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Assessing the leaching behavior of different gunshot materials in natural spring waters

Julian Fäth* and Axel Göttlein

Abstract

Background: Owing to the high environmental risk of lead-based gunshot, especially as the main source of acute lead poisoning in waterfowl, restrictions on its use in European wetlands are being put into place. In order to assess potential risks of alternative gunshot pellets to aquatic systems, we validated a recently published study that compared the leaching behavior of different game shot materials in an artificial solution and their toxicological effects to *Daphnia magna*. We therefore investigated the altered leaching of shot materials in natural spring waters.

Results: The different water conditions (geology/redox conditions) had a strong influence on the leaching behavior of the examined shot types. Spring water originating from siliceous bedrock showed the highest concentrations of nearly all leached metals under aerobic conditions. The results were similar to the former study, which used an artificial standardized medium for daphnids.

Conclusions: According to the conducted leaching tests, Cu- and Zn-based as well as Zn-coated gunshot should be avoided by reason of the high risks they pose to the aquatic environment. Furthermore, the use of Pb-based and Ni-alloyed or -coated game shot also should be hampered owing to their impact on birds or other wildlife. Since some of these shot materials are still on the European market, an effective toxicity screening of alternative gunshot materials is necessary. By conducting standardized leaching tests, in addition to chemical compositional standards and toxicity tests regarding birds, the environmental risks of each game shot would entirely be assessed. The method presented in this study provides a further step for initial ecotoxicological risk assessment of gunshot for aquatic systems, since it additionally assesses minor components, like thin coatings, which also can have a high impact to these ecosystems.

Keywords: Hunting, Ammunition, Aquatic systems, Heavy metal, Lead, Copper, Zinc, Tungsten, Bismuth

Background

Because of mortality of scavenging species after ingesting lead (Pb)-contaminated quarry [14, 19, 30] and the poisoning of waterfowl as a result of the ingestion of Pb shot instead of natural grit and food [27, 34], a general ban on Pb in game ammunition in the European Union (EU) has been recommended by the European Chemicals Agency [6]. Furthermore, many states worldwide and in particular in Europe (23 countries) already have regulated the use of lead shot [28]. For decades, the effects of lead poisoning in waterfowl, raptors, scavengers and terrestrial birds are highly documented [34]. According to comparative investigations, the oral intake of shot made of nickel (Ni), iron (Fe), tin (Sn), copper (Cu) and tungsten (W) did not lead to a higher mortality of mallards (*Anas platyrhynchos*) compared with a control, whereas Pb-based shot did cause significantly higher mortality rates [10, 12, 13, 24]. However, alternatives that are available in the EU, also should be controlled regarding their effects on the environment [42, 44], since some of them may also result in ecotoxicological problems. For example, W alloyed with Ni can cause toxic effects in both, humans and the environment (Ni: [8, 35, 36, 41]; W-compounds: [2, 40]). Furthermore, a study by Levonmäki and Kairesalo [22] revealed the potential for high chromium (Cr) loadings to be released into the soil of shooting ranges from steel shot containing up to 27% Cr. The (eco)toxicological risks of this heavy metal, especially the high carcinogenicity of

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*Correspondence: julian.faeth@tum.de
Professorship of Forest Nutrition and Water Resources, Technical University of Munich, Hans-Carl-von-Carlowitz-Platz 2, 85354 Freising, Germany

Cr(VI), are well known [9, 11, 45] and should not result from such a high Cr content in steel shot, which is commonly seen as nontoxic. As a result of strong leaching, zinc (Zn)- and Cu-based shot may also negatively impact the terrestrial environment [8]. Moreover, the findings of a first comparative investigation on the leaching behavior of game shot in artificial freshwater and the resulting toxicological effects on *Daphnia magna* [7] indicate that shot types leaching Cu or Zn pose a high risk to the aquatic biocenosis. In that study, shot made of Fe and coated with Zn released as much Zn as a pure Zn-based shot and caused nearly 100% mortality of daphnids, indicating that not only the main component but also alloy components and shot coatings should be considered when regulating the use of game shot materials. In order to avoid encouraging the manufacture, trade and use of the above-mentioned critical substitutes for Pb shot in the EU, a mandatory toxicity screening of all alternatives should be adopted. As far as legislation would strictly regulate these substitutes, e.g., in the USA and Canada [43, 46], the European market would already be free from shot types leaching the above-mentioned critical metals. Although every relevant ecosystem (terrestrial and aquatic habitats, avifauna) should be considered, this study focuses on the aquatic compartment.

Since recent studies have demonstrated that the main component is not always the main driver of the environmentally relevant impact of a shot material [7, 8, 35, 36, 41], standardized experimental leaching tests for particular environments are needed as an important step in ecotoxicological risk assessment. Therefore, the Organization for Economic Cooperation and Development (OECD) provides guidelines for assessing the dissolution of metals in aqueous media [32, 33]. These were considered and modified in a hypothesis-driven leaching test described in Fäth et al. [7], representing a worst-case scenario for game shot emitted into aquatic ecosystems. Since that study considered just one standardized artificial freshwater environment adapted to *Daphnia magna*, we decided to extend the experimental design to obtain information about the leaching behavior of shot subjected to natural waters from different bedrock and with different redox conditions.

