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Julian Fäth

Zentrum Wald Forst Holz Weihenstephan
Hans-Carl-von-Carlowitz-Platz 1
85354 Freising

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Preface

This thesis discusses the results of several sub-studies which aim to facilitate a comparative analysis of conventional and alternative shotgun ammunition materials with regard to their ecotoxicological impacts in different ecosystems and their ballistic performance in hunting through the development of standardized testing procedures.

Due to the controversial nature of this topic at both national and international levels, considerable emphasis was placed on presenting the results of this thesis to the professional public in the form of peer-reviewed journal articles (Fäth et al. 2018a; Fäth et al. 2018b; Fäth & Göttlein 2017; Fäth & Göttlein 2019; Fäth et al. 2020) and a conference paper (Fäth & Göttlein 2018). Due to the thematic relevance of this research throughout Germany and Europe, the process was carried out in the form of English and German texts. The latter approach is important because this work partially deals with German standards that are presumably unknown and/or inapplicable in the English-speaking community. Due to the multidisciplinary nature of this thesis, the “Results and Discussion” section was summarized by integrating the results from tables and figures from previous publications. In addition to the above-written publications, other publications (Fäth et al. 2019a, b) that were produced in parallel to this thesis were also included in the discussion.

Project partners for this joint project included the Bavarian Hunting Association (Bayerischer Landesjagdverband e.V.), the Federal Institute of Higher Technical Education and Research (Höhere Technische Bundeslehr- und Versuchsanstalt – EUREGIO HTBLVA Ferlach), the Statistical Consulting Laboratory StaBLab at the Institute of Statistics at the Ludwig Maximilian University of Munich, RUAG Ammotec GmbH, and the Chairs of the Aquatic Systems Biology Department and the Forest Nutrition and Water Balance Department at the Technical University of Munich.

The chemical analyses required for the elution- and bioassays were kindly funded by the Bavarian Ministry of Food, Agriculture and Forestry from the State Hunting Tax. RUAG Ammotec GmbH provided the ammunition and firearm components required for this project as well as the experimental set-ups and premises needed for firing. All other costs were borne by the Associate Professorship of Forest Nutrition and Water Balance at the Technical University of Munich. All further contributions by the above-written project partners can be found in the corresponding chapters of this thesis.

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List of Abbreviations

µmol	Micromole (10^{-6} mole)
Alphamax	Eley Bismuth Alphamax
As	Arsenic
BBodSchV	Federal Soil Protection and Contaminated Sites Ordinance
Bi	Bismuth
BiCarb	Bicarbonate pH8
C.I.P.	Permanent International Commission for the Proof of Small Arms
approx.	approximately
Citro	Citric acid pH4
Cr	Chromium
Cu	Copper
$Deckung_{Energie}$	Number of segments covered by energy on a 16-panel target
$Deckung_{Treffer}$	Number of segments covered by the number of hits on the 16-panel target
DepVerwV	Landfill Utilization Ordinance
DEVA	German Experimental and Testing Institute for Hunting and Sporting Arms
DIN	German Institute for Standardization
EC_{50}	Half maximal effective concentration
ECHA	European Chemicals Agency
Fe	Iron
GPa	Gigapascal
Hubertus	SK Hubertus zinc
Mn	Manganese
Ni	Nickel
nmol	Nanomole (10^{-9} mole)
OECD	Organization for Economic Cooperation and Development
Pb	Lead
PL 34	Fiocchi PL 34
RUAG-Sn	Lead shotgun shell with tin coating
Sb	Antimony
Silver	RWS 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
esp.	especially
W	Tungsten
Waidmannsheil	Rottweil Waidmannsheil
e.g.	for example
Zn	Zinc

Abstract in German

Aufgrund der toxischen Wirkung von Bleimunition auf Greife und Wasservögel ist dessen Verbot sowohl auf nationaler als auch internationaler Ebene ein ständig brisantes Thema. Auf dem europäischen bzw. deutschen Markt für Jagdschrot sind daher inzwischen vielfältige Alternativmaterialien wie z.B. Werkstoffverbindungen oder Legierungen aus Zink, Kupfer, Wismut, Eisen und Wolfram erhältlich. Jedoch sind diese Alternativen besonders im Hinblick auf die zur waidgerechten Jagd notwendige Tötungswirkung sowie ihre Auswirkungen in der Umwelt bislang wenig untersucht. In vorliegender Thesis wurden standardisierte Verfahren zur Untersuchung des Elutionsverhaltens von Schrot in der Umwelt sowie dessen zielballistische Leistung erarbeitet und auf ein Kollektiv, bestehend aus marktrelevanten Schrotmaterialien bzw. –laborierungen, angewandt. Als Ergebnis der Elutionsversuche und Biotests sind Schrote, die Zink oder Kupfer freisetzen, hinsichtlich ihrer ökotoxikologischen Wirkung im aquatischen Bereich als kritisch einzustufen. Konventionelle und beschichtete Bleischrote sowie der Wolfram- und Wismutschrot sorgten hingegen weder für eine Überschreitung der mittleren effektiven Konzentration noch für eine signifikant erhöhte Mortalität des untersuchten Schlüsselorganismus *Daphnia magna*. Für terrestrische Systeme konnten lediglich zwei von drei untersuchten Eisenschroten sowie ein Wismutschrot als unbedenklich bewertet werden. Weiterhin wiesen im Rahmen der zielballistischen Untersuchung alle drei getesteten Eisenschrote aufgrund einer unzureichenden Kornenergie Mängel bei einer Schussentfernung von 35 m auf. Im Rahmen dieser Untersuchung wurde zudem bei einer ohnehin schon größtenteils negativ bewerteten Kupferschrotpatrone eine potenzielle Gefährdung im Jagdbetrieb festgestellt. Im Zuge einer umfassenden Bewertung anhand von aus der Literataur entnommenen bzw. abgeleiteten Grenzwerten gab es unter den untersuchten Jagdschrotpatronen keine Alternative, welche hinsichtlich jedem der untersuchten Aspekte als vollkommen unkritisch zu betrachten ist. Zudem wurde festgestellt, dass die pauschale Bewertung der Wirkung in der Umwelt und der Tötungswirkung von Schrotmunition über die Hauptkomponente des verwendeten Materials, wie z.B. Eisen, nicht möglich ist. Stattdessen müssen diesbezüglich Eigenschaften, wie zum Beispiel eine ausreichende zielballistische Leistung oder die reduzierte Freisetzung toxischer Metalle festgelegt werden. Diese könnten durch die Anwendung der in vorliegender Arbeit dargestellten Verfahren getestet und durch bereits bestehende Simulationsmethoden zur Untersuchung der Aspekte Vogeltoxizität und Wildbrethygiene/Humantoxikologie ergänzt werden. Da hierbei verschiedene, bei der Jagd vorkommende Einflussfaktoren (Waffenkonfiguration, Schussdistanz, Einsatzgebiete) berücksichtigt würden, könnten zusätzlich patronenspezifische Verwendungsempfehlungen abgeleitet werden. Dies konnte zumindest für die in dieser Thesis untersuchten Aspekte „Ökotoxikologie – terrestrische Systeme“, „Ökotoxikologie – aquatische Systeme“ und „Zielballistik“ gezeigt werden. Durch die Einführung eines verpflichtenden, multikriteriellen Bewertungsprozesses für jede auf dem Markt befindliche Schrotmunition würden sich zudem Entscheidungen und Diskussionen über das Verbot bestimmter Materialgruppen komplett erübrigen.

Abstract in English

Due to toxic effects of lead ammunition on birds of prey and waterfowl, its ban is a constantly hot topic on both a national and international level. Consequently, there is a great variety of alternative materials for gunshot on the German and European market, e.g. material compounds or alloys made of zinc, copper, bismuth, iron and tungsten. However, these have been marginally investigated yet, especially with regard to their killing effect on game and their impact on the environment. Therefore, standardized test procedures for examining the leaching behavior of shot in the environment and its target ballistic performance were developed under defined conditions and applied to a collective of market-relevant shot materials and cartridges. As a result of the leaching tests and bioassays, game shots leaching zinc or copper are classified as critical in terms of their ecotoxicological impact in aquatic ecosystems. In contrast, conventional and coated lead shot, as well as tungsten and bismuth, neither caused values exceeding the mean effective concentration nor significantly increased mortality of the key organism *Daphnia magna*. For terrestrial systems only two out of three examined steel shots and one bismuth shot could be rated as harmless. As part of the target ballistic investigation, all three iron shots showed defects at a distance of 35 m due to insufficient grain energy. Furthermore, a copper shot cartridge, which was assessed as critical in most of the shooting scenarios, was identified as potential dangerous considering hunting safety. After a comprehensive assessment based on threshold values, that were taken or derived from literature, there was no alternative catrtridge showing absolutely no negative impact on all aspects investigated in this thesis. Furthermore, it was found that a generalized assessment of the environmental impact or killing effect of shot ammunition via the main material component, e.g. iron, is not possible. Properties such as sufficient target ballistic performance or the reduced release of toxic metals have to be defined, instead. These could be tested by establishing the standardized test methods shown in this thesis and supplemented by already existing simulation methods to investigate additional important aspects such as bird toxicity and game meat hygiene/human toxicology. Since various influencing variables, such as weapon configuration, shooting distance, or different areas of deployment could be taken into account, cartridge-related recommendations of application could be derived. This could be demonstrated at least for the aspects “ecotoxicology - terrestrial systems”, “ecotoxicology - aquatic systems” and “target ballistics” examined in this thesis. The introduction of a mandatory, multi-criteria evaluation process for every game shot ammunition on the market would also make decisions and discussions about the ban of certain material groups completely unnecessary.

1. Background and current state of knowledge

1.1. Lead in the environment

The input of heavy metals in our environment poses a significant problem in many areas. These kinds of metals can enter the food chain directly via absorption or ingestion by plants or animals and often have a toxic effect upon them – even at low concentrations (Calmano 1989). Due to several sources of exposure, as well as accumulation potential in the tissues of organisms (Spehar et al. 1978; Vinodhini and Narayanan 2008), lead (Pb) is considered an environmentally, toxicologically relevant heavy metal (Guderian 2013), which is why its use in industry has been severely restricted (Nriagu 1996) over the years. On the one hand, these restrictions have been put into place through complete material substitutions, such as that of tetraethyl lead as an anti-knock agent in gasoline or lead white in paints (Markowitz & Rosner 2000). On the other hand, lead content in certain materials such as tin (Sn) and solder was reduced by the EU Directive 2011/65/EU to a value that only corresponds to a technical impurity. As a result of bans and restrictions, this element has become increasingly less important in industry over the past few decades (Guderian 2013), while the environmental relevance of other, previously less important sources of lead contamination has consequently increased at the same time. These industries include hunting, which is now considered one of the main sources of Pb release into the environment in industrialized countries (Jørgensen and Willems, 1987; Ma 1989). According to the European Chemicals Agency (ECHA), the use of shotgun ammunition alone is estimated to release 5,000 tons of Pb into wetlands and 14,000 tons into terrestrial environments, which is why this institution is calling for an EU-wide ban on lead in rifle and shotgun ammunition (ECHA 2018).

Despite the relatively low initial ecotoxicological risk of metallic Pb, there is a risk that some of the emitted heavy metal can be released into and spread throughout the environment through natural processes or conditions. This can occur, for example, as a result of oral ingestion by wildlife, as well as through the release of ions (elution behavior) when they accumulate in soil or water. For example, numerous studies have found that birds of prey can suffer fatal intoxication as a result of the dietary ingestion of lead-contaminated offal in the wild and the resulting lead released in their digestive tract (Pain and Amiardtriquet 1993; Kenntner et al. 2001; Müller et al. 2007; Krone et al. 2009). Furthermore, waterfowl have also been known to ingest shot pellets that lands on the bottom of waterbodies instead of grindstones while they are burrowing and may die as a result of lead poisoning (Pain et al. 2019; Mateo & Kanstrup 2019). Due to the potential consequences of Pb released into the environment as just mentioned, its use in hunting should be reduced as much as possible.

1.2. Possible problems caused by the banning of lead in hunting

Because of its toxic effects on waterfowl, Pb has been banned from hunting with shotgun shells in and around wetlands in several US-American states since 1991 (Thomas & Guitart 2003). Today, there are also Pb bans on the use of rifle ammunition (e.g., in the U.S. state of California as well as in several German states) to minimize lead discharge caused by hunting. Due to this current development, numerous alternative materials for hunting ammunition have become available on the market (Table 1).

Table 1: *Alternative materials for hunting ammunition according to Schwarz et al. (2015), Fäth & Göttlein (2015) and Thomas (2019).*

Rifle bullets	Shot pellets
Copper	Bismuth
Copper-zinc alloys	Iron
Tin	Copper
	Nickel
	Tungsten
	Zinc
	Tin

The suitability of these alternatives has been investigated in various studies, e.g., by the German Experimental and Testing Institute for Hunting and Sporting Arms (DEVA 2011) and Kneubuehl (2011), in which exposure from ricocheted lead-free hunting rifle bullets was compared with those containing lead. In this comparison, lead-free bullets had a significantly higher mass and energy level than bullets containing lead. Furthermore, lead-free bullets exhibited a significantly higher range after rebound, which means that hunting safety is less guaranteed when using lead-free solid bullets made of copper (Cu) and copper alloys than with variants containing lead. In response to higher gas pressure (Zeitler 2012) when firing lead-free rifle cartridges, as well as for the comparative investigation of system compatibility, a study was also conducted to investigate the force required to press lead and lead-free bullets through rifle barrel sections (Ettl et al. 2017). Due to the significant variation between the energy curves within the lead-free bullet variants, it was not possible to make a general statement about the system compatibility of lead-free bullets or bullets containing lead. Nevertheless, some Cu-based projectiles were found to have alarmingly high energy peaks, and some of the tests had to be terminated early due to excessive stress being applied to the test setup. Furthermore, a study (Schwarz et al. 2015) on the elution behavior of conventional and alternative hunting rifle bullets in a low-sorption soil surrogate found that some alternatives provided less soil contamination in the environment than lead bullets. However, other bullet designs were found to be at least as critically hazardous as Pb-based bullets, particularly because of the release of large amounts of up to three different heavy metals. Moreover, some bullets that were labeled as ‘lead-free’ released alarming amounts of Pb, the cause being lead-contaminated Sn or lead contents of up to 3.5% in brass.

These high Pb levels in alternative materials, which, in some cases, can lead to a higher release of Pb than with conventional bullets (Schwarz et al. 2015), seriously call into question the current legal situation regarding the use of hunting ammunition in Germany, as well as the controllability of current Pb bans in hunting. In terms of an “environmental deterioration ban” (analogous to Durner 2019), it should be ensured that no permissible alternative material results in a higher risk than lead ammunition. For this reason, direct regulation of hunting ammunition would make sense, i.e., new products could be subjected to an approval process before they enter the market. According to Schwarz et al. (2015), the following five aspects would have to be considered for a comprehensive assessment of hunting ammunition:

- Killing effect
- Ecotoxicology
- Game meat hygiene/human toxicology
- Hunting safety
- System compatibility[1]

[1] In this thesis, the term 'system compatibility' means the compatibility between a weapon and its ammunition.

1.3. Importance of standardized evaluation procedures

Currently, the German Institute for Standardization is developing a standardized procedure for the comparative evaluation of the lethal effect of hunting rifle bullets (DIN 2017). Taking into account different shooting distances relevant to hunting, as well as different game sizes, the specification to be developed (DIN SPEC 91384) will be used to test minimum requirements in order to ensure the killing of hoofed game in a manner appropriate to animal welfare. The focus here is on the reproducibility of the method, which is why the implementation of field tests, such as those according to Martin et al. (2017), cannot be considered for such an assessment. The necessity of introducing standardized methods for the comparative evaluation of alternative hunting ammunition has already been demonstrated by Schwarz et al. (2015) using the example of a comparative evaluation of metal ions released from rifle bullet material. Due to the different material composition of hunting rifle projectiles (core, jacket, possible coating/plating), as well as different electrochemical processes, no comparative conclusion on their environmental impact can be made without a standardized method for the elution behavior of projectile materials. For a comprehensive evaluation of rifle ammunition, a standardization process would, therefore, also make sense for this aspect. Game meat hygiene should also be taken into account in the course of an assessment of the risk of contamination by conventional and, above all, alternative hunting ammunition. There are already some studies on this topic (Schlichting et al. 2017; Gerofke et al. 2018; Martin et al. 2019; Trinogga 2019), which might be included in a standardization process for rifle ammunition.

With reference to the issues mentioned by Schwarz et al. (2015) for the assessment of hunting ammunition (cf. chapter 1.2), it can be clearly stated that there has been a focus on the assessment of hunting rifle bullets in the German-speaking community, whereas shotgun ammunition has received little attention so far. In particular, the ecological relevance of a shotgun shell is significantly higher than that of rifle ammunition (10.5 g per cartridge) due to a higher mass of approx. 36 g, as well as the considerably larger exposed surface area owing to the numerous shotgun shells per cartridge that are emitted into the environment.

Due to the clear lack of knowledge about this ecologically complex and problematic type of hunting ammunition, this thesis will focus on shotgun ammunition. In the following chapter, the current state of knowledge on conventional and alternative shotgun ammunition will be presented and the most important knowledge deficits for each relevant aspect will be elaborated upon, from which the objectives of this thesis will ultimately be derived.

1.4. Aspects of evaluating conventional and alternative shotgun ammunition

1.4.1. System compatibility

As members of the Permanent International Commission for the Testing of Small Arms (C.I.P.), a number of EU countries have signed international treaties committing themselves to binding compliance with a set of rules for safety-relevant testing characteristics and the mutual recognition of certification labels for hunting ammunition. The Federal Republic of Germany is a member of the C.I.P., which ensures the aspect of system compatibility by means of gas pressure tests and specifications of minimum and maximum dimensions for cartridges and cartridge magazines. Therefore, no civilian weapons or ammunition may be placed on the market from or into the area of application of the C.I.P. member states that have not been tested for this set of regulations by official firearms offices (Lampel & Seitz 1983; Böck 2018). In addition, with regard to harder materials, such as steel shells, there is an extended set of rules (C.I.P. 2014), which restricts permissible velocity, maximum muzzle impulse, and choke diameter depending on the diameter of the shell used. This is intended to prevent possible hazards from harder gunshot materials. In addition to cartridge-specific characteristics, a prerequisite for the permissible use of lead-free shells is a weapon with a certification stamp in the form of a lily, which demonstrates their compatibility with harder materials. These requirements for lead-free shotgun shells are specified in Resolution Document XXXII-45 under the C.I.P. (2014), describing required standardized methods for measuring the hardness and deflection properties of lead-free shotgun materials.

Due to the C. I. P.'s highly normative character on a national and international level, the aspect of system compatibility of lead-free shotgun shells is therefore largely addressed by the application of standardized test methods.

1.4.2. Hunting safety

To determine the risks posed by alternative shotgun materials, DEVA determined several relevant parameters, such as residual mass, exit velocity and exit angle of conventional and alternative shotgun shells by firing on various types of material (tree trunks, wooden sticks, stone plates, hard and soft soil, and water) (DEVA 2013; Kneubuehl 2013). Similar to Ettl et al. (2017), there were no significant differences between lead-based and lead-free shells due to the high variance of values within the lead-free group. Nevertheless, Fe and W shot showed significant rebound in some cases when firing vertically at stone plates. The shells made of Pb, bismuth (Bi) and zinc, on the other hand, did not appear to cause any hazards due to rebound. With regard to the shear modulus (deformability) as an indicator of the ability to release energy by deformation (reduction of residual energy), these results are consistent with the properties of the materials studied. For example, Pb, Bi, Cu, Sn and zinc (Zn) have a shear modulus of up to 50 giga-pascals (GPa), while those of Fe and W are significantly higher, with values of 82 and 161 GPa, respectively (Forsythe &Worthing 1925; Kaye & Laby 1993).

Consequently, a restriction on the use of some shotgun shell types would be required; or the hazard area would have to be defined on a shotgun shell type-specific basis.

1.4.3. game meat hygiene and human toxicology

Knowledgeable hunters have the right to market game meat obtained from hunting not only for their own consumption but also for re-sale purposes. Since, in contrast to meat produced from livestock, there is no Pb limit for game meat in Germany, the possibility of Pb contamination of game meat must also be taken into account when evaluating hunting ammunition. It has also been shown that, for game killed with lead-based shotgun ammunition, frequent consumers of waterfowl are exposed to an increased risk of Pb ingestion (Tsuji et al. 1999; Johansen et al. 2004). This can lead to significantly elevated Pb concentrations in blood levels within this group of consumers (Johansen et al. 2006; Tsuji et al. 2008), which can cause central nervous system disorders in children or newborns (in the case of maternal consumption of game) (Lanphear et al. 2000; Canfield et al. 2003; Deutch 2003; Chiodo et al. 2004). For this reason, it is recommended that pregnant women and young children reduce consumption of game killed with lead-based ammunition to no more than once per month (Knutsen et al. 2014). This recommendation comes along with, however, the irrelevance of increased lead contamination in game for an average meat consumer eating respective meat once or twice per year, as explained by Gerofke et al. (2018). Even though frequent consumers (especially those in hunter households), who are exposed to an increased probability of ingesting Pb-contaminated game meat, represent only a very small proportion of the German population (Gerofke et al. 2018), they should nevertheless not be discounted.

However, there are also concerns regarding some alternative materials. For example, according to Tsuji & Nieboer (1997), Bi is considered a concern as well. Furthermore, Bi shells can contain up to 0.68% Pb (Kanstrup et al. 2019), which may be one of the reasons for the concern identified by Tsuji & Nieboer (1997). Furthermore, comparative studies simulating the elution behavior of lead-free hunting rifle bullets in game meat (Paulsen et al. 2015; Paulsen & Sager 2017) revealed that nickel (Ni) is also a concerning alternative material in terms of human toxicological aspects, while Sn is considered harmless. Schlichting et al. (2017) further demonstrated that shotgun shells for game with alternative hunting bullets (e.g., bullets made of Cu or Cu-Zn alloys) posed no risk for human consumption due to excessively high Cu or Zn levels in the meat. Overall, Fe also appears to be a reasonable alternative from a human toxicological point of view (Tsuji & Nieboer 1997), although the alloy components must also be taken into account here. Levonmäki and Kairesalo (2001) also studied iron shells containing up to 27% chromium (Cr). The toxicological risks of this heavy metal, in particular the carcinogenic effect of Cr(VI), are well known (Freeman 1997; IARC 1990; Urbano 2008). Therefore, Cr in such proportions must not be present under any circumstances in iron shotgun shells, which is currently considered to be harmless. W is also a sought-after Pb substitute in bullets, considered non-toxic, due to its outstanding inertness (Heumann & Stolica 1971; Ducros et al. 1999) (Thomas 2019). However, W has not been widely studied with respect to its human toxicological effects, especially in dissolved form. In medicine, this metal is now discouraged as an implant component because dissolved W ions can be toxic or carcinogenic to humans (Idil & Donaldson 2018; VanderSchee et al. 2018; Kalinich et al. 2005).

This example in particular illustrates how important elution tests are for a toxicological evaluation, especially in the case of alternative materials such as W, which have not been largely researched to date. Only by understanding the leaching behavior in a specific environment (meat; digestive tract) it is possible to estimate the effect on human beings through consumption. In order to consider the aspect of “game meat hygiene and human toxicology” in the evaluation of shotgun ammunition, it would be quite possible for a standardized test method to be based on the comparative study according to Paulsen et al. (2015). Hereby, the elements Cu, Zn, Ni, Fe, Sn (Schlichting et al. 2017; Paulsen et al. 2015; Paulsen & Sager 2017) and Bi (Tsuji & Nieboer 1997) discussed in the example of rifle bullets would also have to be re-verified for shotgun shells..

1.4.4. Ecotoxicology

1.4.4.1. Avifauna

The toxic effect of Pb on birds in water bodies must also be taken into account as an original reason for banning Pb in hunting ammunition (cf. Chapter 1.1). In particular, the accidental ingestion of shotgun pellets from the bottom of water bodies can result in severe lead poisoning, often with fatal consequences. The toxic effect of Pb on this class of vertebrates was first published in the 19th century (Fuchs 1842), and numerous studies have been conducted to date, particularly on the acute toxic effects of lead-based shot material in birds. Among other things, large-scale comparative test studies were carried out with mallard ducks (*Anas platyrhynchos*), in which they were administered different shotgun ammunition materials. The differences shown in Table 2 are based on the determination of the mortality rates of *Anas platyrhynchos* determined after the end of the experiment, which were statistically compared to a control group in each study. These were supplemented by results from other studies (right column) that used only one material or no control or another bird species.

