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Steel Shot as a Risk Factor for Soils at the Area of Shooting Activity

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ABSTRACT

This study is follow-up of the steel shot transformation under the influence of environmental factors research (Lisin et al., 2022) and is the initial stage of investigating the iron behavior in soils during steel shot corrosion under a number of factors: the metallic lead in soils, atmospheric precipitation, excess organic matter. The results obtained show that corrosion of steel ammunition is a continuous process, including the formation of a poorly soluble rust crust on the surface of the steel and the mineralization of the metal until it is destroyed. As a result, the metal transformed into rust form, is a constant source of iron ions and dispersed rust particles migrating in soil waters and accumulating in soils. In addition, the aggregation of corrosion products of steel ammunition is the cause of a change in physical and mechanical properties of soils, which leads to a violation of the air and water migration regime of soils and an increase in surface runoff from the territories of shooting activity. The highest environmental risks are observed when steel ammunition is used on shooting areas where metallic lead intensifies steel shot corrosion rate, while the deposited steel shot activates the deterioration of previously encapsulated metal and — if steel and lead ammunition are used at the same time — slows down the encapsulation of newly deposited metallic lead, which catalyses the accumulation and migration of lead in environmental components.

KEY WORDS
steel shot, iron, soil, environmental risk, shooting activity

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1. INTRODUCTION

In 2021, Regulation (EU) 2021/57 banned lead ammunition in or around wetlands; the ban will take effect in 2023. Moreover, the European Chemicals Agency (ECHA) has prepared a proposal to introduce further European-wide restrictions on the use of lead in ammunition for hunting and outdoor sports shooting and fishing tackle (ECHA, 2021). The planned restriction proposal aims to minimize the risks to ecosystems discussed in several papers (Scheuhammer and Norris, 1996; Pain et al., 2010; Bellinger et al., 2013; Pain et al., 2015; Arnemo et al., 2016; Pain et al., 2019; Kanstrup and Thomas, 2020). However, certain studies (Lisin et al., 2020) have demonstrated that the presence of metallic lead does not pose critical risks to the components of terrestrial ecosystems (soils, water, and bottom sediments).

Steel is often viewed as the most preferred alternative to lead, which is explained by the biotoxicity of other proposed metals (cobalt, copper, nickel, tungsten, and zinc) (Grandy et al., 1968; Levengood, 1999; Bardack et al., 2014; Paulsen and Sager, 2017; Thomas, 2016, 2019), as well as certain ballistic and economic factors which were analysed during the preparation of the restriction proposal (ECHA (Annex C), 2021). In this document, the impact of steel and other alternative metals on the environment is assessed with due regard for the following factors: 1) the level of their human health toxicity, aquatic toxicity, and wild life toxicity; 2) their availability and the depletion of raw material resources; 3) the impact on climate change, including the emission of greenhouse gases during the exploration or production of raw materials for non-lead ammunition.

It should be noted that the disputable claim about iron not being characterized by human health toxicity (ECHA, 2021, Annex C, p.246), needs to be clarified because sources from the medical community prove that iron overload can be dangerous. The International Statistical Classification of Diseases and Related Health Problems maintained by the WHO (ICD-10 Version:2019) contains a group of human health conditions associated with the excessive accumulation of iron in organs and tissues (ICD-10: E83.1. Iron metabolic disorders) which

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cause negative cytotoxic effects and leads to disruption of the human immune system (Tarasova and Teplyakova, 2012; Lukina and Dezhenkova, 2015; Orlov, 2020).

Since lead shot use has been partially or totally banned in 23 European countries, interested users switch to non-lead ammunition (mostly steel) (Mateo and Kanstrup, 2019). However, the environmental monitoring of areas with current or prior shooting activities only includes the total lead content, lead mobility and bioavailability (SAAMI, 1996; Lin, 1996; Rooney et al., 1999; Cao et al., 2003; Dermatas et al., 2006; Rauckyte et al., 2009; Hartikainen, H. and Kerko, E., 2009; Lewis et al., 2011; Mera et al., 2015; Okkenhaug et al., 2016; Kelebemang et al., 2017; Lisin et al., 2020), without assessing the same parameters for iron. The risks associated with the presence of steel ammunition in terrestrial ecosystems, which can occur in the case of steel transformation under the atmospheric and soil corrosion factors, were also not analysed in the proposal for a restriction (ECHA, 2021). At the same time, the paper (Lisin et al., 2022) has demonstrated that steel shot is characterized by a high rate of transformation under environmental factors, and the joint presence of steel and lead shot accelerates the corrosion of both metals.

The impact of steel shot deposition into the soil was analysed in papers by Hurley (2004, 2013) which demonstrated that iron catalyses the dissolution of stabilized metallic lead (encapsulated by a coating of poorly soluble lead oxide compounds – hydroxide, carbonate, sulphate) in soils through redox corrosion reactions (Hurley, 2004), and the formed steel corrosion products affect the air and water migration processes of soils (Hurley, 2013).

As there is not enough reliable and detailed information on the behavior of steel shot in terrestrial ecosystems, it is necessary to conduct a comprehensive study of the environmental risks associated with the deposition of steel ammunition into soils, surface waters, ground waters, and sediments, including shooting areas (hunting lands, shooting ranges, and shooting complexes – further SH area) with prior shooting activities and the presence of encapsulated metallic lead in the soils.

This study represents the initial phase of monitoring the behavior of iron in soils when steel shot corrosion occurs under actual environmental factors (atmospheric precipitation, an excess of organic matter, and the presence of metallic lead in soils). The laboratory and field experiments provided the information about: 1) the dynamics of the total iron content, the distribution of Fe forms, and the bioavailability of iron in soils; 2) the effect of iron on the behavior of lead in soils when steel shot and lead shot are present at the same time. The obtained results provide a preliminary assessment of the risks associated with the use of steel shot exposed alone and in combination with lead shot.

2. MATERIALS AND METHODS

The impact of steel shot transformation on iron behavior in soils was analysed in a laboratory experiment with simulating factors affecting the corrosion processes (over a period of 4 months) and in actual environmental conditions in a SH area over a period of 17 months.

2.1. Shot collection

The study used commercial steel shot (2.5 mm diameter) and lead shot #7.5 (2.4 mm diameter) for sports shooting. According to production specifications, the following residual elements are present in steel shot: C (0.6-1.0%), Si (0.7-1.2%), Mn (0.5-1.0%), S (up to 0.07%), P (up to 0.09%). The main residual elements in lead shot are Sb (4–6%), Sn (0.1–0.2%), As (0.2%), Cu (0.02%), Ag (0.002%), and Zn (0.001%).

2.2. Laboratory experiment

The experiment was conducted using the following types of soil: a) the soils of areas with no prior SH activities; b) the soils of SH areas with the presence of metallic lead in the form of lead shot; c) the soils of SH areas with the presence of metallic lead and an additional amount of organic matter (fertile soil layer — a combination of peat, perlite, silica sand, and dolomite fines).

Earlier, it was established that the presence of metallic lead and the increased content of organic acids intensify the processes of steel shot destruction (Lisin et al., 2022). It is known that an increased relative humidity and the presence of condensate on the metal surface increase the steel corrosion rate (Akimov, 2021). To investigate the dynamics of iron behavior in soils, the following factors were simulated in the following order:

1. Varying the presence of metallic lead in the same humidification conditions: a) steel shot deposition into the soils of areas with no prior shooting activities; b) the joint deposition of steel shot and lead shot into the soils of areas with no prior shooting activities; c) steel shot deposition into the soils of SH areas where encapsulated metallic lead was already present in the soil.
2. Varying the soil humidification regime of SH areas by simulating various precipitation amounts.
3. Providing an excess of organic matter in the near-surface soil layer of SH areas, with a humidification regime.

To conduct the short-term experiment and analyse the impact of steel shot transformation on iron behavior in soils, an experimental setup (Fig. 1) was prepared based on the interaction of tested soils with natural atmospheric precipitation with low mineral content and a moderately acidic pH (5–6).