Modifying the experimental setup of the former study, we put different game shot materials in natural spring water originating from different bedrock (siliceous and calcareous) under aerobic and anaerobic conditions at four exposure periods. In order to reflect the market situation in the EU, we assessed (i) three conventional Pb-based shots, (ii) one coated Pb-based shot and (iii) seven alternative shots made of Fe, Zn, W, bismuth (Bi) and Cu.

Table 1 Overview of investigated shot types

Shot name	Abbreviation	Major element	Coating
Rottweil Waidmannsheil	Waidmannsheil	Pb	No
Rottweil Special 36	Special	Pb	No
Fiocchi PL 34	PL 34	Pb	No
Rottweil Silver Selection	Silver	Pb	Yes
Rottweil Steel Game	Steel Game	Fe	No
Fiocchi Steel Shot	Steel Shot	Fe	Yes
Winchester Blind Side	Blind Side	Fe	Yes
SK Hubertus Zink	Hubertus	Zn	No
Rottweil Ultimate	Ultimate	W	Yes
Eley Bismuth Alphamax	Alphamax	Bi	Yes
FOB Sweet Copper	Sweet Copper	Cu	No

For additional information about their full composition see Additional file 1: Data S1

Materials and methods

Shot types

In collaboration with the Bavarian Hunting Association, we selected the most relevant ammunition size and shot materials on the European market, giving a total of eleven types of shotgun ammunition (Table 1). Ammunition comprised the following main components: Pb, Cu, Fe, Zn, W and Bi. The shot cartridges were obtained in size #2 (3.75 mm diameter), with the exception of two shots (*Eley Bismuth Alphamax* and *Fiocchi PL 34*), which were only available with a smaller diameter (3.5 mm). Since our institute is not licensed to manipulate ammunition components, RUAG Ammotec GmbH disassembled all cartridges of the unfired shots and provided the contents of metals in each shot type, as well as the presence and thickness of shot coatings (see Additional file 1: Data S1). Since the cartridges of *FOB Sweet Copper* also contained Cu-coated Pb shot (12% of all pellets), the pure Cu shots were separated to allow a clear assessment of Cu as a shot material.

Game shot exposure

To obtain a relative comparison of the leaching behavior of different game shot materials, our experimental setup was based on the aqueous exposure test described by Fäth et al. [7]. This approach was originally influenced by the OECD guidelines for assessing the dissolution/transformation of metals in aqueous media [32, 33] and was modified to a high-exposure test as a worst-case scenario. Such a scenario was subjected to shallow water resp. wet spots with only a few millimeters water depth, which are typical habitats of daphnids. On hunting hotspots with a high loading of up to 100 pellets per m^2 (more than 100 pellets per each cartridge for this caliber; [7]), a high pellet/water ratio (1 pellet/50 mL)

