Did the advancement of early mediaeval technology of silver and lead smelting cause pollution? A case study of the Łosień - Strzemieszyce region

Způsoboval rozvoj raně středověkých technologií hutnění stříbra a olova znečištění? Případová studie z oblasti Łosień – Strzemieszyce

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Abstract: The early medieval basin of silver and lead metallurgy is partly situated in the catchment area of the Przemsza and Brynica rivers in Southern Poland. The above basin stretches from Olkusz in the east to Bytom and Tarnowskie Góry in the west. In the north it reaches Siewierz and Przeczyce, and in the south – Trzebinia, Chrzanów and Jaworzno. The archaeological sites relating to silver and lead metallurgy that were discovered in this area date back to the second half of the 11th century. The lie of the land is that of a varied horst plateau in which the depressions were filled in with quaternary sands. It has also been strongly anthropogenically transformed. In the mentioned area the highest levels of pollution of metal processing were observed during the Early Middle Ages. The increase in the level of pollution caused by processing metals was closely related to a multi-stage development of the the Piast Monarchy leading to the increase in the demand for metal products. This article will describe primary chemical processes which occur during lead and silver smelting and which produce pollution.

Key words: Early Middle Ages, technology of silver and lead smelting, pollution, Southern Poland

INITIAL REMARKS

The discovery of metal processing methods resulted in the highest levels of pollution ever produced by people. The increase in the level of pollution caused by processing metals was closely related to a multi-stage development of societies leading to the increase in the demand for metal products. This in turn resulted in the exploitation of the natural environment, the traces of which are visible until today.

Is it therefore true that the environmental pollution in the 11th and 12th centuries was an implication of the traces of early medieval lead smelting?

The answer to this question only seems to be easy. It is generally and commonly believed that lead and its compounds are toxic. It can be rightly inferred from this that smelting lead from ore and re-melting it in metallurgic workshops (goldsmith's or bronze) also has toxic character and traces of this toxic effect may be observed in the environment.

Nevertheless, proving the thesis directly is not an easy task and requires the involvement of numerous scientific disciplines and interdisciplinary cooperation. In the situation of the region presented in this article, the examination of pollution caused by prehistoric processes of smelting metals as well as lead, silver and iron in the early medieval period is particularly difficult. It is connected with the fact that at least since the 11th century (or even earlier), extraction and smelting of metals from ores has continued until the present time. This article will present the first research of this phenomenon conducted in the fields common for archaeologists, as well as experts in environmental pollution and the history of metallurgy.

TERRITORIAL RANGE

Several years of archaeological research in the territory of Zagłębie Dąbrowskie (Dąbrowa Basin) resulted in important archaeological discoveries connected with early medieval lead metallurgy. It should be pointed out that the discoveries were made not by one but by several archaeological expeditions working in this territory. Years ago, Czech archaeologist Zdeněk Váňa stated that in case of archaeological research, the so called "law of series" may be sometimes applied, as one discovery leads to other similar discoveries (Váňa 1985, 62). This is not an irrational phenomenon, simply one important discovery makes other researchers aware of a given issue that is essential from a cognitive point of view. The interpretation of archaeological research shall constitute the subject of this article. It can be stressed here that *early medieval silver and lead metallurgical region* was undoubtedly discovered thanks to the research conducted at the turn of the 20th and 21st centuries (Rozmus 2004, 301–305, Bodnar et Rozmus 2004, 9–60, Rozmus 2014).

Early medieval basin of silver and lead metallurgy is partly situated in the catchment area of the Przemsza and Brynica rivers. The above basin stretches from Olkusz in the east to Bytom and Tarnowskie Góry in the west. In the north it reaches Siewierz and Przeczyce, and in the south – Trzebinia, Chrzanów and Jaworzno (fig. 1). The archaeological sites relating to silver and lead metallurgy that were discovered in this area date back to the second half of the 11th century.

At the turn of the 12th and 13th centuries, the settlement structure based on the extraction of near-surface ores collapsed. Production settlements (Zversov aforementioned in historical sours from 1136 AD) either disappeared or were destroyed (Łosień) during military activities. In the 13th century, medieval mining and metallurgic infrastructure based on drift mining was developed. There were several such settlement centres in the area in question. Two of them constitute the subject of this article: Strzemieszyce – Łosień settlement centre (Foltyn 2005, 29–34) and a production settlement in Sosnowiec – Zagórze (Suliga et Rozmus 2012, 250–286).

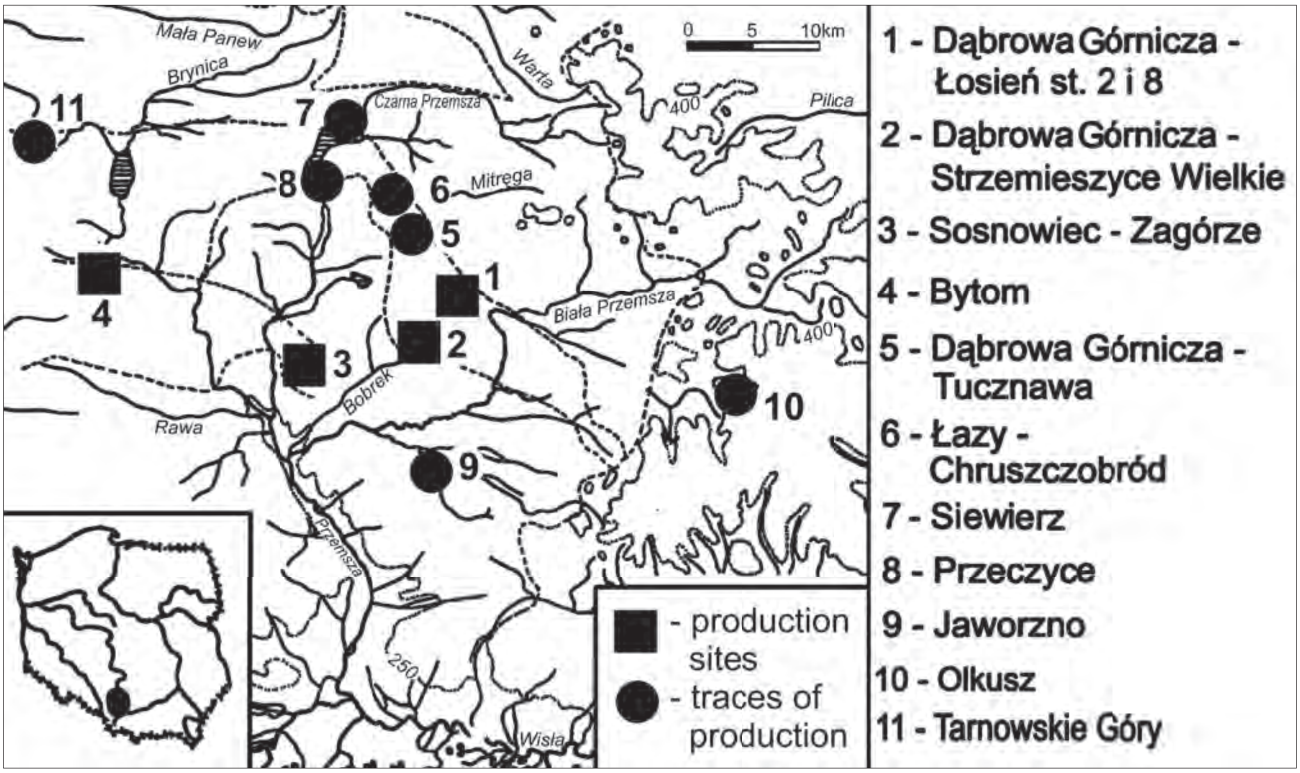


Fig. 1. Schematic location of villages and towns connected with metallurgical sites, traces of lead production and historical sources mentioning silver and lead extraction from the 11th to the 13th centuries.
Obr. 1. Schematické umístění vesnic a měst spojených s metalurgickými místy, stopy výroby olova a historické zdroje zmiňující extrakci stříbra a olova od 11. do 13. století.