Table 2: *Overview of the mortality of Anas platyrhynchos (mallards) after oral ingestion of various shot materials.*

Material	Sigificantly higher mortality	Literature containing comparative studies with *Anas platyrhynchos*	Further studies
Lead	Yes	Grandy et al. (1968), Irby et al. (1967), Locke et al. (1967), Kelly et al. (1998), Sanderson et al. (1997), Brewer et al. (2003)	
Zinc	Yes	Grandy et al. (1968)	Levengood et al. (1999, 2000)
Nickel	No	Grandy et al. (1968)	
Steel	No	Grandy et al. (1968), Irby et al. (1967), Locke et al. (1967), Kelly et al. (1998), Sanderson et al. (1997), Brewer et al. (2003)	Levengood et al. (1999, 2000)
Tin	No	Grandy et al. (1968)	
Copper	No	Irby et al. (1967); Locke et al. (1967)	Franson et al. (2012)
Tungsten	No	Kelly et al. (1998), Brewer et al. (2003)	Ringelmann et al. (1993), Mitchell et al. (2001)
Bismuth	No	Sanderson et al. (1997)	

Table 2 shows that Pb and Zn are significantly more toxic to birds than other shotgun ammunition materials. This is the main reason for current proposals to ban lead, although current knowledge suggests that Zn should also be banned. In order to identify alternative materials of such concern, standardized procedures have already been developed to investigate the toxic effects of shotgun materials on waterfowl as efficiently as possible by means of bird stomach simulations (Kimball & Munir 1971; Levengood & Skowron

2001; Thomas & McGill 2008; Martinez-Haro et al. 2009). These have been implemented in comprehensive toxicity screenings in the USA and Canada, for example (USFWS 1997), in order to comply with the ban of alternatives mentioned in Chapter 1.2. Such a procedure could therefore also be made mandatory in Germany or the EU for ammunition on the market, in particular because of the existence of zinc bullets.

1.4.4.2. Terrestrial systems

The pollution of terrestrial environmental systems (cf. Chapter 1.1) also plays an important role in the evaluation of shotgun ammunition. Soils in the vicinity of highly frequented shooting ranges are particularly affected by lead-dominated debris from hunting and sporting activities. Depending on soil conditions, heavy metals released by ammunition components can lead to severe groundwater contamination (Ampleman et al. 2003; Soeder & Miller 2003). For example, according to Soeder & Miller (2003), sites with low soil pH (affecting the release of dissolved ions from the material) and sandy soil or parent substrate (critical to the sorption capacity of the soil for dissolved heavy metals) can result in high groundwater vulnerability to Pb. Because of this, lead discharge at shooting ranges in Scandinavian countries such as Finland represents one-third of the total sources of their soil and groundwater contamination due to acidic soil conditions ($pH<5$; Salminen et al. 2005) (ECHA 2018).

However, Levonmäki and Kairesalo (2001) report that the use of iron in ammunition with a high Cr content can also result in the corresponding limit values being exceeded in soil. Moreover, in toxicity tests with soil organisms and plants conducted by Strigul et al. (2004), dissolved W also had a strong toxic effect on soil fauna and flora, which is why it would have to be investigated for the European market whether Fe- or W-based ammunition could release Cr or W under similar soil conditions. In response to the lead bans on hunting rifle bullets introduced in Germany at the state level, a study was conducted to investigate metal ions released from bullets in the environment under the development of a standardizable procedure (Schwarz et al. 2015). Due to the main use of rifle ammunition in terrestrial areas, the main focus here was on the impact zone of soil-groundwater. By evaluating the release of heavy metal ions in the soil substrate sand, which is the most unfavorable type of soil from a sorption standpoint, it was determined that, in addition to lead, alternative materials such as copper or brass should also be critically considered. The latter material also released very high amounts of dissolved Pb, which is due to the use of free-cutting brass (which may contain up to 3.5% Pb).

Furthermore, alloyed or coating materials, such as Ni and Zn, also played a role in the evaluation. Sn, on the other hand, appears to be rather unproblematic in terms of contaminating soil and groundwater due to its low solubility rates. In general, this study showed that even small amounts of different elements in bullet materials can determine their elution behavior in the environment. Analogous to Chapter 1.4.3, this repeatedly illustrates the necessity of carrying out standardized solubility tests under defined conditions.

Due to significantly higher material diversity compared to rifle bullets (Table 1), the results of a corresponding elution test for shotgun ammunition should be obligatory. Thomas & Guitart (2003) also describe the necessity of a supplementary investigation of metal elution from shotgun materials within the framework of a standardized test protocol because of the considerable relevance for plants and for organisms living in the soil. The standardized procedure according to Schwarz et al. (2015) could follow this demand relatively easy to estimate the, so far, unexplained leaching behavior of shotgun materials, especially W or Bi, in terrestrial systems. In this context, statements made about the materials Cu, Ni, Zn, Pb and Sn for shotgun shells, which have, so far, been based on experiments with rifle bullets, could also be verified.

1.4.4.3. Aquatic systems

Due to the preferred use of shotguns for hunting waterfowl, aquatic systems are also affected by the resulting release of heavy metals. In addition to intoxication through direct oral ingestion, such as in waterfowl (Chapter 1.4.4.1), there is also the risk of acute toxic effects from heavy metals that dissolve in the water. Numerous studies have already been carried out with various organisms, such as the white sturgeon (*Acipenser transmontanus*; Vardy et al. 2014) or the large water flea (*Daphnia magna*; Khangarot and Ray 1989). According to these studies, the heavy metals Zn and Cu in particular, which are relevant for shotgun ammunition, are considered to be at least as toxic as Pb in dissolved form for the organisms investigated. Furthermore, dissolved Cu has also been shown to affect reproduction and growth of fathead minnows (*Pimephales promelas*; Mount and Stephan 1969) and gene expression patterns of delta smelt (*Hypomesus transpacificus*; Connon et al. 2011). In addition, dissolved Zn may inhibit the growth of grass carp (*Ctenopharyngodon idella*; Chen et al. 2016). However, no data exists on the leaching behavior of shotgun materials in different bodies of water.

Consequently, some alternative shotgun shells may also pose a significant hazard to aquatic systems due to their predominant use in water bodies. As in the case of hunting rifle bullets (Schwarz et al. 2015), no general statement can be made about the elution behavior of shotgun shells in water bodies due to the interaction of several different alloy components (Thomas 2016). For a comparative analysis, data on the elution behavior of different shotgun materials in water bodies and the associated acute toxic effect on aquatic organisms under uniform conditions would also have to be obtained.

1.4.5. Killing effect

According to the German Animal Welfare Act (TierSchG), only hunters are allowed to kill vertebrates without prior anesthetization. Therefore, according to §4 section 1 TierSchG, it is assumed that responsible hunting is carried out in accordance with the laws of hunting. Therefore, no avoidable pain may be caused to game in the course of being killed. This means that the hunter must have the necessary knowledge and skills, whereby the latter also depends, among other things, on the hunting ammunition available on the market.

Compared to rifle ammunition, the lethal effect of shot for hunting is not based on the destruction of vital organs, but mainly on the overstimulation of the peripheral or central nervous system, which causes a so-called shock death in small game species (Kneubuehl 2008). However, little is known about this effect, which is why the killing effect of shotgun ammunition is a constantly controversial topic. This also results from the interaction of several factors that play an important role during hunting. For example, according to Mondain-Monval et al. (2015), in addition to the shotgun ammunition used, wind conditions on the field, as well as judgment, shooting skills, and the shooter's general behavior are all important. Nevertheless, a general estimation of the killing effect of soft iron shot has already been made on the basis of field tests (Hebert et al. 1984; Humburg et al. 1982; Mikula et al. 1977; Pierce et al. 2015), according to which, seems to indicate that it is a suitable alternative. However, conclusions are often drawn too quickly from these findings and positive results are transferred to all application scenarios and other materials. These are, for example, Bi, W, Cu, and Zn, about whose killing effect little is known so far. Furthermore, the regulations imposed by the C.I.P. to ensure system compatibility and the safety of the user restrict the use of these materials. (Chapter 1.4.1) and significantly limit the types of ammunition and weapons available on the market for hunting purposes. Thus, some hard alternative materials can only be used due to a maximum muzzle implse specified by C.I.P. (2017) and may not provide the ballistic performance required to kill game in a manner that is compatible with animal welfare. However, some EU countries, such as Denmark, do not belong to the C.I.P. and are not subject to its strict regulations. This could be the reason why there are clear and different impressions regarding the killing effect of lead-free shotgun cartridges within Europe (Böck 2018).

However, it is essential to consider each material separately under the same conditions in order to identify suitable and unsuitable alternatives. At present, however, there are no precise guidelines for this purpose – only experience-based recommendations for the performance evaluation of conventional Pb shotgun cartridges (Lampel & Seitz 1983; von Wissmann 1967). In view of the considerable lack of knowledge in this area, the evaluation of the ballistic performance of alternative shotgun ammunition should be enabled by developing and applying a new standardized procedure analogous to "DIN SPEC 91384".

1.5.Summary of the current state of knowledge

1. The comparative assessment of alternative shotgun ammunition requires significantly more attention due to its complexity, the pronounced lack of knowledge, and its higher ecological relevance compared to hunting rifle ammunition, especially in Germany and the EU.
2. For almost every aspect that needs to be considered, there is literature describing the concerns of certain alternative materials for shotgun ammunition; therefore, they should be investigated using standardized procedures.
3. Knowledge gaps mainly exist in the aspects of ecotoxicology in terrestrial and aquatic systems, as well as in the ammunition’s killing effect.

1.6. Aims of this thesis

With regard to the knowledge gaps pointed out in Chapter 1.4 for the evaluation of shotgun ammunition, the aspects of ecotoxicology and killing effect in particular should be investigated in more detail. Due to the lack of standardized methods for a comparative evaluation of both conventional lead-based shotgun ammunition and alternative materials, standardizable methods are being developed or further developed within the scope of this thesis and applied to market-relevant shot materials. The aim is to improve the evaluability of different gunshot materials. Furthermore, the spectrum of standardizable test methods for mandatory control of hunting ammunition on the European or German market will be expanded upon.

i. Elutions tests

As discussed in Chapters 1.4.4.2 and 1.4.4.3, a large volume of data is known about the effects of dissolved heavy metals in both terrestrial and aquatic environments. However, the risk of releasing dissolved contaminants from hunting ammunition introduced into the respective systems cannot be estimated by knowledge of the material alone (cf. Chapter 1.3), which is why additional experiments on the release of heavy metal ions (elution experiments) are required.

a. Terrestrial systems

Schwarz et al. (2015) already developed a standardizable method to comparatively assess the release of metals from rifle projectiles in a soil-surrogate. As an indicator for possible contamination of groundwater or pore water, this kind of percolation method according to the requirements of DIN ISO 15799 (DIN 2003) allows an initial risk assessment for ecotoxicological effects in terrestrial systems and was therefore modified and applied for gunshot materials in this paper.

b. Aquatic systems

Analogous to terrestrial environmental compartments, the investigation of solubility behavior of shot materials is also necessary for aquatic systems in order to perform an ecotoxicological risk assessment. Since no uniform procedure exists for this purpose, an experimental test design was developed in order to investigate the leaching behavior of shot in water bodies as realistically as possible, but nevertheless, in a replicable manner. In order to provide a clear ecotoxicological assessment of the released metals, toxicity tests were carried out with a key organism (*Daphnia magna*) for aquatic systems in collaboration with the Chair of Aquatic Systems Biology at the Technical University of Munich (TUM).

ii. Target ballistic investigation

For the uniform testing of the killing effect of alternative and conventional shot ammunition, apart from classical, non-reproducible field studies, there is also no suitable procedure that exists. Only the recommendations of Lampel & Seitz (1983) and Von Wissmann (1967), which are based on empirical values, might be able to provide an initial approach to evaluate the ballistic performance of conventional and alternative shotgun materials by means of modification. For this purpose, weapon technicians and gunsmiths at EUREGIO HTBLVA Ferlach conducted extensive shooting tests with lead-based and lead-free hunting shotgun cartridges. The images of the shots' impact, digitized at Ferlach, were evaluated at the Department of Forest Nutrition and Water Balance at the TUM in cooperation with the Statistical Consulting Laboratory (StaBLab) at the Ludwig Maximilian University of Munich via the application of methods from spatial statitics. Due to the experimental nature of this sub-study, the term ballistic performance is used below instead of the term killing effect.

2. Material and Methods

2.1. Ammunition selection

Taking the European market into account, both conventional Pb shotgun cartridges and alternative cartridges with Bi, Fe, W and Zn as main components of the ammunition were selected in close consultation with the Bavarian State Hunting Association (BJV). A uniform shot diameter of 3.7 mm resp. #2, was specified, as Fiocchi PL34 were only available in a 3.5 mm diameter and Eley Bismuth Alphamax in 3.3 mm. The shotgun cartridges were professionally delaborated by RUAG Ammotec GmbH and the material composition as well as existing coatings of the shotgun ammunition were checked. After it was determined that the shotgun cartridges of FOB Sweet Copper contained two different shotgun ammunition materials, these were each treated as a separate shotgun ammunition type in the elution tests. In addition, Pb shotgun shells coated with Sn were provided to investigate the effect of metal coatings over the lead core. Due to limited resources, not every single shotgun ammunition type could be integrated into all experiments (Table 3).

Table 3: *Overview of the selected shotgun shells and their use in the respective studies.*

Shot designation	Abbreviation	Main element	Coating	Percolation tests	Waterbody simulation	Bioassay with *Daphnia magna*	Target ballistics
Rottweil Waidmannsheil	Waidmannsheil	Pb	No	✓	✓		✓
Rottweil Special 36	Special	Pb	No	✓	✓		✓
Fiocchi PL 34	PL 34	Pb	No	✓	✓	✓	✓
Rottweil Silver Selection	Silver	Pb	Yes	✓	✓	✓	✓
RUAG Sn-Beschichtung	RUAG-Sn	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	✓	✓	✓	✓
FOB Sweet Copper	Sweet Copper	Pb	Yes	✓			

2.2. Elution tests

2.2.1. Terrestrial systems

The aim of the test design for the percolation methodology according to Schwarz et al. (2015) is the comparability of metal ion release from bullets or shotgun materials in a standardized soil surrogate. Therefore, to estimate contamination in the soil-groundwater impact zone, the most unfavorable soil substrate in terms of sorption (quartz sand) was used, in which two shot pellets were embedded for each test replicate. This composition was irrigated a total of eight times with 15 ml each over four weeks with two different model solutions, in accordance with Ettl et al. (2010). Additional drying phases were simulated by removing the plugs and tubes between the irrigation intervals. Two synthetically producible solutions were used as reproducible irrigation media to cover a range of possible pH values in the topsoil. Bicarbonate pH8 (BiCarb) was used as the basic solution, which is the dominant anion in the carbonate buffer range (Blume et al. 2010). The lower pH range was simulated by citric acid pH4 (Citro). Citric acid is one of the naturally occurring organic acids in soil and, according to Schwarz et al. (2015), with a pH of 4, is very similar to natural soil mixtures in terms of its solubility properties. Also, pH4 is generally used by Obermann & Cremer (1992) and in the Landfill Utilization Ordinance (DepVerwV) as the most critical case in elution tests for assessing the long-term behavior of pollutant-containing materials at landfills. The eluate produced in the composition out of pre-filter (prevents the sand from scraping), shotgun shell material, quartz sand and quartz wool (prevents the sand from leaching out) was discharged into sample bottles with a peristaltic pump during each three-hour irrigation test (Figure 1). There were three replicates per variant (n=3).

The heavy metals analyzed were then evaluated using the generally accepted test values set out in the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) for the impact area of soil-groundwater. These take into account various ecosystem effects and also allow a comparative assessment of the concentrations of different elements (Schwarz et al. 2015).

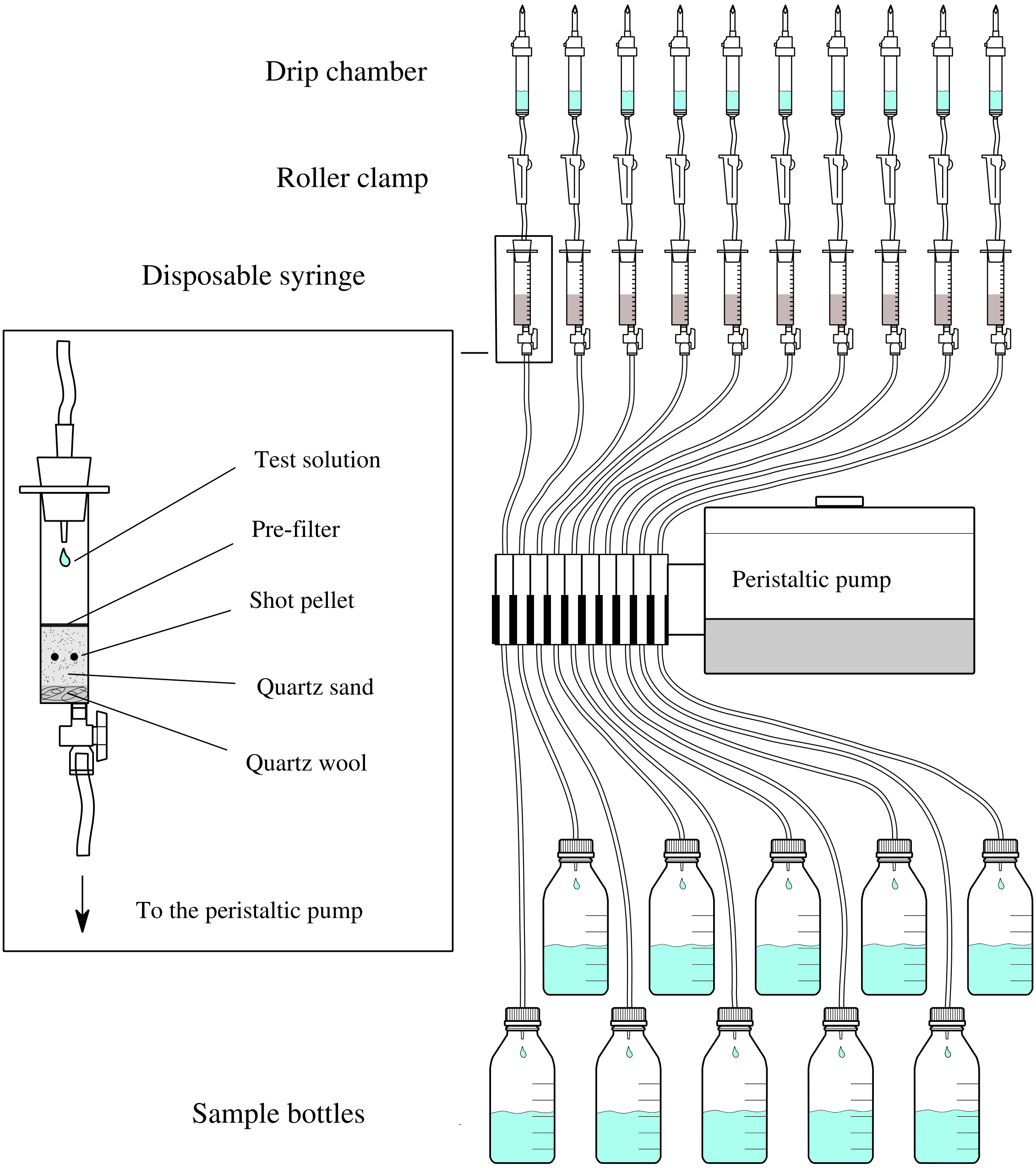


Figure 1: *Percolation test according to Schwarz et al. (2015) modified for shot (from Fäth & Göttlein 2017).*

2.2.2. Aquatic systems

Elution tests

In order to comparatively evaluate the leaching behavior of different shotgun materials in aquatic systems, an elution test was developed that was as natural as possible, yet simple and possible to standardize (Figure 2). This was partly influenced by the Organization for Economic Co-operation and Development's (OECD 2001, 2008) guidelines for risk assessment of potentially toxic substances in aquatic systems, with the solid-liquid ratio and solution media adapted to more natural conditions. For this purpose, naturally derived spring water was used as solution media, which originated, on the one hand, from siliceous parent rock (red sandstone from Spessart; 49°55'37.9" N; 9°23'53.5" E; pH 6.5) and, on the other hand, from calcareous bedrock (Munich gravel plains; 48°23'39.6" N; 11°43'23.6" E; pH 7.6). In modified urine cups, 100 ml of this specific type of water was added to two shot pellets at a time. This kind of scenario can occur in shallow water or puddles with only a few millimeters of water depth at hunting hotspots with up to 100 shotgun pellets per square meter. As another "natural" parameter, redox conditions in the waters, which can vary greatly between flowing and stagnant waters, were manipulated by aerating the nearly closed cups with air (aerobic) or nitrogen (anaerobic). To avoid water loss in the cups, the gases were previously saturated with water in washing bottles. A punctured (a) screw cap allowed excess gas to escape while maintaining a nearly closed system. In accordance with OECD (2001, 2008), both short-term (1 d, 8 d) and long-term (15 d, 22 d) exposures, each with three repetitions, were selected for all shotgun materials, fumigation, and water variants. At each of the four time points, the silicone tubing between the membrane filter (b) (pore diameter: 0.45 µm) and the solution allowed sampling (with a syringe) of a filtered aliquot (12 ml) for chemical analysis. The volume taken was then replenished with fresh water.

Bioassays with *Daphnia magna*

For the bioassays, additional elution experiments had to be carried out with the shot types selected for this purpose (Table 3) in a synthetic medium adapted to the target organism. The so-called "Aachen Daphnia Medium" (ADaM; Klüttgen et al. 1994) has a water hardness of 250 mg/l $CaCO_3$ and consists, per liter, of 333 mg synthetic sea salt, 2.3 ml $CaCl_2$ solution (0.8 mol/l), 2.2 ml $NaHCO_3$ solution (0.3 mol/l), and 0.1 ml SeO_2 solution (0.13 mol/l). The experimental parameters were chosen analogously to the elution experiments described above (2 shot pellets per 100 ml). However, for each shot type, four separate approaches were started simultaneously with three replicates each, sampled (12 ml) for chemical analysis after the expiration of the respective exposure periods (1 d, 8 d, 15 d, 22 d), and then pooled in one container for the Daphnia assay. Purified air was used as the aeration medium in these experiments.

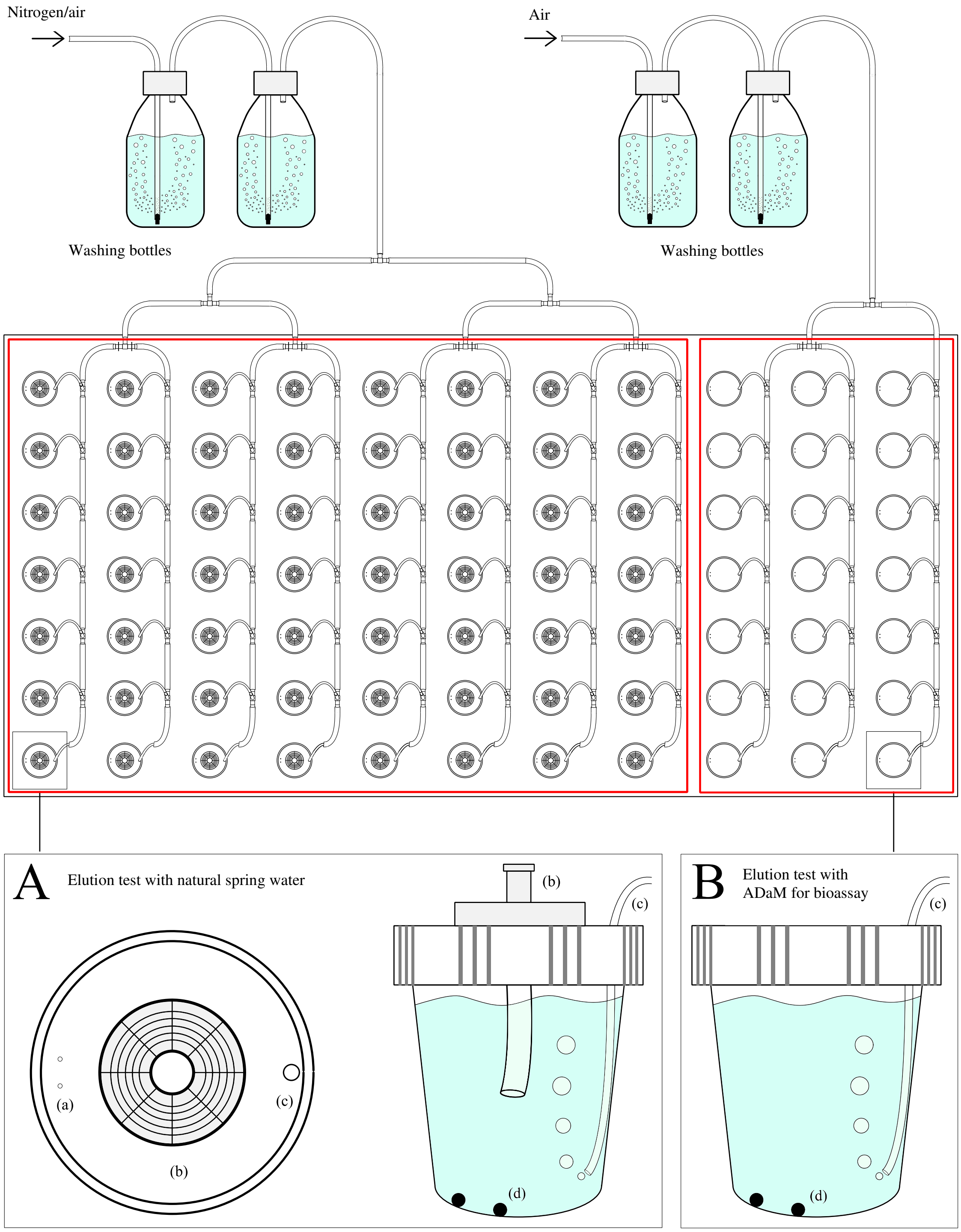


Figure 2: *Experimental design for the leaching behavior of shot in aquatic systems with modified urine cups: a) vent holes, b) membrane filter (pore size 0.45µm), c) gassing tube, d) shot (from Fäth et al. 2018a and Fäth & Göttlein 2019).*

The Daphnia immobilization test was performed by the Chair of Aquatic Systems Biology at TUM according to EN ISO 6341 (DIN 2013) using the Daphnia magna clone K34J in an acclimatized chamber at 20°C and a light:dark cycle of 16:8. For this purpose, six beakers per variant were filled with 40 ml of solution and the remaining solution was used to check the pH value. Another six beakers filled with ADaM served as controls. Five juvenile Daphnia (<24 h, not first offspring) were then transferred to each beaker. After 48 h, the number of immobile daphnia was counted and dissolved oxygen and pH were checked.