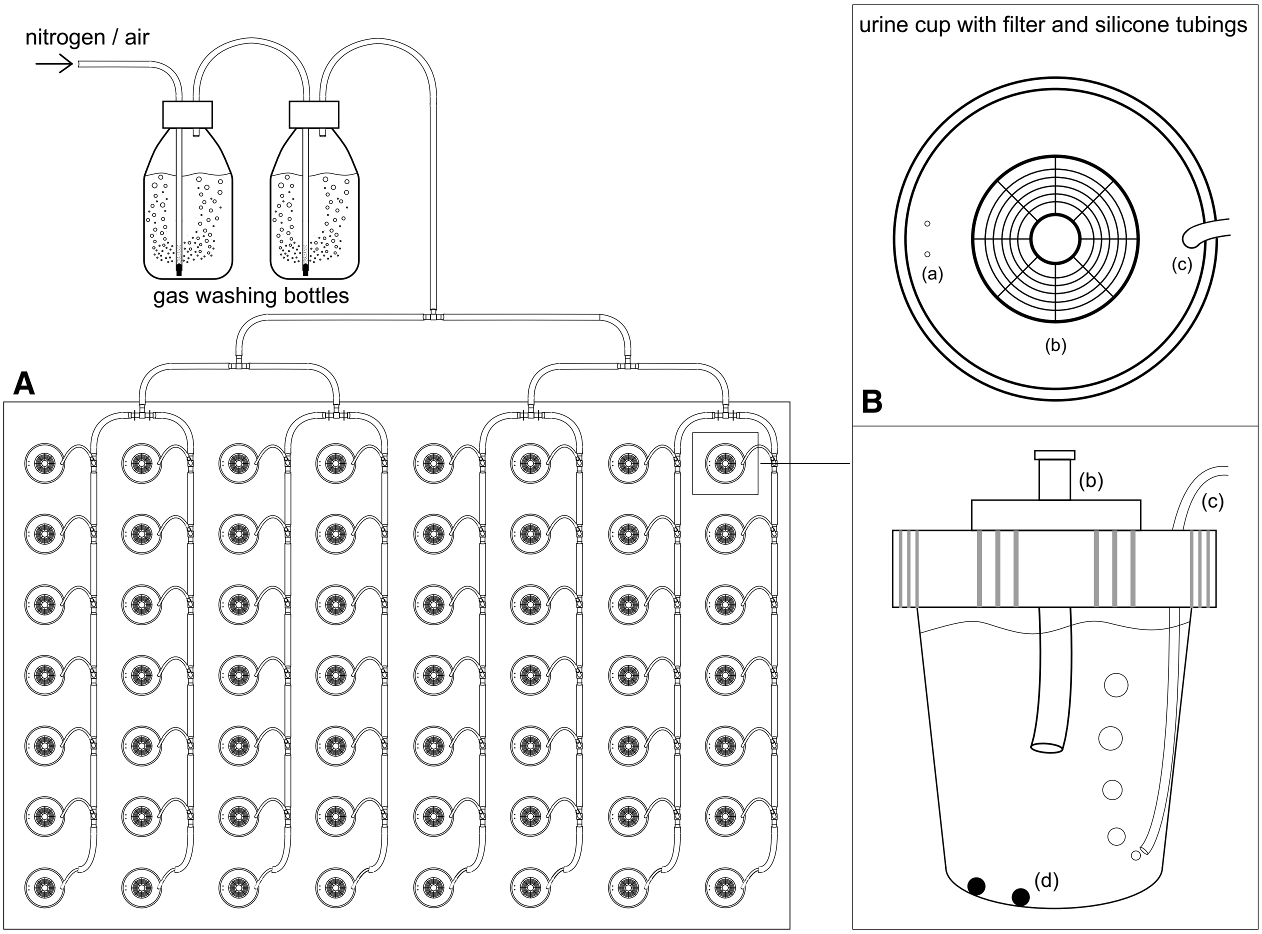

Fig. 1 Experimental setup of the leaching test. **A** Arrangement of the exposure units during the experiment; **B** single exposure unit; (a) punctures for depressurization; (b) membrane filter; (c) silicone tubing; (d) shot pellets

can occur, which was implemented in this study. The leaching test of Fäth et al. [7] comprised a standardized medium termed "Aachener Daphnien Medium" (ADaM; [18]) and thus excluded the effects of natural freshwater with different pH values and redox conditions. To ensure realistic water properties, we sampled water from two springs in Bavaria (Federal State of Germany) rising from siliceous (Red sandstone in the uplands of Spessart; 49°55′37.9″N 9°23′53.5″E; pH 6.5) and calcareous (Munich gravel plain; 48°23′39.6″N 11°43′23.6″E; pH 7.6) bedrock. In order to realize the high-exposure scenario described by Fäth et al. [7], two pellets of each shot type were exposed to 100 mL of the sampled waters in modified medical urine cups (Fig. 1). To manipulate the redox conditions, the cups were flushed with pre-cleaned air (aerobic conditions) or nitrogen gas (anaerobic conditions) through silicone tubings (c).

To avoid water losses, the gases were water saturated (using wash bottles) prior to entering the cups. A punctuated (a) screw cap allowed the escape of surplus gas while maintaining an almost closed system. For each of the four treatments (siliceous aerobic; siliceous anaerobic; calcareous aerobic; calcareous anaerobic) three replicates and four sampling time points (1, 8, 15 and 22 days) were used, in accordance with Fäth et al. [7]. The experimental setup thus provided short-term and long-term exposure periods, as suggested by the OECD [32, 33]. At each of the four time points, the silicone tubing between the membrane filter (b) (pore diameter: 0.45 µm) and the solution permitted the sampling (with a syringe) of filtered aliquots (12 mL) for chemical analysis. After sampling, 12 mL of the respective fresh water was added to each cup.

By applying four natural extrema (water from siliceous and calcareous bedrock under strong aerobic and

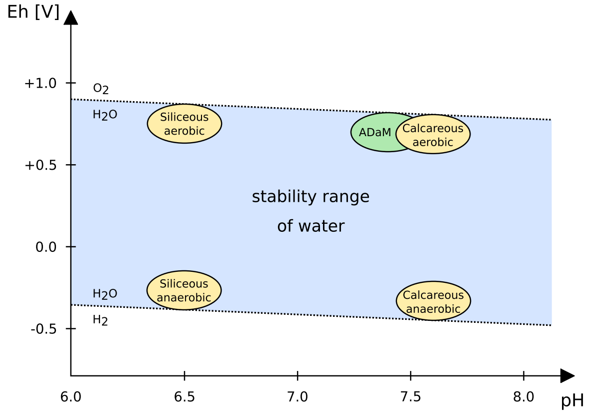

Fig. 2 Schematic placement of the four investigated environments (yellow) as well as the ADaM solution (green) used by Fäth et al. [7] in the stability range of water defined by the redox potential and the pH value at 298.15 K and 10^5 Pa in an Eh/pH chart