CHARACTERISTICS OF POLYMETALLIC DEPOSITS AT THE BORDERLINE OF TODAY'S UPPER SILESIA AND LESSER POLAND

The deposits of zinc and lead can be found in the ore-bearing limestone and dolomite beds. Their approximate total area covers 2500 km^2. These are mainly dolomites from the Middle Triassic, but in some regions there are also dolomites of the Lower Triassic, the so called Buntsandstein, created by bunter sandstone occurring below the Muschelkalk. The next ore-bearing rocks are ore-bearing clays (Gałkiewicz 1983, 15–18). Deposits of zinc and lead are found mainly in dolomites (approximately 93,8 %), whereas they constitute only 6,2 % of limestone. Minor amounts of zinc and lead deposits occur also in sandstones and the Muschelkalk. The above mentioned ores are included in the deposit group of *Mississippi Valley* type that can be found in various locations all over the world (Cabała, Zogała, Dubiel 2008, 694). Chemical compounds, colloquially called galena, constitute the primary lead ore. Generally speaking, these are lead sulphides (PbS). Other compounds that are the products of weathering and other chemical reactions undergone by galena in nature are less important. These are: carbonate ore – cerussite ($PbCO_3$ – sometimes cerussite forms white beautiful crystals) and lead sulphate – anglesite ($PbSO_4$). Lead also occurs in other types of carbonates, such as tarnowskite (lead aragonite) and in calcite, such as plumbocalcite (lead calcite). The economic value of the latter minerals is not big. As it was pointed out in Tadeusz Dziekoński's works, the early lead metallurgy was mainly based on galena processing (Dziekoński 1963, 271). As it was stated before, lead ore is accompanied by an admixture of silver –particularly desired for centuries – that occurs in the form of ore. For example, in silver-bearing galena in Tarnowskie Góry region, silver compounds form solid

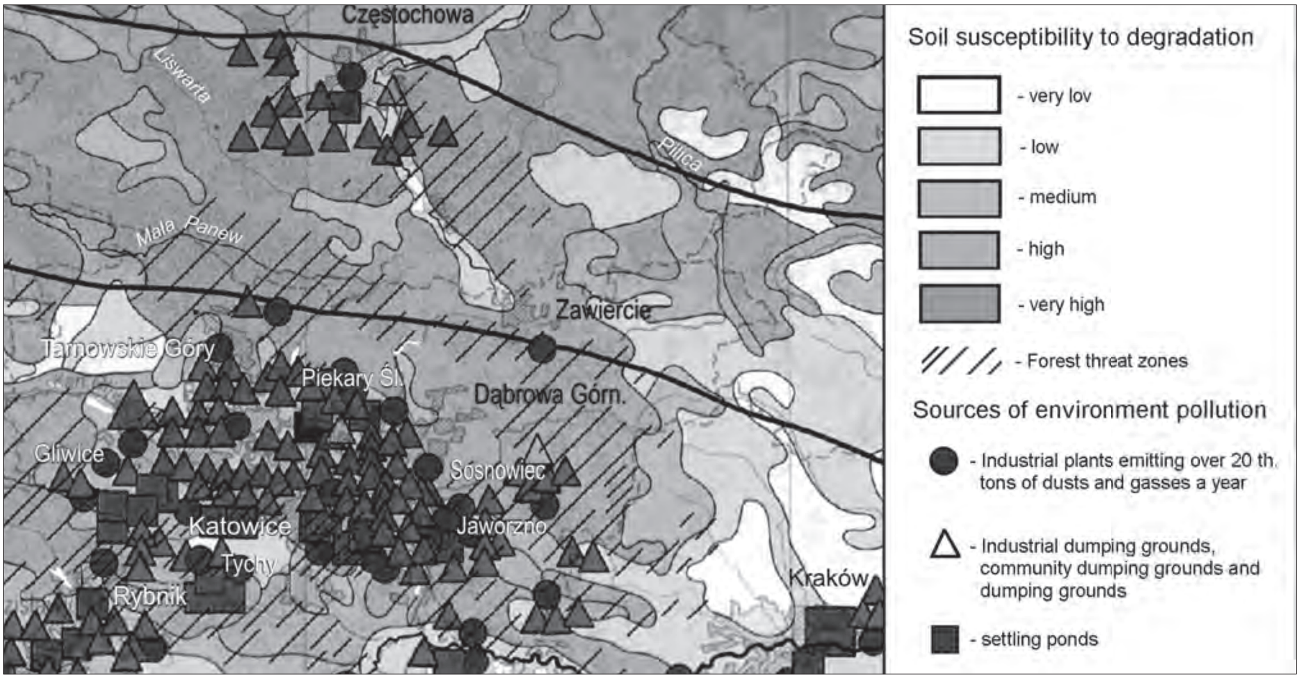


Fig. 2. Sources of the current pollution in the Silesian and Dąbrowa Region. [according to Stopień zanieczyszczeń ołowiem na obszarze śląsko-dąbrowskim. cf. Atlas Rzeczpospolitej Polskiej, ed. M. Najgrakowski, Warszawa 1993–1997].
Obr. 2. Zdroje současného znečištění ve slezském a dąbrowském kraji. [podle Stopień zanieczyszczeń ołowiem na obszarze śląsko-dąbrowskim. cf. Atlas Rzeczpospolitej Polskiej, ed. M. Najgrakowski, Varšava 1993–1997].

solutions or inclusions in the native state, but they predominantly occur in the form of such silver compound as argentite – Ag_2S, pyrargiryte – Ag_3SbS_3, freibergit (Silberfahlerz) – $Ag_6[Cu_4Fe_2]Sb_4S_{13-x}$, silver tetrahedrite (rarely used formula $Cu_3SbS_{3.25}$ + silver admixture), stephanite - Ag_5SbS_4.

In the territory usually referred to as Silesian – Cracow lead and silver deposit region, there are also oxidized zinc ores. They are divided into two groups: blende ore and calamine ore. The main component of calamine ore is zinc carbonate – smithsonite ($ZnCO_3$) or zinc silicate – calamine or hemimorphite ($H_2Zn_2SiO_5$). These minerals impregnate

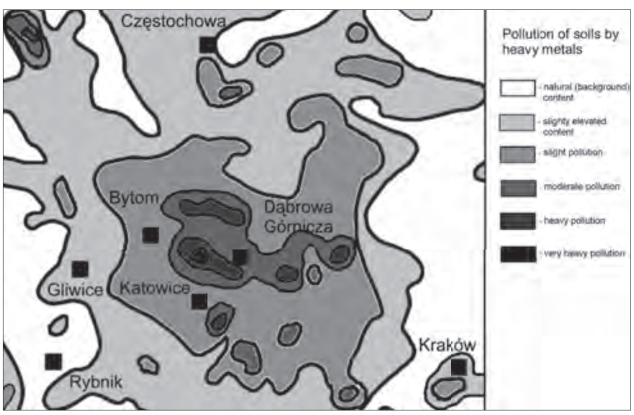


Fig. 3. The degree of lead pollution in the Silesian and Dąbrowa Region. [according to Współczesna skala źródeł zanieczyszczeń w regionie śląsko-dąbrowskim. cf. Atlas Rzeczpospolitej Polskiej, ed. M. Najgrakowski, Warszawa 1993–1997].
Obr. 3. Stupeň znečištění olovem ve slezském a dąbrowském kraji. [podle Współczesna skala źródeł zanieczyszczeń w regionie śląsko-dąbrowskim. cf. Atlas Rzeczpospolitej Polskiej, ed. M. Najgrakowski, Varšava 1993–1997].