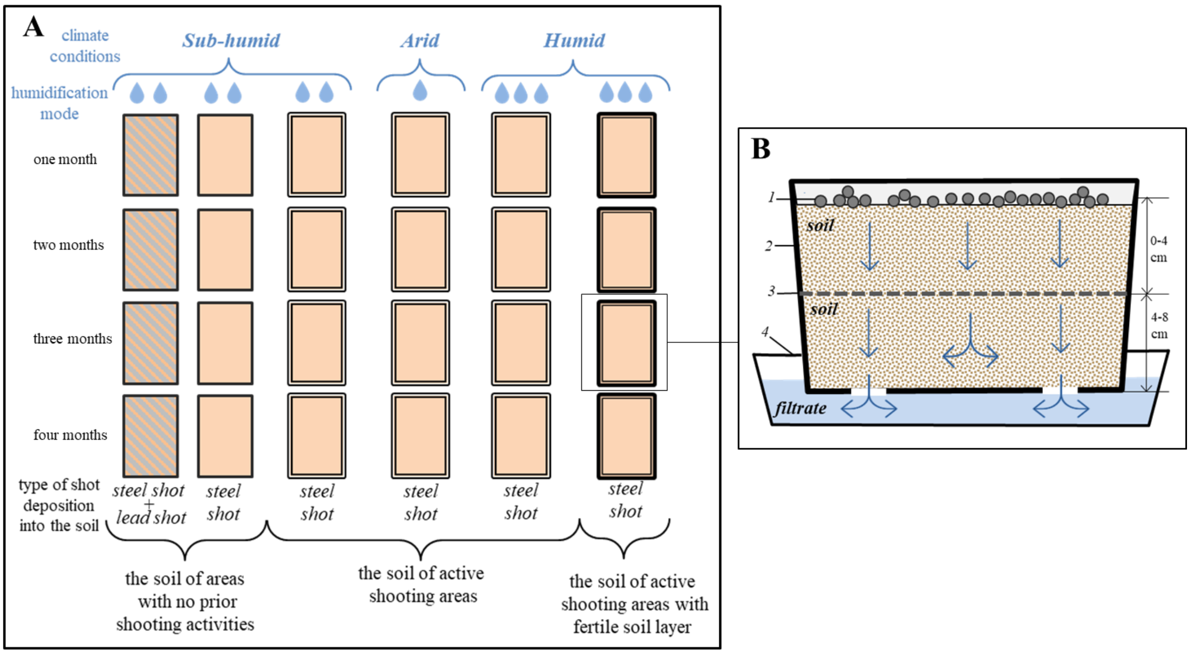

Fig. 1. Experimental setup for estimating the iron concentration dynamics in soils as a result of the transformation of steel shot: (**A**) arrangement of the units (three soil types under different humidity conditions tested simultaneously); (**B**) example, a single unit: 1 - metal shot; 2 - polypropylene container with filtrate holes; 3 - air and moisture permeable material; 4 - polypropylene container for filtrate collection; arrows show the water movement direction in the soil.

The tested air-dried soils were placed into a container with a height of 9 cm and an area of 0.14 sq. m without changing its particle size distribution (reducing the soils to powder) and without sifting foreign inclusions. The soil in the container was separated into the upper layer (0–4 cm) and the bottom layer (4–8 cm) using an air and moisture permeable material. The weight of each soil layer amounted to 0.5 kg, in some of containers 0.1 kg of fertile soil was deposited onto the soil surface to provide an excess of organic matter. 30 g of steel shot or a mix of 30 g of steel and lead shot was deposited onto the soil surface on a single occasion. Each soil/shot/mix shot combination had a set of four containers which corresponded to the period of the experiment in months.

A single watering amount was 150 ml, with the watering frequency determined by the average annual precipitation in arid, sub-humid, and humid climates (400, 700, and 1,500 mm/year, respectively): 1) twice a week for a humid climate; 2) once every ten days for a sub-humid climate; 3) after the entire soil volume in the container dried up completely for an arid climate. The filtrates resulting from the interaction between soil and water were collected after each watering, and the volume of collected water was registered. Some of this water was filtered using a syringe adapter and a membrane filter (with a pore diameter of 0.45 µm) and later conserved using nitric acid (0.3 ml of concentrated HNO_3 per 15 ml of a solution) to evaluate the removal of iron in a dissolved form. The filters with suspended metals were decomposed using a nitric acid (2 ml HNO_3 per 15 ml of a solution) to assess the removal of iron in a suspended form. The acidity, electrical conductivity, and the content of suspended and dissolved forms of iron and lead were determined for each filtrate, and monthly average indicators (for each month) were calculated for the obtained results.

Each month, one container was withdrawn from the experiment, layers of soil (0–4 cm, and 4–8 cm) were air-dried separately, sifted (with a 1 mm mesh), and the fine soil fraction (<1 mm) was reduced to powder in an agate mortar.

2.3. *Field experiment*

In May 2020, a test site was organized in a SH area with the presence of metallic lead in the soil. Steel shot was deposited onto the soil surface on one occasion. The mass of the deposited shot was 20 kg, and the area of distribution was 4 m^2. The field experiment included the visual monitoring of soil surface conditions and regular sampling of soils to assess the dynamics of iron and lead content in the case of steel shot transformation in actual environmental conditions. After sampling, the soil was air-dried and prepared for analysis (the particles exceeding 1 mm were separated, and the analysed fine soil fraction of less than 1 mm was reduced to powder).

2.4. *Analytical methods*

In the soil obtained the mineral composition, the total content of iron and lead, the water-soluble forms of iron and lead (extraction with deionized water, solid-phase:solution = 1:5), loose amorphous Fe oxides (extracts with hydroxylamine (Tessier et al. al, 1979)) and mobile lead (extraction with ammonium acetate (5.4 ml glacial acetic acid, 3.75 ml 25% ammonia) pH 4.8 ± 0.1, solid-phase:solution = 1: 10). In waters after interaction with soil (soil filtrates and water extracts) acidity (pH) and specific electrical conductivity were controlled. The potentiometric pH determination was carried out by "Expert 001" (Econix Expert Ltd.) with measuring glass electrode (type ESL-43-07) and control reference electrode silver/silver chloride electrode Ag/AgCl/KCl (type EVL-1M). Calibration standard buffer solutions (1.08; 3.56; 7.40; 9.18 units) were used. Specific electrical conductivity was evaluated by HM Digital COM80 (HM Digital, Inc.), calibration solutions (10, 84, 1413 µS/cm, OHAUS Corporation) were used. Measurement range 0-9990 µS/cm.

Mineral composition of soils was examined by X-ray diffraction (ULTIMA-IV, Rigaku, Japan), equipped with D/Tex Ultra high speed, position-sensitive detector system. The operation conditions using Ni-filter, Cu-Kα radiation with the X-ray tube operated at 40 kV and 40 mA. Data collection over the angular range of 3 to 65°2θ, per 0.02°2θ step.

The phases of the steel corrosion products in the soil-shot conglomerates were determined using a benchtop powder X-ray diffractometer (Miniflex 600, Rigaku, Japan), equipped with D/TeX Ultra250 high-resolution, high-speed 1D X-ray detector. The measurement conditions: compact Cu radiation X-ray tube operated at 40 kV and 15 mA, Kβ foil filter. Data collection over the scan range 2θ = 3°- 55°, step width: 0.05°, scan speed 5°/min.

Total metal concentrations of the soil fine fraction were analysed using a benchtop Niton FXL 950 energy dispersive X-ray fluorescence spectrometer (ED-XRF, Thermo Fisher Scientific Inc.), equipped X-ray tube (4 Wt, Ag anode, maximum accelerating voltage/current 50 kV/200 µA), and Si-PIN semiconductor detector. Approximately 5 g of powdered soil was placed into XRF sample cups (d=25 mm) with 6 µm thick Mylar X-ray film. Each sample was analysed five times, each sample's measure time was 120 s. Quality control was checked with using of soil reference materials: NIST 2709a, 2710a, 2711a, 2780, 2781, SdAR-M2. The relative standard deviation did not exceed 9% for lead (average 3%), for iron 5% (average 2%).

Iron and lead content in solutions were determined using atomic absorption spectroscopy (AAS; ContrAA®700, Analytik Yena) and inductively coupled plasma mass spectrometry (ICP-MS; ELEMENT2, Thermo Finnigan). The instruments were calibrated using mono element standards of iron and lead ions and a multi-element standard (High Purity Standards).

3. RESULTS AND DISCUSSION

3.1 The characteristics of soil

The physiochemical properties of soils used in the experimental study are shown in *Table S1*. The tested samples are represented by sandy loam, where the matrix consists mainly of quartz (over 60%), with the presence of a plagioclase (albite) and potassium feldspar (microcline), clay and carbonate minerals.