Table 2 Limits of the ICP-AES determined by using the blank value method according to DIN 32645: 2008–11

	LOD [µmol/L]	LOQ [µmol/L]
As	0.09	0.29
Cr	0.03	0.09
Cu	0.04	0.13
Fe	0.02	0.06
Mn	0.01	0.02
Ni	0.06	0.20
Pb	0.05	0.16
Sb	0.06	0.19
Sn	0.06	0.18
Zn	0.06	0.21
Bi	0.08	0.27
W	0.08	0.28

LOD: Limit of detection; LOQ: limit of quantification

anaerobic conditions), a corridor for metal leaching can be covered (Fig. 2).

Chemical analysis

The filtered aliquots of 12 mL were directly analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES; Genesis, Spectro Kleve) for the concentrations of As, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn and Zn. These were corrected for the background concentration of blank samples. Eluates of the *Ultimate* and *Alphamax* shot types were additionally investigated for the contents of Bi and W.

For quality assessment of the metal analysis, we measured ten blank values and ten samples of a referenced standard solution. The relative standard deviation (RSD) of the standard solution ranged from three to ten percent for all quantifiable metals in this study. Recovery was between 95% and 107%. According to the blank value method of DIN 32645: 2008–11 [4], the limits of detection (LOD) and limits of quantification (LOQ) were determined by the threefold, respectively, tenfold standard deviation of the measured blank values (Table 2). In the following, all concentrations are given in µmol/L.

Statistical analyses

The presented analytical data only reports quantifiable element concentrations (i.e., > LOQ). In order to compare the results with the leaching data of Fäth et al. [7], we merged the first two (1 day, 8 days) and last two (15 days, 22 days) exposure periods (short term/long term) and compared the mean metal concentrations for each investigated treatment. To statistically compare the different treatments with the results of Fäth et al. [7], we conducted an analysis of variance (ANOVA) of the leached metals for each exposure period and for every shot type that showed a potentially toxic leaching.

Results

Leaching in natural spring water

During exposure, the three uncoated Pb shots *Waidmannsheil*, *Special* and *PL 34* caused high Pb concentrations and differed in their leaching behavior across the four treatments (Fig. 3a, b). In the water from siliceous bedrock under aerobic conditions, these shots showed the highest Pb release compared with the other natural waters, whereas the measured values of the calcareous anaerobic variant were almost always below the LOQ. The opposite pattern was observed for leached Sb concentrations, exceeding the LOQ in the calcareous variants. Only relatively low concentrations were found for As in the calcareous aerobic treatment for the shot type *Special*. By contrast, the coated Pb shot *Silver* leached only Ni, with concentrations exceeding the LOQ in all media and highest values in the siliceous anaerobic environment. The coated Fe-based shot *Blind Side* leached similar Zn concentrations as the pure zinc shot *Hubertus*. The Zn leaching rates in the solutions of *Blind Side* and *Hubertus* were highest in the siliceous aerobic variant. Furthermore, *Blind Side* leached low Cr concentrations, exceeding the LOQ in the water from siliceous bedrock. Pure copper pellets of the shot type *Sweet Copper* only released quantifiable amounts of Cu in the aerobic treatments, with the concentrations in the siliceous aerobic variant being highest. Iron, released by