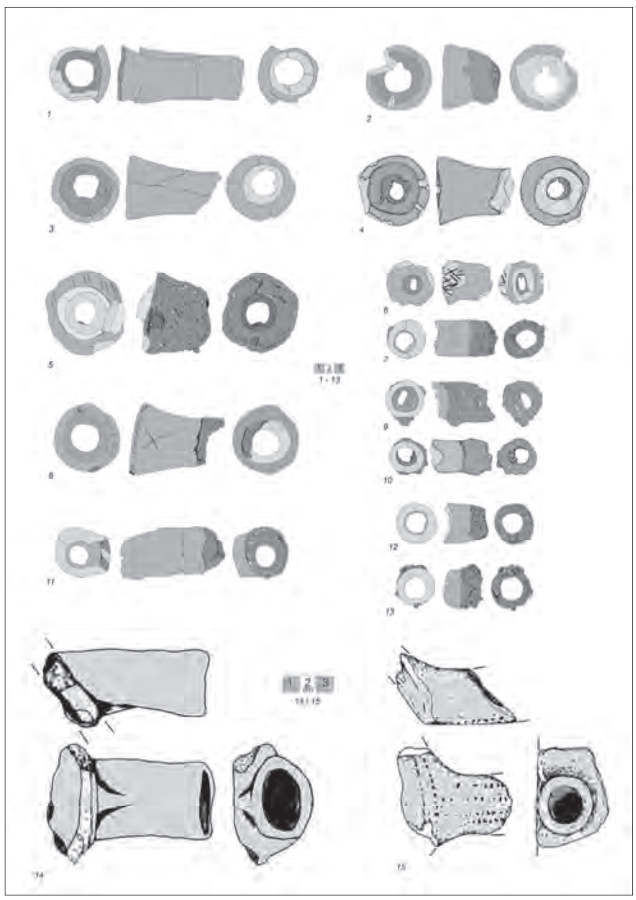


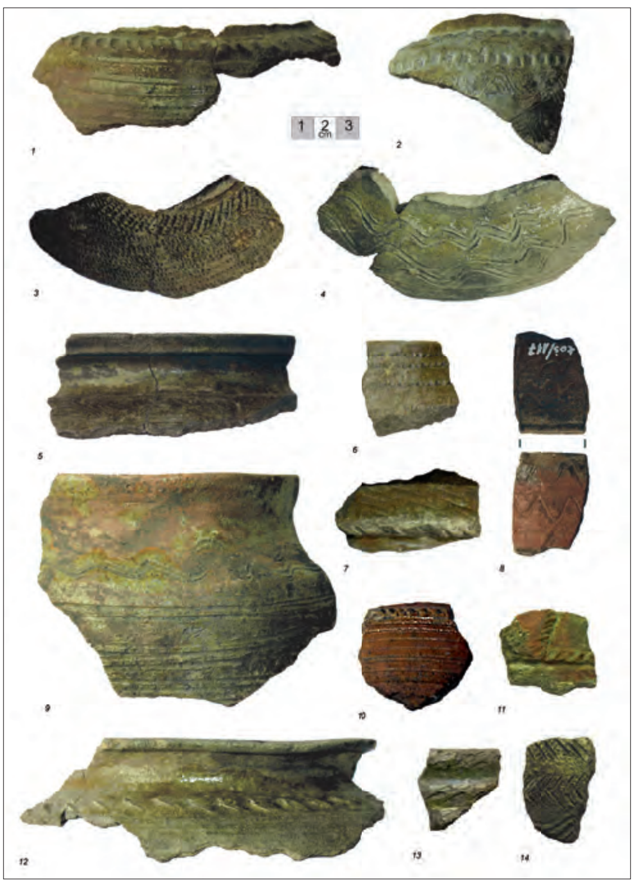
Fig. 4. Relics connected with smelting and foundry. Tuyères, shank ladles.
Obr. 4. Relikty spojené se tavbou a slévárenstvím. Tuyères, tyčové naběračky.

olomites or create a net of small veining and irregular clusters. The next zinc compound and the main component of blende ore is sphalerite, that is zinc sulphide (ZnS), sometimes containing over 60 % of this metal. Pure zinc was not important for the medieval economy, therefore zinc smelting in this period will not be discussed in details here. It must be pointed out, however, that contrary to popular belief, people of the Past had limited knowledge how to produce pure zinc (Craddock 1998, 1). The issue of the application of zinc compounds in the production of brass cannot be ignored. This is a crucial issue due to a considerable number of antique brass objects found as relics of Greco-Roman civilization or the Middle Ages in Europe and other parts of the world, for example in India (Krawczuk 1956, 435–458, Krawczuk 1957, 283–287, Szmoniewski 2009, 118–121). Teofil Prezbiter described medieval techniques of brass production. This is brass produced on the basis of copper alloys and zinc compounds by mixing calamine with molten copper (Teofil Prezbiter 1998, 120). There were also other techniques known in Antiquity of producing brass by adding zinc oxide covering the walls of metallurgic kilns to copper (Krawczuk et Piaskowski 1958, 331). In some regions of the area in question, the ores of the above mentioned metals occur together with deposits of iron ore. At some places they were extracted in large amounts, leaving huge waste dumps (Nowak, 1994, 23). These were mainly sulphides FeS_2. In the weathering layers, those that were easily accessible to medieval miners, there are also deposits of limonite ($2Fe_2O_3 * nH_2O$). In fact, metal deposits in the area where ore-bearing dolomites can be found are polymetallic. Frequently, ore minerals Zn and Pb (sphalerite, galena) and Fe (pyrite, marcasite) occur together.

The above geological complexity clearly conditions increased levels of heavy metals content in soil, including of course lead. The levels increase considerably when ores are systematically extracted and smelted (Cęckiewiczet al. 1977, 137–140).

The occurrence of ores and also rich deposits of coal in the area of today's borderline of Upper Silesia and Lesser Poland resulted in the development of the biggest industrial centre in this part of Central Europe. There is every reason to believe that mining and metallurgical traditions in this area started a thousand years ago. This development leads also to pollution concentration and degradation of natural environment (compare fig. 2, 3). The differentiation of medieval pollution from modern pollution constitutes the most difficult problem in our research.

Pollution with lead compounds is assumed to have accumulated over a few hundreds years. Moreover, anthropogenic pollution adds up to a naturally high level of lead and zinc compounds in soil.



