Science of the Total Environment 409 (2010) 430–438

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Historical biomonitoring of fluoride pollution by determining fluoride contents in roe deer (*Capreolus capreolus* L.) antlers and mandibles in the vicinity of the largest Slovene thermal power plant

Ida Jelenko *, Boštjan Pokorny [1]

ERICo Velenje, Ecological Research and Industrial Cooperation, Koroška 58, SI-3320 Velenje, Slovenia

ARTICLE INFO

Article history:
Received 7 July 2010
Received in revised form 9 October 2010
Accepted 12 October 2010
Available online 20 November 2010

Keywords:
Historical bioindication
Fluoride
Roe deer
Antler
Mandible
Slovenia

ABSTRACT

Roe deer antlers/mandibles are a useful tool for determination of ambient fluoride pollution. Antlers have a well-defined annual cycle of growth, therefore they represent a natural standardisation of samples during winter months. On the contrary, mandibles accumulate fluorides during the whole life of an organism, thus they reflect aggregated effect of fluoride pollution trough the life-span of an organism. Both tissues are easily available; mandibles are often systematically collected with the purpose of cognitive management and control, and antlers could be gathered from private well-dated hunters' collections.

Considering these benefits, fluoride contents were measured in 141 antlers (period 1960–2007) and 220 mandibles (period 1997–2009) of roe deer, shot in the vicinity of the largest Slovene Thermal Power Plant of Šoštanj (ŠTPP) as one of the major sources of fluorides in Slovenia. Fluoride contents in antlers significantly differed among age categories, and ranged from 110 to 1210 mg/kg in yearlings, 130 to 2340 mg/kg in young adults, and 250 to 2590 mg/kg in older adults, respectively. Fluoride levels in mandibles were also significantly different among age categories, and ranged from 30.0 to 227 mg/kg in fawns, 33.8 to 383 mg/kg in yearlings, and 61.5 to 1020 mg/kg in adults, respectively.

Comparison of these results with previously reported fluoride contents in antlers and mandibles of roe deer from different areas of Europe revealed that the study area has never been extensively contaminated with fluorides. Moreover, trends of fluoride contents in both tissues confirmed a significant decrease of fluoride pollution in the area after the years 1995 and 2000, when flue-gas cleaning devices were constructed on the ŠTPP. Indeed, highly positive correlations between annual emissions from the ŠTPP and mean annual fluoride contents in antlers/mandibles confirmed that both tissues may be a useful tool for assessing temporal trends in ambient fluoride pollution.

1. Introduction

Fluorides are natural compounds of the geosphere and are the 13th most abundant element in the earth crust (WHO, 2002). They derive from natural sources such as volcanic activity, bedrock weathering, or are a part of marine aerosols. However, anthropogenic activity (e.g. aluminium smelting; iron, steel, copper or nickel production; production and use of fertilizers; glass, brick and ceramic production; and combustion of fossil fuels) can significantly contribute to increased fluoride concentrations in the environment (Tataruch and Kierdorf, 2003; Weinstein and Davison, 2004). These increased concentrations often have a negative impact on living organism, both humans (Fordyce et al., 2007; Ozsvath, 2009) and wildlife (Suttie et al., 1987; Kierdorf et al., 1989; Pius and Viswanathan, 2008), which can be manifested as osteofluorosis (WHO, 2002; Fordyce et al., 2007) or dental fluorosis (Kierdorf et al., 1996a; Jelenko et al., 2010a). Therefore, in the last decades a number of studies of the impact of fluorides on animals have been carried out, concentrated mainly on ungulates and especially cervides (Kay, 1975, 1976; Walton and Ackroyd, 1988; Machoy et al., 1991; Kierdorf et al., 1996a, 1997; Hell et al., 1995; Vikøren et al., 1996; Kierdorf and Kierdorf, 1999, 2000a, 2001a,b, 2005, 2006; Sedláček et al., 2001; Zakrzewska et al., 2005; Zemek et al., 2006; Pokorny, 2006a; Jelenko et al., 2010b).

Elevated fluoride contents in the body of ruminants are mostly the consequence of feeding on contaminated plant material; other potential uptake route is also the accidental ingestion of soil and/or water that contains high concentrations of fluorides (Khandare and Rao, 2006; Fordyce et al., 2007). 50% of the ingested fluorides are absorbed into the blood of the animal (Whitford, 1994; Ozsvath, 2009), and mostly all of the absorbed fluorides (97–99%) are finally accumulated in bone tissues (Whitford, 1994; Pius and Viswanathan, 2008).