The average pH of the water extraction of all analysed soils is 8.0±0.1. The soils of SH areas are characterized by the lowest specific electrical conductivity of the water extraction which amounts to 250±40 μS/cm. When a fertile soil layer is deposited onto such soils, the specific electrical conductivity of the water extraction increases to 360±20 μS/cm. The natural content of organic carbon in soils varies between 1.5 and 2.5%. In soils with an additional fertile layer, the content of C_{org} is over 9%.

The natural iron content in soils is determined by the weathering of parent rock material and may vary depending on the exact location within the site where soil samples are taken for the experiment. The total iron content in the fine soil fraction of areas with no prior shooting activities is 17,400±540 mg kg^{-1}, in the soils of SH areas — 21,500±340 mg kg^{-1}, in case of the deposition of a fertile soil layer with an iron content of 4,770±40 mg kg^{-1} into the soils of SH areas, the total iron content of the soil mix is 18,700±210 mg kg^{-1}. The average total iron in the studied soils is not higher than the abundances of iron in urban soils (22,000 mg/kg (Alekseenko and Alekseenko, 2014))

The total lead content in the fine soil fraction is determined by the load from shooting.

3.2 Iron behavior in the soil during the steel shot corrosion under the environmental factors

The steel shot transformation under environmental factors results in the formation of suspended (flocculent) and mobile soluble iron compounds and complexes which can become irreversibly assimilated by the soils and migrate in soil solutions (Lisin et al., 2022). The impact of environmental factors on the iron behavior in soils was analysed by assessing the following parameters: 1) the dynamics of the total iron content in soils in the case of steel shot deposition onto the soil surface; 2) the maximum amount of Fe that can be irreversibly assimilated by the fine soil fraction; 3) the weight percentage of Fe forms in soils; 3) the dynamics of iron removal and the distribution of the forms of iron migration in soil water. The proportion of iron forms migrated with soil water was calculated using the data obtained during the collection of regular soil filtrates, while the monthly amount of iron migration was determined by taking into account the remaining amount of iron in the water extraction.

According to the obtained results, the iron content in the lower soil layer (4–8 cm) did not show fundamentally changes compared to the initial soil content over the laboratory experiment period (*Table S2*) which indicates that there is limited vertical migration of iron in the short term. The analysis of the behavior of iron forms in the upper soil layer (0–4 cm, *Table S2*) is presented further. The data were obtained for the fine soil fraction. The weight percentage of this fraction for soils that do not initially contain metallic lead is 50%, and for soils of SH areas — 40%, for soils of SH areas with a fertile layer — 50%. The maximum amount of iron irreversibly assimilated by the fine soil fraction during steel shot corrosion was calculated based on the fraction mass of 0.2 kg.

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After the redox conditions of regular filtrates (*Table S3*) and water extractions (*Table S4*) were identified, it was seen that under any conditions simulating the interaction between soil, shot, and precipitation, the pH of soil water varies within the range of near-neutral and weakly alkaline values (from 7.2 to 8.4). This corresponds to the usual conditions of the upper part of the soil profile where, in the conditions of free exposure to oxygen and pH ≥7, the solubility of the main steel shot corrosion product — $Fe(OH)_3$ — is extremely low (solubility in water — $2.03 \cdot 10^{-8}$ g/100 ml^{-1}), and iron migration in soil solutions mostly occurs in a suspended form.

Factor — Metallic lead (in conditions of humidification)

The factor was analysed with steel shot deposited into the soil of a SH area which already contained encapsulated metallic lead, as well as with steel shot and a combination of steel and lead shot deposited into the soil of an area with no prior shooting activities.

As a result of steel shot deposition into the soil of areas with no prior shooting activities, the total iron content in the fine soil fraction increases 1.2-1.3 times compared to the initial level (Fig. 2, A). The corresponding amount of iron irreversibly assimilated by the fine fraction (both chemically and mechanically) is 4.7% of the deposited shot mass. If both steel and lead shot is used in such areas, the amount of iron in the fine soil fraction increases 1.3 times in the first month, compared to the initial level. The maximum amount of content is observed during the second month when the concentration of iron increases 1.4 times compared to the initial level (Fig. 2, B), with up to 6.5% of the deposited shot assimilated in the fine fraction.

If steel shot is deposited in a SH area, the concentration of iron in the fine soil fraction increases and reaches 1.2 times the initial level in the first month (Fig. 2, C). Later, the total iron content increases, reaching 1.4 times the initial level. The maximum amount of iron irreversibly assimilated by the fine soil fraction reaches 5.8% of the deposited shot mass.

Within the first month of the transformation of steel shot deposited alone, the total iron content in the soil of an area with no prior shooting activities increases slower than in the soil of a SH area. Δ_{Fe} amounts to 3,700 and 4,200 mg/kg respectively (Fig. 2, D-*a* and D-*b*). The maximum increase in the total iron content is observed when steel shot and lead shot are deposited together: Δ_{Fe} amounts to 5,500 mg/kg (Fig. 2, D-*c*).

During the third month, the iron content in the fine soil fraction decreases in all the experiment scenarios — a trend that continues later (Fig. 2 A-C). This is explained by the aggregation of shot and steel corrosion products (Fe (III) compounds) with organic residues and mineral particles in the soil, with the formation of shot and soil aggregates (Fig. 2, E-F). The composition of the aggregates' cementing agent includes lepidocrocite (γ-FeO(OH), 34%), quartz (50%), feldspar and plagioclase (9%), calcite (3%), and mica (1%). These massive aggregates accumulate a significant part of iron (both in the form of shot and its corrosion products) in the skeletal soil fraction (>1 mm) and partly limit further iron assimilation in the fine soil fraction.

When both steel and lead shot are deposited in soil, the maximum amount of iron accumulated in the fine fraction (taking into account the fraction's weight percentage) is higher than in the case of the deposition of steel shot alone (5.8–6.5% and 4.7% of the deposited shot mass, respectively). This confirms the information about the faster destruction of steel shot in the presence of metallic lead presented in the paper by Lisin et al. (2022).

The analysis of the iron forms in soils (*Table S5*) indicates that the natural distribution patterns do not change significantly under external impact: the share of water-soluble iron is less than 0.01% of the total content, iron is mostly present in the form of poorly soluble amorphous (hydro)oxides, whose proportion increases by 1-2% relative to the initial level, and residual fractions, including corrosion crust particles.

As a result of steel shot transformation in the soil of areas with no prior shooting activities, iron removal by soil waters more than doubles compared to the initial level (Fig. 3, A). In the oxidizing conditions of the near-surface layer of the soil profile, iron is mostly migrated in soil water in suspended forms (*Fig*. 3, B-1), with their proportion increased in case