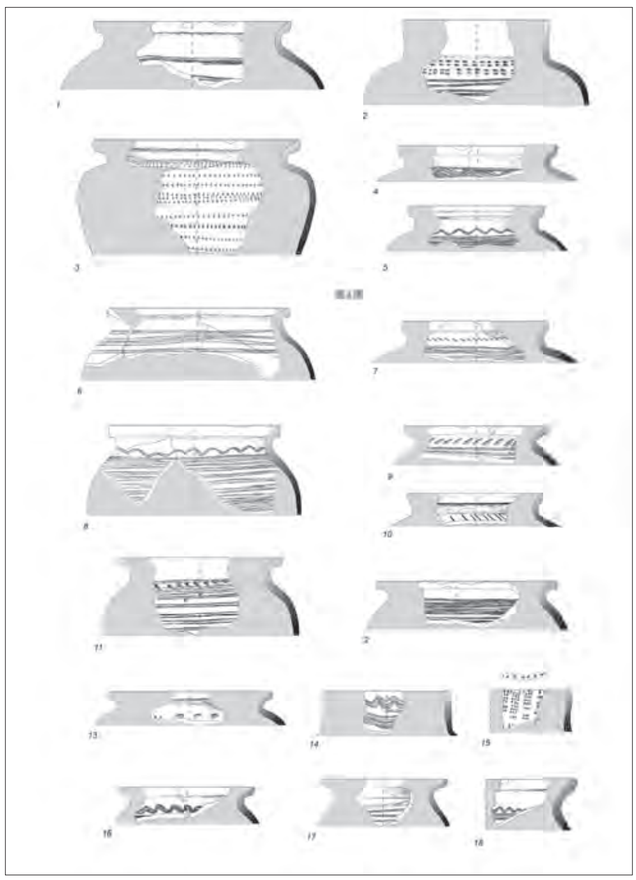


Fig. 5a and 5b. Glazed ceramics from Dąbrowa Górnicza – Łosień.
Obr. 5a a 5b. Glazovaná keramika z Dąbrowa Górnicza – Łosień.

EARLY MEDIEVAL LEAD AND SILVER SMELTING PLANTS

This article will describe here primary chemical processes which occur during lead and silver smelting and which produce pollution.

Technological processes described for two sites shall serve as the basis for the discussion of this issue. These are: site no. 5 in Sosnowiec – Zagórze and site no. 8 in Dąbrowa Górnicza – Łosień. In those sites, all most important features of medieval smelting plant infrastructure can be observed. Additionally, in 2006 a collection of silver coins and silver clumps including silver cut coins, the so called "Steelworker's Hoard", was found. The hoard consists of 1106 coins, of which 1067 were either placed in a glazed vessel or right next to it, and the remaining denars were found during subsequent excavation works in 2007 and 2008. The main part of the hoard are the coins of the brot-hers Ladislaus II the Exile and Boleslaus the Curly. There is also a coin of Boleslaus III the Wrymouthed and a cross denar. Apart from the coins, there were also 179 silver clumps in the pot. At present, the Dąbrowa Górnicza City Museum has 1124 coins that can be directly associated with the "Steelworker's Hoard". Moreover, there is one coin of Ladislaus II the Exile discovered in 2004, which probably is not a part of the hoard and which was lost in the 12th century in some other circumstances (Rozmus 2012, 7).

The most important elements of metallurgical production settlement included metallurgical kilns, a pit shaft, cobblestones surrounding the kilns, waste dumps and traces of posts indicating the existence of roofs over the kilns. During the examination of the settlement numerous pieces of tuyères were found as well as objects that served as shank ladles and crucibles (fig. 4). Hundreds of pieces of tuyères indicate that particular kilns were used numerous times. Glazing ceramics was an important part of the production and had purely decorative aspect. Rich ornaments and forms of the ceramics are unique on the national level (Bodnar et al. 2006, Auch 2012, 199–246). "Lead paste" (lead – silica recipe) that was obtained at the production settlement was used for decorating the walls of vessels. Lead compounds were used for obtaining multi-colour, mainly green and green-olive glaze on the ceramics (fig. 5a and 5b). There is much evidence proving that the ceramics produced in the Strzemieszyce – Łosień settlement centre and in the area near Siewierz in the 11th and 12th centuries were sent to many parts of Poland.

When describing a production settlement that deals with lead metallurgy, an important distinction has to be made between the sites where lead was remelted and the sites where it was smelted from its ore. Whereas the remelting sites on the territory of Piast Poland and the whole Slavic territory are commonly known, the sites of lead smelting which constituted the source of this metal for the whole Central Europe in the 11th and 12th centuries can only be associated with the Harz Mountains and to a lesser extent with the ore-bearing areas in Slovakia (Hunka 2005, 103, Górecki et Sermet 2009, 104, Labuda 2004, 203) which in the early Middle Ages were politically ruled by the dynasty of the Hungarian Arpads. The latest discoveries showed that the sites of silver (and lead) smelting were situated in today's Silesia – Lesser Poland borderland. In the region where the early medieval silver and lead smelting centre was founded, the ore-bearing deposits were clearly polymetallic (zinc and lead ores with the admixtures of silver and iron ore). Thanks to the occurrence of iron ore, it was possible to develop a lead smelting technique with the use of iron compounds. Such smelting technique was found during the examination of the sites in Dąbrowa Górnicza (Łosień and Strzemieszyce Wielkie) and in Sosnowiec (Karbowniczek et Suliga 2005, 135–143, Karbowniczek et al. 2006, 36–40, Rozmus et Suliga 2012, 250–286, Suliga et al. 2013, 151–174). Another smelting technique that was commonly used was based on the reaction of lead ore with carbon compounds.

Metallic lead may be obtained from the ore that most frequently occurs in the natural form – that is from galena, in many different ways. The easiest of them is divided into two stages. In the first stage galena is roasted and lead oxide (litharge) is obtained as a result of this process:

$$PbS + 3/2O_2 \rightarrow PbO + SO_2$$
$$PbS + 2PbO = 3\ Pb + SO_2$$

Other techniques of obtaining metallic lead include the reduction of litharge with the use of carbon and carbon oxide:

$$PbO + C = Pb + CO$$
$$PbO + CO = Pb + CO_2$$

The above step-by-step methods of lead compounds reduction can be best illustrated by the diagram in the article about lead smelting in Chęciny area in Poland (Karwan, Suliga 2002, 165–176).

The following reactions show lead smelting technique with the use of iron and iron compounds.

$$PbS + Fe = Pb + FeS$$
$$2PbS + 2FeO = 3Pb + 3FeS + SO_2$$
$$3PbS + Fe_2SiO_4 = 3Pb + 2FeS + SO_2 + SiO_2$$

As it can be inferred from the above chemical reactions formulae, smelting lead from galena was really a multi-stage process. Oxides were obtained from sulphides, pure metal was obtained in the next stage, and impurities, including silver, were separated from the pure metal. The multi-stage process of lead smelting is considerably different from the process of copper smelting. In the latter one, the transformation of the copper ore – malachite in the process of smelting in a metallurgical kiln into black copper oxide indicates smelting failure (Cole 1977, 187). The next stage of technological processes was isolating the admixture of silver from the smelted lead. Presumably there were several methods of obtaining silver. Among other tools, crucibles were used for this purpose. A piece of such a crucible was found with a drop of silver stuck to the edge of the pot.

The above reactions show various methods of obtaining lead from its ore. The results of the research conducted so far show that iron and its compounds played an important role in obtaining lead in the Strzemieszyce – Łosień microregion. What is surprising here is the fact that this method was not mentioned in historical sources until the 16th century (Dziekoński 1963, 284). It has been now discovered that this method of metallurgical production was present in Poland at least one century earlier than in other European areas, that is in the Schwarzwald (Black Forest) or in the Harz Mountains (Goldenberg 1990, 157, Brockner 1992, 153).

Apart from the possibility of obtaining lead and silver from galena (PbS), there was another method of lead smelting based on cerussite ($PbCO_3$), which is carbonate lead ore. Cerussite ore occurs close to galena. In some special cases in natural conditions, shallow deposits of galena were converted into cerussite. The examiners of the lead smelting production site in Przeczyce near Siewierz assumed that cerussite ore was the starting point for the production of lead (Bartczak et al. 2011, 44).

$$PbCO_3 = PbO + CO_2 \text{ (temperature over } 300^0\text{C)}$$
$$PbO + CO = Pb + CO_2$$
$$PbO + C = Pb + CO_2$$

However, there is no other (published) evidence, apart from the presence of cerussite ore near Przeczyce (it must be pointed out here that galena is also present there) that it was cerussite ore not galena that was the basis for the early medieval production of lead in Przeczyce.

