133/mcs2020

Volmer K, Herzog A (1995) A closer look at roe deer - investigations on roe deer (in German). Schriftenreihe des Arbeitskreises Wildbiologie an der Justus-Liebig-Universität Gießen eV, Heft 22. Verlag J. Neumann-Neudamm, Melsungen.

von Raesfeld F, Neuhaus AH, Schaich K (1978) Roe deer, 8th edn (in German). Parey, Hamburg

von Storch F, Costa-Cabral M, Hagner C, Feser F, Pacyna J, Pacyna E, Willand A, Buchsteiner D, Höke S, Kaufmann-Boll C (2014) Development of technical, legal and organizational foundations for adaptation to climate change from the view of soil protection. Umweltforschungsplan des Bundesministeriums für Umwelt, Naturschutz, Bau und Reaktorsicherheit, Forschungskennzahl 7371 71 213/01, UBA-FB 1857, Texte 56/2014. Umweltbundesamt, Dessau-Roßlau

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