By considering four natural extremes of (siliceous aerobic, siliceous anaerobic, calcareous aerobic, calcareous anaerobic), as well as an artificial variant (ADaM) of freshwater, a comprehensive range of elution behavior of shotgun materials was able to be covered and, therefore, an initial hazard assessment for aquatic systems was able to be performed (see Figure 3).

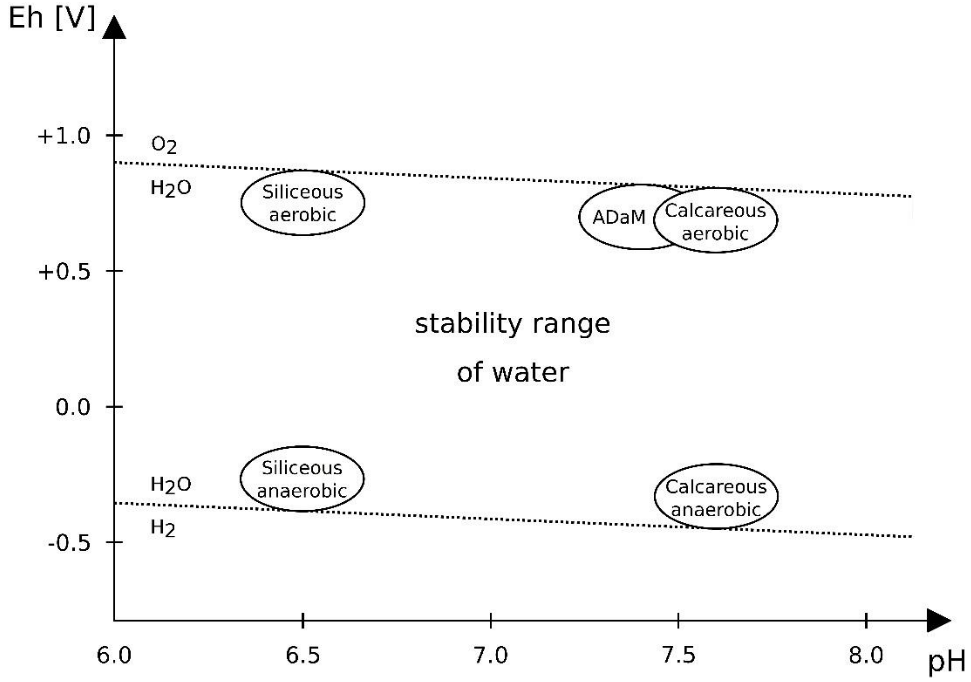


Figure 3: *Schematic integration of the investigated variants for aquatic systems in the stability range of water, defined by the redox potential and pH at 298.15 K and 10^5 Pa in an Eh/pH diagram (from Fäth & Göttlein 2019).*

To evaluate the results of the different variants, the first two (day 1 and day 8) and the last two experimental dates (day 15 and day 22) were summarized as short-term and long-term leaching behavior and the mean concentration of each toxicologically relevant metal released in the corresponding water variants was compared with the EC_{50} value for *Daphnia magna* from Khangarot and Ray (1989) and Okamoto et al. (2015).
For the statistical comparison of different leaching behaviors of the shotgun material between the water variants, a variance analysis (ANOVA) was carried out for each relevant metal released and shotgun material type.

2.2.3. Chemical analysis

All samples were filtered using membrane filters (pore size 0.45 µm) and then analyzed for their levels of As, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn and Zn using inductively coupled plasma atomic emission spectrometry (ICP-AES; Genesis, Spectro in Kleve, Germany). In addition, eluates of the Alphamax and Ultimate shot were analyzed at the ICP for their Bi and W concentrations. The concentrations of all samples were corrected via their background concentration (determined via "blank runs").

To increase both precision and accuracy, a matrix-adapted (Citro, BiCarb) calibration was performed at ICP, especially for measuring the percolated samples. The naturally obtained samples and the artificially prepared ADaM solutions were measured with the method adapted to the matrix of the bicarbonate solution used in the percolation test. Following the blank method according to DIN 32645 (DIN 2008), the limits of detection (NWG) and limits of quantification (BG) were determined by three times and ten times the standard deviation of ten measured blank values, respectively (Table 4). In the table below, all concentrations are given in nmol/l.

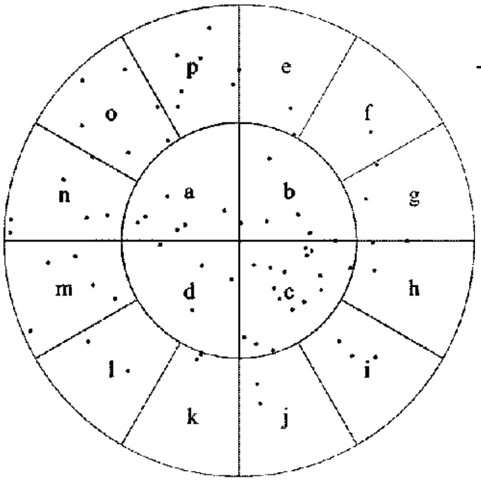
Table 4: *Matrix-adjusted limits of detection (NWG) and limits of quantification (BG) in nmol/l of the ICP according to the blank method performed according to DIN 32645 (DIN 2008).*

	NWG Citro	BG Citro	NWG BiCarb	BG BiCarb
As	130	433	86	287
Cr	28	92	26	87
Cu	34	114	38	127
Fe	61	205	17	57
Mn	3	11	5	17
Ni	50	168	59	197
Pb	84	280	47	157
Sb	87	290	56	187
Sn	64	213	55	183
Zn	97	322	62	207
Bi	82	274	52	173
W	83	277	51	170

2.3. Target ballistic investigation

2.3.1. Derivation of the experimental design

As already mentioned in Chapter 1.4.5, a test method (Wannseer Standard) exists for the reproducible investigation of ballistic performance of shotgun cartridges, which was developed exclusively for lead-based shotgun shells (Lampel & Seitz 1983; von Wissmann 1967). This represents an important basis for the investigation of ballistic criteria, although a modification is necessary for the comparability of different materials. Analogous to the legal minimum requirement for rifle ammunition in Germany of 1,000 or 2,000 J of impact energy at 100 m, depending on the game species being hunted, ballistic reference values based on lead shotgun ammunition were defined as minimum requirements, taking into account the literature references of Lampel & Seitz (1983). The core criterion in this sub-study, taking into account the size of the wild animal, is the target coverage of the material, for which at least five shots must hit a defined 16-field target. The target, which has a diameter of 75 cm and is divided into 16 equally sized fields, is checked after the shot for pellet distribution and number of hits. Lampel & Seitz (1983) only give evaluation criteria for shotgun cartridges up to 3.5 mm in diameter (game scenario “rabbit”). In order to be considered covered for this in terms of sufficient ballistic performance, two adjacent fields (an area of two fields: 552 cm^2 ~ projection area of a rabbit) must, together, have at least five hits with a 3.5 mm shot, from which the $\text{Coverage}_{\text{Hits}}$ can be determined (Figure 4). In order to establish comparability of the alternative materials, which primarily differ from lead in terms of their density, taking into account the specified requirements for lead-based shotgun material, the $\text{Coverage}_{\text{Energy}}$ was derived as a further criterion in addition to the $\text{Coverage}_{\text{Hits}}$. Using energy values taken from literature at a prescribed test distance of 35 m for the shot diameter recommended for hunting a rabbit, and taking into account the minimum number of hits (five hits of 5.9 J each), a minimum impact energy of 29.5 J per two fields (hereinafter referred to as segment) was derived. This criterion is important in that alternative shotgun materials have a very differentiated potential to transfer energy to the wild animal's body surface to produce a shock death. Pierce et al. (2015) also presents material density as an important criterion for evaluating the performance of a shotgun cartridge, which is why $\text{Coverage}_{\text{Energy}}$ was also considered in the studies described below. The kinetic energy per pellet can be calculated by velocity and pellet weight analysis and is compared with the minimum requirement (29.5 J) per segment, from which the $\text{Coverage}_{\text{Energy}}$ can be determined. Figure 4 shows the scheme already established by Lampel & Seitz (1983) for determining the coverage$_{Hits}$ and the Coverage$_{Energy}$ criterion derived in this study.



Segment *Segment*	Treffer *Hits*	Deckung$_{Treffer}$ *Coverage$_{Hits}$*	E_{kin}	Deckung$_{Energie}$ *Coverage$_{Energy}$*
a + b	6 + 6 = 12	Yes	12*5,0 J = 60 J	Yes
b + c	6 + 16 = 22	Yes	22*5,0 J = 110 J	Yes
c + d	16 + 4 = 20	Yes	20*5,0 J = 100 J	Yes
d + a	4 + 6 = 10	Yes	10*5,0 J = 50 J	Yes
e + f	2 + 1 = 3	No	3*5,0 J = 15 J	No
f + g	1 + 3 = 4	No	4*5,0 J = 20 J	No
g + h	3 + 2 = 5	Yes	5*5,0 J = 25 J	No
h + i	2 + 3 = 5	Yes	5*5,0 J = 25 J	No
i + j	3 + 2 = 5	Yes	5*5,0 J = 25 J	No
j + k	2 + 2 = 4	No	4*5,0 J = 20 J	No
k + l	2 + 2 = 4	No	4*5,0 J = 20 J	No
l + m	2 + 5 = 7	Yes	7*5,0 J = 35 J	Yes
m + n	5 + 6 = 11	Yes	11*5,0 J = 55 J	Yes
n + o	6 + 6 = 12	Yes	12*5,0 J = 60 J	Yes
o + p	6 + 7 =13	Yes	13*5,0 J = 65 J	Yes
p + e	7 + 2 = 9	Yes	9*5,0 J = 45 J	Yes
Number of covered segments	Coverage$_{Hits}$	12	Coverage^{Energy} (at 5.0 J acc. Korn)	9

Figure 4: *From Lampel & Seitz (1983) and von Wissmann (1967) derived and modified scheme for determining Coverage$_{Hits}$ and Coverage$_{Energy}$ using the 16-field grid. For the determination of Coverage$_{Energy}$, an energy of 5.0 J per shot was assumed as an example (from Fäth et al. 2020).*

2.3.2. Technical implementation of the shooting tests

All cartridge types were each shot with three identical shotgun barrels using interchangeable chokes from different manufacturers (Beretta, Browning, Perazzi) with 12/76 caliber (cartridge chamber according to C.I.P. 2015). Five different choke shapes (full, ¾, ½, ¼ and cylinder chokes) were used per choke manufacturer. The shooting tests were each conducted at three different distances (15 m, 25 m, 35 m) on a paper target (side-to-side length: 110 cm) with the shotgun barrel configurations clamped in an HPI firing block. Despite the test distance of 35 m specified by Lampel & Seitz (1983) for lead-based shotgun shells, the different shooting distances are very important due to the additional investigation of different shotgun shell materials with a lower kinetic energy in this study, in order to be able to derive recommendations for this aspect, if necessary. Analogous to the minimum specification of Lampel & Seitz (1983), each variant was shot in fivefold repetition. In addition, the average velocity of the entire shot sheaf was determined on the basis of five repeat measurements by means of radar detection for each variant and distance. With this method and by determining the average pellet weight from five delaborated cartridges of each type, the kinetic grain energy was calculated.

2.3.3. Data processing

All of the paper targets shot at were digitized at HTBLVA Ferlach using a large-format scanner. The pellet hits per scan were recorded via an optoelectronic program in the form of x and y coordinates and transmitted to the Professorship of Forest Nutrition for further evaluation. In order to accurately project all digital shot images to the center of a digital test disk, a center point correction was used, applying the median of the x- and y-coordinates. The median was chosen because rim hits can strongly distort the center of a target (Lampel & Seitz 1983).

2.3.4. Statistical evaluation

With regard to the criteria explained below, it should be noted that in discussing the results of this study, the main focus is on the $\text{Coverage}_{\text{Hits}}$ and $\text{Coverage}_{\text{Energy}}$ criteria. Other criteria such as Inner $\text{Circle}_{\text{Hits}}$ appear exclusively in the developed shiny app "huntR" (cf. Chapter 3.3.2).

In order to capture important differences in the target criteria depending on shotgun ammunition and other variables, a Generalized Linear Model (GLM; Fahrmeir et al. 2007) was used for each evaluation characteristic. This was able to provide a model-based estimation of the target criterion as a function of choke shapes and manufacturer, as well as shot distance and ammunition used. Here, a full interaction model was estimated for each criterion. The distribution assumption was adjusted to the corresponding variable type of each target criterion. For the criteria $\text{Coverage}_{\text{Hita}}$, $\text{Coverage}_{\text{Energy}}$ and the number of hits in the inner circle, respectively on the total target surface or on the area of a rabbit, the Poisson distribution (log-link) was assumed in each case; for the energy criteria per area, as well as the target radius, the assumption of a normal distribution (identity link) was made. The analyses were performed with the statistical program R (R Core Team 2020). In addition to the basic module, the package ggplot2 (Wickham 2016) was used to display the results.

3. Results and Discussion

3.1. Elution behavior in a standardized terrestrial system

3.1.1. Leaching behavior

The main parts of the following results have already been published in Fäth & Göttlein (2017).

In the section below, the elements eluted in the percolation test that caused the limit values to be exceeded in accordance with the BBodSchV will be discussed. For As and Cr, there was no significant release rate compared to the test values. Since all shot types showed the highest release rate in the acidic solution (Citro), this is shown in its temporal course by Figure 5. Solution rates in the basic solution (BiCarb) are therefore only described in the text and in Tables 5 and 6.

The **conventional lead-based** shot types Special, Waidmannsheil and PL 34 showed an *extreme* or *very high* release of lead in the acidic solution right at the beginning (Tables 5 & 6). The only threshold value exceedance in the akaline solution was a *low* (0.15 µmol/l) exceedance of the antimony value by Special at the beginning. Towards the end of the test in the acidic variant, the three conventional types of lead-based shot were at a significantly *higher* concentration level in their Pb release and with respect to exceeding the threshold value for Pb; all were then in the class *extreme* (Waidmannsheil: 22.24 µmol/l; Special: 32.15 µmol/l; PL 34: 28.87 µmol/l). Likewise, towards the end of the test, they exceeded the corresponding limit in the basic solution due to a *higher* Sb release, with Special being assigned to the exceedance class *obvious* (0.49 µmol/l) and Waidmannsheil and PL 34 being assigned to a *low* (0.18 µmol/l; 0.21 µmol/l) exceedance of the Sb test value. The dominant Pb leaching rate and limit exceedance in the acidic variant (without exceeding the threshold values for any other heavy metal) and the only limit exceedance for Sb in the basic solution is in agreement with the results of Schwarz et al. (2015) and Fäth & Göttlein (2015) on rifle bullets. This electrochemical behavior of lead shot is essential for their ecotoxicological assessment, as well as for the search for solutions to reduce Pb inputs into the environment.

Looking at the **lead-coated shot**, it was apparent that Sweet Copper also released *high* Pb concentrations (3.57 µmol/l) at Citro at the beginning of the test along with Cu (8.75 µmol/l) (Table 5 & 6). While the Cu exceedance class remained constant (*high*; 32.69), the exceedance increased over the course of the experiment for Pb up to a *very high* class

(9.80 µmol/l), with no noticeable change in the ratios between release rates over time (Figure 5). In contrast, Silver shot, which are also coated, showed a *obvious* excess of the Ni limit at the beginning of the test (7.59 µmol/l) as well as a *high* excess of the Pb test value (5.20 µmol/l). At the end of the test, *extreme* Pb (22.32 µmol/l), *obvious* Ni (4.46 µmol/l) and *low* Cu leaching rates (1.23 µmol/l) exceeded the threshold value, which clearly shows the temporal changes in the solution behavior of this type of shotgun ammunition. This strongly differentiated leaching behavior is presumably due to the different coatings, whereby these, even in an intact state, clearly do not have sufficient strength to prevent Pb release from the shotgun shell. The *high* Pb limit exceedance at the beginning of the test and the *very high* or *extreme* leaching towards the end suggests that a Cu/Ni coating on Silver and the Cu coating on Sweet Copper only initially provide some protection of the lead core from dissolving. In the course of the experiment, they seemed to dissolve successively at particularly weak points, which is why a Pb release favored by the electrochemical voltage series (Pb is significantly less noble than Ni and Cu) dominated leaching behavior very strongly towards the end of the test. In the case of the tin-coated lead shot RUAG-Sn, on the other hand, only Sn ions dissolved; this means that only the threshold value for Sn was *low* exceeded both at the beginning (0.44 µmol/l) and towards the end of the test (0.75 µmol/l) under acidic conditions. Since there was otherwise no further metal ion release in the percolate test of this lead-coated shot, the Sn coating appeared to protect the lead core from dissolving compared to Silver and Sweet Copper. This is plausible in that Sn has outstanding corrosion resistance, particularly due to its high passivation capacity through the formation of outer oxide layers (Li et al. 2015).

The pure copper shot **Sweet Copper** only released Cu and small amounts of Fe ions (Figure 5). Iron (Fe), which occurs in small amounts in Cu as an alloy component or due to impurities and which can be released significantly due to its lower electrochemical standard potential than Cu, was not evaluated due to the low ecological relevance of the measured concentration ranges. Thus, only in the acidic case, a *high* Cu limit exceedance (17.32 µmol/l) at the beginning of the test and a *very high* one (40.78 µmol/l) at the end (Table 5 & 6) is of importance for this shot material.

The **Hubertus** and **Blind Side** shots released *immense* amounts of zinc ions in the acid test solution (Figure 5). Due to the significantly higher Zn threshold values compared to Pb, Cu and Ni, only *low* (16.01 µmol/l; 27.67 µmol/l, 33.29 µmol/l) and *obvious* (50.35 µmol/l) threshold excesses occurred at the beginning and at the end of the test, respectively (Table 5 & 6). The very high solubility rate of metallic Zn is due to its very low inertness, as well as its low potential due to the formation of oxide layers (Macdonald et al. 1998; Thomas et al. 2012). The similarly high Zn release from the Fe-based iron shot Blind Side, as in the case of the Pb-coated shots, is most likely due to a Zn-based coating, whose core was probably not exposed at any point due to the lack of Fe ions in the percolate. Furthermore, the Cr ions detected were conspicuous in both the acidic and basic variants, which, according to Levonmäki and Kairesalo (2001), may be due to certain proportions in the material. However, since these were leached in a very low concentration range (up to 0.18 µmol/l), this did not result in any threshold values being exceeded in accordance with the BBodSchV.

Like Silver, the tungsten shot **Ultimate** showed an ion release for three different metals (Fe, Ni, Sn), but only in the second half of the test period (Figure 5). While there was no threshold value exceedance according to the BBodSchV at the beginning, Ultimate *lowly* exceeded the values for Ni and Sn towards the end of the test (Table 5 & 6). These metals occur as alloying constituents to W and thus can also be released (Thomas 2016). However, since this shotgun material also has a coating, the origin of the released ions could not be clearly identified.

Although **Steel Shot** is coated and **Steel Game** is not, the elution behavior of the two iron shot types was almost identical (Figure 5). Both showed a high level of Fe and a relatively low level of Mn released with a constant level towards the end. Although some heavy metals were detected, the threshold values according to BBoDSchV were not exceeded at the beginning or at the end of the two test environments (Table 5 & 6).

Similarly, no test values were exceeded for the Bi shot **Alphamax** (Table 5 & 6), although no limit values exist for the released Bi ions. The Pb ions detected at the beginning of the acidic variant also did not exceed the corresponding limit value. Nevertheless, it can be assumed here that, similar to Kanstrup et al. (2019), Pb-contaminated Bi material (with up to 0.68% Pb) is present.

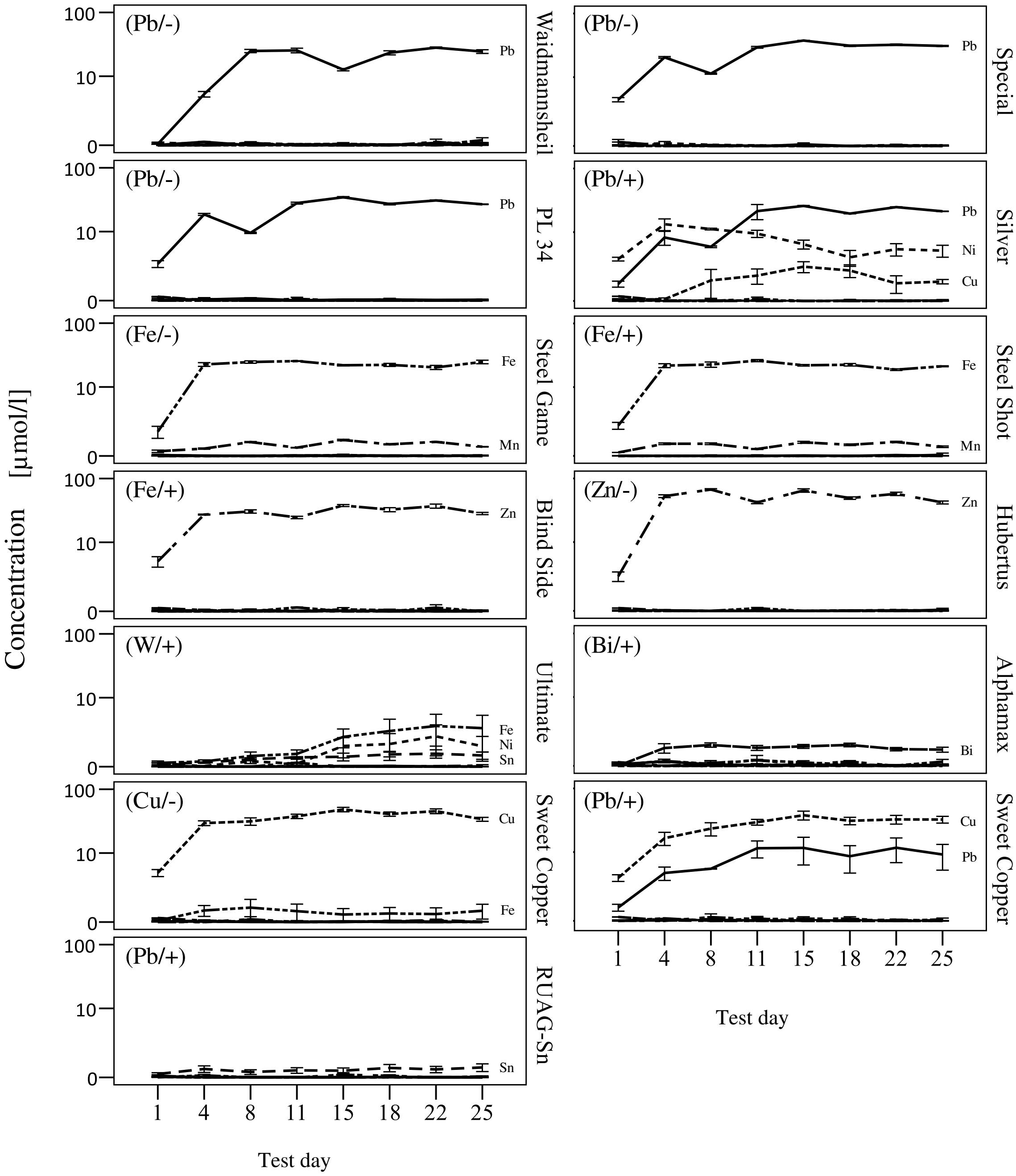


Figure 5: *Time series with the leaching behavior of the shots investigated in the percolation test with citric acid pH4 over four weeks. The charts show the mean concentration [µmol/l] for Pb, Bi, Fe, Cu, Mn, Ni, Zn and Sn (± standard error; logarithmic scale) with a material label (Element / "+" for coating, "-" for no coating) of each shot according to Table 3. A measurement of the Bi concentration was only done for the percolate of the shot types Ultimate and Alphamax (from Fäth & Göttlein 2017).*