The technological processes described above were conducted in kilns discovered mainly in Dąbrowa Górnicza – Łosień, Dąbrowa Górnicza Strzemieszyce Wielkie and Sosnowiec – Zagórze. The kilns may be divided into several types. Initially, 7 types of metallurgical kilns were described, basing on the condition in which they were preserved.

In 2002, the biggest ever metallurgical kiln of 15 m^2 was discovered – object 1/2002. The examined structure was rectangular (5 × 3 m) with rounded corners (Bodnar et Rozmus 2004, 34–35). In the southern part, there was a pavement made of calcareous stones and a well preserved strip of pugging. From the southern, western and partly from the northern side, there was a clay strip bordering the kiln which surrounded the hearth of the kiln. The fill of the kiln consisted of layers of slag (iron compounds and lead oxide), ash, charcoal and pugging (fig. 6). The kiln was abandoned in the course of the metallurgical process (working of the kiln). The basic smelting process took place between the layer of lead compounds and the layer of iron compounds. The bottom of the kiln was filled with pieces of ceramics, clay tuyères and relics made of iron and of lead compounds in the form of PbO clumps. Below the clay hearth of the kiln there was a hollow where archaeologists found animal bones, ceramic relics with intentionally engraved patterns, lead objects (lead weights) and everyday objects.

The remaining objects that were classified as kilns had a very similar structure (stone hearth covered with clay, clay or stone walls; fill that consisted of iron compounds, lead compounds, pugging, ceramics, pieces of clay tuyères bearing visible signs of high temperature) and were designed for smelting lead. In some of the cases, the remains of the metallurgical objects can be classified as open kilns, the so-called “ Rostfeuerung” (Rogaczewska 2004, s. 166–171) or just surrounded by stones without permanent walls, used for smelting, casting or roasting iron ore (roasting kilns), or as objects of a different than metallurgical character (utility kilns). Kilns surrounded by stones are also known in the territory of the Czech Republic (Hrubý 2011, 133, obr. 142), however they are younger – they date back to the 13th century.

Most of the kilns were multi-use. Such an object was broken after smelting, the clay bottom was cleaned, and then clay walls of 5–10 cm thickness were built once again (on a construction made of small branches). As a result of a very high temperature in the kilns the inner side of the walls was glazed and turned to the olive colour Numerous pieces of glazed clay from kiln walls were found. On one of the pieces, a trace of fingerprints left during the modelling of the kiln walls was found (Rozmus, Rybak, Bodnar 2005, p. 25, photo. 12). Exceptionally large amounts of broken glazed ceramics (fig. 5a and 5b) found near kilns indicate that vessels were glazed right next to the kilns. Some of the vessels were not resistant to high temperature and broke into pieces which were not removed.

In this site, remains of a huge, rectangular roofed hall, resting on posts (of 30 cm in diameter) that were surrounded by stones and placed every 350–370 cm, were found. The fact that such a building was constructed is connected with the necessity of protecting kilns from unfavourable weather conditions. Figure 7 shows a diagram with traces of the posts holes and metallurgical objects. Cobbled pavements constituted an integral part of metallurgical production settlements. They were particularly well preserved in the site no. 5 in Sosnowiec – Zagórze. Figure 8 shows the location of the kilns in relation to the remains of the cobbled pavement.

Heaps of iron compounds prepared to serve as a potential kiln charge may be located near lead smelting kilns. Several such heaps were found in Sosnowiec - Zagórze.

The discovery of relics of metallurgical kilns made it possible to systematize the knowledge concerning their appearance, which lead to the preparation of the first large typology of this category of archaeological finds. The finds of other metals, such as tin or alloys in the form of lumps or brass and bronze objects, indicate that apart from smelting, craftsmen working in the settlements also took up goldsmithing. Apart from metallurgical plants, there were goldsmith’s workshops that dealt with such metals as lead, silver, copper, zinc compounds (calamine) and tin. When casting particular objects, craftsmen used shank ladles (fig. 4). Goldworking was not found in this area. Iron ore was roasted in smelting plants in order to be later used as a reducing agent in lead smelting process.

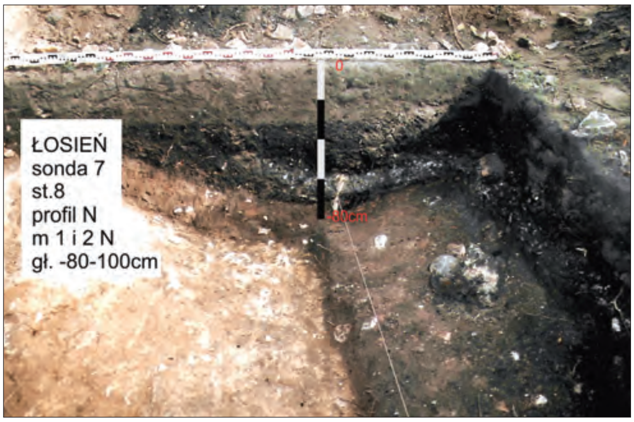


Fig. 6. A section of a metallurgical kiln object 1/2002. The section shows the layers of the charge in the form of lead compounds and iron compounds.
Obr. 6. Řez metalurgického pecního objektu 1/2002. Řez ukazuje vrstvy vsázky ve formě olověných sloučenin a železných sloučenin.

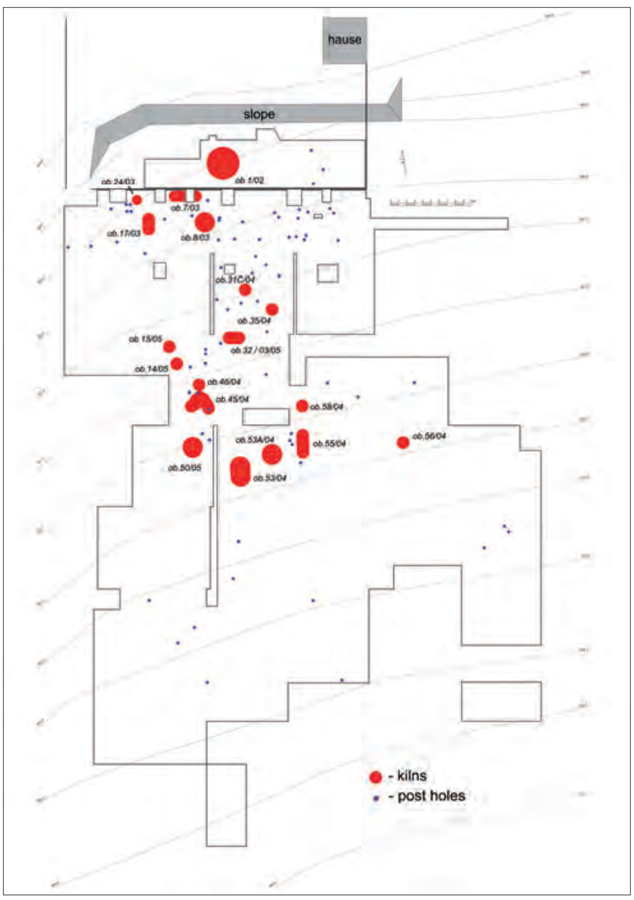


Fig. 7. A diagram showing the location of metallurgical objects and posts holes. Dąbrowa Górnicza – Łosień site 8.
Obr. 7. Schéma znázorňující umístění metalurgických objektů a děr věží. Dąbrowa Górnicza – Łosień místo 8.