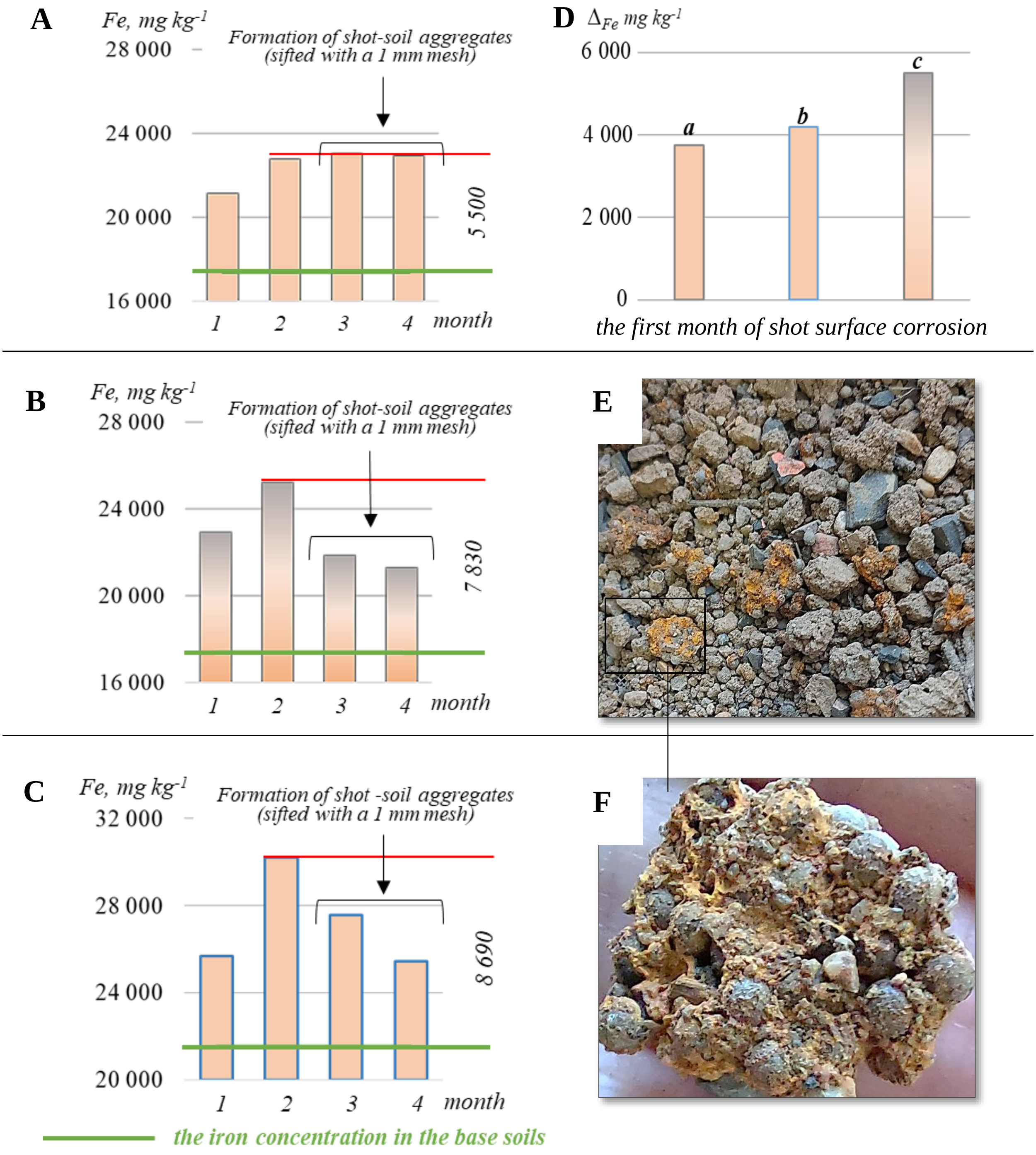
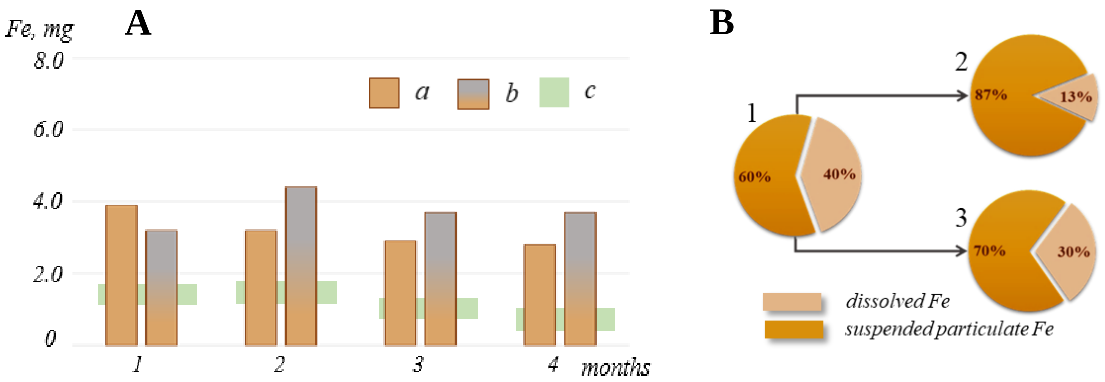


Fig. 2. The content of iron in the fine soil fraction (<1 mm) (**A-C**) and example of shot-soil aggregates in skeletal soil fraction (> 1 mm) (**E-F**). **(A)** the content of iron in the fine soil fraction (<1 mm) into the soil of area with no metallic lead, use of steel shot alone; **(B)** the content of iron in the fine soil fraction (<1 mm) into the soil of area with no metallic lead, use mix of steel shot and lead shot; **(C)** the content of iron in the fine soil fraction (<1 mm) into the soil of shooting area, where metallic lead is encapsulated, use of steel shot alone; **(D)** increment of total iron (Δ_{Fe}) in fine soil fraction at the first month of shot surface corrosion: ***a*** **-** steel shot, the soil of areas with no prior shooting activities; ***b*** **-** steel shot, the soil of areas with shooting activities; ***c*** -steel shot and lead shot, the soil of areas with no prior shooting activities; **(E)** mix of shot, Fe (III) compounds organic resiues and mineral particles in the soil, soil fraction >1 mm; **(F)** example of shot-soil aggregate.

of steel shot deposition (*Fig*. 3, B-2). Over time, the formation of shot and soil aggregates limits the level of iron migration which decreases but remains above the initial level (*Fig*. 3, A-c, in the case of a one-time steel shot deposition onto the soil surface over the entire experiment period).

If steel and lead shot are deposited and transformed together, iron remains in the dissolved form longer (*Fig*. 3, B-3), that causes a higher level and constant value of metal removal with soil water (*Fig*. 3, A-b).



The value of the monthly iron removal was determined considering its residual reserve in the water extract

The relative distribution dissolved and suspended particulate Fe in regular filtrates

Fig. 3. Iron removal by soil waters (**A**): a) steel shot exposed alone at the soil of area with no metallic lead; b) a combination of steel shot and lead shot exposed at the soil of area with no metallic lead; c) base soil without metal shot exposed; and Iron forms transported with soil water (**B**): 1) the soil after one month's interaction; 2) the soil with steel shot after four months interaction; 3) the soil with mix steel shot and lead shot after four months interaction.

Factor — Various of the humidification conditions for the soil of SH area

In arid climate conditions, quite large (3–5 cm) shot and soil aggregates form after just 2 months (*Fig*. 4, D), which limits the release of iron into the analysed soil fraction when new portions of steel shot corrode. The maximum total iron content is 1.1 times the base soil iron content (*Fig*. 4, A); up to 2% of the mass of iron caused by deposited steel shot is irreversibly assimilated by the fine soil fraction.

In sub-humid climate conditions, the release of iron into the fine soil fraction intensifies due to the alternating cycles of humidification and drying up. The maximum amount of iron content is 1.4 times the initial level (*Fig*. 4, B), and up to 5.8 % of the mass of iron caused by deposited steel shot is irreversibly assimilated. After that, the release of iron into the fine fraction slows down due to the accumulation of iron in the skeletal soil fraction and its removal from the analysed sample during the sample preparation (*Fig*. 4, E).

In humid climate conditions, the total iron content grows linearly throughout the entire interaction period — at the end of the period, the content of iron in the fine soil fraction reaches 1.4 times the initial level (*Fig*. 4, C). During the sifting, loose corrosion crust on shot and fine corrosion dust could be seen, while the skeletal fraction contained several small aggregates (*Fig*. 4, F). The accumulation of iron in the fine soil fraction reaches the maximum level of 6% of the mass of iron caused by deposited steel shot.

Thus, in the case of steel shot transformation, an increase in the total iron content in the fine fraction of the upper soil layer is controlled by the climate conditions with various humidification regimes. In humid climate conditions, the process of shot and soil aggregate formation is secondary, while the prevalent process is the gradual accumulation of iron in the fine fraction of the upper soil layer.

The changes in the humidification regime do not affect the distribution of iron forms in the soil profile (*Table S5*). Like in the previous example, iron is mostly present in the form of poorly soluble amorphous (hydro)oxides and residual fractions, with the proportion of water-soluble iron less than 0.01% of the total content.

