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COMPARATIVE ANALYSIS OF FLUORIDE CONTENT IN SHEEP MANDIBLES FROM ARCHEOLOGICAL EXCAVATIONS IN SZCZECIN ACCORDING TO INDIVIDUAL AGE AND TIME OF BEING DEPOSITED IN SOIL

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Abstract

Bones can be a very good marker of environmental contamination by fluoride. Bones in a living organism have a different composition than in a dead one. As a result of adsorption from soil, bones from archeological excavations usually have more fluoride than those in a living body, and a significant portion of the fluorides they contain are acquired after death.

This paper presents the results of a studies on fluoride content of sheep mandibles from archeological excavation sites in Szczecin. An attempt was undertaken to define how the chronological age of the bones and the time they had been lying in soil affected the bones.

The material consisted of sheep mandibles from several excavations sites: Szczecin Mścięcino, Szczecin Rynek Warzywny, and Szczecin Zamek Książąt Pomorskich (Szczecin Castle of Pomeranian Dukes). Cultural layers in these excavations were mostly formed from humus and humus with sand and clay. The fluoride content was determined by an ion-selective electrode with the pH/mV Orion 920A.

Fluoride content was determined in 270 mandibles, which were classified into sheep age categories and according to the archeological age of the bones. The individual and archeological age of the sheep bones was determined by archeologists during the initial tests of the bones. A comparative evaluation of the significance of differences in the average

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fluoride content in the bones was performed by means of a single factor analysis of the orthogonal variance. The least significant differences were estimated by Tukey's test.

The results show that the fluoride content depends on the individual age of animals and the chronological age of bones. The fluoride content of the sheep mandibles increased along with the individual age of the animals. Moreover, chronologically younger bones contained significantly less fluoride than older ones. In the sheep mandibles which lay longer in soil, the fluoride content tended to increase with the chronological age, while in chronologically youngest bones the tendency was reverse.

Key words: fluoride, fossil bones, mandibles, sheep.

ANALIZA PORÓWNAWCZA ZAWARTOŚCI FLUORKÓW W ŻUCHWACH OWIEC Z WYKOPALISK ARCHEOLOGICZNYCH MIASTA SZCZECINA W ZALEŻNOŚCI OD WIEKU OSOBNICZEGO I CZASU ZALEGANIA W GLEBIE

Abstrakt

Kości mogą być bardzo dobrymi biomarkerami skażenia środowiska fluorkiem. Inny jest skład kości w organizmie żywym, a inny w martwym. W wyniku adsorpcji z gleby kości archeologiczne zazwyczaj zawierają więcej fluorków niż świeże, a znaczącą część fluorków stanowią te wbudowane po śmierci.

W pracy przedstawiono wyniki badań zawartości fluorków w żuchwach owiec z wykopalisk archeologicznych miasta Szczecina. Podjęto próbę określenia, w jaki sposób wiek osobniczy oraz czas zalegania kości w glebie wpływa na zmianę stężenia fluorków w żuchwach owiec.

Materiał do badań stanowiły żuchwy owiec z terenów, w których prowadzono wykopaliska archeologiczne: Szczecin Mścięcino, Szczecin Rynek Warzywny i Szczecin Zamek Książąt Pomorskich. Warstwy kulturowe w tych wykopaliskach tworzyły głównie próchnica oraz próchnica z domieszką piasku i gliny. Zawartość fluorków w kościach oznaczano potencjometrycznie z zastosowaniem elektrody jonoselektywnej z użyciem pH/jonometru firmy Orion 920A. Przebadano zawartość fluorków łącznie w 270 żuchwach, które posegregowano według utworzonych kategorii wieku osobniczego owiec i wieku archeologicznego kości. Wiek osobniczy oraz archeologiczny kości owiec został ustalony przez archeologów podczas wstępnych badań kości. Oceny porównawczej istotności różnic między średnimi zawartościami fluorków w kościach dokonano za pomocą jednoczynnikowej analizy wariancji ortogonalnej. Najmniejsze istotne różnice obliczono testem Tukeya.