It was discovered that, apart from lead and silver, litharge – that is lead oxide (PbO) was the final product of metallurgical and goldsmith's (that is lead and bronze) workshops. Lead oxide briquettes were specially formed to be traded. They were probably used for the production of lead glass, which since the 11th century was more frequently used in the Polish territory as the material for such products as for example glass beads. Lead was also formed into the so called "rolls", billets, small bars and huge bars weighing several kilograms with a rectangular intersection, just like the relics found in the settlement in Siewierz (Dobrakowski et Dobrakowska 2013, 111. fig. 10).

One of the main products made of lead were lead weights of various forms and weight (Bodnar, Rozmus, Szmoniewski 2007). The next product, temple rings were probably produced in Dąbrowa Górnicza - Łosień. The silver discovered in Łosień contained various levels of impurities, reaching between 10 and 20 %, which meant that it was used only as a semi-product for the production of coins. After it was transported to the mint, purified from lead and refined with for example an admixture of copper and gold, it could be used for minting denars. Silver was traded with the use of iron weights which were plated with bronze and which were found in big numbers in the settlements situated in the region under discussion.

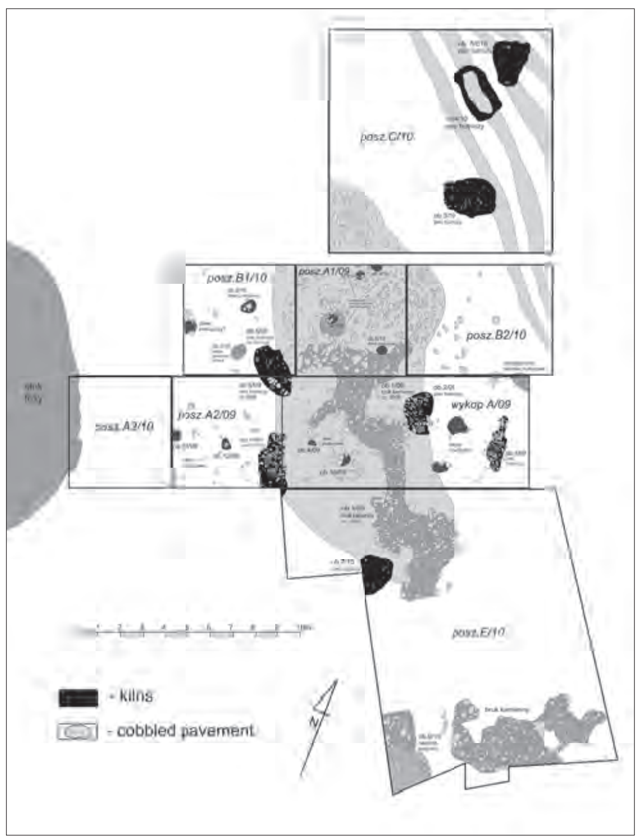


Fig. 8. A diagram showing the location of metallurgical objects and cobbles. Sosnowiec – Zagórze.
Obr. 8. Schéma zobrazující umístění metalurgických objektů a valounů. Sosnowiec – Zagórze.

THE EXAMINATION OF LEAD POLLUTION – OUTLINE OF THE SUBJECT MATTER

Better knowledge of lead ore dates back to the turn of the 5th and 4th millennium (Gilfillan 1965, 55, Drasch 1982, 200), when its compounds were extracted, such as cerussite ($(PbCO_2)_3$ – lead carbonate or white lead ore), and in particular galena (PbS) – lead sulphide (Retief et Cilliers 2006, 148), litharge (PbO ; Pb_3O_4) and lead acetate II ($[Pb(CH_3COO)_2]$ (Retief et Cilliers 2006, 149). According to Gale and Stos-Gale, lead was the first metal in history that was remelted (Stos et Stos-Gale 1981, 178), which can be proved by the oldest find of beads from Anatolia dating back to approximately 6500 B.C (Catal Hüjük settlement 7000–6000 B.C.), made of lead remelted from galena (Stos et Stos-Gale 1981, 178–179, Łęczycki 2010, 208). In the 80s of the previous century, the above researchers put forward a very interesting thesis that the knowledge how to process lead ore, due to the lack of practical applications, was forgotten and than discovered again several times in various places independently without the influence of any external factors, and it was only the development of lead remelting around 4000 B.C. that brought back this soft metal to life (Stos et Stos-Gale 1981, 178–180). The production of lead bronze was started.

In the era of copper, bronze and iron, the extraction of lead increased gradually as a result of the increasing demand for various products made of non-ferrous metals (Nriagu 1983). It was extracted in the biggest quantities in the times of Greco-Roman civilization. The biggest intensity of the extraction and processing of lead, and also high levels of pollution connected with it, were noted in the period from 500 BC and 300 AD (Emsley 1994, 14, Eliot 1995, 732).

The scale of environmental pollution may be illustrated by the calculations of the number of tons of lead deposited in the Greenland glaciers, which show that during 800 years of intense lead exploitation in the Roman period, 400 tons of this metal were deposited there (see Retief et Cilliers 2006, 147 for bibliographical references). In the period under discussion, approximately 80 000 tons of lead were processed annually, which is equivalent to the amounts from the times of the Industrial Revolution over 2000 years later (see Borsos et al. 2003, 8 for bibliographical references). The literature of this subject makes an assumption that the decrease in the intensity of extraction and processing of lead occurred simultaneously with a gradual fall of the Roman Empire. At the beginning of the Middle Ages, lead extraction and processing reached the lowest level of several hundred tons a year, and beginning with the year 1000 it started to increase considerably (Borsos et al. 2003, 9). When expressed in terms of pollution caused by the production of lead in the Mediterranean calculated in the Greenland glaciers samples, the values are as follows: from 3,170 kilotons per year in the Bronze Age, through 14,960 kilotons per year in the Roman Empire period (50 B.C.–500 A.D.), to the decrease to 4,250 kilotons per year in the period from 500-1000 AD (Retief et Cilliers 2006, 149).

Some researchers even think that lead secretly contributed to the fall of the Roman Empire (for example Gilfillan 1965, Nriagu 1983, 661–663m Woolley 1984, 353–361), whereas others claim that the influence of pollution caused by lead was not significant at all (for example Gaebel 1983, 431m Drasch 1952, 226, 227). Nevertheless, the scale of lead ore exploitation in the Roman period, taking into account technological advancement, is impressive.

Information concerning lead harmfulness can be found in the works of ancient authors. Xenophon (434–359 BC) and Lucretius (98–55 B.C.) (Weeber 1990) mentioned polluted smoke from lead mines in Attica that was harmful to people's health. Roman authors such as Vitruvius in *De architectura* (De architectura VIII. 6.10.) and Pliny the Elder in *Naturalis Historia* warn about the toxic character of lead fumes and inform that the waters in the vicinity of lead ore extraction sites were harmful.

Apart from dust pollution, metallurgy leaves huge waste stockpiles in the form of burrows and metallurgical dumps. At the beginning of the Migration Period, there were numerous metallurgical centres in the Danubian Region. As it was described by Michael McCormick, a historian specializing in the economic history, on the basis of an account of Rutilus Namatianus from the 5th century, over a million tons of slag were left in the above mentioned territory after remelting of galena (M. McCormick 2007, 55).

As it was mentioned before, overlapping of various types of industrial pollution over the centuries hinders chronological classification. In order to cope with this challenging task, several methods were applied to measure different types of soil pollution in production settlements in Dąbrowa Górnicza – Łosień site 2 and 8 and in Sosnowiec – Zagórze. The analysis of potential unfavourable influence of pollution on living organisms has initially been commenced.