Table 5: *Evaluation of the averaged initial metal leaching in the elutents citric acid pH4 (Citro) and bicarbonate pH8 (BiCarb) by means of threshold value exceedance classes according to Schwarz et al. (2015) with indicated mean concentrations [µmol/l]. The classification scheme regarding the exceedance of the thresholds according to the BBoDSchV (in brackets below the elements) according to Schwarz et al. (2015) is given at the bottom of the table. Only values above the detection limit (Table 4) were given (from Fäth & Göttlein 2017). The material label of the shot materials is composed as follows: (Element / "+" for coating, "-" for no coating).*

			Element - *element* [µmol/l]							
Lösung *solution*	Schrot Abkürzung *shot abbreviation*	Materialkennung *material label*	As (0,13)	Cr (0,96)	Cu (0,79)	Ni (0,85)	Pb (0,12)	Sb (0,08)	Sn (0,34)	Zn (7,65)
Citro pH4	Waidmannsheil	(Pb/-)	-	-	-	0,05	**15,18**	-	-	-
	Special	(Pb/-)	-	-	-	-	**12,47**	-	-	-
	PL 34	(Pb/-)	-	-	-	-	**11,04**	-	-	-
	Silver	(Pb/+)	-	-	0,06	**7,59**	**5,20**	-	-	0,43
	RUAG-Sn	(Pb/+)	-	-	-	-	-	-	**0,44**	-
	Steel Game	(Fe/-)	-	-	-	-	-	-	-	-
	Steel Shot	(Fe/+)	-	-	-	-	-	-	-	-
	Blind Side	(Fe/+)	-	0,18	-	-	-	-	-	**16,01**
	Hubertus	(Zn/-)	-	-	-	-	-	-	-	**27,67**
	Ultimate	(W/+)	-	-	-	-	-	-	0,13	-
	Alphamax	(Bi/+)	-	-	-	-	0,11	-	-	-
	Sweet Copper	(Cu/-)	-	-	**17,32**	-	-	-	-	0,25
	Sweet Copper	(Pb/+)	-	-	**8,75**	-	**3,57**	-	-	0,35
BiCarb pH8	Waidmannsheil	(Pb/-)	-	-	-	-	0,09	0,07	0,13	-
	Special	(Pb/-)	-	-	-	0,07	-	**0,15**	-	0,10
	PL 34	(Pb/-)	-	-	-	0,08	-	-	-	0,07
	Silver	(Pb/+)	-	-	-	0,22	-	-	-	-
	RUAG-Sn	(Pb/+)	-	-	-	-	-	-	-	-
	Steel Game	(Fe/-)	-	-	-	-	-	-	-	-
	Steel Shot	(Fe/+)	-	-	-	-	-	-	-	-
	Blind Side	(Fe/+)	-	0,11	-	-	-	-	0,06	-
	Hubertus	(Zn/-)	-	-	-	-	-	-	-	0,32
	Ultimate	(W/+)	-	-	-	-	-	-	0,06	-
	Alphamax	(Bi/+)	-	-	-	-	-	-	0,08	0,12
	Sweet Copper	(Cu/-)	-	-	0,05	-	-	-	-	0,16
	Sweet Copper	(Pb/+)	-	-	0,05	0,10	-	-	-	-

Klassifizierung der Überschreitungsfaktoren der Prüfwerte nach BBODSCHV für den Wirkungspfad Boden-Grundwasser *Classification based on exceedance factors of the test values (pathway soil-groundwater) according to BBODSCHV*	keine *no* 0 - 1	**gering** ***low*** **1 - 5**	**deutlich** ***obvious*** **5 - 10**	**hoch** ***high*** **10 - 50**	**sehr hoch** ***very high*** **50 - 100**	**extrem** ***extreme*** **> 100**

Table 6: *Evaluation of the averaged final metal leaching in the elutents citric acid pH4 (Citro) and bicarbonate pH8 (BiCarb) by means of threshold value exceedance classes according to Schwarz et al. (2015) with indicated mean concentrations [µmol/l]. The classification scheme regarding the exceedance of the thresholds according to the BBoDSchV (in brackets below the elements) according to Schwarz et al. (2015) is given at the bottom of the table. Only values above the detection limit (Table 4) were given (from Fäth & Göttlein 2017). The material label of the shot materials is composed as follows: (Element / "+" for coating, "-" for no coating).*

			Element - *element* [µmol/l]							
Lösung *solution*	Schrot Abkürzung *shot abbreviation*	Materialkennung *material label*	As (0,13)	Cr (0,96)	Cu (0,79)	Ni (0,85)	Pb (0,12)	Sb (0,08)	Sn (0,34)	Zn (7,65)
Citro pH4	Waidmannsheil	(Pb/-)	-	-	0,13	-	**22,24**	-	-	0,82
	Special	(Pb/-)	-	-	-	-	**32,15**	-	-	-
	PL 34	(Pb/-)	-	-	-	-	**28,87**	-	-	-
	Silver	(Pb/+)	-	-	**1,23**	**4,46**	**22,32**	-	-	-
	RUAG-Sn	(Pb/+)	-	-	-	-	-	-	**0,75**	-
	Steel Game	(Fe/-)	-	-	-	-	-	-	-	-
	Steel Shot	(Fe/+)	-	-	-	-	-	-	-	-
	Blind Side	(Fe/+)	-	0,04	-	-	-	-	-	**33,29**
	Hubertus	(Zn/-)	-	-	-	-	-	-	-	**50,35**
	Ultimate	(W/+)	-	-	-	**1,40**	-	-	**0,52**	-
	Alphamax	(Bi/+)	-	-	-	-	-	-	-	-
	Sweet Copper	(Cu/-)	-	-	**40,78**	-	-	-	-	-
	Sweet Copper	(Pb/+)	-	-	**32,69**	-	**9,80**	-	-	-
BiCarb pH8	Waidmannsheil	(Pb/-)	-	-	-	-	-	**0,18**	-	-
	Special	(Pb/-)	-	-	-	-	-	**0,49**	-	-
	PL 34	(Pb/-)	-	-	-	-	-	**0,21**	-	-
	Silver	(Pb/+)	-	-	-	0,08	-	-	-	-
	RUAG-Sn	(Pb/+)	-	-	-	-	-	-	-	-
	Steel Game	(Fe/-)	-	-	-	-	-	-	-	-
	Steel Shot	(Fe/+)	0,12	-	-	-	-	-	0,06	0,23
	Blind Side	(Fe/+)	-	0,05	-	-	-	-	-	1,67
	Hubertus	(Zn/-)	-	-	-	-	-	-	-	5,67
	Ultimate	(W/+)	-	-	-	-	-	-	-	-
	Alphamax	(Bi/+)	-	-	-	-	-	-	-	-
	Sweet Copper	(Cu/-)	-	-	0,07	-	-	-	-	-
	Sweet Copper	(Pb/+)	-	-	0,13	-	-	-	-	-

Klassifizierung der Überschreitungsfaktoren der Prüfwerte nach BBoDSchV für den Wirkungspfad Boden-Grundwasser *Classification based on exceedance factors of the test values (pathway soil-groundwater) according to BBoDSchV*	keine *no* 0 - 1	**gering** ***low*** **1 - 5**	**deutlich** ***obvious*** **5 - 10**	**hoch** ***high*** **10 - 50**	**sehr hoch** ***very high*** **50 - 100**	**extrem** ***extreme*** **> 100**

3.1.2. Ecotoxicological evaluation

The results show, that for the estimation of the leaching behavior of shotgun materials in standardized terrestrial systems, the exclusive consideration of the main components, such as Fe, W or Pb, is insufficient. Furthermore, according to EN ISO 18772 (DIN 2014), the sole consideration of the total amount of a contaminant introduced into the soil is inadequate for estimating the impact on soil or groundwater due to the elution of heavy metals as well as their subsequent removal by water. Therefore, each different shot composition must be considered separately, even if the main component is the same.

As expected, the **three conventional lead-based shotgun ammunition types** Waidmannsheil, Special and PL 34 should be classified as very critical in acidic conditions due to their *extreme* excess of Pb threshold values according to BBodSchV. In addition, the exceedance of the Sb test value up to the class *obvious*, the test clearly shows that conventional lead-based shotgun material is also of concern with regard to the toxicological effect in terrestrial systems even under basic conditions, where other elements such as Cu or Ni dissolve to a lesser extent or not at all. This is especially important for shooting ranges, as they are responsible for different levels of groundwater contamination due to the increased ammunition input depending on the soil environment (Soeder & Miller 2003). For example, one widely used solution is the liming of shooting ranges, which can significantly reduce the solubility and mobility of lead by increasing soil pH (USEPA 2005; Geebelen et al. 2002). However, increasing pH increases the preferential solubility of antimony, which is why some shooting ranges, even without liming (on lime-rich sites), do not have a lead problem but do have an antimony problem.

Even the **Silver and Sweet Copper (Pb/+)** shotgun materials were not able to prevent the release of lead despite their surface coating, which is probably due to their low coating thickness. Due to their exceedance of additional elemental limits (Cu, Ni), these types of ammuniton should be evaluated even more critically than conventional Pb shotgun materials, which is why such coatings should be avoided from a terrestrial and ecotoxicological point of view. The tinned lead variant **RUAG-Sn,** on the other hand, appears to be a thoroughly viable solution for preventing Pb release. However, since possible damage in the course of shooting cannot be ruled out, the durability of the protective coating must be tested by examining fired shot pellets. Nevertheless, Sn has good corrosion resistance and would therefore be a promising alternative from an ecotoxicological point of view – not only potentially as a coating but also as a core material.

The **Hubertus' and Blind Side's** shot materials are clearly less conspicuous than the (coated) Pb materials with regard to the exceedance classes shown in Tables 5 and 6. This is mainly due to the significantly higher test value for Zn, which was nevertheless exceeded due to the very high Zn concentrations in the percolate (up to 50.35 µmol/l) test. According to Baath (1989), dissolved Zn also has a high toxicity potential for microorganisms in the soil. These two examples highlight the concern associated with toxic coatings, even if they are in the µm range. If classified according to its main component, the Fe-based shotgun material Blind Side would have been classified as non-toxic, although, according to the percolation tests carried out, it must be classified as equally critical as the zinc shotgun material Hubertus.

With regard to the up to *very high* Cu value exceedance (40.78 µmol/l), the pure copper material (Cu/-) from **Sweet Copper's** cartridges must also be classified as critical. If the entire contents of the shotgun cartridge are considered, the copper-coated Pb shot (Pb/+) took up a proportion of up to 12% in the cartridge, which additionally released *high* to *very high* Pb concentrations, and this must also be taken into account.

The leaching behavior of the W-based shot **Ultimate** was extremely complex. While the ammunition seemed harmless in the first half of the test due to its low solubility rates, it released three different metals (Fe, Ni, Sn) at the end of the test, two of which exceeded the limit value of the BBodSchV. In contrast, W-ions that are potentially toxic to plants were not released in a detectable concentration. In view of the above-mentioned threshold value exceedances, the tungsten shotgun material Ultimate should nevertheless be rated as critical in this context.

After the percolation tests, the **Steel Game, Steel Shot and Alphamax** ammunition types can be described as the least critical variants in terms of their terrestrial ecotoxicological effect, since they did not cause any threshold values to be exceeded in accordance with the BBodSchV or release any other metal contents that are toxic in a dissolved form.

3.1.3. Shot vs. rifle bullets

Due to the good reproducibility of the percolation procedure described in Chapter 2.2.1, the mass-related elution behavior of shotgun shells can be compared with that of previously studied rifle bullets (Fäth & Göttlein 2015). This enables an initial comparative assessment of the different ecological effects of rifle bullets and shot loadings in the environment.

Looking at the copper ammunition, for example, the Sweet Copper cartridge has a significantly higher mass-related Cu release (75.7 µmol/l per g) than the Barnes TTSX copper rifle bullet studied by Fäth & Göttlein (2015) (9.3 µmol/l per g). Comparing the lead-based materials, for example, the shot Special (53.4 µmol/l per g) released more than 20 times as much dissolved Pb as the rifle bullet RWS DK (2.5 µmol/l per g), bearing in mind that Pb bullets are jacketed with steel or tombac, which is why, after bullet deformation, an undefinable surface influences the elution of Pb.

This finding is also highly relevant, for example, for highly frequented clay target shooting ranges, since the powerful elution behavior and the large weight of up to 36 g of shot per cartridge (up to 200 bullets) leads to significantly greater groundwater contamination levels compared to shooting ranges for rifle ammunition (Lucks 1991; Soeder & Miller 2003), especially in Scandinavian countries (cf. Chapter 1.4.4.2). The significantly higher ecological relevance of shotgun ammunition, as proven by percolation tests, thus confirms the assumption made in Chapter 1.3 and also emphasizes the necessity of creating mandatory ecological test criteria for shotgun ammunition available on the German or European market.

3.1.4. Evaluation of the methodology

In order to establish a procedure that is as realistic and reproducible as possible for the comparative evaluation of the elution behavior of shot in terrestrial systems, washed quartz sand was used as a surrogate for soil with minimal sorption capacity instead of natural soil samples in the irrigation test. This represents the worst case scenario in the event of contamination, as dissolved heavy metals can enter the groundwater directly via water filtration with almost no sorption. In order to evaluate the elution behavior for this environmental impact, the corresponding threshold values of the BBodSchV, which are also used for the evaluation of leachate analyses, are suitable. Hereby, an initial assessment of possible risks to groundwater from heavy metals eluted from different shot materials in the soil were made under comparative conditions. It should be noted, however, that this should not be used to infer the mobility of metals in real soils, since heavy metals have different affinities for sorption on solid surfaces depending on pH and clay content (Herms & Brümmer 1984).

In the course of the four-week percolation process, there were significant drying phases between the total of eight irrigation test dates, which promoted the corrosion of the introduced shot pellets (Figure 6). This provides a realistic scenario, since, in nature, soil desiccation usually also occurs with resulting corrosion processes. Furthermore, this underlines the suitability of the selected percolation period, since "long-term" processes such as corrosion can already be observed in this relatively short period. Changes in leaching behavior have also already occurred. This was, for example, evident in the case of Silver with an elution behavior dominated by Ni and Pb at the beginning and by Pb, Ni and Cu towards the end, which is why the consideration of the initial and final leaching stages (Table 5 & 6) is very important.

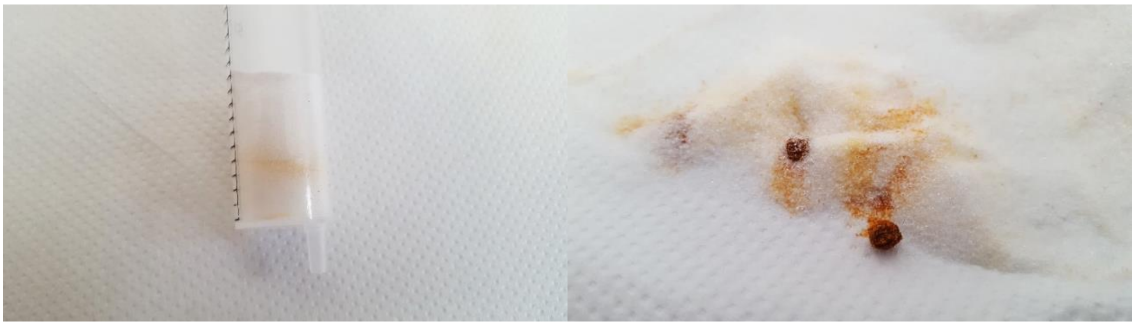


Figure 6: *Disposable syringe with corroded iron shotgun shell material (Rottweil Steel Game) in quartz sand and quartz wool (left) and shotgun shell material removed from the disposable syringe with quartz sand (right) after the last irrigation date.*

An equally good level of reproducibility is provided by the model solutions used, Citro and BiCarb, which can be prepared relatively easily. While the BiCarb solution was derived from the carbonate buffer range, Schwarz et al. (2015) first had to investigate the chemical solution properties of soil and humus solutions for the acidic range in order to find a suitable surrogate. According to this, citric acid with pH4 is most similar to natural humus lysimeter solutions regarding its solution properties for heavy metals. This is supported by the specification of pH4 as the worst case scenario in the investigation of long-term behavior of materials containing pollutants in landfills by Obermann & Cremer (1992) and in the DepVerwV. As citric acid is also very well suited as an extracting agent in other soil studies, such as the determination of plant-available nutrients (Fäth et al. 2019a, b), it seems to simulate relatively realistic mobilization mechanisms in the soil – not only for heavy metals but also for essential nutrients such as calcium, magnesium, potassium or phosphorus.

Due to the simulation of realistic corrosion and elution processes in the soil, the percolation method used is therefore well-suited for a comparative assessment of possible ecotoxicological effects in terrestrial systems caused by hunting ammunition. Due to the simple manageability and reproducibility of the method, it should be included in a standardization process analogous to "DIN SPEC 91384" so that every rifle and shotgun ammunition on the market can be tested.

3.1.5. Conclusion

1. The percolation method is well-suited as a standardized method for a comparative evaluation of the elution behavior of shotgun materials in sorption-weak soils (ecologically worst-case).
2. A general statement about the ecotoxicological risk of certain material groups or main components for terrestrial systems is not possible on the basis of the results obtained in this sub-study.
3. Only the shotgun ammunition Steel Game, Steel Shot and Alphamax were considered uncritical for terrestrial systems under the applied test conditions due to their rather harmless leaching behavior.
4. All other shotgun ammunition types were classified as critical due to increased elution of the elements lead, zinc, nickel or copper. Respective ions were shown to be equally toxic even if they originated from alloyed additives or coatings.

3.2. Elution behavior in a standardized aquatic system

3.2.1. Leaching behavior

Most of the results presented and discussed below have already been published in Fäth et al. (2018a) and Fäth & Göttlein (2019).

The three **conventional lead-based** shot types Waidmannsheil, Special and PL 34 released very high Pb concentrations, whereby the respective four variants differed greatly (Figure 7). In water from siliceous rock, the highest Pb release (up to 10.3 µmol/l) occurred from these shots under aerobic conditions compared to the other variants. In the calcareous anaerobic variant, the measured concentrations were almost always below the limit of quantification for these shots. Due to the higher pH in the calcareous water, surface passivation of the Pb material probably occurs due to the formation of insoluble lead oxide or lead carbonate, according to Lyon (2010). In contrast, the milieus which had been designed to be anaerobic with nitrogen probably caused extensive resistance of metallic Pb to dissolve (electrochemical immunity; Lyon 2010). In contrast, solubility rates of Sb (up to 1.7 µmol/l) and As (up to 0.4 µmol/l) were highest in the calcareous variants, but at a much lower level than Pb concentrations. This corresponds to the results of the percolation experiments for terrestrial systems (Chapter 3.1.1) as well as to recent studies (Klitzke & Lang 2009; Schwarz et al. 2015) and should particularly be considered for waters in dolomitic or calcareous landscapes.

The coated **Silver** shot material released nickel in all environments, with the highest concentrations (up to 2.1 µmol/l) in the anaerobic and aerobic variants of the water from siliceous rock. In contrast, concentrations of up to 0.8 µmol/l were measured in the alkaline water. As already discussed with respect to the percolation experiments (Chapter 3.1.1), the dissolved Ni probably originated from the coating. In contrast, however, no determinable Cu or Pb release occurred in the four water variants, which is presumably due to the significantly higher pH values (6.5 and 7.6, respectively) and the lower complexing properties of the natural water compared to that of citric acid.

As in the percolation tests, **Blind Side** did not resemble classic Fe-based shot material in terms of its leaching behavior, but rather the pure Zn shot material **Hubertus**. Zinc concentrations were highest in the siliceous aerobic variant (up to 59.0 µmol/l). Due to the fact that metallic Zn undergoes surface passivation or immunization against solubility in aqueous media above a pH of 8.5 only (Macdonald et al. 1998; Thomas et al. 2012), these materials can release very high dissolved Zn contents into an aquatic environment, especially in siliceous rock waters. Additionally, very low Cr concentrations were also measured in the eluate from Blind Side in this experiment for the siliceous variants.

The pure copper shot **Sweet Copper** (Cu/-) mainly released quantifiable amounts of Cu in the aerobic environments, with concentrations being highest in the siliceous aerobic variant (up to 6.5 µmol/l; Figure 7). Otherwise, the lowest Cu concentrations (mainly below the limit of quantification) were found in the N_2-aerated variants, which is due to the high electrochemical immunity of metallic Cu in reductive environments (Talkeno 2005).

The relatively moderate amount of Fe released by the **Steel Game** and **Steel Shot** material (up to 3.0 µmol/l) was most highly concentrated in the siliceous water, although this decreased with increased exposure time. In addition, the two iron shots released Mn, the concentration of which was highest in the siliceous aerobic medium, but was also within a low range (up to 1.5 µmol/l).

The W shot **Ultimate** only released Sn ions under anaerobic conditions. As in the percolation tests (Chapter 3.1.1), the leaching behavior cannot be clearly explained due to the unknown composition of the coating, as well as the combination of several elements in the alloy (Fe, Ni, Sn). Nevertheless, the metallic Sn in the investigated water variants seems to convert mainly into tin oxide (Talkeno 2005), which presumably leads to surface passivation in each of the investigated environments (pH6.5/pH7.6; aerobic/anaerobic).

Due to low leaching of Bi in all variants (only up to 0.9 µmol Fe/l or 0.07 µmol Mn/l; Figure 7), neither detectable Bi ions nor other environmentally relevant substances were observed in the Bi-based shotgun ammunition **Alphamax**.

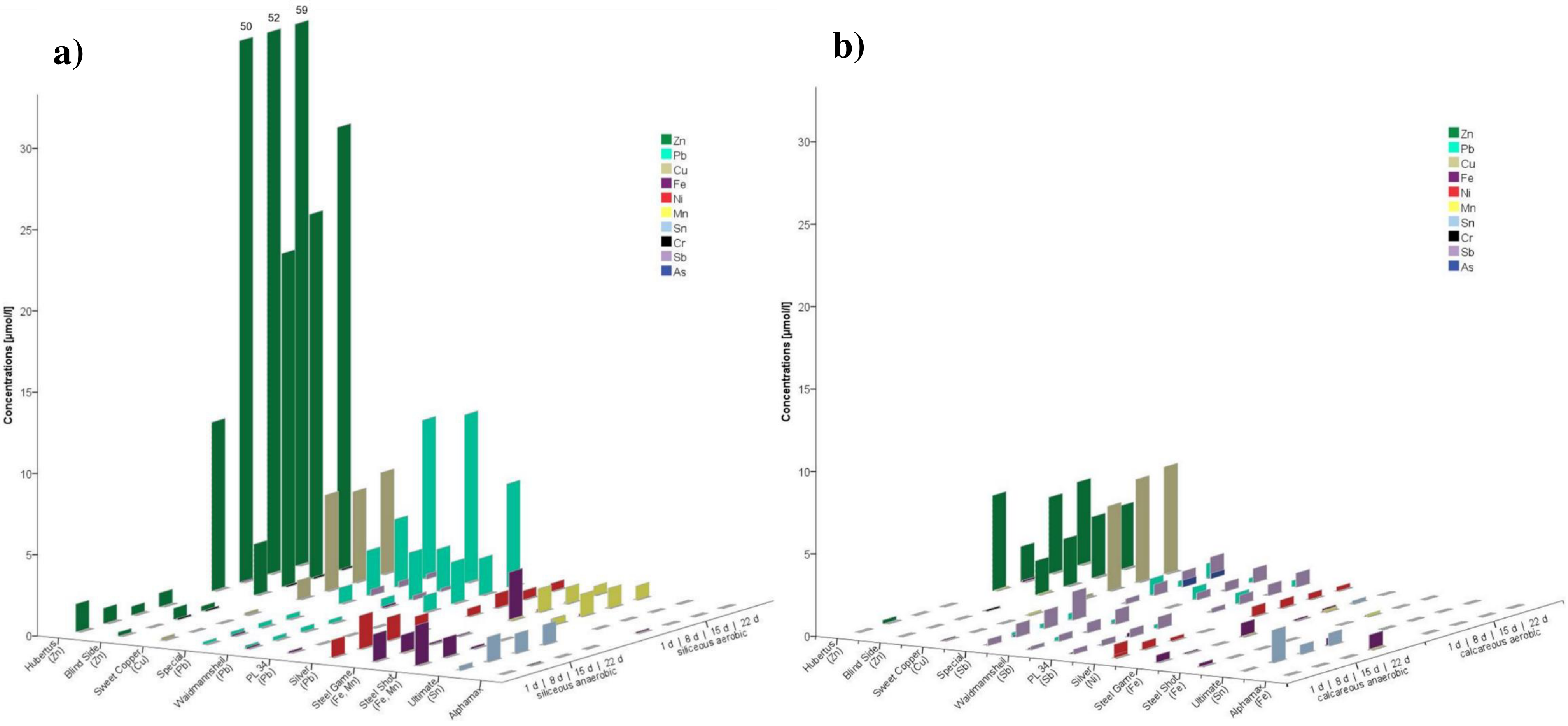


Figure 7: *Mean concentration of leached metals [µmol/l] above the limit of quantification (Table 4) after 1, 8, 15 and 22 days of shotgun material exposure in a) siliceous and b) calcareous water under aerobic and anaerobic conditions. The main metal released is given in brackets (from Fäth & Göttlein 2019).*

3.2.2. Ecotoxicological analysis

In the following section, the risks of the investigated shotgun materials for aquatic systems will be presented and discussed on the basis of the results from the acute toxicity tests with *Daphnia magna* carried out at the Chair of Aquatic Systems Biology. Furthermore, the results of the elution tests with the four water variants using EC_{50} values for Daphnia will be taken into account.