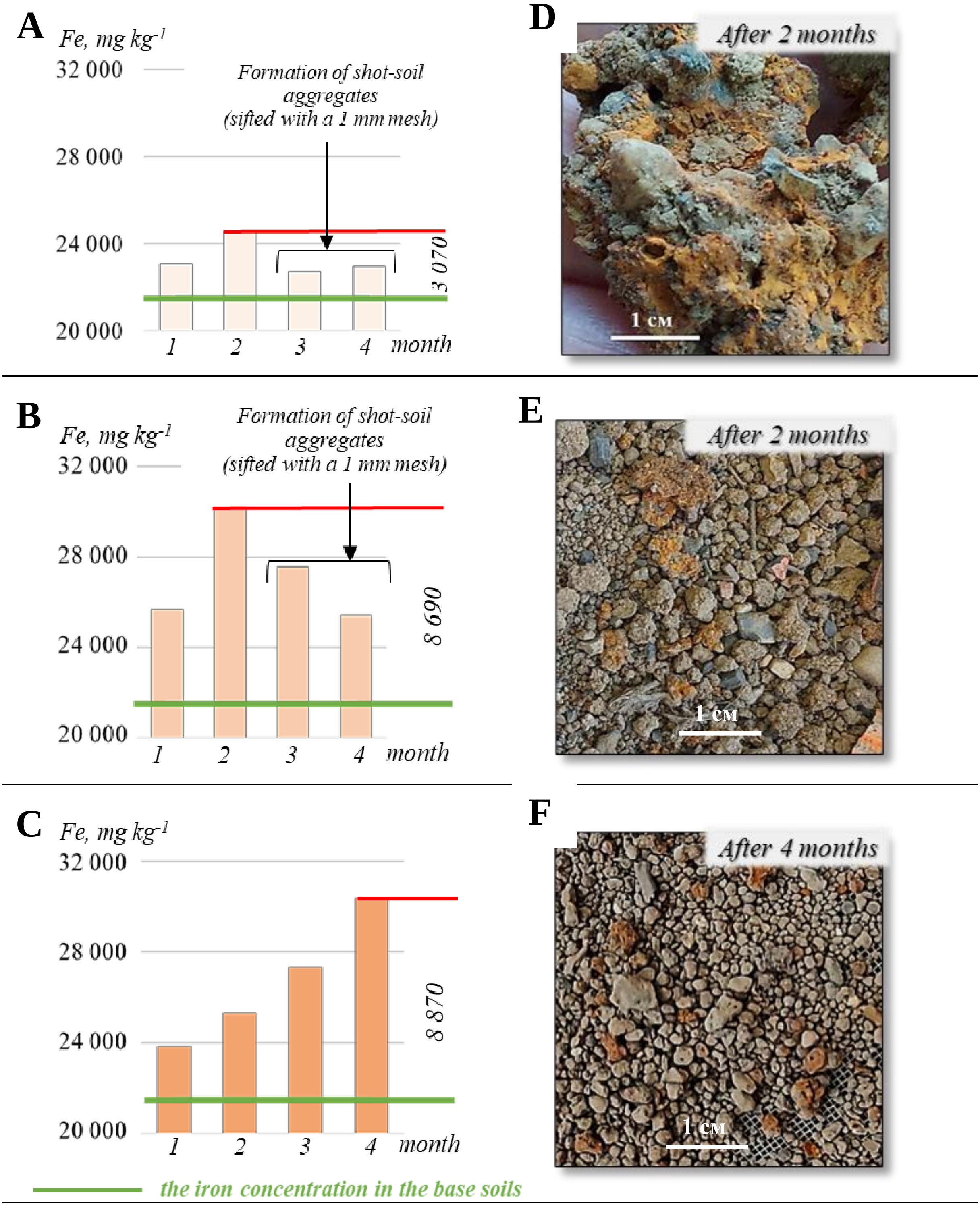
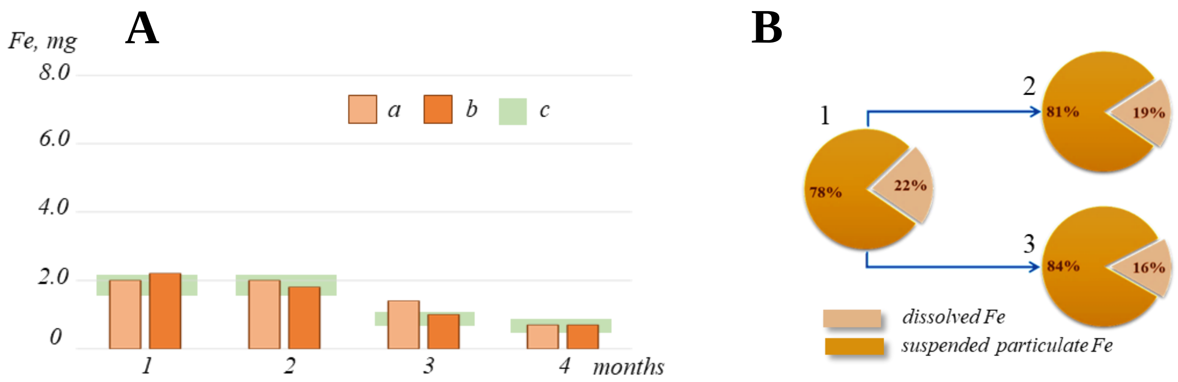


Fig. 4. The content of iron in the fine soil fraction (<1 mm) (A-C) and example of shot-soil aggregates in skeletal soil fraction (> 1 mm) (D-F) in various climate conditions. (A) the content of iron in the fine soil fraction (<1 mm) into the soil of shooting area at arid climate conditions, use of steel shot alone; (B) the content of iron in the fine soil fraction (<1 mm) into the soil of shooting area at sub-humid climate conditions, use of steel shot alone; (C) the content of iron in the fine soil fraction (<1 mm) into the soil of shooting area at sub-humid climate conditions, use of steel shot alone; (D-F) orange is shot-soil aggregate, mix of shot, Fe (III) compounds organic residues and mineral particles in the soil, soil fraction >1 mm.

The proportion of amorphous iron (hydr)oxides noticeably increases in a humid climate - by 4-6% relative to the initial level, and by 1-3% in other conditions.

The accumulation of iron in the soil as finely dispersed corrosive particles and amorphous (hydr)oxides in the oxidative environment of the near-surface horizon of soils limits the removal of iron with soil waters. Iron removal by soil waters under conditions of precipitation infiltration corresponds to the initial level (Fig. 5, A). The redistribution of metal transfer forms in soil waters towards an increase in the proportion of suspended forms (Fig. 5, B) was noted by the end of the experimental period



The value of the monthly iron removal was determined considering its residual reserve in the water extract

The relative distribution dissolved and suspended particulate Fe in regular filtrates

Fig. 5. Iron removal by soil waters (**A**): a) sub-humid climate conditions, a steel shot exposed alone at the soil of shooting area; b) humid climate conditions, a steel shot exposed alone at the soil of shooting area; c) base soil of shooting area with lead shot; and Iron forms transported with soil water (**B**): 1) the initial stage of the interaction of shooting area soil and steel shot; 2) sub-humid climate conditions, the soil of shooting area with steel shot interaction over four months, distribution of the dissolved and suspended particulate Fe over four months on average; 3) humid climate conditions, the soil of shooting area with steel shot interaction over four months, distribution of the dissolved and suspended particulate Fe over four months on average.

Factor — The SH area soil with an excess of organic matter (under humid conditions)

In the case of an excess of organic matter, like with the permanent humidification conditions, the total iron content in the upper soil layer increases gradually (*Fig*. 6, A-B). This is explained by the fact that no massive shot and soil aggregates are formed in these conditions (*Fig*. 6, C-D), and the corroded shot is present in the soil as separate inclusions. The iron content increase in the fine soil fraction is significant over the entire observation period. The maximum increase in the iron content compared to the initial level amounted to 12,270 mg/kg, while the total content of iron irreversibly assimilated by the fine soil fraction in case of an excess of organic matter is 10% of the mass of iron caused by deposited shot.

The high content of organic matter and permanent humidification resulted in a tenfold increase in the water-soluble iron forms compared to the initial level (6.5 and 0.6 mg/kg, respectively) in the first month of the interaction between steel shot and the soil (*Table S5*). The proportion of water-soluble iron forms increases relative to the initial level (<0,01%) and amounted to 0.03%, no changes in the general distribution of iron forms: poorly soluble amorphous (hydro)oxides - 21% of the total content, while residual fractions - 79%.

According to the conditions of the experiment, steel shot is deposited onto the surface of the fertile soil which is located above the main soil layer. Thus, in the first month of the interaction between steel shot and fertile soil, mobile complex iron organic compounds are formed which is indicated by the change in the prevalent form of iron migration from the suspended to the dissolved form (*Fig*. 7, B-1,2). The same period also corresponds to the maximum level of iron removal by soil waters (*Fig*. 7, A-b). Over time, the removal level reduces to the initial values (*Fig*. 7, A-c), however, iron migration mostly occurs in the dissolved form (*Fig*. 7, B-3).