Stwierdzono, że zawartość fluorków w żuchwach owiec była zależna zarówno od wieku osobniczego zwierząt, jak i wieku archeologicznego kości. Zawartość fluorków w żuchwach owiec zwiększała się wraz z wiekiem osobniczym zwierząt. Ponadto kości młodsze pod względem wieku archeologicznego zawierały istotnie mniej fluorków niż kości starsze. W żuchwach owiec zalegających dłużej w glebie stwierdzono także tenedencję wzrostu zawartości fluorków wraz z wiekiem osobniczym zwierząt, natomiast w kościach najmłodszych pod względem archeologicznym tendencja ta była odwrotna.

Słowa kluczowe: fluorki, kości archeologiczne, żuchwy, owce.

INTRODUCTION

Fluoride content in living organisms has a significant meaning for evaluation of the environmental contamination by this element. Bones, nails, antlers, hair, teeth, snails' shells or birds' egg shells as well as urine and blood are used as biomarkers of the fluoride environmental contamination (MANDAT et al. 1990, GUTOWSKA et al. 2002, PIOTROWSKA et al. 2006). Friedrich (2002) claims that up to 90% of the retained fluorides in an organism is deposited in bones, teeth, nails and hair.

Fluorine is deposited in bones as hydroxyapatite. The hydroxyl ion is substituted by the F^- ion forming fluoroapatite, in which the distance between the calcium and fluoride ions is smaller. Fluoroapatite crystals are bigger, more stable, more resistant to dissolving and less subject to rebuilding (GRYNPAS 1990). According to MACHOY (1987) the fluoride ion can substitute the hydroxyl ion in bones even up to 5.7%, and according to DĄBKOWSKA et al. (1995) – in a range of several per cent.

The composition of bones in a living organism is different from that of bones in a dead animal. When a bone is buried in soil, the physiological equilibrium which was earlier established between this tissue and the surroundings is disturbed. In soil there follows a dynamic interaction between bones and the geochemical forces. The influence on the diagenetic bone tissue have: the pH of soil, microorganisms, structure of soil, mineralogy, and the organic content, so called external factors. The internal factors are: density, volume, microstructure and bone biochemistry (SZOSTEK, BAŁUSZYŃSKA 1997).

The reason of the fluoride accumulating in bones, mainly, after the death, is the influence of surrounding remains of the soils mainly (NOCEŃ et al. 1994). As a result of the adsorption from soil, archaeological bones contain more fluoride than the living ones, and a significant part of fluorides constitute those which were sorption after the death (CHLUBEK et al. 1996). Posthumously, in the soil environment, bone enrichment in the fluorides is a very slow process. That is why a significant increase of the fluoride content in the archaeological bones remains is evident only in the bones which lay in soil tens of years or even several centuries (NOCEŃ 1997).

This paper concerns an evaluation of the fluoride content in sheep mandibles from the archeological excavations of Szczecin, as well as an attempt of defining a dependence of the mandible fluoride content in the individual sheep age and the chronological age.

MATERIALS AND METHODS

The material for the study consisted of sheep mandibles from archaeological excavations in Szczecin. The bones for the analysis were rendered by the Chair of Animal Anatomy of University of Agriculture in Szczecin. The animal remains come from three archaeological excavation sites: Szczecin Mścięcino, Szczecin Rynek Warzywny, and Szczecin Zamek Książąt Pomorskich (Szczecin Castle of Pomeranian Dukes, latter called the Castle).

The material from Mścięcino site was excavated in 1954 while unearthing the remnants of an early Middle Age settlement and later, in 1968, during archaeological excavations of an early Middle Age castle. The sheep were probably kept for wool and hide rather than meat (KUBASIEWICZ 1955, STĘPIEŃ 1994).

The excavations from the Castle come from the sites set in different places. The material was excavated in the castle yard and basement in the 1970s. The sheep were a cross of the bigger copper sheep with the smaller peat sheep (KUBASIEWICZ 1960).

The last site – Szczecin Rynek Warzywny – was located close to the Castle, between Castle and the Odra River. The excavations were conducted between 1954 and 1965. The excavated bones were mainly mandibles of the ancient copper sheep, with very few bones of the peat sheep (KUBASIEWICZ 1957, KUBASIEWICZ, GAWLIKOWSKI 1967).

The individual and chronological age of the sheep bones was established by the archaeologists during initial tests of the bones.

Cultural layers in these excavations were mostly formed from humus and humus with sand and clay (GARCZYŃSKI 1955).

Fluoride content in 270 bones was determined (Table 1). The mandibles were classified into categories embracing individual sheep age and chronological age of bones. These categories and numbers of mandibles in each category are given in Tables 2 and 3. Adult individuals are those of above 24 months of age.