As in the aquatic variants, the conventional lead-based shot **PL 34** also showed a significant release of Pb in the ADaM solution used for the toxicity test (short-term: 1.81 µmol/l; long-term: 0.60 µmol/l). However, there was no significantly increased mortality *of daphnids in the* bioassay compared to the control group (Figure 8). Even the significantly higher release rates of **Waidmannsheil, Special and PL 34** (up to 10.3 µmol Pb/l; Figure 7) in siliceous aerobic water compared to ADaM (Table 7) did not exceed the EC_{50} value of 17 µmol Pb/l for *Daphnia Magna*. Also, the Sb concentrations released in the basic environments did not cause any corresponding limit exceedance. However, the measured Pb concentrations are higher than the LC_{50} value (0.54 µmol/l) of the Mexican amphipod (Borgmann et al. 2005), which is why a potentially acute toxic effect of such concentrations on other key organisms cannot be excluded. Furthermore, concentrations released in this manner may cause long-term effects in organisms, which cannot actively regulate metal concentrations in their tissues, particularly because of the bioaccumulation potential of Pb (McGeer et al. 2003). Nevertheless, the shot material Waidmannsheil, Special and PL 34 can be classified as non-critical, at least for the Large Water Flea.

In the case of the Pb shot material **Silver**, which was presumably coated with Cu/Ni, there was also no significant increase in mortality in the acute daphnia test (Figure 8) despite a clear release of Ni (up to 2.1 µmol/l; Figure 7), nor was the corresponding EC_{50} value (124 µmol/l) exceeded, which is why this material can also be classified as harmless for aquatic environments on the basis of the tests carried out.

In contrast, significantly increased mortality rates of up to 100% occurred in *Daphnia magna* after elution of the **Blind Side** and **Hubertus** shot materials (Figure 8). There was also an exceedance of the EC_{50} threshold value (8.57 µmol Zn/l) in the siliceous aerobic aquatic variant (Table 7 & Figure 7). Therefore, these forms of ammunition should be classified as critical for aquatic systems due to their very high Zn release rate. This also confirms the concern of dissolved Zn ions for other aquatic life, such as grass carp, discussed in Chapter 1.4.4.3 (Chen et al. 2016). In addition, since no limit exceedance occurred in the calcareous and anaerobic variants, it can be assumed that the identified concerns apply primarily to flowing waters in siliceous landscapes. However, this assumption would have to be verified on the basis of further near-natural experiments with suitable organisms.

The Cu-based **Sweet Copper** shotgun matierial also exceeded the EC_{50} values (1.46 µmol Cu/l) in all aerobic variants (Table 7). Accordingly, the daphnia tests also resulted in significantly increased mortality rates of up to 100%. The already extensively established toxic effect of dissolved Cu ions on aquatic organisms (Knauer et al. 1997; Tollett et al. 2009; Azevedo and Cássio 2010; Khangarot and Das 2010; Vardy et al. 2014; Shuhaimi-Othman et al. 2011; Khangarot and Ray 1989; Mount and Stephan 1969; Connon et al. 2011) was thus also confirmed based on the bioassay with *Daphnia magna* for shot materials combined with elution experiments. Therefore, the pure copper shot material should be classified as a concern for aquatic systems. Due to the very low EC_{50} value for Cu in Daphnia, it can be assumed that the Cu-coated Pb shot Sweet Copper (Pb/+) would also exceed the limit value due to its leaching behavior. The failure to exceed the EC_{50} in the anaerobic variants, whose Cu concentrations were even almost always below the limit of quantification, could possibly limit the inferred concern of copper shotgun material or coatings to flowing waters. However, since this has not been verified by further elution experiments and bioassays, the worst case must be used for the overall evaluation for aquatic systems (as was also the case for Blind Side and Hubertus) in accordance with this precautionary principle.

Despite the negligibleleaching behavior of the Fe-based shotgun materials **Steel Game** and **Steel Shot**, iron-based shot material cannot generally be regarded as harmless according to the results of this sub-study. In order to guarantee this statement beyond a doubt, other alloyed elements and coatings such as Cr have to be taken into account. This is illustrated by the high release of Zn in the steel-based shotgun material **Blind Side**, which contributed to an equally critical assessment as the pure zinc-based shotgun material **Hubertus**. Despite thes findings, the steel-based shot material **Steel Game** and **Steel Shot** can be classified as harmless for aquatic systems.

In spite of its coating and its Sn solubility rate (up to 2.0 µmol Sn/l; Figure 7),the W-based shot material **Ultimate** can also be classified as harmless with regard to its ecotoxicological effect in aquatic systems (EC_{50} for Sn in *Daphnia magna*: 182 µmol

Sn/l) (Table 7). The passivation behavior of Sn that was already discussed with regard to the percolation tests (Chapter 3.1.1) was also confirmed in the aquatic elution tests (Chapter 3.2.1), which is why the use of this metal should also be promoted with regard to its safety in this type of system.

Due to non-quantifiable release rates, as well as the absence of significantly increased Daphnia mortality, the Bi shot material **Alphamax** can also be considered non-critical for aquatic systems.

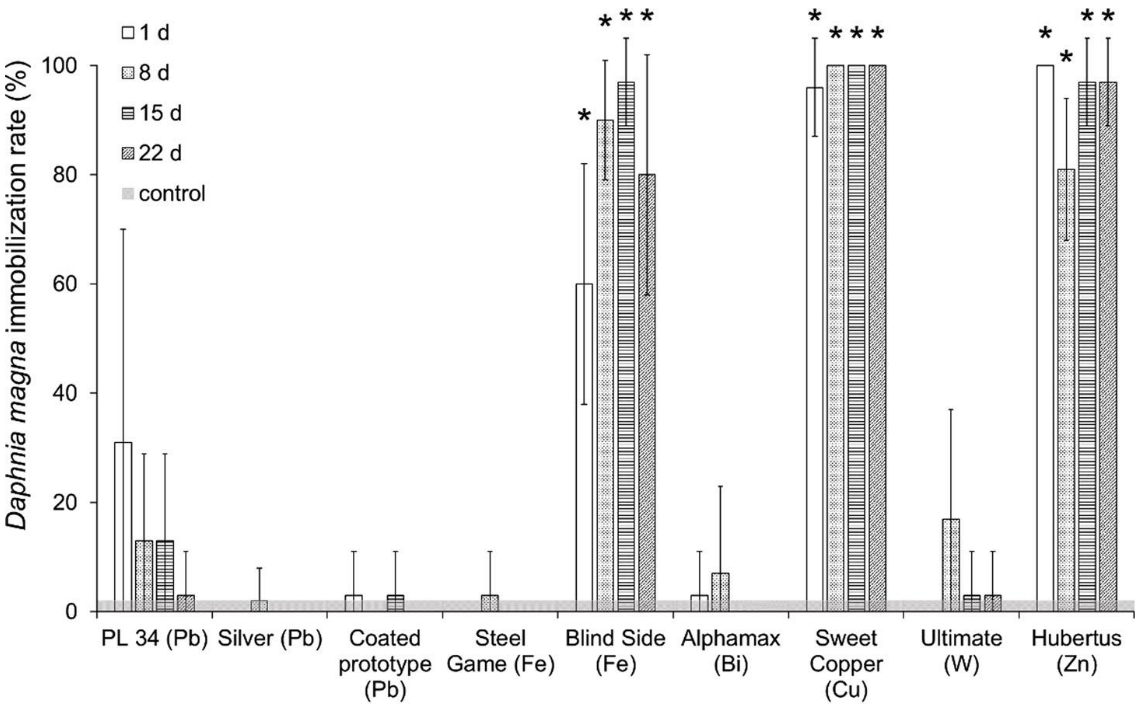


Figure 8: *Average immobilization rate and standard deviation after the 48-hour toxicity test with Daphnia magna after 1, 8, 15 and 22 days of shot material exposure in ADaM. Asterisks mark significant differences (p<0.05) from control. The main component of the shots is indicated in parentheses (from Fäth et al. 2018a).*

Table 7: *Mean and standard error of relevant heavy metal concentrations [µmol/l] per water variant for the short-term (1 d; 8 d) and long-term (15 d; 22 d) behavior during the elution experiments for the aquatic compartment (from Fäth & Göttlein 2019).*

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

[a] BG = Limit of qualififcation; [b] NWG = Limit of determination; The values in bold show homogeneous sub-groups determined by ANOVA with a significantly higher mean value than the rest of the solution media examined. Gray cell staining indicates concentrations exceeding the EC value for Daphnia magna according to Khangarot and Ray (1989).

3.2.3. Methodology

Critical reflection

The replicable methodology of the elution tests makes it possible to estimate the leaching behavior of various shot materials in freshwater systems in direct connection with potentially ensuing ecotoxicological effects (verified by bioassays). This is an important step towards being able to develop comprehensive and practical test methods for assessing potential ecological impacts of shot materials on the environment, which has also been advocated by other ecologists on several occasions (Thomas 2019; Thomas and Guitart 2003).

In order to create conditions that are as realistic as possible, two natural types of water were used for the ion release experiments in addition to the ADaM solution that was produced synthetically for the bioassay. Due to the wide range of geological substrates available, two types of spring water were selected for this purpose, one originating from siliceous bedrock (red sandstone) and the other from a calcareous rock (Munich gravel plain). The additional setting of aerobic and anaerobic conditions (aeration with air or N_2), which simulate redox conditions that vary in part strongly between flowing and stagnant waters, served as a supplementary environmental factor that is important for the leaching behavior of metals. Due to limited resources, additional use of different sediments was not possible. In addition, other waters with a very low pH level, such as water from marshes, could not be included in this study, which would have been important for further verification of the results. Nevertheless, a comprehensive range for the elution behavior of shot materials in freshwater was reported (Figure 3), and a significant influence of geology and redox conditions (Table 7) on the leaching behavior of different shot materials in freshwater was found. Although the ADaM solution is more similar to the calcareous water in terms of its pH level (Figure 3), solubility rates still occurred therein that were significantly different from the calcareous variant. At the same time, despite significant pH differences, there was, for the most part, no significant difference between the ADaM solution and the siliceous aerobic variant with respect to the solubility rates of elements of concern (Table 7). This could be due to the high ionic strength of the ADaM solution caused by its synthetic composition (Chapter 2.2.2).

Deriving a standardizable test procedure

To summarize, the synthetic version and the siliceous aerobic variant of the test represents the most critical scenario, i.e., the situation with the highest heavy metal solubility. Since the properties of naturally extracted water can vary considerably and are thus not reproducible, the ADaM solution would consequently be ideally suited for a standardizable elution procedure for the assessment of ecotoxicological effects of shot materials in aquatic systems. Due to the mostly significantly higher solubility rates in the aerobic version compared to the anaerobic one, aeration with air is recommended for the worst case scenario. Regarding the extensive availability of literature data for the assessment of toxicological effects of dissolved metals on aquatic organisms, especially for *Daphnia magna* (Khangarot and Ray 1989; Okamoto et al. 2015), it would be sufficient to evaluate the concentrations measured in the elution experiments using the corresponding EC_{50} values.

3.2.4. Conclusion

1. As a result of the elution tests and bioassays, shot materials that release zinc or copper should be classified as critical in terms of their ecotoxicological effects in aquatic environments.

2. Conventional and coated lead-based materials, as well as tungsten and bismuth material, did not exceed EC_{50} values and did not significantly increase the mortality rates of *Daphnia magna.*

3. Since coatings can dominate the elution behavior, it is not possible to generalize the ecotoxicological risks for aquatic environments based on the material group or the main component of shot.

4. The bioassay with *Daphnia magna* was the first study that provided a direct link between the leaching behavior of shot material in freshwater and potentially associated ecotoxicological risks.

5. For a standardized evaluation of different shot materials with regard to their ecotoxicological effects in aquatic systems, the elution test conducted in the standardized ADaM solution using EC_{50} values available in literature is recommended.

3.3. Target ballistic performance

Parts of the results presented in the following section have already been published (Fäth et al. 2018b; Fäth et al. 2020).

3.3.1. Results based on technical criteria

Since some anomalies already occurred during the firing tests, these will be described below and will serve as an additional basis for the discussion of the results in Chapters 3.3.3 and 3.4.1.

For the alternative shotgun shell material FOB Sweet Copper, many shot pellets remained stuck in the cup casing as they exited the muzzle and impacted the wooden panel behind the target as a large "projectile" (Figure 9). The shot caked together in the casing, resulted in reduced coverage and therefore reduced ballistic performance (see results for coverage).

Figure 9: *Stuck shot lump in the cup and the wood panel after shooting with FOB Sweet Copper (from Fäth et al. 2018b).*

In addition, a higher grain mass (0.32 g) was found in the course of the weight analysis of this type of shotgun shell at up to 12%, which is more than would have been expected from pure copper shotgun shell material (~ 0.26 g) at this diameter (3.75 mm). The corresponding proportions of the heavier shotgun shells were taken into account in the calculation of the shot material's energy.

In preliminary tests, it was also determined that firing the Ultimate tungsten shotgun shell at the full and ¾ chokes results in a very high level of stress on these two choke shapes and that the overall experiment was jeopardized due to the risk of irreversible damage to the shotgun barrel configurations used. Therefore, the full and ¾ chokes of all manufacturers were not fired with this shotgun cartridge.

3.3.2. Presentation and modeling of the results in huntR

Since the development of standardized procedures for the evaluation of conventional and alternative shotgun ammunition represents a sub-section of this thesis, the application "huntR", with the shiny package (Chang et al. 2020), was developed in cooperation with the StaBLab at the LMU Munich. In particular, due to the numerous variants and variables involved, its use greatly facilitated the presentation of the statistical analysis and results. The app was developed in two steps, whereby the basic platform (1st step) was developed with the shells of the reference barrel as a training dataset and made accessible in the form of a web application (https://hunt-r.shinyapps.io/shinyapp/) (Fäth et al. 2018b). In the second step, this application was extended by implementing additional variables of the remaining shelling variants (choke shape and manufacturer) (Fäth et al. 2020). The app contains different sections, and when opened, the descriptive-statistical section appears, wherein different descriptive metrics (e.g., $\text{Coverage}_{\text{Energy}}$ and $\text{Coverage}_{\text{Hits}}$) and the individual shotgun shell images of all variants were specified (Figure 10).

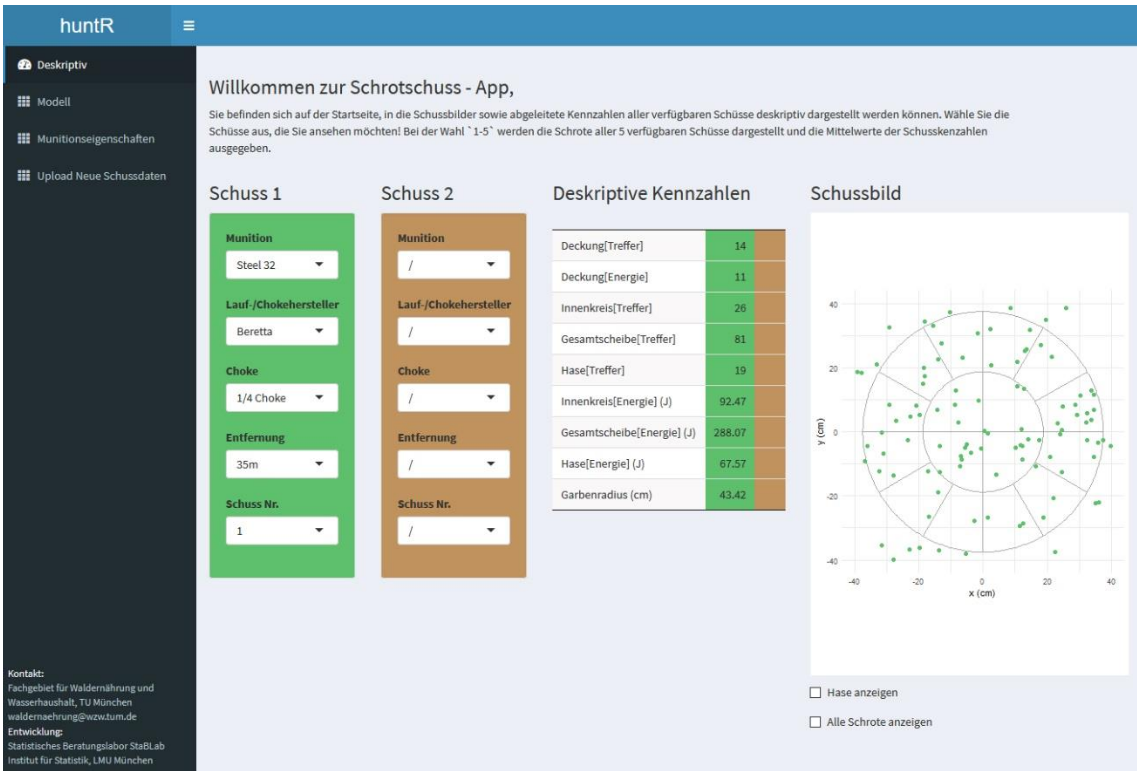


Figure 10: *Descriptive-statistical section of the shiny app "huntR" for illustrating the ballistic results (from Fäth et al. 2020).*

In the "Modell" area, the results of the statistical modeling (see Capter 2.3.4) are shown, which can be selected depending on the variant or ballistic indicator. For each of the ballistic criteria, the estimated regression model can also be used to determine the probability that a specifiable threshold value will be exceeded by the selected criterion for a ballistic variant. This value can also be entered in the diagrams.

Furthermore, in the "Munitionseigenschaften" tab, various information on the physical properties of the shots, such as velocity or weight, can be viewed on a variant-specific basis. This is made easier by an additional search function.

The interface for uploading new data (Figure 11) was used for evaluating future firing data. Here, the user can simultaneously load and evaluate several coordinate files of a shotgun shell variant in the form of .csv files. The requirement is that each file contains the two columns 'x' and 'y' with the coordinates of the individual shot with one line per shell. Additional columns are ignored by the program. Furthermore, the coordinate files are expected to originate from a 300 dpi scan of the shot targets. In addition, the uploaded firing data are automatically centered on the digital 16-field disc by means of a center point adjustment using the median value. With the help of the display of each single shot image, quality assurance of the hit coordinates is possible. Analogous to the descriptive-statistical area, the target criteria of the additional shots can be evaluated directly after entering the grain energy [J]. By clicking on "Zeige mittlere Schusskennzahlen", the respective criteria are displayed in the form of a mean value along with the associated 95% confidence interval (if the number of uploaded shots is $n \geq 5$, in parentheses behind it). The data can be downloaded as a table in the form of a text file. An additional feature is the comparison of uploaded shots with all variants of the total data set developed in this study. The new results are displayed with the label "New Data" as an additional category on the x-axis with an estimated 95% confidence interval at $n \geq 5$.

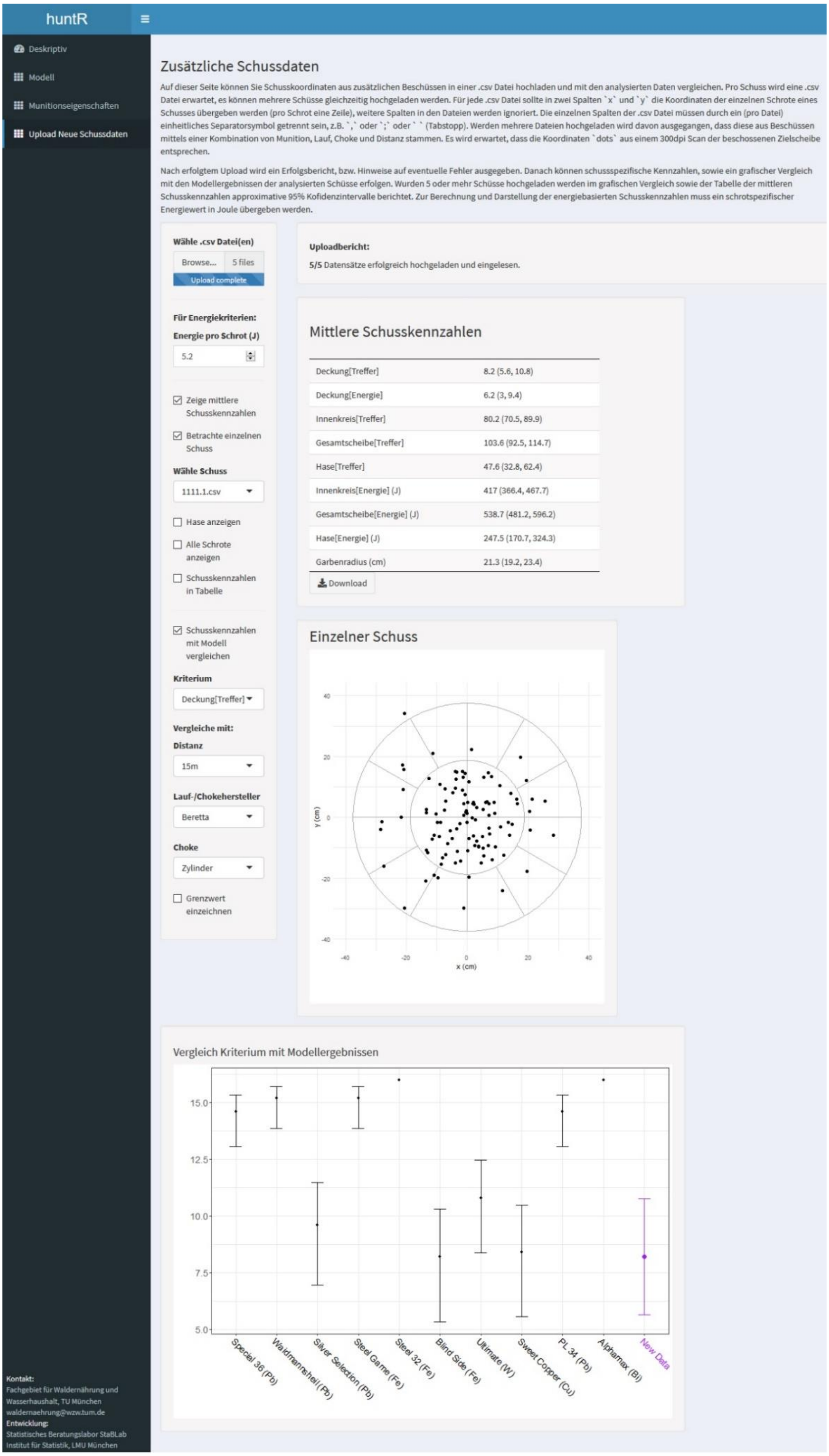


Figure 11: *Interface for uploading new data in the shiny app "huntR" (from Fäth et al. 2020).*

3.3.3. Evaluation & discussion

Methodology

The Wannseer test method from Lampel & Seitz (1983), an established evaluation method for the ballistic performance of alternative and conventional hunting ammunition, was applied and modified for the evaluation of the shot shelling (cf. Chapter 2.3). The additionally derived criterion $Coverage_{Energy}$, with added consideration of kinetic energy per area to the previously simply considered hit counts ($Coverage_{Hits}$), establishes a better comparison of different materials under the various test conditions involved (e.g., choke shape & manufacturer as well as distance). To clarify the question of weighting the criteria $Coverage_{Hits}$ and $Coverage_{Energy}$, results for the lead-based shotgun shell Special 36 and Waidmannsheil at 35 m should be considered. In these variants, $Coverage_{Hits}$ and $Coverage_{Energy}$ are always identical (Tables 8 and 9). This can be explained by the similarity of the grain energy to the energy derived from Lampel & Seitz (1983) for a lead-based shot pellet of the same diameter at 35 m. The alternative materials, Special 36 and Waidmannheil, show the same $Coverage_{Hits}$ and $Coverage_{Energy}$ at 35 m. The $Coverage_{Hits}$ and $Coverage_{Energy}$ results are identical in these variants (Tables 8 and 9). On the other hand, the alternative materials at 35 m show a clear difference in $Coverage_{Hits}$ and $Coverage_{Energy}$, which is why an equal consideration of both criteria is necessary. According to Lampel & Seitz (1983), the "rabbit" scenario requires at least nine segments to be covered for sufficient ballistic performance on a target. In accordance with this equal consideration principle, both Coverage Criteria ($Coverage_{Energy}$ and $Coverage_{Hits}$) must therefore reach a value of at least nine, so that the respective shelling variant fulfills the minimum performance requirement.