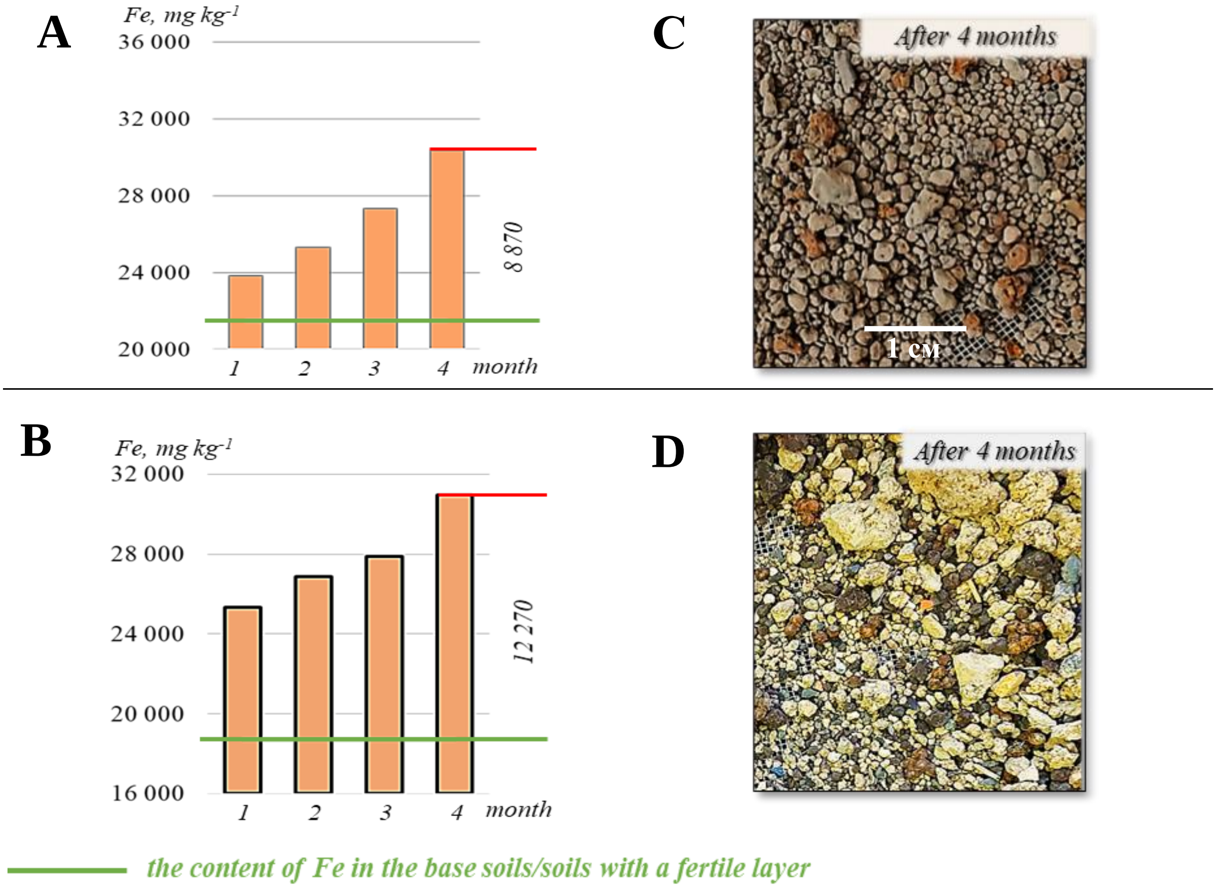
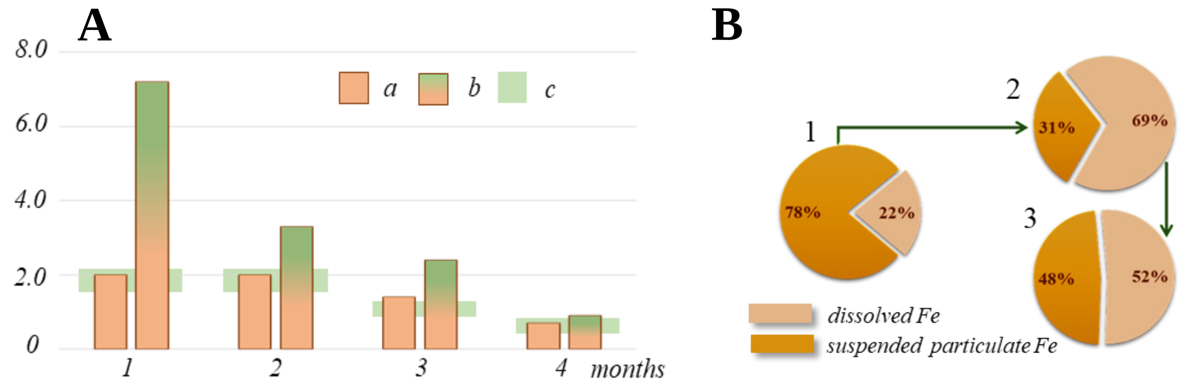


Fig. 6. The content of iron in the fine soil fraction (<1 mm) (**A-B**) and example of shot-soil aggregates in skeletal soil fraction (> 1 mm) (**C-D**) into soil of shooting area with an excess of organic matter. **(A)** the content of iron in the fine soil fraction (<1 mm) into the soil of shooting area without a fertile soil layer, a low level of organic matter, use of steel shot alone; **(B)** the content of iron in the fine soil fraction (<1 mm) into the soil of shooting area with a fertile soil layer, an excess of organic matter, use of steel shot alone; **(C-D)** orange is shot-soil aggregate, mix of shot, Fe (III) compounds organic residues and mineral particles in the soil, soil fraction >1 mm.



The value of the monthly iron removal was determined considering its residual reserve in the water extract

The relative distribution dissolved and suspended particulate Fe in regular filtrates

Fig. 7. Iron removal by soil waters (**A**): a) a low content of organic matter, a steel shot exposed alone at the soil of shooting area without a fertile soil layer; b) an excess of organic matter, a steel shot exposed alone at the soil of shooting area with a fertile soil layer; c) base soil of shooting area with lead shot; and Iron forms transported with soil water (**B**): 1) the initial stage of the interaction of shooting area soil without a fertile soil layer and steel shot; 2) the initial stage of the interaction of shooting area soil with a fertile soil layer and steel shot; 3) after four months of the interaction of shooting area soil with a fertile soil layer and steel shot.

3.3 *Iron influence on the lead behavior in soils with the mix of steel and lead shot*

When lead and steel shot are deposited jointly into the soil of an area with no prior shooting activities and the initial lead content of 26 mg/kg, the total lead content in the soil increases up to 2,700 mg/kg in the first month of the experiment and continues to grow, reaching up to 4,400 mg/kg in the second month (*Table S2*). Later, with the formation and strengthening of shot and soil aggregates which keep lead shot and its degradation products in the skeletal soil fraction, the total lead content in the fine soil fraction remains at the stable level of 2,750 mg/kg. If lead and steel shot are transformed at the same time, the weight percentage of mobile lead forms in the soil remains at a constant level between 11 and 14% of the total content, while water-soluble lead forms constitute under 0.04% of the total lead content (*Table S6*). The obtained results correspond to the fact that the presence of steel shot increases the period of lead shot encapsulation by oxygen compounds. This information is presented in the paper by Lisin et al. (2022). It should be noted that in this case lead mostly migrates in its suspended form instead of the typical dissolved form (*Table S6*). This occurs due to the deposition of lead ions on the corrosive particles Fe(III) formed at the same time and can increase the depth of lead migration in the soil profile (due to the mechanical migration).

In SH areas, metallic lead is mostly present in the soil volume in an encapsulated form (SAAMI, 1996; Lisin et al., 2020). When steel shot alone is deposited onto the soil surface, the contact between steel shot and metallic lead is limited, the total lead content remains at the level of 3,200–3,500 mg/kg (*Table S*2, for the soil of SH areas in the experimental simulation conditions), the proportion of mobile and water-soluble lead forms (2–3% and less than 0.01% of the total content, respectively) does not change significantly compared to the base soils (before the deposit of steel shot), the main form of lead transport in soil waters is suspended *(Table S6).*

The risk of direct contact between steel shot and encapsulated lead shot (which can develop in a SH area over time) was evaluated based on a simulation experiment where a mix of steel shot and encapsulated lead shot was deposited into the soil with an initial lead content of 26 mg/kg. A month later, the content of lead in the upper soil layer increased to 450 mg/kg. When encapsulated lead shot was deposited alone (in analogue conditions of experiment), the increase in the total lead content in the upper soil layer was half as great and amounted to 250 mg/kg.