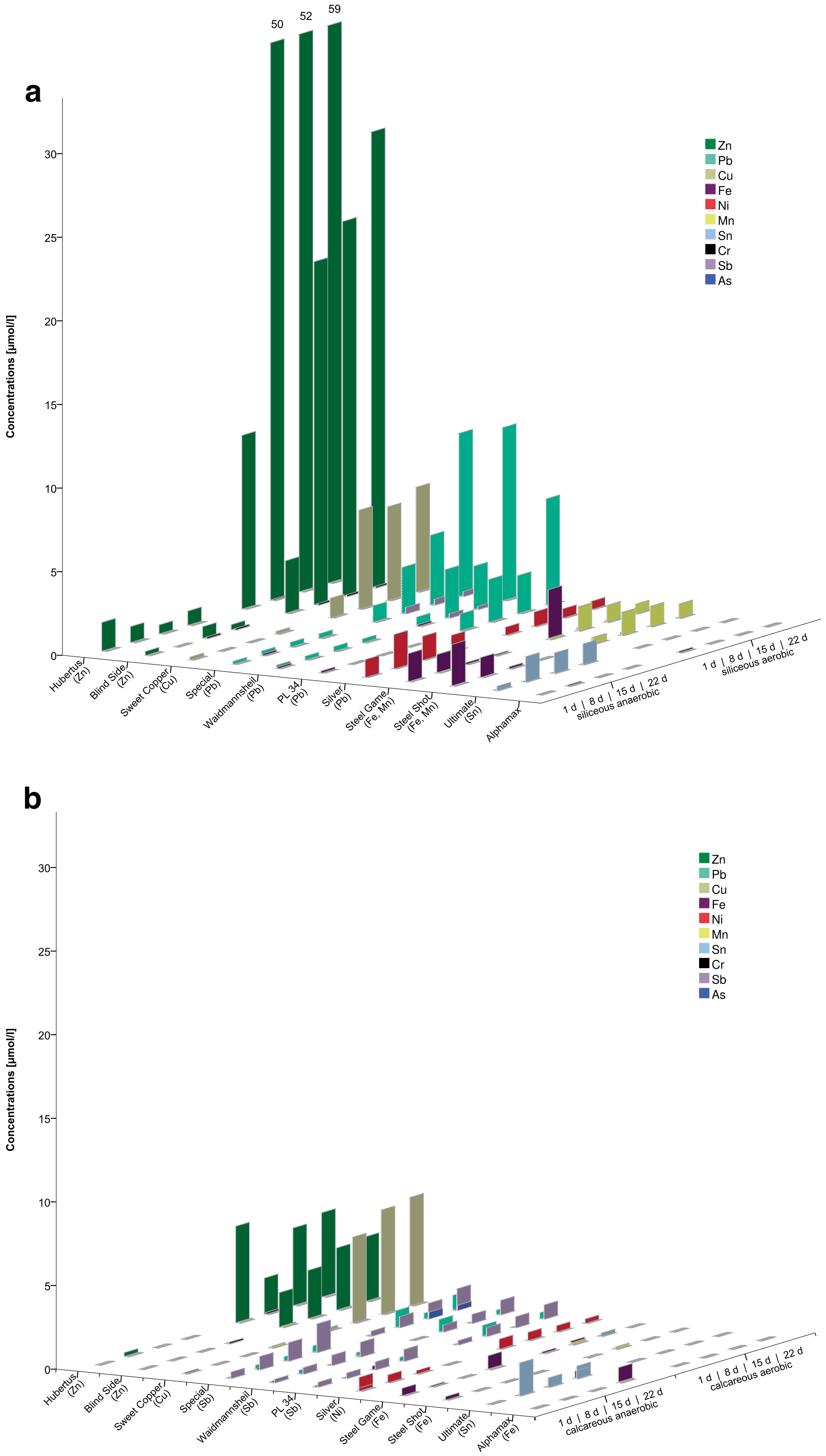

Fig. 3 **a** Mean concentrations (µmol/L; $n = 3$) of leached metals exceeding the LOQ (Table 2) after 1, 8, 15 and 22 days of shot exposure in water from siliceous bedrock under aerobic and anaerobic conditions. The mainly leached metal is given in parentheses. **b** Mean concentrations (µmol/L; $n = 3$) of leached metals exceeding the LOQ (Table 2) after 1, 8, 15 and 22 days of shot exposure in water from calcareous bedrock under aerobic and anaerobic conditions. The mainly leached metal is given in parentheses

Table 3 Mean ± standard error of relevant heavy metal concentrations [μmol/L] for each shot type during short-term (1 day; 8 days) and long-term exposure (15 days; 22 days) leaching tests, including the results for ADaM given by Fäth et al. [7]

shot type (main component)	leached element	ADaM	siliceous aerobic	calcareous aerobic	siliceous anaerobic	calcareous anaerobic
short term period						
PL 34 (Pb)	Pb	**1.81 ± 0.26**	**1.77 ± 0.36**	0.32 ± 0.15	<LOQ	<LOQ^{a}
	Sb	<LOD^{b}	<LOQ	**0.39 ± 0.06**	<LOQ	**0.31 ± 0.08**
Blind Side (Fe)	Zn	**13.39 ± 3.35**	**11.82 ± 3.91**	2.47 ± 0.26	0.21 ± 0.01	<LOD
Hubertus (Zn)	Zn	**33.79 ± 4.56**	**29.99 ± 9.02**	3.96 ± 0.81	1.33 ± 0.19	<LOQ
Silver (Pb)	Ni	0.59 ± 0.08	**0.68 ± 0.09**	0.55 ± 0.06	**1.56 ± 0.47**	**0.65 ± 0.10**
Sweet Copper (Cu)	Cu	**1.91 ± 0.51**	**3.53 ± 1.06**	**2.63 ± 1.12**	0.14 ± 0.01	<LOQ
Ultimate (W)	Sn	<LOD	<LOD	<LOD	0.89 ± 0.29	0.89 ± 0.44
long term period						
PL 34 (Pb)	Pb	0.60 ± 0.25	**4.30 ± 1.12**	0.20 ± 0.09	<LOQ	<LOQ^{a}
	Sb	<LOQ	<LOQ	**0.75 ± 0.05**	<LOQ	0.59 ± 0.05
Blind Side (Fe)	Cr	<LOQ	0.10 ± 0.00	<LOQ	0.10 ± 0.01	<LOQ
	Zn	**34.70 ± 0.92**	24.82 ± 1.29	3.78 ± 0.16	0.49 ± 0.11	<LOD^{b}
Hubertus (Zn)	Zn	30.48 ± 1.79	**55.71 ± 3.75**	4.83 ± 0.15	0.69 ± 0.10	<LOQ
Silver (Pb)	Ni	**1.34 ± 0.19**	0.52 ± 0.02	0.31 ± 0.04	**1.20 ± 0.23**	<LOQ
Sweet Copper (Cu)	Cu	4.11 ± 0.37	**5.92 ± 0.27**	**6.35 ± 0.10**	<LOQ	<LOQ
Ultimate (W)	Sn	<LOQ	<LOD	<LOD	**1.23 ± 0.07**	0.65 ± 0.08