The requirement for the $Coverage_{Energy}$ criterion is specified as minimum energy per area. Accordingly, the minimum energy of 29.5 J required for coverage in a segment can also be fulfilled by 30 shots with 1.0 J each, although the amount of energy from a single shell above which several shots can trigger a shock in the tissue of the corresponding game species is unknown. Therefore, an additional minimum grain energy level must be required, which must be as high as that of a standard lead-based shot for hunting a rabbit at 35 m according to Lampel & Seitz (1983), i.e. 5.9 J.

Since the minimum requirements derived by Lampel & Seitz (1983) provide an expanded and contemporary basis for an evaluation according to the current state of knowledge, differences in ballistic performance on a target for various firing options with simultaneous consideration of $Coverage_{Energy}$ and $Coverage_{Hits}$, as well as grain energy will be discussed below on the basis of an evaluation matrix.

Results & evaluation

In general, the shotgun ammunition types investigated met the limits in most cases at short range with a cylinder choke and, in some cases, with a ¼ choke, and at longer range with the narrower chokes (¾ and full choke) (Table 11). The lower coverage value with narrow chokes and a short shooting distance (Table 8 & 9) is due to the specific counting system of the field target (Figure 4). Here, not only were the coverage values of central segments considered, but also that of the outer field target combinations, in order to achieve sufficient ballistic performance – even in the case of a poorer hit location. Furthermore, significant differences were found between choke manufacturers (e.g., Beretta vs. Browning) with the same choke configuration (e.g., full choke or cylinder choke). For the iron-based shotgun shell Steel Shot with a cylinder choke, there were very large differences in the grain energy – even at the same distance (35 m) – with values between 3.8 J (Browning) and 3.0 J (Beretta). The distinct difference in energy is decisive for $Coverage_{Energy}$ and suggests dimensional differences between choke manufacturers with cylinder bores. Blind Side and Steel Game also showed similar differences at 15 m when fired with full, ¾ and ½ chokes. Furthermore, variants containing lead (Silver Selection, Special 36 and Waidmannsheil) had a higher average grain energy, and thus, a higher $Coverage_{Energy}$ level than most of the lead-free alternatives (Table 9 & 10). On the other hand, lead-based shotgun cartridges contain a lower number of shot pellets for the same original weight due to the high density of Pb and deliver a correspondingly lower $Coverage_{Hits}$ value compared to less dense materials (Table 8). An example of this is the Silver Selection shotgun shell type, where the $Coverage_{Hits}$ value is often considered to be decisive in joint evaluation (Table 11). Therefore, this shotgun shell seldom meets the minimum requirement for this Coverage criterion at longer shooting distances, especially for the ½ and cylinder chokes. However, this may also be due to its lower mass of 32 g, compared to 36 g for Special 36. This means that it is not only the shape of choke, the choke manufacturer or the distance that have a significant influence on the target ballistic performance of shotgun cartridges, but also the mass. Waidmannheil and Special 36, on the other hand, meet the minimum requirements for almost every type of firing. The failure to meet the $Coverage_{Hits}$ requirement could be eliminated for the few affected variants by increasing the weight distribution.

At a distance of 35 m, the main limiting factor in the shot shelling with PL34, apart from the $Cover_{Energy}$, was the grain energy, which did not meet the required minimum energy of 5.9 J. The light gray coloring indicates this in the respective cases (Table 11). Particularly in the case of the iron shot Blind Side, Steel Shot and Steel Game, the evaluation of the grain energy is also relevant. If both coverage criteria were to be considered alone, they would be rated similarly to the lead-based shotgun shell Waidmannsheil and Special 36 for the respective shelling variants examined. Assuming an additional minimum energy of 5.9 J per shell for sufficient ballistic performance on a target is required, this is not achieved by the iron-based shotgun shell at 35 m. Steel Shot meets all three required limits with each choke manufacturer only with ¼ and cylinder chokes at 15 m. Steel Game, on the other hand, achieves the three minimum requirements at 25 m with all variants, as well as with ¼ and cylinder chokes at 15 m. Blind Side also achieves sufficient results at 25 m and with a ¼ choke at 15 m with all choke manufacturers, both in terms of the coverage criteria and the grain energy. In general, for all iron-based chokes, it was observed that the minimum grain energy could not be achieved at 35 m in any case (Table 10). This finding coincides with the maximum permissible muzzle velocity according to C.I.P (2017) described in Chapter 1.4.5, which is why iron-based shotgun cartridges in the Member States concerned cannot deliver the necessary performance at this distance.

The shotgun shell diameter of the Alphamax Bi variant is somewhat smaller at 3.3 mm, but it is still possible to test whether this cartridge meets the minimum requirements for hunting a rabbit depending on the defined shelling variants, taking into account the $Coverage_{Energy}$ and grain energy. Analogous to the iron-based shotgun shell, evaluating the grain energy is most relevant here, whereby only in the case of the 25 m variant with a ½ choke does every choke manufacturer achieve all three limit values. At the greatest distance (35 m), Alphamax is likely to have an insufficient $Coverage_{Energy}$ value when using a small choke.

With the exception of a short distance of 15 m, the Ultimate tungsten shotgun ammnuition meets all three minimum requirements, although full and ¾ chokes were not used for firing this type of ammunition due to problems in preliminary tests (cf. Chapter 3.3.1). Due to their high density, the required grain energy was clearly exceeded by the tungsten shot – with values between 9.3 and 18.0 J under all test conditions; but at 15 m, the ½ and ¼ choke variants showed a problematic $Coverage_{Hits}$ value.

As expected due to the factors mentioned in Chapter 3.3.1, the Sweet Copper shotgun ammunition type provided a relatively poor $Coverage_{Hits}$ value in multiple firing conditions without any specific pattern. The stuck shot in the plastic cup, which resulted in an unpredictable flying clump of material and, ultimately, poor coverage. For this type of shotgun ammunition only, there were also shelling variants in which none of the required limit values (black coloring in Table 11) were met.

Table 8: *Evaluation of the $Coverage_{Hits}$ based on Lampel & Seitz (1983). Values < 9 are shaded gray (from Fäth et al. 2020). Translator's note: Table headers from left to right: Cylinder, ¼ choke, ½ choke, ¾ choke, full choke. All commas represent decimal points.*

$Coverage_{Hits}$		Zylinder			1/4 Choke			1/2 Choke			3/4 Choke			Vollchoke		
		Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi
Silver Selection (Pb)	15m	9,6	15,4	11,0	9,4	14,2	8,6	8,8	15,0	5,4	5,2	13,2	4,0	4,2	9,4	4,0
	25m	6,6	10,4	8,8	6,6	11,2	9,6	11,2	12,0	13,4	13,2	14,6	11,4	11,8	15,8	10,2
	35m	4,8	7,4	4,4	5,8	6,6	5,6	5,6	5,8	11,8	10,6	9,6	13,2	14,2	13,4	12,6
Special 36 (Pb)	15m	14,6	15,6	14,0	14,4	15,6	11,2	9,8	14,6	4,0	5,4	11,8	4,0	4,0	6,6	4,2
	25m	10,4	13,6	12,2	11,6	13,6	14,8	12,8	14,0	15,0	15,0	14,4	14,8	11,2	15,2	12,6
	35m	9,4	9,0	9,4	7,4	9,6	11,6	13,4	9,8	15,6	12,8	11,2	15,2	14,6	14,6	14,6
Waidmannsheil (Pb)	15m	15,2	15,4	14,4	14,0	15,8	8,0	8,0	14,6	4,2	5,4	12,2	4,0	4,0	5,2	4,0
	25m	12,6	12,6	13,2	13,2	15,2	15,0	14,6	14,4	14,2	14,6	14,6	13,2	13,8	15,2	13,4
	35m	11,6	10,6	9,4	8,2	11,8	13,4	13,6	12,6	15,0	14,2	14,2	16,0	15,0	15,0	15,4
PL 34 (Pb)	15m	14,6	15,0	15,4	16,0	15,8	14,2	13,2	15,6	6,0	9,6	14,4	4,0	4,0	8,6	4,2
	25m	14,2	15,2	13,2	13,6	14,4	15,6	16,0	14,2	15,8	15,6	15,8	15,4	15,8	15,8	14,2
	35m	10,8	12,0	11,8	11,8	12,8	12,8	15,2	12,6	14,8	15,8	14,0	16,0	15,2	15,4	16,0
Steel Shot (Fe)	15m	16,0	16,0	16,0	15,2	16,0	12,2	8,0	15,4	11,8	4,2	11,6	6,0	5,2	6,4	7,0
	25m	16,0	15,8	15,8	15,8	16,0	15,6	16,0	16,0	16,0	15,8	16,0	15,8	15,2	15,8	14,8
	35m	14,4	14,8	15,2	15,6	13,4	15,4	15,8	15,8	15,8	16,0	15,6	16,0	15,8	16,0	15,8
Steel Game (Fe)	15m	15,2	16,0	15,8	15,8	15,6	10,2	5,4	13,4	5,6	4,8	8,4	5,0	4,6	6,2	5,0
	25m	16,0	16,0	15,6	15,8	15,8	16,0	15,6	15,8	16,0	15,6	15,6	15,2	13,2	15,2	13,6
	35m	13,8	14,0	13,4	12,8	13,3	14,6	15,2	14,4	15,8	15,8	15,0	15,8	15,8	16,0	14,8
Blind Side (Fe)	15m	8,2	12,6	7,4	9,6	10,0	10,6	8,2	11,8	8,0	7,6	13,2	8,0	5,8	11,8	5,4
	25m	14,2	15,4	14,8	15,2	16,0	16,0	14,8	15,8	15,6	15,2	16,0	15,6	15,2	16,0	15,6
	35m	15,4	15,2	15,2	15,0	14,8	13,8	14,8	15,0	15,4	15,2	15,4	15,4	14,2	15,6	15,4
Alphamax (Bi)	15m	16,0	16,0	16,0	16,0	16,0	15,8	15,2	16,0	12,4	12,0	16,0	8,2	5,8	10,6	5,0
	25m	16,0	16,0	16,0	16,0	16,0	16,0	16,0	16,0	16,0	16,0	16,0	16,0	16,0	16,0	16,0
	35m	11,0	14,2	12,2	14,2	14,8	15,0	15,8	15,0	15,6	16,0	15,6	16,0	15,8	16,0	16,0
Ultimate (W)	15m	10,8	11,2	10,2	7,4	11,2	5,0	4,6	9,6	4,0	System compatibility!					
	25m	14,2	14,4	15,6	13,4	14,8	14,0	13,2	12,8	9,4						
	35m	14,2	13,8	13,4	13,8	13,8	14,0	14,0	12,8	14,6						
Sweet Copper (Cu)	15m	8,4	10,6	8,4	7,0	9,8	7,6	6,8	8,8	6,0	4,4	6,8	6,0	5,0	6,6	4,8
	25m	9,6	10,2	8,8	8,0	11,0	12,8	11,8	11,0	12,2	11,4	11,8	13,6	12,0	12,8	13,0
	35m	5,2	9,4	4,4	5,8	4,6	12,0	11,4	7,8	13,0	12,0	9,2	14,8	13,0	11,8	14,6

Table 9: *Evaluation of the $Coverage_{Energy}$ based on Lampel & Seitz (1983). Values < 9 are shaded gray (from Fäth et al. 2020). Translator's note: Table headers from left to right: Cylinder, ¼ choke, ½ choke, ¾ choke, full choke. All commas represent decimal points.*

$Coverage_{Energy}$		Zylinder			1/4 Choke			1/2 Choke			3/4 Choke			Vollchoke		
		Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi
Silver Selection (Pb)	15m	13,4	16,0	15,6	15,4	16,0	14,0	12,0	16,0	9,4	8,6	15,4	5,6	5,2	13,8	4,8
	25m	10,4	15,2	12,6	11,6	14,6	14,4	14,4	14,4	15,0	15,4	15,6	14,6	14,2	16,0	13,8
	35m	7,0	10,0	7,2	5,8	11,2	8,2	5,6	10,4	14,2	10,6	12,6	14,4	15,2	14,8	14,4
Special 36 (Pb)	15m	15,8	16,0	15,4	15,6	16,0	15,2	13,8	15,8	6,6	9,4	15,0	6,2	4,2	12,2	6,8
	25m	12,6	14,4	13,6	14,4	14,6	16,0	15,6	15,6	15,8	15,8	16,0	15,8	13,4	16,0	15,0
	35m	9,4	9,0	9,4	7,4	9,6	11,6	13,4	9,8	15,6	12,8	12,4	15,4	14,6	14,6	14,6
Waidmannsheil (Pb)	15m	16,0	16,0	15,8	16,0	16,0	13,8	11,4	15,4	6,8	7,2	15,4	5,2	4,4	11,8	6,4
	25m	14,6	13,8	15,6	15,4	16,0	15,6	15,6	15,6	15,2	15,4	15,6	15,6	15,6	16,0	15,8
	35m	11,6	10,6	9,4	8,2	11,8	13,4	13,6	12,6	15,0	14,2	14,2	16,0	15,6	15,8	15,6
PL 34 (Pb)	15m	16,0	16,0	16,0	16,0	16,0	15,4	15,4	15,8	7,8	13,4	15,6	4,8	4,0	11,4	4,4
	25m	14,8	15,8	14,8	13,6	15,6	15,8	16,0	15,0	15,8	15,8	16,0	15,8	16,0	16,0	15,6
	35m	8,2	8,8	9,6	6,2	4,2	11,0	14,2	10,6	14,2	14,6	12,0	15,2	15,0	14,8	15,4
Steel Shot (Fe)	15m	16,0	16,0	16,0	15,6	16,0	13,8	9,6	16,0	13,4	6,6	14,4	7,4	7,0	7,0	7,8
	25m	15,4	15,8	15,8	15,8	15,8	15,6	16,0	16,0	15,8	15,8	16,0	15,6	14,8	15,8	13,6
	35m	4,2	10,6	11,8	9,0	8,0	13,0	15,2	13,0	14,6	15,8	14,8	12,8	14,6	15,6	13,4
Steel Game (Fe)	15m	16,0	16,0	16,0	16,0	16,0	14,8	8,6	15,4	8,0	7,0	13,8	8,2	6,6	10,6	6,8
	25m	16,0	16,0	15,6	16,0	16,0	16,0	16,0	15,8	16,0	16,0	16,0	15,6	14,6	15,4	14,8
	35m	12,4	10,4	10,6	9,6	11,5	14,2	14,4	13,2	15,6	14,8	13,8	15,4	15,8	15,2	14,6
Blind Side (Fe)	15m	11,2	15,6	11,4	12,6	11,4	14,0	12,6	14,4	12,6	11,0	14,2	11,8	8,2	14,6	8,4
	25m	14,2	15,6	14,8	15,2	16,0	16,0	14,8	15,8	15,6	15,2	16,0	15,6	15,2	16,0	15,6
	35m	10,0	13,4	14,0	6,6	10,8	9,4	10,2	13,6	13,0	11,2	14,8	13,8	12,4	14,0	14,4
Alphamax (Bi)	15m	16,0	16,0	16,0	16,0	16,0	15,8	15,2	16,0	12,4	12,0	16,0	8,2	5,8	10,6	5,0
	25m	15,6	14,8	15,2	15,2	14,4	16,0	16,0	16,0	16,0	16,0	16,0	15,8	16,0	16,0	16,0
	35m	0,8	0,4	0,4	0,8	2,2	3,6	5,4	3,8	10,8	9,6	6,2	9,0	10,0	10,8	11,4
Ultimate (W)	15m	16,0	15,2	15,6	14,0	15,8	11,2	11,2	14,6	5,0	System compatibility!					
	25m	15,2	15,8	16,0	15,4	15,8	15,4	14,8	16,0	12,8						
	35m	15,4	15,0	15,6	15,2	15,0	14,8	15,0	15,0	16,0						
Sweet Copper (Cu)	15m	12,4	14,8	13,0	12,0	15,0	9,8	10,2	14,4	9,6	6,8	11,6	7,8	7,8	9,6	6,6
	25m	11,6	13,2	11,6	10,6	12,6	13,4	13,4	15,2	14,0	13,8	13,8	15,2	14,2	13,8	14,2
	35m	4,0	9,4	4,4	3,6	3,0	9,0	11,4	7,8	13,0	10,2	9,2	13,6	11,0	11,8	12,8

Table 10: *Single grain energy of the shots [J]. For values < 5.9, the fields are shaded gray (from Fäth et al. 2020). Translator's note: Table headers from left to right: Cylinder, ¼ choke, ½ choke, ¾ choke, full choke. All commas represent decimal points.*

Grain energy		Zylinder			1/4 Choke			1/2 Choke			3/4 Choke			Vollchoke		
		Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi
Silver Selection (Pb)	15m	14,7	14,2	15,5	15,7	15,9	16,0	14,0	12,9	15,9	14,7	14,5	17,0	15,6	15,7	16,8
	25m	10,6	10,3	10,7	11,3	11,1	10,7	10,0	9,1	11,2	10,2	10,5	11,5	11,2	10,8	11,2
	35m	7,4	7,5	7,7	7,1	7,7	7,5	7,1	7,8	8,0	6,6	7,5	7,8	7,8	7,7	7,7
Special 36 (Pb)	15m	11,9	12,6	13,9	14,0	14,0	14,6	13,9	14,7	14,6	13,8	14,2	15,4	13,7	14,8	14,9
	25m	8,9	9,1	9,7	10,0	9,6	10,0	10,1	10,4	9,7	9,8	10,1	10,6	9,8	10,3	10,5
	35m	6,7	6,3	6,7	6,5	7,0	7,3	6,9	7,0	6,2	6,5	7,4	7,4	7,1	7,3	7,2
Waidmannsheil (Pb)	15m	13,4	13,7	14,7	14,1	15,0	15,1	13,7	14,7	15,8	14,4	14,2	15,6	15,1	15,5	16,1
	25m	9,5	9,6	10,1	10,1	10,2	10,3	9,5	10,2	10,3	10,1	9,8	10,7	10,6	10,5	11,0
	35m	6,8	7,1	6,9	7,2	7,1	7,1	6,5	7,0	7,0	6,5	6,8	7,5	7,4	7,8	7,6
PL 34 (Pb)	15m	10,8	12,1	11,2	10,2	10,4	12,3	11,4	11,9	12,3	11,4	12,1	12,8	12,0	12,5	11,8
	25m	7,6	7,9	7,4	7,0	7,5	7,9	7,7	8,9	7,9	7,9	8,1	8,8	8,5	8,5	7,9
	35m	5,3	5,6	5,0	4,6	3,7	5,1	5,0	5,5	5,5	5,2	5,3	5,6	5,5	5,6	5,3
Steel Shot (Fe)	15m	7,6	8,4	8,5	8,6	8,1	8,6	9,0	8,7	9,1	9,2	9,0	8,5	8,5	9,8	8,1
	25m	5,1	6,1	5,8	5,9	5,6	5,8	6,1	5,7	5,9	6,1	6,7	5,5	5,9	6,6	5,5
	35m	3,0	3,8	3,7	3,6	3,7	3,9	3,7	3,5	3,8	3,8	3,8	3,5	3,9	4,0	3,5
Steel Game (Fe)	15m	10,5	11,6	11,7	11,3	11,1	12,1	12,1	11,2	12,0	11,7	12,7	11,1	12,3	12,6	11,2
	25m	7,2	8,0	7,7	8,0	7,6	8,1	8,2	7,8	8,2	7,6	8,6	7,5	8,3	8,4	7,5
	35m	4,9	5,4	5,3	4,6	5,1	5,1	5,0	5,1	5,4	4,8	5,9	5,0	5,5	5,7	5,4
Blind Side (Fe)	15m	11,7	10,8	12,1	9,9	9,7	11,2	9,9	11,2	10,4	10,7	11,6	10,8	10,2	11,2	10,5
	25m	6,8	7,5	7,3	6,2	6,1	7,0	6,2	7,1	6,4	6,8	7,8	7,1	6,1	7,3	7,0
	35m	4,0	4,4	4,4	3,1	3,4	4,2	3,6	4,8	4,2	4,0	5,0	4,4	3,8	4,4	4,4
Alphamax (Bi)	15m	5,6	5,4	5,4	5,7	6,1	6,3	6,2	6,6	6,5	6,5	6,3	6,4	6,2	6,8	7,0
	25m	3,6	3,5	3,2	3,3	3,8	3,8	3,9	4,5	3,7	4,2	4,5	4,3	4,0	4,4	4,4
	35m	2,3	1,8	2,0	2,3	2,5	2,4	2,2	2,9	2,7	2,6	2,7	2,6	2,3	2,7	2,9
Ultimate (W)	15m	16,0	18,4	17,2	17,5	17,9	18,0	16,5	17,1	18,0	System compatibility!					
	25m	12,4	13,7	12,9	13,2	13,3	13,4	12,4	13,0	13,5						
	35m	9,7	10,2	9,8	9,6	9,5	9,8	9,3	9,4	9,9						
Sweet Copper (Cu)	15m	11,8	12,8	13,4	11,1	12,3	13,6	12,0	14,2	12,5	12,2	12,7	11,9	11,6	14,0	12,4
	25m	8,4	9,0	9,3	8,4	8,7	8,8	8,6	10,0	8,1	8,5	9,2	8,2	8,2	9,2	7,6
	35m	5,1	5,9	6,5	5,3	5,8	5,9	6,1	7,1	5,9	5,3	6,2	5,5	5,5	6,2	5,3

Table 11: *Summarized assessment of the shelling variants based on the evaluation from Tables 8, 9 and 10. Variants that meet both coverage criteria (values > 9) and the minimum grain energy (values > 5.9 J) are highlighted in white. If one of the two coverage criteria is not met, the fields (regardless of the minimum grain energy) are colored dark gray. For respective cases, the individual criteria which were not achieved are inserted in the relevant fields. Variants that met both coverage criteria but not the minimum grain energy are highlighted in light gray. If no single threshold value was met, the cells are black (from Fäth et al. 2020).*
Translator's note: *Table headers from left to right: Cylinder, ¼ choke, ½ choke, ¾ choke, full choke. Legend from lightest to darkest color: All limit values achieved; Coverage limit values, but not E_{kin}, per grain achieved; Coverage limit values not achieved; No limit value achieved.*

		Zylinder			1/4 Choke			1/2 Choke			3/4 Choke			Vollchoke		
		Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi	Beretta	Browning	Perazzi
Silver Selection (Pb)	15m						DT	DT		DT	DT & DE		DT & DE	DT & DE		DT & DE
	25m	DT		DT	DT											
	35m	DT & DE	DT	DT & DE	DT & DE	DT	DT & DE	DT & DE	DT							
Special 36 (Pb)	15m									DT & DE	DT		DT & DE	DT & DE	DT	DT & DE
	25m															
	35m				DT & DE											
Waidmannsheil (Pb)	15m						DT	DT		DT	DT		DT	DT & DE	DT	DT & DE
	25m															
	35m				DT & DE											
PL 34 (Pb)	15m															
	25m															
	35m	DE & Ekin/Korn	DE & Ekin/Korn		DE & Ekin/Korn	DE & Ekin/Korn										
Steel Shot (Fe)	15m							DT			DT & DE		DT & DE	DT & DE	DT & DE	DT & DE
	25m															
	35m	DE & Ekin/Korn				DE & Ekin/Korn										
Steel Game (Fe)	15m							DT & DE		DT & DE	DT & DE	DT	DT & DE	DT & DE	DT	DT & DE
	25m															
	35m															
Blind Side (Fe)	15m	DT		DT				DT		DT	DT		DT	DT & DE		DT & DE
	25m															
	35m				DE & Ekin/Korn											
Alphamax (Bi)	15m												DT & DE	DT & DE		DT & DE
	25m															
	35m	DE & Ekin/Korn	DE & Ekin/Korn	DE & Ekin/Korn	DE & Ekin/Korn	DE & Ekin/Korn	DE & Ekin/Korn	DE & Ekin/Korn	DE & Ekin/Korn			DE & Ekin/Korn				
Ultimate (W)	15m				DT		DT	DT		DT & DE	System compatibility!					
	25m															
	35m															
Sweet Copper (Cu)	15m	DT		DT	DT		DT	DT	DT	DT	DT & DE	DT	DT & DE	DT & DE	DT	DT & DE
	25m			DT	DT											
	35m			DT & DE				DT & DE								

Alle Grenzwerte erreicht	Deckungsgrenzwerte nicht erreicht
Deckungsgrenzwerte aber nicht E_{kin} pro Korn erreich	Keinen Grenzwert erreicht

DT: $Coverage_{Hits}$

DE: $Coverage_{Energy}$

$^{Ekin}/_{Korn}$: Grain energy

3.3.4. Methodology

Statistics

A discrete modeling of the coverage criteria presented in this thesis is closely oriented to the criteria established by Lampel & Seitz (1983) using a 16-field grid to assess the ballistic performance of lead-based shotgun ammunition. In a modern approach based on perspective, the modeling that has been done using GLMs could be replaced by a simplified modeling method using the point process of the shot. Target criteria could then be derived directly from the estimated point process, although such an approach would require more complex statistical methods for reliable results, as well as a larger number of shot repetitions.