Table 1

Specification of the analyzed bones

Site of excavations	Number of mandibles	Chronological age (century)
Szczecin Mścięcino	26	9^{th} - 11^{th}
Szczecin Zamek	123	2^{nd} half 7^{th} - 20^{th}
Szczecin Rynek Warzywny	121	2^{nd} half 9^{th} - 1^{st} half 13^{th}
Total	270	2^{nd} half 7^{th} - 20^{th}

Table 2

Categories of individual sheep age and number of mandibles in categories

Categories of individual sheep age		Number of bones
1.	<6 months	17
2.	6-12 months	80
3.	12-18 months	36
4.	18-24 months	27
5.	> 24 months	108

Table 3

Categories of chronological bones age and number of mandibles in categories

Categories of chronological bones		Number of bones
I	2^{nd} half 7^{th} - early 9^{th}	10
II	9^{th} - 11^{th}	159
III	late 11^{th} - 2^{nd} half 12^{th}	41
IV	late 12^{th} - 14^{th}	42
V	early 16^{th} - 18^{th}	10
VI	19^{th} - 20^{th}	7

The fluoride content in the bones was determined by potentiometry using a pH/mV Orion 920A with an ion-selective fluoride electrode, according to Durda et al. (1986).

All analyses were performed in three replications. The comparative evaluation of significance differences in mean fluoride contents in bones was executed by ANOVA. The LSD values were estimated by Tukey's test. In order of determine how the individual age and the time of lying in soil influenced the fluoride content in mandibles, there was a 3D surface matched for the experiment data, by means of the method of the smallest squares with the distance weighing. It depicts the tendency of changes in fluoride content according both to individual age and chronological age of bones.

RESULTS AND DISCUSSION

The results of the experiment showed that the fluoride content in the sheep mandibles depended on both the individual sheep age and the chronological age of the bones.

According to the individual age, the mean fluoride content in the mandibles was the lowest in the bones of sheep age 6-12 months (category 2), where it was 123.4 mg $F^{-}\cdot kg^{-1}$ (Figure 1a). The bones of the youngest individuals contained 128.0 mg $F^{-}\cdot kg^{-1}$. As SZOSTEK, BAŁUSZYŃSKA (1997) claim that a higher fluoride content in mandibles of the youngest sheep, compared with sheep 6-12 months of age, can be caused by higher mineralization of bones in younger animals and easier fluoride sorption from soil by bones of young dead individuals. From the group of bones of the young individuals

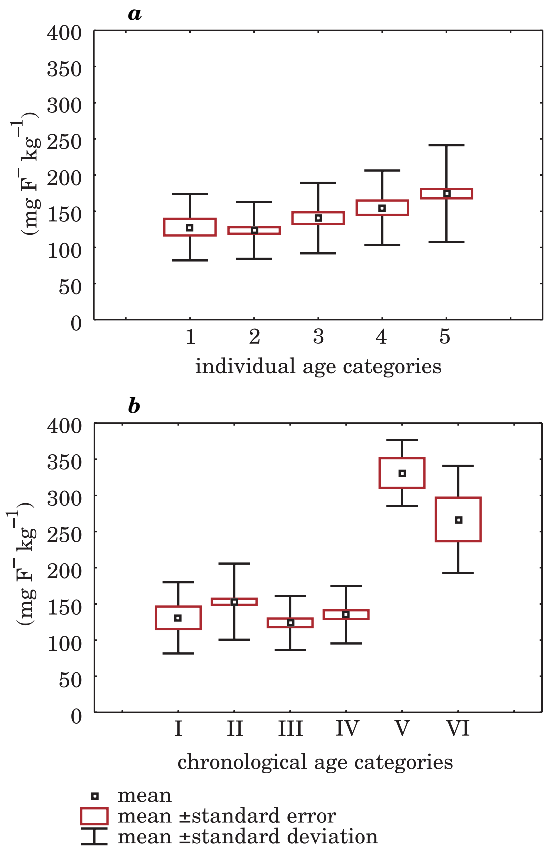

Fig. 1. The fluoride content in sheep mandibles from Szczecin excavations according to individual age of sheep (*a*) and chronological age of bones (*b*)

(6-12 months of age) on, the fluoride content tends to increase as the age of sheep goes up. A highly significant statistical difference in the fluoride content was observed between the categories 2 and 5 ($p < 0.001$ – Table 4). ALSO NOCEŃ (1997) claimed that along with the individual age increase, the accumulation of fluorides increased in archeological bones.