LOQ: Limit of quantification; LOD: limit of detection; bold values indicate homogeneous subsets with the significant highest concentrations among the tested environments determined by ANOVA. Grey shading represents those values that exceeded the EC_{50} for *Daphnia magna* according to Khangarot and Ray [15]

the shot types *Steel Game* and *Steel Shot*, was highest in the siliceous environment, showing decreasing concentrations with increasing exposure time. These two shots also leached quantifiable Mn concentrations, which were greatest in the siliceous aerobic media. The W-based shot *Ultimate* only caused quantifiable Sn leaching when exposed to an anaerobic environment. Owing to its weak and unspecified metal leaching (measured Fe concentrations only after 22 days of exposure in the calcareous anaerobic variant), the shot type *Alphamax* could not be associated with quantifiable Bi release or to the release of other potentially toxic metals relevant to the aquatic environment.

Comparison with the standardized ADaM solution

Over the short term, ADaM and the siliceous aerobic treatment resulted in the highest levels of Pb leaching for the conventional Pb shot *PL 34*; however, during long-term exposure, this changed to dominant Pb release solely in the siliceous aerobic treatment (Table 3). The marked Zn leaching from *Blind Side* and *Hubertus* was highest in ADaM (short term: 13.39 and 33.79 µmol/L, respectively; long term: 34.70 and 30.48 µmol/L, respectively) and the siliceous aerobic solutions (short term: 11.82 and 29.99 µmol/L, respectively; long term: 24.82 and 55.71 µmol/L, respectively). In addition, the Fe-based shot *Blind Side* released very low (but quantifiable) concentrations of Cr (0.10 µmol/L) in the two siliceous treatments over the long term. Nickel leaching from the coated Pb shot *Silver* reached its highest value either in the ADaM media (long term: 1.34 µmol/L) or in the siliceous anaerobic environment (short term: 1.56 µmol/L). The highest levels of Cu leaching from *Sweet Copper* were measured in the following three solutions: ADaM (short term: 1.91 µmol/L), siliceous aerobic (short term: 3.53 µmol/L; long term: 5.92 µmol/L) and calcareous aerobic (short term: 2.63 µmol/L; long term: 6.35 µmol/L). Among these, the siliceous aerobic variant always contained the highest concentrations during both terms. Heavy metal leaching from the W shot *Ultimate* was quantifiable for Sn in the anaerobic environments only (up to 1.23 µmol/L). Both in the short-term and the long-term period EC_{50}-values for *Daphnia magna* were exceeded by the metal leaching of Blind Side (Zn) and

Hubertus (Zn) in ADaM as well as in the siliceous aerobic environment and for Sweet Copper (Cu) also in the calcareous aerobic variant.

Discussion

Justification for the study

Since the Daphnia test described by Fäth et al. [7] only considered metal leaching in a single standardized but artificial solution, we investigated two natural waters to validate this game shot adapted and comparative approach. This is an important step forward in providing comprehensive test procedures for assessing the potential ecological impact of shot, which has already been claimed by ecologists [42, 43]. Despite the great variety of geological substrates, we minimized the treatments to two extrema of spring water, rising from siliceous and calcareous bedrock. The manipulated oxygen content, which differs between standing and running waterbodies, provides an additional environmental factor. The additional application of sediments and organic compounds was not possible because of the high number of potential treatments that would result. Furthermore, waters with low pH, e.g., sump water, could not be addressed in this study and have to be investigated soon. Nevertheless, a direct impact of different geologies and redox conditions on the leaching behavior of the shot materials in water could be significantly detected.