A comparison of the obtained data shows that when steel and lead shot corrode together in an area with no prior shooting activities, the encapsulation of lead shot slows down, and as a result, the total lead content in soils continues to grow, and the proportion of mobile lead forms increases: their content is significantly higher than in SH areas where lead shot is present in an encapsulated form. Over time, iron may initiate the destruction of the encapsulating coating on lead shot surface and activate the release of lead ions into the soil.

Steel corrosion products have a higher density than the soil matrix (3.24-5.24 g/cm^3 and 1.2-2.4 g/cm^3, respectively). As noted in Hurley (2013), over time, formation of secondary a ‘iron-pan’ in the soil profile, consisting of steel shot corrosion products and shot-soil conglomerates. The fixation of lead shot in their composition and the sorption of lead ions by corrosive particles of Fe(III) assimilating in the soil will cause to the "burial" of lead in ferruginous interlayers.

3.4 *The soil condition and composition monitoring on the experimental site of the territory of shooting activity*

Steel shot deposited onto the surface of soil with the presence of lead (*Fig.* 8., A) was covered with a red coating of iron oxides within the first month. Over time, spots of iron oxide particle (rust) dispersion formed in the areas of steel shot accumulation, and three months later (*Fig*. 8., B) it led to the formation of a denser crust which consisted of steel and lead shot, as well as rust and soil particles. A year later, dense shot and soil aggregates formed in the areas of steel shot accumulation in the near-surface soil of the test site (*Fig*. 8., C), while separate thin iron spots were observed in the soil profile (*Fig*. 8., D). After 17 months, a dense and fragile shot and soil crust with a thickness of around 1 cm is observed on the soil surface (*Fig*. 8., F), and a ferriferous layer with a thickness of up to 1.5 cm has formed in the soil profile (*Fig*. 8., E).

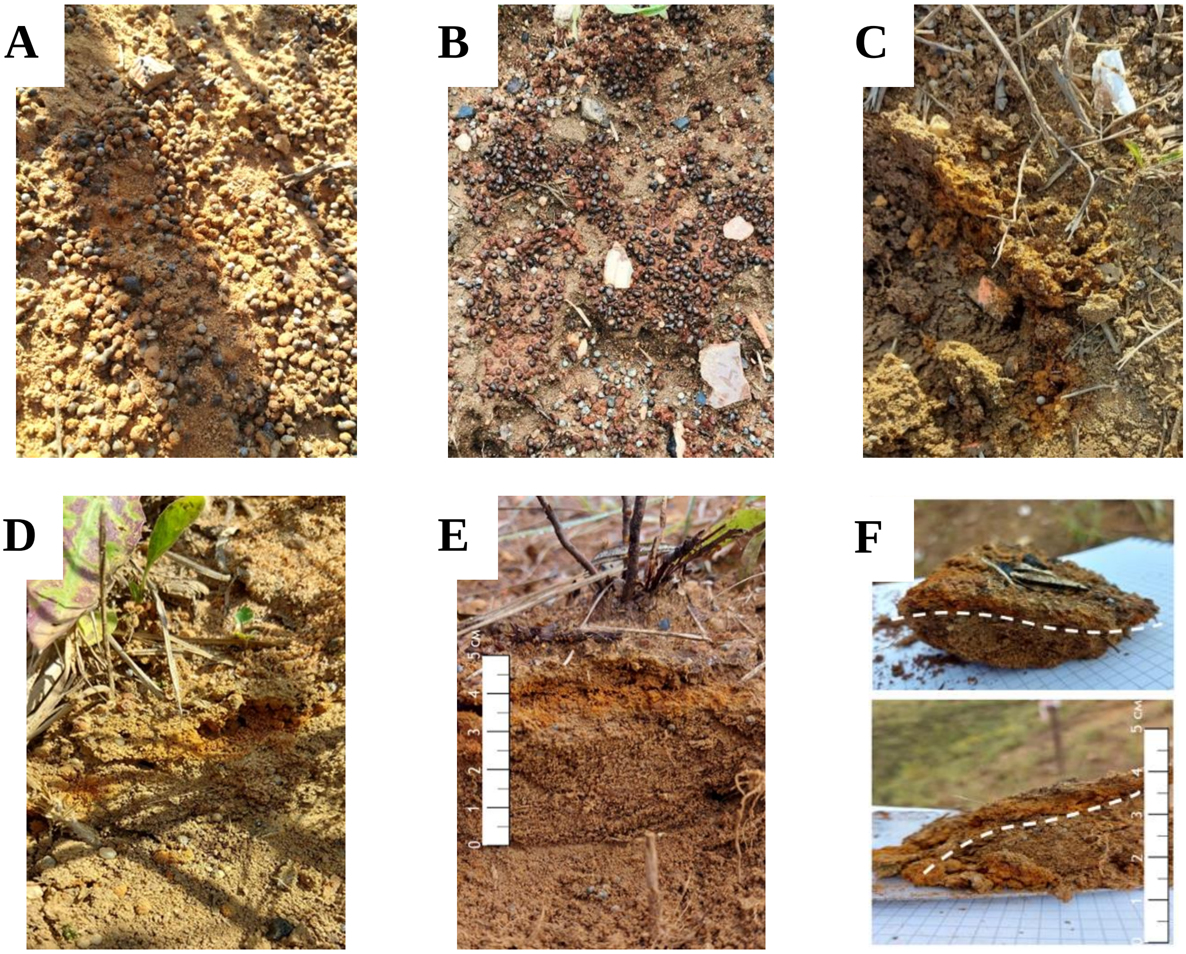


Fig. 8. Visually observable soil changes because of steel shot transformation: **(A)** the experimental site exposition 1 month. A friable corrosion crust of poorly soluble Fe (III) (hydr)oxide forms on the shot surface; **(B)** the experimental site exposition 3 months. Aggregation of steel corrosion products with organic residues and mineral particles in the soil; **(C)** the experimental site exposition 11 month. Formation of shot -soil aggregates; **(D)** the experimental site exposition 13 month. Iron spot in the soil profile; **(E-F)** the experimental site exposition 17 month: **(E)** ferriferous layer in soil profile; **(F)** shot -soil layer on soil surface.

The total content of iron and lead in the experimental site's soils was monitored throughout the observation period (*Fig*. 9), and the monitoring showed that within one month of steel shot deposition, the total content of iron in the soil increased nearly 1.5 times (from 16,590 mg/kg to 23,120 mg/kg). After that, the increase in the total content of iron slowed down due to the formation of shot and soil aggregates which limit the release of iron into the soil. The intensification of increase in the total iron content in April 2021 was influenced by the ample soil humidification in the seasonal increase in humidity. However, later, the process of iron accumulation in the fine soil fraction once again slowed down due to the formation of a dense shot and soil layer.

When steel shot is deposited alone onto the surface of areas where metallic lead is present mostly in an encapsulated form, the contact between steel shot and metallic lead is limited. Over the sampling period, the total content of lead in the soils varied between 1,200 and 1,600 mg/kg. The increased lead concentration in the last month of the sampling period (with the symbatic diagrams of the total content of Fe and Pb on Fig. 9) may indicate the activated transformation of previously encapsulated metallic lead. At the same time, it cannot be ruled out that the transformation of the newly deposited lead shot causes this process.