Affinity of fluorides towards accumulation in bones, which characterised them as bone-seeking pollutants, has a great importance for bioindication purposes, allowing also a retrospective approach

* Corresponding author. Tel.: +386 3 898 19 51; fax: +386 3 898 19 42.
E-mail addresses: ida.jelenko@erico.si (I. Jelenko), bostjan.pokorny@erico.si (B. Pokorny).
[1] Tel.: +386 3 898 19 89; fax: +386 3 898 19 42.

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doi:10.1016/j.scitotenv.2010.10.012

(i.e historical biomonitoring). In this context, the most appropriate target species for bioindication of fluoride pollution in terrestrial ecosystems in Europe is the European roe deer (*Capreolus capreolus* L.), due to its favourable ecological and socio-biological characteristics (Tataruch and Kierdorf, 2003; Pokorny, 2003), the pan-European distribution (Apollonio et al., 2010), and much smaller home ranges in comparison with most other deer species, which enables monitoring with rather high spatial resolution (Kierdorf and Kierdorf, 2000a, 2003). Moreover, it is also one of the most important hunting species throughout Europe; therefore, antlers of roe deer bucks are regularly kept at homes as trophies and their mandibles are in many countries often systematically collected with the purpose of cognitive management and control of the hunting system. In this way, both tissues are easily accessible also for the research purposes (Kierdorf and Kierdorf, 2005; Zemek et al., 2006; Jelenko et al., 2010a; Pokorny et al., 2009).

Antlers are bony cranial appendages that develop on the top of permanent frontal outgrowths (pedicles) of male deer and undergo a periodic annual replacement (Kierdorf and Kierdorf, 2005). During their growth (in the period November–March/April) fluorides, with other essential minerals, accumulate and deposit in mineralized antler tissue (Tataruch and Kierdorf, 2003; Kierdorf and Kierdorf, 2005). When the antler growth is finished, the further intake of fluorides into the tissue is stopped. Roe deer antlers, therefore, reflect a cumulative intake of fluorides fixed to a specific time span of some late autumn/winter months, and are thus natural standardised environmental samples (Tataruch and Kierdorf, 2003; Pokorny, 2006a).

On the contrary, fluoride contents in other bone tissues, such as mandibles, represent their cumulative intake into the organism during its entire life (Kay et al., 1976; Kierdorf et al., 1989; Vikøren et al., 1996). Consequently, it is always needed to take into account also the age of studied animal, when comparing the results of fluoride levels in mandibles (Kierdorf et al., 1989; Jelenko et al., 2010a).

Measurement of the fluoride contents in antlers and/or mandibles of roe deer is known to be a useful tool for the assessment of the temporal and geographical changes in the fluoride pollution of the environment (Suttie et al., 1987; Walton and Ackroyd, 1988; Vikøren et al., 1996; Kierdorf and Kierdorf, 1999, 2000a, 2000b, 2001b, 2002; Sedláček et al., 2001; Pokorny, 2006a). Indeed, suitability of the ungulate's (particularly roe deer) antlers and mandibles as pollution bioindicators was confirmed in the past with the determination of the strong positive correlation between the fluoride concentrations in the environment and: (i) fluoride levels in antlers of different deer species (Kierdorf et al., 1997; Kierdorf and Kierdorf, 2000b, 2002, 2003, 2005, 2006; Pokorny, 2006a); (ii) fluoride levels in mandibles of cervids (Machoy et al., 1991; Kierdorf and Kierdorf, 1999, 2000a; Zakrzewska et al., 2005). The importance of antlers and/or mandibles as a tool for assessing historical trends in ambient pollution is especially emphasised in areas where fluoride load is measured rarely or is not measured at all (Suttie et al., 1987; Machoy et al., 1991). Moreover, such a retrospective approach is very important also for the assessment of the efficiency of the remediation measures done in a certain area (e.g. construction of air-cleaning devices on point emission sources), which has been proven with some previous studies (Vikøren et al., 1996; Kierdorf and Kierdorf, 1999, 2000a, 2001a, 2003; Pokorny, 2006a).