Patterns of metal leaching

As expected, the uncoated Pb-based shots *Waidmannsheil*, *Special* and *PL 34* released quantifiable amounts of Pb, Sb and As. The lower Pb leaching rate under the calcareous aerobic environment probably resulted from surface passivation, through the formation of insoluble lead oxide or lead carbonate around the shot pellet because of a relatively high pH value of the water [25]. Furthermore, the N_2-flushed treatments might have induced resistance against dissolution of the metallic Pb (electrochemical immunity). By contrast, releases of Sb and As were highest in the calcareous treatments, which is in line with recent studies [8, 17, 38]) and should be considered in dolomite or limestone environments. The coated Pb shot *Silver* leached only low concentrations of Ni in patterns comparable to those of Pb release, probably resulting from similar electrochemical processes (as mentioned above). As discussed by Fäth et al. [7], Ni originated from the coating. With respect to its metal ion release, *Blind Side* did not resemble a classical Fe-based shot but was rather similar to the pure Zn shot *Hubertus*. As result of the alkaline pH range (> 8.5), which causes surface passivation or immunity of metallic Zn against dissolution in water [26, 44], high loadings of dissolved Zn can be released to the aquatic environment (up to 55,71 µmol/L; Table 3) particularly in waters rising from siliceous bedrock. With a concentration of up to 6.4 µmol/L, Cu leaching of *Sweet Copper* exceeded the EC_{50} values in all aerobic environments and both exposure periods, posing a potential hazard to these waters. The comparatively moderate Fe-(maximum: 3.0 µmol/L) and Mn-leaching rates (maximum: 1.5 µmol/L) of *Steel Game* and *Steel Shot* should not be considered a real threat to the aquatic environment, since the effect concentrations for relevant organisms (EC_{50} for *Daphnia magna* of Fe: 129 µmol/L and Mn: 151 µmol/L; [15]) are relatively high. Therefore, consideration of these two elements in such a leaching test is not deemed necessary. A similarly low leaching potential was observed for the W-based shot *Ultimate*, only releasing small amounts of Sn in anaerobic environments, which is almost negligible considering the relatively low risk of < 1.2 µmol Sn/L to the environment (EC_{50} for *Daphnia magna*: 182 µmol/L). Owing to the corrosion-resistant properties of metallic Sn [3, 23], rapid surface passivation may be the reason for the nonquantifiable amounts of dissolved Sn in the aerobic treatments.

Ecotoxicological game shot assessment

The distinctly higher leaching rates of the three uncoated Pb-based shot types (up to 10.3 µmol/L; Fig. 3a) in the siliceous aerobic environment as compared with ADaM (Table 3), however, did not exceed the EC_{50} Pb-threshold for *Daphnia magna* (17 µmol/L). With regard to the coated Pb shot *Silver*, which released Ni instead of Pb, it is noted that Ni should also be avoided in game ammunition because of its carcinogenic effects on wildlife when present in living tissue [41]. Since the shot coating of *Silver* may be damaged during firing, additional leaching of Pb should be expected in reality. Despite the coating a Pb intoxication of waterfowl [10, 12, 13, 24] has to be assumed as a result of grinding activities and the very acidic environment in their gizzard [37]. Therefore, with respect to the avifauna Pb in game shot should be avoided. This is even more important because additional Pb alloy components (e.g., Sb and As) can potentially be leached in alkaline environments.

According to our results, pure Zn shot (*Hubertus*) and Zn-based coatings (*Blind Side*) cause hazardous loadings of dissolved Zn that exceeded the EC_{50}-values for *Daphnia magna* by far (Table 3). Furthermore, Zn should be prevented as a component of shot materials for use in hunting since there is a high hazard potential to aquatic [7] and terrestrial environments [8] as well as to avian species [20, 21]. The measured concentrations in the aerobic environments containing the *Sweet Copper* shot were also very critical since they were at least as high as the Cu concentrations measured in ADaM, which resulted in

100% mortality of daphnids [7]. The high toxicity of Cu to aquatic wildlife is well known [1, 15, 29, 39, 47]. Pure Cu must therefore not be used in game shot, which is mainly emitted to wetlands. Furthermore, the admixing of Cu-coated Pb pellets to pure Cu shot in *FOB Sweet Copper* cartridges (which may be considered a consumer fraud) emphasizes the need for legal regulation of game shot materials. Despite the negligible Fe and Mn leaching from *Steel Game* and *Steel Shot*, Fe-based shot must not automatically be regarded as nontoxic. The presence of a potentially toxic coating should be evaluated before classifying an Fe-based shot as non-harmful, as underlined by the high Zn leaching from *Blind Side*, which led to a similar risk as that of the pure Zn shot *Hubertus*. In relation to the likely low risk of leached Sn to aquatic systems from the shot type *Ultimate*, assessing the element content of this W-based alloy is crucial. Since this shot contains up to 10% Ni (S1), probably resulting in carcinogenic effects on wildlife with shot present in their tissue [41], this kind of alloy should be viewed as critical. However, from an ecotoxicological point of view, Sn seems to be a suitable substitute for Pb in game shot because of its corrosion-resistant properties. The nonquantifiable metal release of the Bi-based shot type *Alphamax* suggests little risk to aquatic biota (also see [7]).