During the evaluation of the coverage criteria (mean coverage from five repetitions), Lampel & Seitz' (1983) specifications were strictly applied to check the minimum requirement of nine covered segments in terms of energy as well as hits. However, an evaluation of the model probabilities derivable from the regression models described in Chapter 2.3.4 could also be considered. For example, one could demand achieving a minimum probability of 80% for a certain criterion. This would offer a higher degree of reliability compared to an evaluation via a mean value specified by Lampel & Seitz (1983). However, the threshold values applied in Chapter 3.3.3 (e.g., $\text{Coverage}_{\text{Energy}} \geq 9$) would then also have to be adjusted, since the requirements that have to be met via model probabilities would otherwise be significantly stricter and not in line with reality. However, no specifications or empirical values exist on which combinations of minimum requirements and model probabilities could represent a meaningful approach to assessing the ballistic performance of shotgun ammunition, which is why the application of Lampel & Seitz' (1983) criteria is currently the only option.

Evaluation procedure

In general, the lead-based shotgun ammunition provided almost identical values for $\text{Coverage}_{\text{Energy}}$ and $\text{Coverage}_{\text{Hits}}$ at 35 m (Tables 8 & 9), which is due to the similar values obtained for the grain energy of 5.9 J taken from Lampel & Seitz (1983). In contrast, with the exception of Blind Side, the iron-based shotgun ammunition provided similar values of both coverage criteria at a distance of 25 m, which is consistent with the evaluation results for the minimum grain energy of 5.9 J (Table 10). This testifies to the equally high relevance of the grain energy in addition to the energy per area, although it is unclear what the minimum energy per individual grain must be to cause shock death in game. Furthermore, it must be taken into account that alternative metals deform significantly less than lead and therefore most likely have different effects, which cannot be represented holistically by kinetic energy alone. In subsequent studies, the deformation of certain alternative materials after impact with selected simulants should therefore be investigated, and material-specific limit values should be derived therefrom. The impact pattern is also distorted when moving targets are fired upon and achieves different values in reality, which is why the use of the criteria presented here can lead to more differentiated results between the various cartridges. This should also be considered in future studies. Notwithstanding this outlook, Table 11 provides an initial overview for all the shelling variants investigated, from which initial recommendations for the use of shotgun ammunition for hunting can be derived. The additional identification of criteria that have not been achieved also constitutes an important tool for the further development of practical shotgun ammunition.

In general, the results show that a standardized test of the ballistic performance of shotgun cartridges on the market would be very useful. Above all, the significant differences in the $Coverage_{Energy}$ between the choke manufacturers for iron-based shotgun ammunition Steel Shot, with the same choke shape and distance, underline the usefulness of such a test. The relevance of a limit value to be defined for testing a minimum energy level per area ($Coverage_{Energy}$) as well as a minimum grain energy level could also contribute to the comparability of different shotgun materials in this study. The limit values were derived together with the $Coverage_{Hits}$ criterion from data on lead-based shotgun cartridges by Lampel & Seitz (1983) for hunting a rabbit. The shiny app "huntR", which was developed within the scope of this thesis, also provides an important initial approach for recording the ballistic performance of shotgun cartridges on a target and could be taken into account as part of a relevant standardization process for the development of universally applicable standards.

The minimum grain energy taken from Lampel & Seitz (1983), as well as derived coverage limits, would actually have to be empirically tested and possibly reformulated. However, due to the many influencing factors that exist (choke shape, choke manufacturer, distance, shot loading), a general evaluation of shotgun materials is very difficult – even under standardized test conditions – which is why findings from field studies must be viewed critically because of the additional factors mentioned in Chapter 1.4.5 that must be taken into account. Furthermore, Lampel & Seitz' (1983) evaluation criteria, which have so far been valid for lead ammunition, offer both verifiable and effective references for practical shot shelling in hunting, which is why the firing and evaluation procedure presented in this thesis, taking into account various evaluation criteria, represents an initial and viable approach for a comparative ballistic evaluation of conventional and alternative shotgun ammunition.

3.3.5. Conclusion

1. Due to the relevance of many different variables, the target ballistic performance of conventional and alternative shotgun ammunition cannot be generalized by the material or the main component.

2. Based on the shooting tests, it is nevertheless possible to derive initial recommendations (Table 11) on useful combinations between weapon, ammunition and application scenarios.

3. All three iron-based shotgun ammunition types did not meet the minimum requirements at 35 m in any of the variants examined. For iron-based shotgun ammunition to be suitable at this distance, C.I.P. regulations must be adapted.

4. The alternative shotgun cartridge Sweet Copper must be viewed critically – not only with regard to its target ballistic performance, but also with regard to potential hazards during hunting. The proportion of lead-based shot mixed into the cartridge also represents a consumer deception.

5. Therefore, building upon these studies, standardized testing of all shotgun ammunition on the market meant for hunting would be necessary.

3.4. Interdisciplinary discussion

3.4.1. Results of the sub-studies

Given the standardized character of the tests carried out in this thesis on the aspects of "ecotoxicology in terrestrial systems", "ecotoyicology in aquatic systems" and "ballistic performance on targets", their results will be compared and discussed in the following section. A direct comparison of other aspects, such as wild game hygiene, is only possible to a limited extent due to various possible scenarios, as well as the lack of results under standardized conditions. Although the worst case should be used when in doubt, it is equally important to consider how often it occurs. For example, in the standardized test procedure for elution behavior in terrestrial systems (Chapter 3.1), an acidic soil sample with pH4 is the most critical case for most heavy metals, which, according to the results of the Germany-wide forest soil inventory (Wellbrock et al. 2016), corresponds to the median pH values in topsoil. In the field of game meat hygiene/human toxicology, on the other hand, the risk depends on the game meat consumption behavior of humans (Chapter 1.4.3), which, according to Gerofke et al. (2018), is not relevant in terms of its frequency on average, even in the case of increased lead contamination. The most critical case possible here (frequent eaters, such as hunter households) thus does not occur on a representative basis compared to acidic soil with pH4 and therefore cannot be directly compared. In addition, for the time being, standardizable simulation methods, such as those according to Paulsen et al. (2015), would have to be applied for this purpose. Based on the data obtained on target ballistics, a direct comparison with other literature, e.g., on potential ricochet behavior (aspect of hunting safety, Chapter 1.4.2), is also not possible due to the high dependence of physical values of shotgun material on the corresponding configuration of weapon and ammunition components (choke shape, choke manufacturer, shot pattern, shot diameter, etc) and different application scenarios (distance, forest/water bodies). Accordingly, standardized tests would also have to be carried out for this purpose beforehand, taking into account the variables written above. In order not to neglect these aspects, which should be considered for a comprehensive evaluation, these literature references are considered in the following section in addition to the aspects examined in more detail in this thesis and are shown in Table 12 as supplementary references. These should also be understood as a demand for further research into the investigation of shotgun cartridges using standardized procedures.

Lead-based shotgun ammunition

The Pb release of Waidmannsheil, Special 36 and PL34 ammunition detected in the elution tests should be viewed critically according to the evaluation of terrestrial conditions (cf. Chapter 3.1.2). In contrast, in the studies on aquatic environments, the EC_{50} value of Pb for *Daphnia magna* was not exceeded in any of the water-based variants (Figure 7, Table 9) and there was no significantly increased daphnia mortality rate observed in the bioassay (Figure 8). In contrast, the coatings of the two Pb-based meals Silver Selection and RUAG-Sn material painted a different picture. The release of three heavy metals (Cu, Ni, Pb), all of which exceeded the limit values of the BBodSchV (Table 5 & 6), meant that Silver, in contrast to aquatic environments (no significantly increased daphnia mortality and EC_{50} exceedance), also needs to be regarded as critical for terrestrial environments. The coated shotgun material from RUAG-Sn, on the other hand, showed only a minor limit exceedance for Sn (Table 6) in the standardized terrestrial system test, which is why this coating could be a promising alternative due to its positive elution properties (Chapter 3.1.2). In this regard, however, it should be noted that intact shotgun material was used. Accordingly, the coatings may be damaged when the material is shot, which could lead to altered release behavior of the shotgun material (Schwarz et al. 2015), especially in the stomach of birds. Regarding the considerable importance of potentially exposing of the core of coated lead-based shotgun material to other environmental aspects, such as avifauna and game meat hygiene (Table 12), this should be taken into account in future investigations regarding the promising Sn coating. With respect to ballistic performance on a target, on the other hand, it was clear that the lead-based variants met the ballistic requirements in most cases due to their increased grain energy (Table 10) compared to the alternative cartridges (Table 12). This is important because it takes into account the material density, which, according to Pierce et al. (2015), is also decisive for determining the killing power of shotgun material in hunting.

In general, the elution behavior of Pb shot in terrestrial systems should be further investigated. In addition, the aspects of avifauna and game hygiene should be further investigated – especially with regard to coated shot – if possible, under standardized conditions. With regard to the aspect of game meat hygiene in particular, the relevance of lead contamination by shotgun ammunition for different consumer groups (analogous to Gerofke et al. 2018) should be taken into account.

Iron-based shotgun ammunition

The two Fe-based shot types Steel Game and Steel Shot did not show any concerning elution behavior in the ecotoxicological test procedures. Nevertheless, in the case of the iron-based shotgun material, it is not possible to generalize the main component with respect to each of the aspects investigated in this thesis. This was demonstrated by the Zn-coated iron-based shotgun material from Blind Side, which showed a dominant release of Zn for both terrestrial and aquatic environments. The zinc coating, which protects against corrosion, caused such high concentrations (Figure 5 & 7) that both the already very high threshold values for the impacted soil-groundwater (Table 5 & 6) and the EC_{50} and mortality values for *Daphnia magna* (Figure 8) were clearly exceeded. In this context, it must also be taken into account that the dominant release of Zn from the iron-based shotgun material, which is actually considered to be generally "non-toxic", could also have an influence on avifauna, since Zn can also have a toxic effect on birds (cf. Chapter 1.4.4.1). The case of chromium contents in iron-based shotgun material of up to 27% already mentioned in Chapter 1.4.4.2, which, according to Levonmäki and Kairesalo (2001), must be regarded as critical with regard to their effect in different types of soil and for humans (IARC 1990; Freeman 1997; Urbano 2008) due to their increased elution, also emphasizes the problem of generalizing the (eco)toxicological effects of iron-based shotgun material.

In terms of target ballistics, Fe-based shotgun materials must also be considered in a very nuanced manner, which was made considerably more difficult by the differences in grain energy of this type of shotgun material found in some cases between the various choke manufacturers (Table 10). Nevertheless, under the same test conditions, the three iron-based shot material types achieved all three minimum requirements in terms of target ballistics in fewer of the cases investigated (< 50%) compared to the lead-based shotgun material, especially at longer ranges. For the positive shooting scenarios, however, recommendations for respective cartridges can be inferred on the basis of Table 11. The need for a nuanced approach thus contradicts the general conclusions from field studies that iron-based shotgun material is generally equal to that of lead-based shotgun material in terms of target ballistic performance (Hebert et al. 1984; Humburg et al. 1982; Mikula et al. 1977; Pierce et al. 2015). In addition, it should be noted that, according to DEVA (2013) and Kneubuehl (2013), iron-based shotgun material is likely to rebound under certain scenarios due to its increased shear modulus (cf. Chapter 1.4.2), which is why this aspect should be critically examined again in the future with regard to this group of materials. Since the iron-based shotgun material from Blind Side should be considered critical with regard to every aspect examined in detail in this thesis, it is not possible to pronounce iron-based shotgun cartridges generally harmless when the aspect of hunting safety is also taken into account. The use of such cartridges would have to be subject to strict restrictions, which could be worked out on the basis of standardized procedures. In addition, the test characteristics for harder shotgun materials according to the C.I.P (2017) would have to be adapted for this group of materials in order to eliminate the restriction of target ballistic performance by means of a maximum muzzle velocity as described in Chapter 3.3.3.

Zinc-based shotgun ammunition

With regard to the ecotoxicological evaluation of standardized test procedures for terrestrial and aquatic systems carried out in this thesis, the uncoated zinc shotgun material Hubertus should be evaluated at least as critically as the Zn-coated iron-based shotgun material Blind Side (cf. Chapter 3.1.2). Due to the additional acute toxic effect of metallic zinc in birds (Table 12), the heavy metal Zn is thus of particular concern from an ecotoxicological point of view, both as a coating and as a main component in shotgun ammunition.

Due to limited resources, the shotgun ammunition type Hubertus could not be included in the target ballistic tests, which is why no results exist for this purpose.

Copper-based shotgun ammunition

The most conspicuous type of shotgun material with regard to every aspect examined in this thesis was Sweet Copper. The grain mass determinations already made after delaborating the shot cartridges showed a clear discrepancy, which can be explained by 12% of the total shot loading being copper-coated pellets with a lead core (88% of this type of shotgun material was purely copper-based). In addition to the elution tests for terrestrial systems (Figure 5), a subsequent compression test provided clear evidence of the significantly higher plasticity of the heavy metal in the proportionally mixed shot material (Figure 12).

Figure 12: *Shot of the FOB Sweet Copper cartridge (declared as lead-free) after a compression test; left: copper shot; right: copper-coated lead shot (from Fäth et al. 2018a).*

Both the elution tests for terrestrial (up to a very high exceedance of the Cu limit value according to BBodSchV; Chapter 3.1.2) and aquatic environments (exceedance of the EC_{50} values for *Daphnia magna*; Chapter 3.2.2) and the bioassay carried out with daphnia (significantly increased mortality rate of daphnia by up to 100%; Figure 8) illustrate the ecotoxicological concern of copper, an alternative material that is normally considered non-toxic for birds (Chapter 1.4.4.1). In addition to the target ballistics scenarios (Table 12), which were already evaluated negatively for the most part, the plastic cup filled with the shot (Figure 9), as a large and heavy projectile, also represents a clear risk of accidents in hunting practice due to its significantly higher cross-sectional impact and flight range, as well as its unpredictability, which is why this type of shotgun material must be viewed critically in terms of target ballistics and hunting safety.

However, due to added lead-based shot, as well as the stuck shot in the plastic cup, these results cannot be generally applied to pure Cu as a shot material, with the exception of the evaluations of elution behavior in terrestrial and aquatic systems (copper-based shotgun material and coated lead-based shotgun material were considered separately). However, this type of consumer deception (FOB Sweet Copper is sold as a Pb substitute; Nobel Sport 2015) illustrates the need for standardized and mandatory testing procedures for shotgun ammunition meant for hunting that is available on the market, in addition to the concerns raised by both types of shotgun material used.

Tungsten-based shotgun ammunition

The heavy metals Ni and Sn released by the tungsten-based shotgun material in the elution tests should be assessed differently depending on the environmental category under consideration. As already mentioned in Chapter 1.4.4, the elution of small amounts of Sn is harmless for terrestrial and aquatic environments as well as for avifauna, which has now been proven, at least for the most part (low exceeding of the Sn limit in the percolation test; Chapter 3.1.2), by the tests conducted. However, the released Ni ions also represent a problem for terrestrial environments due to the additional exceedance of the Ni test value (Table 6) for the impacted soil-groundwater, whereas aquatic systems should not be regarded critically in this respect. With regard to the main component (W), however, no elution took place in either solubility tests. When examining the target ballistics criteria, the barrel of the full choke variant was damaged in preliminary testing and, for safety reasons, the ¾ and full chokes were not fired in the main test. Therefore, this cartridge was excluded from the case evaluation on target ballistics presented in Table 12. For this reason, a general evaluation of the target ballistic performance of this type of shot material was not possible, but should be considered in accordance with Table 11, depending on the application scenarios that were not investigated in their entirety.

In addition to the ecotoxicity concern of Ultimate in terrestrial systems, the aspect of hunting safety should still be considered (Table 12).

Bismuth-based shotgun ammunition

Due to its very low level of heavy metal release, the bismuth shotgun ammunition Alphamax was rated as harmless in the elution tests for terrestrial and aquatic areas. Nevertheless, the Pb release presented in Chapter 3.1.1 must be taken into account, which was not relevant in the context of the evaluation for terrestrial systems (Chapter 3.1.2) because of the low concentration tested. However, these results confirm the Pb contamination of Bi-based shotgun material found by Kanstrup et al. (2019) (up to 0.7%), which, even at these low levels, can already cause a risk of lead poisoning in birds (Kanstrup et al. 2019). However, in the course of standardized bird gizzard simulations, this would need to be verified for the bismuth shotgun material studied. Furthermore, according to Tsuji & Nieboer (1997), Bi should also be considered critical with regard to the aspect of game meat hygiene and/or human toxicology (Table 12). Similar to the iron-based shotgun ammunition, the evaluation of the ballistic performance of Alphamax on a target was most dependent on the minimum grain energy value, and it fulfilled the minimum target ballistic requirement in only 20% (Table 12) of the cases, whereby the smaller shot diameter must be taken into account for this matter.

Therefore, with regard to this type of shotmaterial, target ballistics and game meat hygiene or human toxicology, in particular, must be critically examined in the future.

Table 12: *Final evaluation of the aspects examined in this thesis for the comparative consideration of conventional and alternative shotgun ammunition with reference to other aspects additionally indicated as being of concern on the basis of literature. A negative evaluation of the elution tests is marked by indicating the leached heavy metals in gray cells. A "+" marks an ecological harmlessness of the shots' elution behavior. For the aspect aquatic systems only those shot types were marked, whose evaluation was verified by the bioassay with Daphnia magna. To evaluate target ballistics, the percentage of cases in which the minimum target ballistic requirement was met was calculated (see Table 11). Cells with respective cases < 50% are colored gray. Due to the smaller diameter, cases of Fiocchi PL 34 and Eley Bismuth Alphamax shot are shown in italics. Cells of the shotgun cartridges not examined for the respective aspect were left blank.*

Shot name	Main element	Coating	Ecotoxicology: Terrestrial systems	Ecotoxicology: Aquatic systems	Target ballistics	Literature references on the risks of the main element
Rottweil Waidmannsheil	Pb	No	Pb		80%	Avifauna[1] Game meat hygiene[2]
Rottweil Special 36	Pb	No	Pb		84%	
Fiocchi PL 34	Pb	No	Pb	+	*67%*	
Rottweil Silver Selection	Pb	Yes	Pb, Ni, Cu	+	60%	
RUAG Sn-Coating	Pb	Yes	Sn	+		
Rottweil Steel Game	Fe	No	+	+	49%	Hunting safety[3]
Fiocchi Steel Shot	Fe	Yes	+		31%	
Winchester Blind Side	Fe	Yes	Zn	Zn	49%	
SK Hubertus Zink	Zn	No	Zn	Zn		Avifauna[4]
Rottweil Ultimate	W	Yes	Ni, Sn	+		Hunting safety[3]
Eley Bismuth Alphamax	Bi	Yes	+	+	*20%*	Game meat hygiene[5]
FOB Sweet Copper	Cu, Pb	No	Cu, Pb	Cu	44%	Avifauna[1], Game meat hygiene[2], Hunting safety[6]

[1]Grandy et al. (1968), Irby et al. (1967), Locke et al. (1967), Kelly et al. (1998), Sanderson et al. (1997), Brewer et al. (2003); [2]Tsuji et al. (1999), Johansen et al. (2004), Lanphear et al. (2000), Canfield et al. (2003), Deutch (2003), Chiodo et al. (2004); [3]DEVA (2013), Kneubuehl (2013); [4]Grandy et al. (1968), Levengood et al. (1999, 2000); [5]Tsuji & Nieboer (1997) ; [6] Chapter 3.1.1

3.4.2. The Problems of generalization

The final evaluation in Table 12 clearly shows that there is no alternative shotgun cartridge among the products that could be rated positively with regard to each of the aspects investigated. Moreover, there are literature references for at least one further area that was not examined in detail in this thesis (e.g., avifauna or game meat hygiene) on the corresponding risks related to the main component of the material. However, according to the results of this thesis, a generalization about the main component of shotgun materials, especially for aspects that are more closely examined by means of standardized tests, is not conclusive. Rather, properties such as a low release of heavy metals into the environment, as well as a minimum target ballistic performance must be called for and tested depending on different scenarios. Likewise, it is not conclusive in any case to compare all alternative materials as a single group in terms of their properties with those of conventional lead-based shotgun materials. The different chemical and physical properties of Fe, Cu, Bi, Zn or W cause such a high deviation in the parameters investigated (e.g., target ballistics or elution behavior) by means of a combined consideration of all alternative materials that, ultimately, no significant differences can occur (cf. Chapters 1.2 & 1.4.2). A conclusion to be derived from this process should therefore not be the assumption that, due to there being no significant difference, all materials represent a real alternative, but rather that there are some materials that justify substitution in each case with regard to the aspect under consideration and that there are others that do not.

Furthermore, when discussing the ecotoxicity of ammunition components, the focus often lies on the protection of specific bird species – also with equally sweeping generalizations about the principal component. Therefore, the term "non-toxic shot" is usually used as a synonym for "non-lead shot”, which, however, is not correct, firstly by means of terminology and secondly from empirical evidence, among other things, due to the toxicity of zinc to birds, which was presented in Chapter 1.4.4.1. Moreover, the results presented in Chapter 3.1.1 for the elution test in terrestrial environments support the risk of the existence of Pb-contaminated Bi material (with up to 0.7% Pb) published by Kanstrup et al. (2019). According to these findings, even the low Pb content in bismuth shot can cause the risk of lead poisoning in birds according to the same pattern of poisoning from pure lead shot (Kanstrup et al. 2019). Other toxic metals may also be present in shotgun materials in the form of alloys or coatings, some of which are at least as important as the main element of the material, especially for elution behavior in different environments (see Chapters 3.1.5 and 3.2.4). This issue was shown, among other things, by the acute toxicity test for aquatic environments, in which an iron-based shot (Blind Side), which is actually officially classified as generally having non-toxic main material, caused almost 100% mortality of the tested daphnia species due to its zinc coating. The percolation tests also showed that the coated lead-based shot from the Silver Selection released additional amounts of Ni and Cu, which should also regarded as critically as alternative elements. Due to additional alloyed materials, the tungsten shot (Heumann & Stolica 1971; Ducros et al. 1999), which was considered generally inert in the same test, also released significant Ni concentrations. Due to this, the results on the partial aspects of ecotoxicology (Table 12) refer not only to the main elements, but also to alloyed materials and coatings.

The comparative examination of the ballistic properties of alternative and conventional shotgun ammunition on a target also showed that blanket statements about any one material are impossible. The firing tests carried out under standardized conditions proved that a large number of factors (distance, shot grain size, assembly, choke shape, choke manufacturer) have an added influence on the ballistic performance of hunting shotgun cartridges on a target, which is why each individual variant can be considered separately and, at best, recommendations can be derived therefrom. Even with the three iron-based shotgun ammunition types examined, Steel Shot, Steel Game and Blind Side, the results were so different for the same shelling variants that they had to be analyzed in detail and evaluated depending on the firing scenario (cf. Chapter 3.3.3). For this reason, as well as for reasons of influences from other factors (e.g., judgment, shooting skills and the general behavior of the hunter, as well as wind conditions; Mondain-Monval et al. 2015), blanket statements on the killing effect of shotgun shells derived from field studies (Hebert et al. 1984; Humburg et al. 1982; Mikula et al. 1977; Pierce et al. 2015) should be viewed in a critical manner.

3.4.3. Necessity of standardized procedures

Due to the issue of generalizations discussed in Chapter 3.4.2, a comparative evaluation, especially for alternative shotgun ammunition, would make sense by applying standardized test procedures to check every type of shotgun ammunition available on the market. In doing so, the required properties, such as reduced environmental impact or sufficient ballistic performance on a target, could be tested in detail.