THE FIRST METHOD

In site no. 2, researchers conducted the examination of iron compounds pollution in the area where one of the metallurgical objects is situated (object 1/1999), paying special attention to magnetic susceptibility. The table below shows how the smelting of lead during which iron compounds are used as reducing agents is reflected in the analysis of stratigraphic layout of the site. The table also shows the level of contemporary pollution in the upper soil layers, particularly the percentage of heavy metals from industrial dust that were deposited in the soil. The method of magnetic susceptibility measurement is based on the conversion in high temperatures of different kinds of sulphide iron - contained in natural solid fuels (coal and wood) and in smelted ore – to ferromagnetic iron oxides, whose presence causes a considerable increase in magnetic susceptibility. This method can be used to determine the range of a given site that bears traces of activity. The table was worked out by prof. Z. Strzyszcz from the Polish Academy of Sciences.

Tab. 1. According to the research conducted by prof. dr hab. inż. Z. Strzyszcz – Institute of Environmental Engineering of the Polish Academy of Sciences with the use of MS2F „Bartington" sensor.
Tab. 1. Podle výzkumu provedeného prof. dr hab. inż. Z. Strzyszczem – Ústav environmentálního inženýrství Polské akademie věd s použitím čidla MS2F „Bartington".

Measurement depth [cm]	**Magnetic susceptibility [10^{-8} m³/kg]**	**Remarks**	
0–5	105	Dark grey sand	Contemporary susceptibility resulting from the emission of industrial pollution, particularly in the last 80–100 years
5–10	110	Dark grey sand	
10–15	56	Dark grey sand	
15–25	20	Dark grey sand	
25–30	30	Dark grey sand	
30–40	57	Dark grey sand	
40–50	390	Sand + slag	
50–60	1440	Slag	"Archaeological susceptibility"
60–70	240	Sand + slag	
70–80	12	Yellow sand	
80–90	6	Yellow clay	
90–100	0	Limestone	
125–130	4	Yellow clay	

When analysing the results from the table, it is obvious that magnetic susceptibility really increases at two stratigraphic layers. The first of them is the upper layer of contemporary humus up to 10–15 cm where both pollution from blast kiln dust and remains of pollution ploughed from deeper layers overlapping culturally accumulate. The next layer is at the depth of 40–70 cm, but the highest level of magnetic susceptibility, which prof. Z. Strzyszcz called the level of "archaeological susceptibility" (this is a wor-king expression used for the sake of this research), occurs at the depth of 50–60 cm. In the Łosień sites, a stratigraphic layer connected with early medieval settlement, and in this case with production settlements in particular, can usually be noticed at this depth. This certainly cannot be regarded as a uniform layer in a large area. On the other hand, the fact that metallurgical kilns are scattered around gives researchers the chance to locate the layer containing archaeological finds in a wider range than only locating single metallurgical objects, especially at the moment of a limited exploration range.

THE SECOND METHOD

This method is connected with the examination of the chemical composition of ash in the fill of a metallurgical kiln. It is of prime importance due to the process of recognizing a given kiln as a metallurgical object used for smelting lead.

The fact of identifying metallurgical kilns for smelting lead introduces a new category of archaeological sources to the Polish academic research. Very little trace remains of smelting ore with the use of free blast in the so-called "sztosy" (kilns for smelting silver and lead in the form of free-standing piles) where the basis is the reduction of galena through the reaction with coal ($PbS \rightarrow PbO$, $PbS + 3/2O_2 \rightarrow PbO + SO_2$, and then $PbO + C = Pb + CO$ and $PbO + CO = Pb + CO_2$). Final products, that is lead and silver, were obviously taken away. It is therefore possible to discover an ash-filled hearth which must not be associated with lead smelting and will be classified as a trace of a fire burning in the same place for many years and used for cooking. In case of such hearths, no tuyères were found nearby.

Smelting ore with iron compounds brings about further difficulties in the interpretation of such a find for an archaeologist who has never had a chance to deal with similar issues before. The use of iron compounds in the process that can be described as $PbS + Fe = Pb + FeS$, $2PbS + 2FeO = 3Pb + 3FeS + SO_2$, $3PbS + Fe_2SiO_4 = 3Pb + 2FeS + SO_2 + SiO_2$ observed in Łosień, Strzemieszyce and Zagórze, leaves very clear archaeological traces in the form of iron compound traces. The ash in the post-production slag may contain small amounts of lead (approximately 3% in the slag in Zagórze, compare table no. 2), however this cannot be determined without conducting proper analyses. As it was mentioned before, smelted lead was taken away, and testing of the chemical composition of slag from kilns is not a standard and cheap archaeological analysis. The traces of iron slag may suggest the existence of iron metallurgy, particularly to inexperienced archaeologists, instead of lead metallurgy. In such situations, archaeologists may be wrong about the nature of the finds they examine. Thanks to the recognition of this category of archaeological objects, such mistakes may be avoided in the future.

Tab. 2. According to the analysis of dr. A. Garbacz – Klempka AGH University of Science and Technology.
Tab. 2. Podle rozboru dr. A. Garbacze – Klempka AGH Univerzita vědy a technologie.

Sosnowiec-Zagórze Object 3/2010	**Sample 1**	**Sample 2**	**Sample 3**
Signal loss	17%	15%	10%
Iron	78.49	76.75	82.70
Cobalt	0.24	0.35	0.97
Titanium	ok.0.5	ok.0.5	ok.0.5
Manganese	–	–	–
Copper	0.38	0.34	0.79
Zinc	0.81	0.63	0.58
Gallium	–	–	–
Zirconium	1.11	0.98	0.74
Niobium	ok.1	ok.1	ok.1
Molybdenum	ok.1	ok.1	–
Silver	0.04	<0.02	0.03
Tin	0.20	0.11	0.03
Antimony	–	–	–
Gold	–	–	–
Lead	<0.02	**2.997**	**2.169**
Bismuth	–	–	–

THE THIRD METHOD

The third method consists in the examination of the chemical composition of the soil in the area where kilns were found and directly between the metallurgical objects. Metal-bearing minerals are represented by carbonates Zn and Pb, sulphides Fe – Zn – Pb, oxides Fe and unstable sulphates Fe, Zn, Pb. (…). Among minerals Zn – Pb – Fe present in soil, smithsonite, cerussite and iron oxide and hydroxide prevail. In the area of historical and contemporary metallurgical and mining waste dumps, the processes of sulphide oxidation are clearly visible in the crystallization of sulphates Ca and Fe on plant roots (Cabała 2009). Iron, zinc and lead, primarily as sulphides, are the main components of metal ores present in the areas in question. Taking these factors into consideration, the examination of the chemical composition of the pollutants was conducted in the area close to the metallurgical kilns in site no. 8. The following minerals were found: cerussite - $PbC0_{3,}$ oxides - Pb0, as well as metallic lead, barite - $BaS0_{4,}$ silica glaze and aluminosilicate, and also phosphoric lead compounds such as pyromorphite – $Pb_5\,[Cl|(P0_4)_3]$ (Cabała, Szeląg, Rozmus, in press). As it is clearly visible, it can be inferred from the pollutants composition of lead compounds in soil whether the site in question is the place of metallurgical processing of lead ore. In this case, lead oxide PbO can only come from the processing of other lead compounds, mainly lead sulphide PbS. This is a very important conclusion that can be used when making decisions concerning the search of lead and silver ore kilns.