In Slovenia, the Šoštanj Thermal Power Plant (ŠTPP) is one of the largest anthropogenic sources of fluorides. Fluoride emissions from the ŠTPP have been much altering over the last decades, due to the changes in the rate of coal burning (huge peak in 1980s) and up-following continuous decrease after the installation of cleaning devices in 1995 and 2000 (for details, see the description of the study area).

Since there is a lack of data on fluoride pollution, its trends and exposure of wildlife to fluorides in the study area, the main aims of this study were as follows: (i) reconstruction of temporal trend in fluoride pollution in the vicinity of the ŠTPP (the Šalek Valley) based on the analysis of fluoride contents in antlers and mandibles of roe deer, shot after the year 1960; (ii) comparison of fluoride contents (and their trend) in roe deer antlers and mandibles from the Šalek Valley with the data from regions elsewhere in Europe; (iii) assessment of the efficiency of the remediation measures done on the ŠTPP, and to compare the mean annual fluoride contents in antlers/mandibles with the data on annual emissions from the ŠTPP; (iv) comparative evaluation of advantages and drawbacks of roe deer antlers and mandibles as tools for historical biomonitoring of fluoride pollution.

2. Material and methods

2.1. Study area

The study area (the Šalek Valley with its hilly surroundings) is situated in the northern part of Slovenia (Fig. 1). The bedrock of this area is very various, with both silicate and carbonate rocks being very frequent. Natural vegetation represents different types of deciduous or mixed forests, with beech, spruce, Scotch pine, sessile oak, and chestnut as the most frequent tree species. The Valley gained its present shape in Pliocene, when thick layer of lignite (with high fluoride concentrations: 104–145 mg/kg; Beričnik Vrbovšek, 2002), was also formed. Lignite has been continuously mined since the beginning of the 20th century and consumed in the Šoštanj Thermal Power Plant, which has been the main (only important) source of (fluoride) pollution in this area. However, after the construction of flue-gas cleaning devices on the ŠTPP in 1995 and 2000, emissions have significantly decreased, which resulted in much lower exposure of different parts of biota and in continuous improvements of both terrestrial and aquatic ecosystems (Pokorny et al., 2004; Poličnik and Batič, 2004; Poličnik et al., 2008; Al Sayegh Petkovšek et al., 2008; Pokorny, 2006a; Jelenko et al., 2009; Mazej et al., 2010).

The exact data on fluoride emissions from the ŠTPP are not known. However, since 1960 the ŠTPP burned over 150 million tons of lignite, which resulted in approximately 110,000 tons of emitted dust (Rotnik, 2010). Considering the average fluoride contents in lignite and residual ash, the average annual amount of emitted fluorides in the period 1980–1999 was assessed at 516 tons (Beričnik Vrbovšek, 2002; Rotnik, 2010). In 1995 and 2000 two flue-gas cleaning devices were constructed on the ŠTPP, which resulted in a drastic decrease of annual dust emissions, as follows: 8121 tons in 1993, 1845 tons in 1996 and 467 tons in 2001, respectively (Rotnik, 2010). Consequently, the fluoride emissions from the ŠTPP drastically decreased as well, i.e. to 76 tons per year in the period 2004–2007 (ARSO, 2009).

2.2. Sample collection

Antlers of 141 roe deer bucks, shot in the period 1961–2007 in the Šalek Valley, were collected from the local hunters (owning trophies at their homes) of the hunting ground Oljka, Šmartno ob Paki. All animals were shot within the distance of 6 km south from the ŠTPP (in the direction of prevailing winds above the power plant), between 300 and 700 m above sea level (just below the upper layer of the frequent thermal inversion, which in winter months disables emitted gasses to leave the study area).

Antler bone samples were taken following the method described by Kierdorf and Kierdorf (2005). To eliminate the possibility of secondary contamination, antlers were thoroughly cleaned with a nylon brush; moreover, the upper bone surface (approximately 0.5 mm in depth) was removed by grinding. Afterwards, a hole was drilled into the back of each beam approximately 1.5 cm above the antler–pedicle junction, with a tungsten-carbide cutter fitted to a hand-held electric drill. Between 1 and 3 g of bone powder was collected for an individual animal.

Contrary to antlers, which can be collected in hunters' collections for decades and even centuries back in single sample episode, mandibles can generally not be found in such collections. Therefore, they can in principle be used in spatial (for which they should even be preferred in