According to the chronological age of bones, an average fluoride content in archeological bones was found in mandibles from the late 11th-2nd half 12th century (category III) and in mandibles lying in soil longest, from the 2nd half of the 7th- early 9th century (category I), where it reached123.7 mg $F^{-} \cdot kg^{-1}$ and 130.8 mg $F^{-} \cdot kg^{-1}$, respectively (Figure 1b). The highest F^{-} content appeared in bones from the early 16th to the 18th century (category V) – 331.0 mg $F^{-} \cdot kg^{-1}$, and in bones from the 19th- 20th century (category VI) – 226.8 mg $F^{-} \cdot kg^{-1}$. The bones which lay in soil the shortest time showed the highest content of fluoride. This can be attributed to the surface layers of the excavation soil containing more fluoride than the deeper ones. The

Table 4

Statistical analysis of differences between the fluoride content in sheep mandibles from Szczecin excavations

According to the individual sheep age		
Individual age categories	(mg $F^{-} \cdot kg^{-1}$)	
	mean	standard deviation
1.	128.0	45.92
2.	123.4	39.33
3.	140.4	48.71
4.	154.9	51.42
5.	174.3	66.89
Statistical analysis of difference	2-5***	
According to the chronological bones age		
Chronological age categories	(mg $F^{-} \cdot kg^{-1}$)	
	mean	standard deviation
I	130.8	49.31
II	153.0	52.56
III	123.7	37.42
IV	135.0	39.78
V	331.0	45.78
VI	266.8	74.03
Statistical analysis of difference	I-V***, I-VI***, II-V***, II-VI***, III-V***, III-VI***, IV-V***, IV-VI***	

same conditions are observed in areas subjected to fluorine emissions (e.g. the Police Chemical Plant near Szczecin, which emits large amounts of fluorine). The excavation layers from which the bones used for our examinations were excavated contained large amounts of humus, which retained fluoride (MEINHARDT 1994, GAŁĄZKA 1996). The statistical analysis showed highly significant differences between the bones of the two youngest groups, and the other categories of the chronological age of bones (Table 4).

The surface diagram of the fluoride content according to the individual age of sheep and the chronological age of bones can suggest that in the bones from the period of up to 2nd half of the 12th century (I, II and III categories of chronological age) the fluoride content increased only slightly along with the individual sheep age, while in the bones which lay in soil a shorter time a reverse tendency was observed – the fluoride content in mandibles decreased along with the individual sheep age (Figure 2). It was also ascertained that in all the categories of individual age of sheep, the fluoride content in mandibles increased as the time they had been deposited in soil was shorter, a tendency which was most evident in the youngest bones (category 1 and 2).

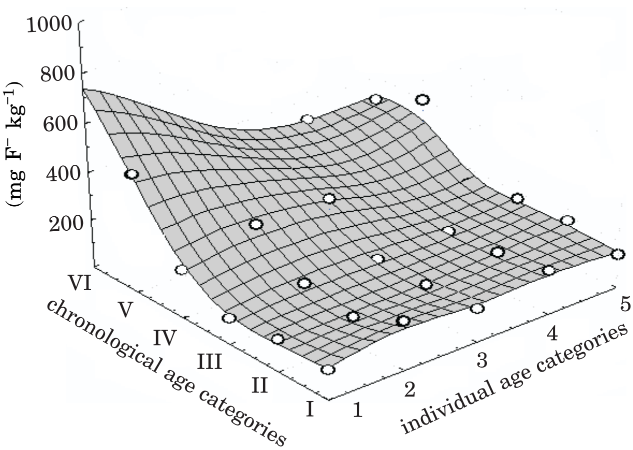

Fig. 2. Tendency of the fluoride content in sheep mandibles from Szczecin excavations according to individual sheep age and chronological bones age

CONCLUSIONS

1. The fluoride content in the sheep mandibles from the archeological excavations in Szczecin increased along with the individual age of animals.

2. As regards the chronological age, the younger bones contained significantly more fluorides than the older ones.

3. In the sheep mandibles which lay in soil longer, an increasing tendency in the fluoride content along with the individual age of animals occurred, while in the youngest chronological bones a contrary tendency was noticed.

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