THE FOURTH METHOD

This method consists in the examination of human remains to check if they contain any lead compounds and also to check the potential harmfulness of the compounds. This method, however, will be developed during future research. Archaeological and zoological examination of several animal burial grounds located close to kilns in the area under discussion brought interesting results. Until now, burial grounds of four cows were examined. Three of them were situated on the east – west axis and covered with cobbles, and a lead ornament was found in one of the graves.

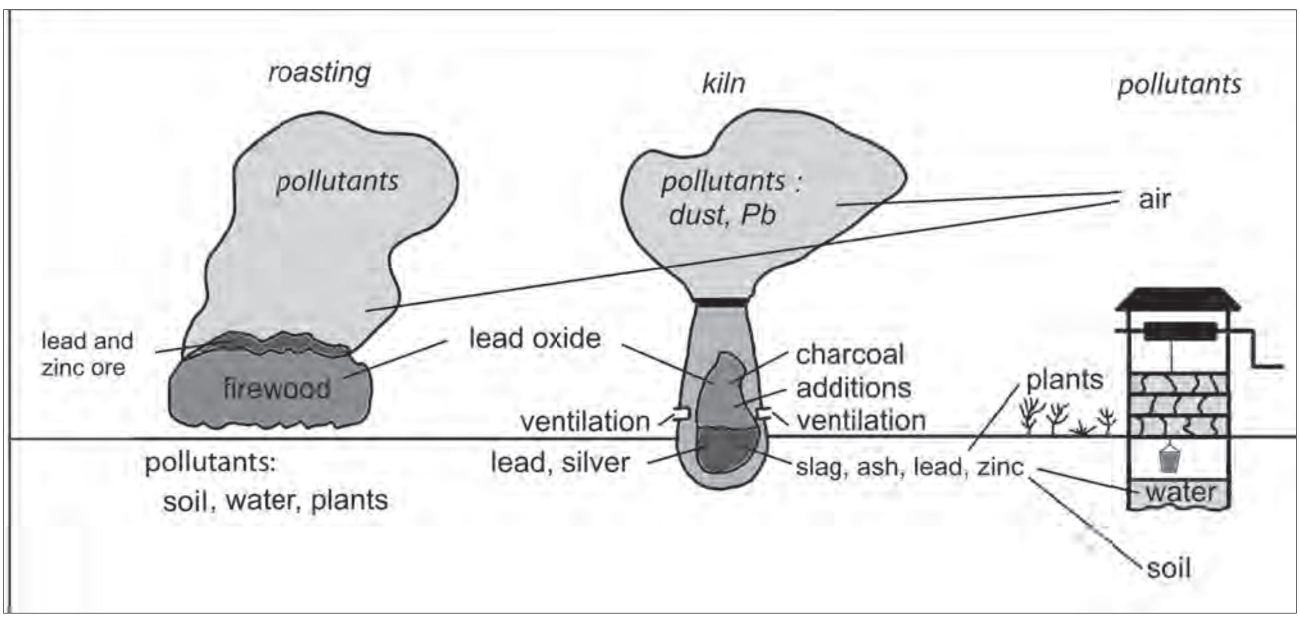


Fig. 9. A diagram showing the spreading of heavy metals pollution.
Obr. 9. Schéma znázorňující rozšíření znečištění těžkými kovy.

Two of the graves can serve as examples: object 19/2003 – burial of a cow under cobbles and object 29/2005 – burial of a cow without cobbles. Archaeological and zoological examination showed that, in the first case, the long bones heads fused with the shafts at a later age, the usual age being between 3.5 to 4, and the degree of ossification of the limbs indicates the age between 3.5 and 5 years, while the parallel attrition of molars in the mandible indicates the age of about 5 to 7. In the second case, the age of the cow determined on the basis of attrition of molars in the mandible is between 5 to 7 years with the ossification indicating the age of 3.5 to 4 years. It can be inferred that the delay in the maturity of the animals, showed by the discrepancy in the determination of the animals age as indicated by molars and by skeleton bones, was influenced by lead compounds. Accumulation of lead compounds in bones was studied in industrial regions in Germany. The data obtained from bone material from burial mounds in the Harz Mountains coming from the 18th century was analysed and an increased content of lead in bones was found. The content appeared to be higher in the 18th century than in the modern times (Schutkowski, Fabig, Herrmann 2000, 96–99).

The pollution spread in a fairly simple way (Deicke et Ruppert 2000, 78–82): toxic compounds got to the air directly from smoking chimneys, and from the air to the soil and groundwater (fig. 9).

CONCLUSIONS

The Dąbrowa Górnicza settlement micro-region (Strzemieszyce – Łosień settlement centre, compare Foltyn 2005, 29–34) and, as it is known today, the regions of Sosnowiec and Siewierz in the Middle Ages, are famous for a large number of non-standard archaeological finds. Currently conducted research proves that this should be regarded as one of the most important production centres in Central Europe for archaeologists. The development of industry in this region must have exerted a considerable influence on the changes of the geographical environment. The anomalies shown in the analysis of cow skeletons may serve as an example of unfavourable influence of this development on living organisms.

Examination of the archaeological remains of lead and silver smelting requires cooperation of specialists from various fields, not only archaeology but also geology, metallurgy and environmental pollution.

SOUHRN

V části povodí řek Przemsza a Brynica v jižním Polsku se nachází raně středověký areál s doklady metalurgie stříbra a olova. Rozprostírá se od Olkusze na východě až k Bytomi a Tarnowským Horám na západě. Na severu sahá po Siewierz a Przeczyce a na jihu po Trzebiniu, Chrzanów a Jaworzno.

Ložiska zinku a olova se nachází v rudonosných vrstvách vápenců a dolomitů, jejichž celková rozloha je přibližně 2500 km^2. Jedná se většinou o dolomity střednětriasového a v některých oblastech i spodnětriasového stáří, takzvaný Buntsandstein (pestrý pískovec) nacházející se pod lasturnatým vápencem (Muschelkalk). Dalšími zdrojovými horninami jsou rudonosné jíly (T. Gałkiewicz 1983, 15–18). Ložiska zinku a olova se většinou nachází v dolomitech (přibližně 93,8 %), zatímco ve vápencích tvoří jejich podíl pouze 6,2 %. Menší naleziště zinku a olova se vyskytují také v pískovcích a lasturnatém vápenci. Zdejší krajina má charakter hrásti s prohlubněmi vyplněnými čtvrtohorními písky. Celé území bylo silně poznamenáno působením antropogenních vlivů.

Archeologické lokality s doklady metalurgie stříbra a olova, které byly objeveny v této oblasti jsou datovány do druhé poloviny 11. století. Na přelomu 12. a 13. století se sídlištní struktura založená na připovrchové těžbě rud rozpadla. Sídliště výrobního charakteru (Zversov zmiňovaný v písemných pramenech k roku 1136) buďto zanikla nebo byla zničena (Łosień) v důsledku vojenských akcí. V průběhu 13. století se pak rozvinula středověká hornická a metalurgická infrastruktura založená na hlubinné těžbě.

Středověký sídlištní mikroregion Dąbrowa Górnicza a také regiony Sosnowiec a Siewierz jsou známy díky velkému množství netypických archeologických nálezů. Právě probíhající archeologický výzkum dokazuje, že toto území je možné považovat za jedno z nejvýznamnějších výrobních center v rámci střední Evropy. Vývoj průmyslu v tomto regionu musel mít značný vliv na změny v okolní krajině. Anomálie zjištěné analýzou koster hovězího dobytka jasně ilustrují nepříznivý vliv výše zmíněného vývoje na živoucí organizmy. Zkoumání archeologických dokladů hutnictví olova a stříbra si vyžaduje spolupráci odborníků z různých oborů – nejen archeologie, ale také geologie, metalurgie a environmentální chemie.

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