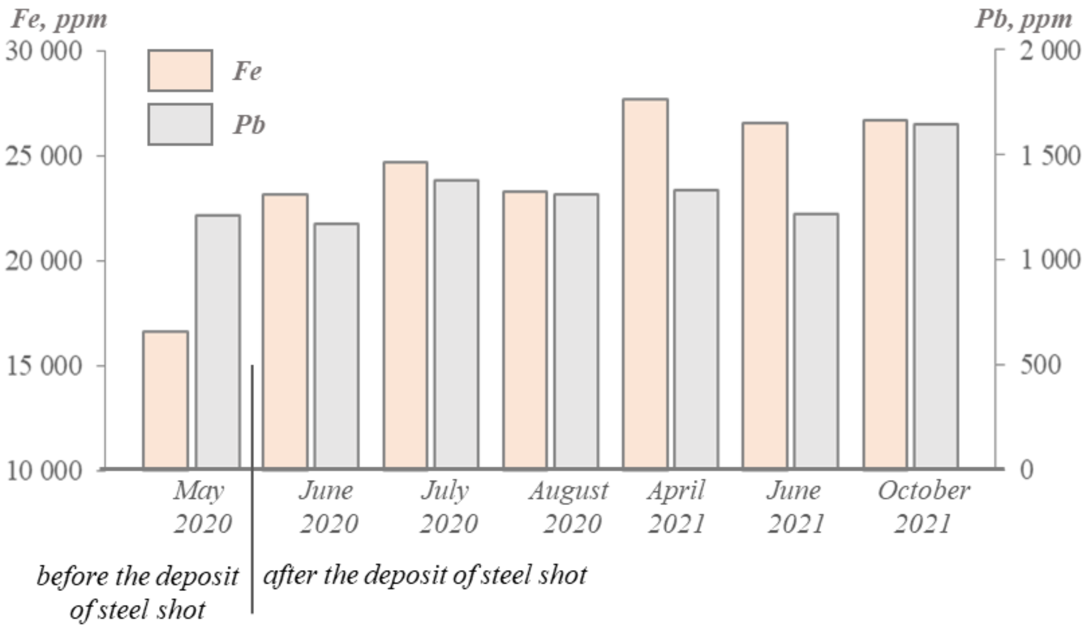


Fig. 9. Total content of Fe and Pb in the upper soil layer (fraction <1 mm)

3.5 *The environmental risks associated with steel shot used in the operation of shooting ranges*

The obtained results indicate that steel shot transforms under the impact of the environmental factors in several stages (*Fig*. 10):

I. Exposed to air on the soil surface, shot is covered with a thin black and red primary oxidation coating that contains Fe (II) and (III) oxides $FeO \cdot Fe_2O_3$. When exposed to moisture, Fe (II) and (III) oxides form poorly soluble iron hydroxides and oxyhydrates — $Fe(OH)_3$, α, γ – FeO(OH). Thus, a friable corrosion crust of poorly soluble Fe (III) (hydr)oxide forms on the shot surface. Over time, this crust may peel off the shot surface and disperse in the soil; in case of wind erosion, it also presents a source of the atmospheric dispersion of particles (PM 2.5 and PM 10.0).

II. As shot gets deeper into the soil layer, it starts interacting with soil water, and Fe (III) particles are migrated with the soil solution. Organic (humic and fulvic acids) contained in soil water increase the solubility of Fe (III) compounds, intensifying the steel corrosion process. Thus, in addition to the suspended Fe (III) particles, complexes of Fe^{3+} with organic chelates $[FeFu]^+$ are formed in the soil solution — they are hydrolysis-resistant, migrate with soil water, and can become part of a soil adsorption complex. At the same time, the primary oxidation coating continues to grow inward inside the steel shot.

III. A secondary coating of steel corrosion products is formed — it consists of Fe (III) compounds mixed with organic residues and mineral particles in the soil. This process is accompanied by the deposition of corroded metal particles in the form of mechanical impurities into the soil, as well as the migration of complex iron organic compounds in soil water.

IV. The growth of aggregates and the contact between pellets result in the formation of dense watertight and airtight aggregates in the near-surface soil — inside these aggregates, iron is mineralized (the primary oxidation coating grows inwards inside the steel shot) until its complete destruction. Therefore, apart from the mechanical assimilation of corroded metal particles in soil, and the migration of organic iron compounds in soil water, the upper soil layer gradually becomes denser, increasing the surface runoff.

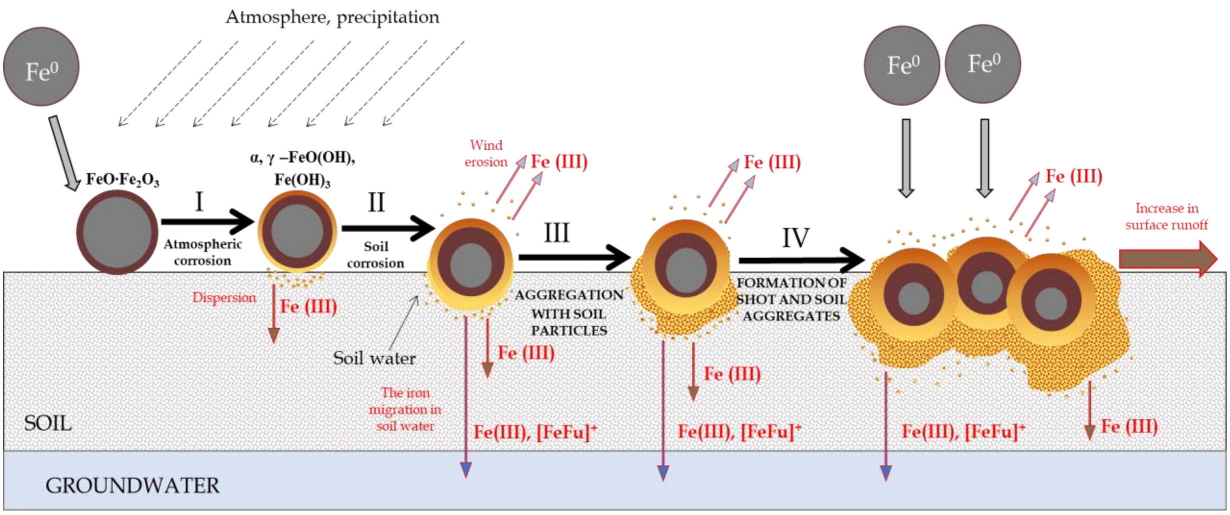


Fig. 10. Steel shot transformation on the soil surface under the environmental factors

Unlike the cyclical process of lead shot corrosion (Lisin et al., 2020), the corrosion of steel shot is a continuous process during which iron is mineralized (Fe (II) and (III) oxides) and poorly soluble rust (a crust of Fe (III) (hydr)oxide) forms until the complete destruction of iron. Iron transforms into a rust formation which constantly releases both iron ions into natural waters, and dispersed particles of Fe (III) (hydr)oxide up to irreversible assimilation of iron in the environment. Thus, steel shot transformation in the environment leads to the contamination of the following environmental components:

– ambient air — due to the release of dispersed friable and easily peeled off formations of insoluble Fe(III) (hydr)oxide in case of wind erosion ($PM_{2.5}$ and PM_{10});

– the surface soil layer — due to the disruption of the air and water migration processes of soils and the increase in the surface runoff from SH areas;

– the lower soil layers — due to the increased migration depth associated with the suspended form of metals;

– groundwater — in case of vertical migration of aqua and organic complexes and suspended iron formed as a result of soil corrosion;

– sediments — due to the accumulation of corrosion products of shot deposited into water bodies;

– surface water — due to the entering of aqua and organic complexes and suspended forms of iron; surface and subsurface runoff from SH areas; secondary contamination due to the migration of iron from sediments associated with the changes in physical and chemical conditions.

4. CONCLUSION

Iron is one of the main components of the lithosphere and one of the most abundant elements in soil, and two features of its existence in the environment:

- there are no requirements for iron concentration in soils;
- iron concentration in soils shows volatility in case of small changes caused by anthropogenic iron deposition.

These peculiarities create an illusion that iron presents no hazard to the environment — because of this idea and the metal’s high availability, iron is most often suggested as the best alternative for lead in ammunition. However, the study of steel shot transformation in natural conditions has demonstrated that intense steel corrosion is observed within 1–2 months of steel shot deposition, resulting in the entering of significant number of corrosive particles (friable iron (hydr)oxides) into the soil, and increasing the total iron content in the fine soil fraction.

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Over time, a dense shot and soil layer forms on the soil surface, and ferriferous layers in the soil profile. The monitoring of iron content has shown that the increase in the total iron content depends on the seasonal humidification regime.

The highest environmental risks occur when both steel and lead shot have been used in SH areas where metallic lead intensifies steel shot corrosion rate, while the steel shot itself activates the destruction of previously encapsulated metal and slows down the encapsulation of newly deposited metallic lead, which catalyses the accumulation and migration of lead in environmental components.

Fixation of lead shot in shot-soil conglomerates and sorption of lead ions by corrosive particles of iron (III) assimilating in the soil will cause to “burial” of lead with steel shot corrosion products. With an unfavorable change in physicochemical conditions (for example, the occurrence of an anaerobic environment), it is possible to restore iron from corrosion products. In this case lead will become mobile and released into the soil water.

Negative implications are also expected in case steel ammunition is used on wetlands where, due to the permanent flooding and an excess of organic matter, the corrosion processes may intensify with the formation of a large number of mobile iron complexes with organic ligands.

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