Need for obligatory standardized test methods

According to our results, a general toxicity screening for conventional and alternative game shot should be adopted in the EU. For this purpose, defined methods must be conducted under standardized conditions to guarantee that the impact of metal leaching on aquatic and terrestrial ecosystems is as low as possible. Furthermore, already established methods for testing the toxicity of shot materials for birds, e.g., according to Kimball and Munir [16] which is also implemented in the USFWS [46] protocol, should be adopted in Europe. The study of Fäth et al. [7], however, delivered a reliable proof of concept to investigate metal leaching from game shot in aquatic environments, combined with a first orienting assessment of potential ecotoxicological impacts on this ecosystems. Although the pH of ADaM is quite similar to that of the calcareous spring water investigated in this study, it caused high leaching rates that were similar to the siliceous aerobic treatment, except for the case of Pb. This was likely a result of the high ionic strength, resulting from the artificial composites ($CaCl_2$, $NaHCO_3$, SeO_2, synthetic sea salt) in this standardized medium. Currently, the German Institute for Standardization develops methods for testing the minimum requirements for the killing effect of hunting rifle bullets [5], serving as a guideline for respective manufacturers, which could possibly be advanced to a European standard. In analogy to this, a related guideline could be implemented to assess the leaching of potentially hazardous metals from game shot in aquatic systems. Since the properties of natural waters are not reproducible, we suggest the ADaM solution and a flushing of the cups with precleaned air as a standardized worst-case simulation for the aquatic environment. Regarding the broad availability of EC_{50}-values for *Daphnia magna* [15, 31], it is sufficient to evaluate the leached metal concentrations using these literature thresholds without conducting a real toxicity test. By providing chemical compositional standards for alternatives to Pb, which were inter alia derived from the extremely complex USFWS [46] test protocol, Thomas [42] recently argued for a quite simple screening of alternative game shot materials. With regard to the detected Cu-coated Pb pellets in the *FOB Sweet Copper* cartridge, this would be a first step to a legal regulation of Pb substitutes in Europe. Nevertheless, the procedures according to USFWS [46] neglect marginally contained elements such as the Zn coating (thickness: up to 3 µm; S1) of the Fe-based shot *Blind Side*. This small amount (maximum 0.33% mass fraction) would not exceed the suggested 1% limit for Zn but dominates the leaching of toxic ions, resulting in 100% mortality of *Daphnia magna* [7]. By conducting standardized leaching tests, the risks of each game shot material for terrestrial and aquatic habitats could be comprehensively assessed, including the effects caused by coatings. Furthermore, the toxicity of European game shot materials to avian species also has to be controlled.

Conclusions

According to the leaching tests, Cu- and Zn-based as well as Zn-coated gunshot should be hampered by reason of the high risks they pose to the aquatic environment. Referring to other recently published studies (see chapter 4.3), the use of Pb-based and Ni-alloyed or -coated game shot also should be avoided owing to their impact on birds or other wildlife. In our leaching tests, the different water conditions (geology/redox conditions) caused marked differences in the amounts of leached metals among the examined shot types. The natural spring water from siliceous bedrock under aerobic conditions showed the highest concentrations for all alternative metals among the four treatments that were quite similar to the results of the former study using a standardized medium. We therefore suggest the use of the reproducible ADaM solution for future game shot adapted leaching tests to yield a standardizable worst-case scenario. In addition to the total chemical composition, this method could serve as a further test for conducting initial ecotoxicological risk assessments of game shot materials for aquatic systems. As shown by our leaching tests, other minor components like coatings are of great importance for the environmental impact of game shot.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s12302-019-0249-2.

Additional file 1: Data S1. Element content [%] of the investigated game shot materials and thickness of a coating provided by RUAG Ammotec GmbH after disassembling all selected cartridges. Since the cartridges of *FOB Sweet Copper* contained pure Cu- and Cu-coated Pb pellets, the content is presented for the two shot types of this cartridge.

Abbreviations

ADaM: "Aachener Daphnien Medium"; Alphamax: Eley Bismuth Alphamax; As: arsenic; Bi: bismuth; Blind Side: Winchester Blind Side; Cr: chromium; Cu: copper; EC_{50}: half maximal effective concentration; ECHA: European Chemicals Agency; EU: European Union; Fe: iron; Hubertus: SK Hubertus Zink; ICP-AES: inductively coupled plasma atomic emission spectrometry; LOD: limit of detection; LOQ: limit of quantification; Mn: manganese; Ni: nickel; OECD: Organization for Economic Cooperation and Development; Pb: lead; PL 34: Fiocchi PL 34; Sb: antimony; Silver: Rottweil Silver Selection; Sn: tin; Special: Rottweil Special 36; Steel Game: Rottweil Steel Game; Steel Shot: Fiocchi Steel Shot; Sweet Copper: FOB Sweet Copper; Ultimate: Rottweil Ultimate; W: tungsten; Waidmannsheil: Rottweil Waidmannsheil.

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Authors' contributions

JF performed the experiments, was involved in the conception, design, analysis and interpretation of the data and wrote the paper. AG headed the study, made substantial contributions to the conception, design, analysis and interpretation of the data, and substantially improved the manuscript. Both authors read and approved the final manuscript.

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Availability of data and materials

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

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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