Thomas (2019) also points out the problem of sweeping considerations regarding the main component of shotgun materials and attempts to simplify this generalization for alloy components, which can also have toxic effects on the environment. Here, reference was made to the legally applicable testing protocol (USFWS 1997) for the approval of shotgun ammunition in the U.S.A.. In the first stage thereof, this procedure is mainly based on theoretical considerations of the effect of heavy metals in the environment. In aquatic environments, for example, it is assumed that a shot grain dissolves completely in one cubic foot of water, from which a concentration of dissolved ions can be calculated, which is then compared with literature values such as EC_{50} for *Daphnia magna*. Due to the very different leaching behavior of alternative shotgun materials (see Chapters 3.1.1 and 3.2.1), such estimates are not realistic. They ignore inertness and, consequently, electrochemical behavior, as well as the formation of insoluble products (e.g., metal oxides) of some metals such as tungsten, which would never dissolve completely in nature. Although complete solubility of a shotgun grain could be a kind of "most critical case," additional elution tests must be performed to determine whether components (e.g., thin coatings) with low mass fractions at a higher solid-liquid ratio are nevertheless ecotoxicologically relevant. For example, the shot coating from Blind Side, with a thickness of up to 3 µm, would not exceed the 1% Zn limit proposed by Thomas (2019) due to a maximum mass fraction of 0.33% (Fäth & Göttlein 2019). Nevertheless, the Zn coating dominated the leaching behavior of the Fe-based shotgun material (cf. Chapter 3.2.1, Figure 7) and caused almost 100% mortality of the daphnia species (cf. Chapter 3.2.2, Figure 8). Thus, simplified threshold values for major components, alloys, and coatings, such as those according to Thomas (2019), should be complemented by standardized elution tests for terrestrial and aquatic environments (see also Thomas & Guitart 2003). This would allow the risks of any shot material, including the effect of coatings on the environment, to be comprehensively assessed. Thomas' (2019) material threshold values, which should nevertheless be applied, could detect and prevent potential consumer deception, such as the proportion of Cu-coated Pb-based shot material in FOB Sweet Copper cartridges. Also, the toxic effect towards birds should not be neglected in this regard. Due to their very high Zn release, the Hubertus and Blind Side shotgun materials probably have a negative effect not only on aquatic (cf. Chapter 3.2.2) and terrestrial habitats (cf. Chapter 3.1.2), but also on avifauna. Therefore, in addition to the limits called for by Thomas (2019), existing tests using avian gizzard simulations

(Kimball & Munir 1971; Levengood & Skowron 2001; Thomas & McGill 2008; Martinez-Haro et al. 2009) should be conducted.

An equally comprehensive test for shotgun ammunition available on the market must be carried out with regard to its killing effect. Due to the problem of generalizing the results from field studies discussed in Chapter 3.4.3, this test must be carried out under standardized conditions for different firing scenarios. In particular, the considerable differences between choke manufacturers (cf. Chapter 3.3) require additional consideration of this important parameter in addition to distance and choke characteristics. Since the Wanseer standard method by Lampel & Seitz (1983) has, to date, been the only test method available for use hunting, the method modified in this thesis, which was used as an example for a species of game (rabbit) to be hunted with the shot diameters investigated, should be used for the evaluation of both conventional and alternative shotgun cartridges for reasons of topicality.

3.4.4. Outlook

In order to ensure a reduction of negative environmental impact for shotgun ammunition on the market while simultaneously ensuring sufficient target ballistic performance of such ammunition, the methods described in Chapters 3.1, 3.2 and 3.3 would need to result in a standardization procedure analogous to "DIN SPEC 91384" and thus be asserted as a recommendation for the industry. Due to the additional aspects to be considered according to Table 12, these could also be extended to include the bird gizzard simulation tests mentioned in Chapter 1.4.4.1 (coverage of the avifauna environments), which are already established in the USA, for example. Furthermore, a standardizable procedure already exists for the field of game meat hygiene or human toxicology (Paulsen et al. 2015), which could also be used to test shotgun ammunition. However, a prioritisation of the different evaluation aspects cannot be derived in this thesis. It is difficult or nearly impossible to determine whether the life of a water flea is more or less valuable than the life of a duck or an earthworm. Therefore, a prioritisation or focusing would ultimately have to be determined by policy with reference to the respective standards or methods.

If such mandatory standards or methods were established in Germany or the EU, it would not be necessary to make a blanket statement about main components in shot materials for the evaluation of different alternative materials, which can often be a product of politics in favor of simplified solutions or decisions, e.g., banning the use of lead.

4. General Conclusions

The results of this thesis show that the multidisciplinary evaluation of conventional and alternative shotgun ammunition is very complex – even under standardized conditions - and, therefore, mandatory test methods for shotgun cartridges meant for hunting that are available on the market would be useful. The knowledge gaps of the effects of shot materials, particularly in the areas of ecotoxicology and target ballistics, described at the beginning of this work, could be bridged by the development and application of standardized test procedures for the elution behavior of shot material in the environment and for its target ballistic performance, at least for the types of shotgun ammunition that were studied. In this context, there was no alternative among the tested cartridges that could be considered non-critical with respect to each of the investigated aspects. In addition, it was found that a blanket evaluation based on the main component of the shot material, such as iron, is insufficient for both environmental aspects and killing effect. Instead, properties such as a reduced release of toxic metals or sufficient target ballistic performance must be established, against which each type of hunting shotgun ammunition on the market should be tested. Since additional influential factors, such as shotgun barrel configuration (choke shape, choke diameter), other cartridge characteristics (loading, shot weight, shot diameter) or deployment scenario (distance, water vs. forest) play a role here, additional usage recommendations for each shotgun cartridge could be derived from these results. An investigation that is independent of the main components of shot material would ultimately identify the cartridges that are truly non-critical with respect to the aspects mentioned in this thesis, such as ecotoxicology, killing effect, game meat hygiene/humantoxicology, and hunting safety. Among these factors, innovative lead-based shot materials (e.g., with a heavy tin coating) could be considered, if they meet all the requirements. The introduction of a corresponding evaluation process for hunting shotgun ammunition available on the market would also make decisions and debates on the banning of certain groups of materials unnecessary.

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Zeitler R. (2012): Wirklich besser, schneller, gesünder? Jagd in Bayern 5, S. 37-38.

6. List of Previous Publications

Publications

Fäth J., Feiner M., Beggel S., Geist J., Göttlein A. (2018a): Leaching behavior and ecotoxicological effects of different game shot materials in freshwater. Knowledge and Management of Aquatic Ecosystems 419, 24, doi:10.1051/kmae/2018009.

Fäth J., Goretzko D., Pargent F., Gessinger M., Pfeiffer W., Brack L., Liu T., Warter T., Günther F., Kuchenhoff H., Göttlein A. (2018b): Investigating target ballistic characteristics of conventional and alternative shotgun ammunition for the applicability in hunting. Allgemeine Forst und Jagdzeitung 189, S. 161-172, doi:10.23765/afjz0002028.

Fäth J., Göttlein A. (2017): Comparative investigation of the metal leaching from conventional and alternative game shot in a percolation experiment. Allgemeine Forst und Jagdzeitung 188, S. 222-232, doi:10.23765/afjz0002016.

Fäth J., Göttlein A. (2019): Assessing the leaching behavior of different gunshot materials in natural spring waters. Environmental Sciences Europe 31, 57, doi:10.1186/s12302-019-0249-2.

Fäth J., Günther F., Gessinger M., Langer F., Küchenhoff H., Göttlein, A. (2020): Target ballistic properties of conventional and alternative shot ammunition with different shotgun configurations. Allgemeine Forst und Jagdzeitung 191, S. 37-49, doi: 10.23765/afjz0002058.

Conference papers

Fäth, J., Göttlein, A. (2018). Vergleichende Bewertung der Metallionenfreisetzung konventioneller und alternativer Jagdschrotmaterialien. In: Berichte des Forschungszentrums Waldökosysteme der Universität Göttingen, Reihe B, Band 83, Forstwissenschaftliche Tagung 2018 in Göttingen; ISBN 978-3-940617-11-8, S. 398.

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lfd. Nr.	Jahr	Autor	Titel	Bezugs-preis*
222	2022	J. Fäth	Vergleichende Betrachtung konventioneller und alternativer Schrotmaterialien hinsichtlich ihrer Wirkung in der Umwelt sowie ihrer zielballistischen Eigenschaften anhand standardisierter Verfahren; 96 S.	20,00 €
221	2021	K. Stimm (Hrsgb.)	Die Eiche - Facetten zu Ökologie, Naturschutz, Wachstum und waldbaulichen Perspektiven; 306 S.	30,00 €
220	2020	J. Ewald, A. Göttlein, J. Prietzel, M. Kohlpaintner, B. Reger, M. Olleck	Alpenhumus als klimasensitiver C-Speicher und entscheidender Standortfaktor im Bergwald; 154 S.	25,00 €
219	2021	B. Felbermeier, B. Stimm (Hrsgb.)	Waldbau weltweit 2.0 - Festschrift anlässlich der Verabschiedung von Prof. Dr. Dr. Reinhard Mosandl; 282 S.	30,00 €
218	2020	J. Hamberger (Hrsgb.)	Beiträge zur Forstgeschichte: Festschrift zur Ruhestandsversetzung von LWF-Präsident Olaf Schmidt; 214 S.	30,00 €
217	2017	E. Thurm	Mixed stands of Douglas-fir and European beech compared to pure stands: Patterns and growth analyses in dependence of site conditions	25,00 €
216	2017	J. Hamberger (Hrsgb.)	Forum Forstgeschichte - Festschrift zum 25-jährigen Bestehen des Arbeitskreises Forstgeschichte; 162 S.	25,00 €
215	2016	A. König, M. Scheingraber, J. Mitschke	Energiegehalt und Qualität der Nahrung von Rehen (Capreolus capreolus) im Jahresvergleich in zwei unterschiedlich geprägten Habitaten	25,00 €
214	2015	A. Wallner, R. Seitz, (Hrsgb.)	Der gepixelte Wald - Reloaded; 148 S.	25,00 €
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212	2014	A. Göttlein, K. Katzensteiner, A. Rothe	Standortsicherung im Kalkalpin - SicALP; Abschlussbericht zum Forschungsprojekt INTERREG BY/Ö J00183	18,00 €
211	2012	S. Korten, J. Hamberger, R. Pausch	Beiträge zur Forstlichen Arbeitswissenschaft und Angewandten Informatik - Festschrift zur Emeritierung von Prof. Dr. Walter Warkotsch	15,00 €
210	2011	B. Michler, A. Fischer	Arzneipflanzen in Bayerischen Wäldern: Analyse des natürlichen, nachhaltig nutzbaren Potenzials	15,00 €
209	2010	O. Schmidt, R. Seitz	Der gepixelte Wald - Forstliche Fernerkundung vor dem Hintergrund aktueller Entwicklungen in Umwelt und Technik	15,00 €
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206	2009	J. Hamberger	Forum Forstgeschichte Festschrift zum 65. Geburtstag von Prof. Dr. Egon Gundermann	25,00 €
205	2007	E. Gundermann, O. Schmidt	Forum Forstgeschichte Ergebnisse des Arbeitskreises Forstgeschichte in Bayern 2005 - 2007	15,00 €
204	2007	S. Korten	Holzernteschäden an Fichten-Buchen-Verjüngung Ausmaß, Verteilung, Prognose und Bewertungsansätze	41,00 €
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96	1989	KOLLOQUIUM	Der EG-Binnenmarkt. Chancen und Risiken aus Sicht von Forst- und Holzwirtschaft	7,50 €
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89	1988	U. Pröbstl	Auswirkungen des Waldsterbens auf Erholung und Fremdenverkehr in waldreichen Mittelgebirgslandschaften Bayerns	10,00 €
88	1988	H. Löffler	Langzeitlagerung von Stammholz und Schnittholz	11,00 €
87	1988	B.-M. Liss	Versuche zur Waldweide - Der Einfluss von Weidevieh und Wild auf Verjüngung, Bodenvegetation und Boden im Bergmischwald der ostbayerischen Alpen	vergriff.
86	1988	R. Hüser, K.-E. Rehfuess	Stoffdeposition durch Niederschläge in ost- und südbayerischen Waldbeständen	7,50 €
85	1987	W. Warkotsch, R. Neubert	Untersuchungen zur Erhöhung der Tragfähigkeit von forstlichen Fahrwegen und deren Nachweis mittels dynamischer Verdichtungsprüfung	7,50 €
84	1987	W. Philipp	Die Aufforstung als Beitrag zur Lösung des Überschußproblems in der Landwirtschaft Bayerns	15,50 €
83	1987	H. Röhle	Entwicklung von Vitalität, Zuwachs und Biomassestruktur der Fichte in verschiedenen bayerischen Untersuchungsgebieten unter dem Einfluss der neuartigen Walderkrankungen	7,50 €
82	1987	A. Knorr	Ernährungszustand, Standortansprüche und Wuchsleistung der Esche (Fraxinus excelsior L.) in Bayern	10,00 €
81	1987	T. Preuhsler	Wachstumsreaktionen nach Trassenhieb in Kiefernbeständen	10,00 €
80	1987	KOLLOQUIUM	Die Produktion nachwachsender Rohstoffe auf bisherigen landwirtschaftlichen Flächen aus Sicht von Forst- und Holzwirtschaft	vergriff.
79	1987	K. Foerst, U. Sauter, W. Neuerburg	Bericht zur Ernährungssituation der Wälder in Bayern und über die Anlage von Walddüngeversuchen	6,00 €
78	1987	U. Ammer et al.	Der Einfluss des Altmühlüberleiters bei Gunzenhausen auf die Entwicklung des Artenspektrums, die Vitalität und das Wachstum der benachbarten Kiefernbestände	8,50 €
77	1987	K. v. Gadow	Untersuchungen zur Konstruktion von Wuchsmodellen für schnellwüchsige Plantagenbaumarten	7,50 €

76	1986	H. Weiger	Experimentelle Untersuchungen in nordbayerischen Nadelwaldbeständen über den Wasserhaushalt und den Stickstoffeintrag nach Stickstoffdüngungen	15,50 €
75	1986	Ch. Bosch	Standorts- und ernährungskundliche Untersuchungen zu den Erkrankungen der Fichte (Picea abies (L.) Karst.) in höheren Gebirgslagen	10,00 €
74	1986	R. Amtmann	Dynamische Windbelastung von Nadelbäumen	vergriff.
73	1986	R. Mössmer	Verteilung der neuartigen Waldschäden an der Fichte nach Bestandes- und Standortsmerkmalen in den Bayerischen Alpen	7,50 €
72	1986	KOLLOQUIUM	Produktionsziele, Zielsortimente und Rohholzvermarktung aus Sicht von Forst- und Holzwirtschaft	5,00 €
71	1986	R. Plochmann, Ch. Hieke	Schadensereignisse in den Wäldern Bayerns - Eine Zusammenstellung der forstlichen Literatur seit Beginn des18. Jahrhunderts	7,50 €
70	1986	E. Kennel, A. Reitter	Waldschadensinventur Bayern 1985	vergriff.
69	1986	E. Reigber, G. Braun, H. Tränkner	Forstliche Bioindikatoruntersuchungen in Bayern - Die Kombination von Luftbildauswertung und Bioindikatoruntersuchung, dargestellt am Beispiel Oberallgäu 1983	10,00 €
68	1985	E. Reigber, G. Braun	Forstliche Bioindikatoruntersuchungen in Bayern - Methodik und erste Ergebnisse 1981/ 1982 -	10,00 €
67	1985	G. Zwirglmaier, H. Löffler, W. Patzak	Struktur und Frühinvalidität der Waldarbeiterschaft der Bayerischen Staatsforstverwaltung	7,50 €
66	1985	KOLLOQUIUM	Forderungen an eine Bundeswaldinventur aus der Sicht von Forst- und Holzwirtschaft	5,00 €
65	1985	H. Pretzsch	Wachstumsmerkmale süddeutscher Kiefernbestände in den letzten 25 Jahren	7,50 €
64	1985	E. Kennel, G. Zwirglmaier	Waldschadensinventur Bayern 1984	vergriff.
63	1985	E.-M. Mössmer	Einflußfaktoren für die Blaikenerosion auf beweideten und aufgelassenen Almflächen im kalkalpinen Bereich der Landkreise Miesbach und Rosenheim	6,50 €
62	1984	G. Maier	Aufnahme und Auswertung von Fichtenbeobachtungsflächen in Bayern	5,00 €
61	1984	R. Mosandl	Löcherhiebe im Bergmischwald	vergriff.
60	1984	KOLLOQUIUM	Der Holzaußenhandel als Problem von Forst- und Holzwirtschaft	6,00 €
59	1984	C.-Th. Bues	Radiodensitometrische Untersuchung der Variation von Jahrringbreite und Holzdichte in südafrikanischen Pinus radiata-Beständen unter dem Einfluss des Klimas und verschiedener Durchforstungsmaßnahmen	6,50 €
58	1984	K. Uebelhör	Struktur und Dynamik von Nothofagus-Urwäldern in den Mittellagen der valdivianischen Anden Chiles	10,00 €
57	1983	E. Kennel	Waldschadensinventur Bayern 1983 - Verfahren und Ergebnisse -	7,50 €
56	1983	W. Mergner	Einfluss des Schalenwildes auf die bäuerliche Waldwirtschaft	vergriff.
55	1983	H.-U. Grosse	Untersuchungen zur künstlichen Verjüngung des Bergmischwaldes	vergriff.
54	1983	KOLLOQUIUM	Möglichkeiten der Stabilisierung des Rohholzmarktes als Problem von Forst- und Holzwirtschaft	6,00 €
53	1982	H. Rodenkirchen	Wirkungen von Meliorationsmaßnahmen auf die Bodenvegetation eines ehemaligen streugenutzten Kiefernstandortes in der Oberpfalz	vergriff.
52	1982	KOLLOQUIUM	Beschränkungen in der Produktion durch externe Einflüsse als Problem von Forst- und Holzwirtschaft	6,50 €
51	1982	H. Röhle	Struktur und Wachstum von Stieleichen-Mischbeständen auf grundwasserbeeinflußten Standorten in den Auewäldern Südbayerns	7,50 €
50	1982	A. Karameris	Analyse und Prognose der Erholungsnachfrage in Wäldern als forstlicher Beitrag zur Raumplanung	8,50 €
49	1981	KOLLOQUIUM	Die Statistik über Forst- und Holzwirtschaft - Bestandsaufnahme und Folgerungen	6,00 €
48	1981	M. Horndasch, F. Franz	Die Standortserkundung in den Staatswaldungen der Oberforstdirektion Augsburg	6,50 €
47	1981	W. Laatsch, B. Zenke	Verfahren zur Reichweiten- und Stoßdruckberechnung von Fließlawinen	7,50 €
46	1980	KOLLOQUIUM	Öffentlichkeitsarbeit als Problem von Forst- und Holzwirtschaft	6,00 €
45	1979	T. Preuhsler	Ertragskundliche Merkmale oberbayerischer Bergmischwald-Verjüngungsbestände auf kalkalpinen Standorten im Forstamt Kreuth	7,50 €

44	1979	A. van Laar	Biometrische Methoden in der Forstwissenschaft; Teil I: Verfahrensgrundlagen, Teil II: Auswertung forstlicher Versuche	7,50 €
43	1979	KOLLOQUIUM	Marktordnung für Rohholz als Problem für Forst- und Holzwirtschaft	7,50 €
42	1978	SYMPOSIUM	100 Jahre Forstwissenschaft in München	7,50 €
41	1978	E. Gundermann	Die Beurteilung der Umwelteinwirkungen von Forststraßen im Hochgebirge	7,50 €
40	1978	W. Kroth, G. Gleißner	Leistungen der bayerischen Forstbetriebe zur Verbesserung der Erholungs- und Schutzfunktion des Waldes	7,50 €
39	1978	KOLLOQIUM	Mobilisierung der Nutzungsrückstände und Nutzungsreserven im Kleinprivatwald als Problem der Forst- und Holzwirtschaft	7,50 €
38	1977	P. Burschel, R. Eder, K.-E. Rehfuess, D. Kantarci	Waldbauliche, ökologische und bodenkundliche Untersuchungen in jungen Kiefernökosystemen nach unterschiedlichen Bodenbearbeitungen	7,50 €
37	1977	P. Burschel, H. Löw, C. Mettin	Waldbauliche Untersuchungen in den Hochlagen des Werdenfelser Landes	7,50 €
36	1977	U. Ammer, A. Pohlmann	Beispiele zur Rekultivierung von Aufschüttungen und Abgrabungen in stadtnahen Wäldern	7,50 €
35	1977	R. Mößmer, U. Ammer	Reiten in stadtnahen Wäldern - Modellplanung Forstenrieder Park München	7,50 €
34	1977	R. Lammel, R. Plochmann	Die Nutzung des Kleinprivatwaldes in Ostbayern und Perspektiven ihrer künftigen Entwicklung	7,50 €
33	1977	W. Warkotsch	Entscheidungshilfen zur Planung von Holzerntemaßnahmen	7,50 €
32	1977	G. Braun, A. v. Schönborn, E. Weber	Zur Feststellung und Bewertung von Waldschäden durch Immissionen	7,50 €
31	1977	H. Bleymüller	Untersuchungen über den Einfluss von Wirkstoffbehandlung, Pfropfung und Umweltveränderung auf das vegetative Wachstum und die Blühinduktion bei Fichte und Kiefer	7,50 €
30	1976	A. van Laar	Einzelbaum-Parameter der Fichte unter dem Einfluss von Standort und Umwelt	7,50 €
29	1976	KOLLOQIUM	Die Holzaufkommensprognose für Bayern - Folgerungen für Forst und Holzwirtschaft	7,50 €
28	1976	H. Rall	Ziele und Struktur holzwirtschaftlicher Betriebe - Grundlagen und Ergebnisse empirischer Zielforschung im Landkries Rosenheim	7,50 €
27	1976	R. Lammel	Untersuchungen über die Struktur bäuerlicher Betriebe mit Wald und die Einstellungen und Ziele bäuerlicher Waldbesitzer	7,50 €
26	1976	J. Timinger	Beitrag zur Entwicklung eines Informationssystems für die Holzernte	7,50 €
25	1975	P. Bartelheimer, B. Frhr. v. Droste zu Hülsoff	Möglichkeiten der Zusammenarbeit von Forst- und Holzwirtschaft - Eine Modellkonzeption für die Optimierung der Wertschöpfung	7,50 €
24	1975	R. Stitzinger, M. Plettenberg, W. Guglhör, J. Timinger	Beiträge zum Rücken von Nadelschwachholz und zur Kalkulation von Maschinenkosten	7,50 €
23	1975	E. Seltzer	Untersuchungen über Struktur und Wachstum von Flurgehölzen in Oberbayern	7,50 €
22	1975	KOLLOQIUM	Schalenwildbestände und Leistungsfähigkeit des Waldes als Problem der Forst- und Holzwirtschaft	7,50 €
21	1974	F. Bichlmaier, E. Gundermann	Beiträge zur Quantifizierung der Sozialfunktion des Waldes im bayerischen Hochgebirge	7,50 €
20	1974	KOLLOQIUM	Die Rohstofffunktion im Rahmen der Waldfunktionsplanung	7,50 €
19	1974	B. Nille	Ertragskundliche Untersuchungen von Aufforstungsbeständen im Rekultivierungsgebiet der Bayerischen Braunkohle-Industrie AG in Wackerdorf/Oberpfalz	7,50 €
18	1973	B. Deckelmann	Bayerische Waldinventur 1970/71; Inventurabschnitt III: Listenstichprobe	7,50 €
17				
16	1973	KOLLOQIUM	Ergebnisse der Bayerischen Waldinventur 1970/71 - Folgerungen für die Forst- und Holzwirtschaft	7,50 €
15	1973	F. Franz, E. Kennel	Bayerische Waldinventur 1970/71; Inventurabschnitt I: Großrauminventur Kartenband	7,50 €
14	1973	F. Franz, E. Kennel	Bayerische Waldinventur 1970/71; Inventurabschnitt I: Großrauminventur Sondertabellen	7,50 €

13	1973	F. Franz, E. Kennel	Bayerische Waldinventur 1970/71; Inventurabschnitt I: Großrauminventur Strukturtabellen	7,50 €
12	1973	F. Franz, E. Kennel	Bayerische Waldinventur 1970/71; Inventurabschnitt I: Großrauminventur Basistabellen	7,50 €
11	1973	F. Bachler, B. Deckelmann, E. Kennel, R. Kennel, A. Schmidt, U. Wotschikowsky	Bayerische Waldinventur 1970/71, Inventurabschnitt I: Großrauminventur Aufnahme- und Auswertungsverfahren	7,50 €
10				
9	1973	A. van Laar	Nadel-Biomasse, Zuwachs und Zuwachsverteilung von Pinus Radiata in Südafrika unter dem Einfluss von Astung und Durchforstung	7,50 €
8	1972	KOLLOQIUM	Der Rohholzpreis als Problem der Forst- und Holzwirtschaft	7,50 €
7	1972	R. Kennel	Die Buchendurchforstungsversuche in Bayern von 1870 bis 1970	7,50 €
6	1972	R. Erlbeck, H.-W. Jordan	Erholungsplanung für den Naturpark Bayerischer Wald	7,50 €
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4	1972	E. Gundermann	Untersuchungen zur Erfassung, Wertung und Ordnung der Erholungsfunktion von Waldbeständen im Bayerischen Hochgebirge	7,50 €
3	1971	J. Timinger	Arbeitsuntersuchung bei der Seilbringung in Nadelholzhieben oberbayerischer Gebirgsforstämter	7,50 €
2	1971	F. Franz	Grundlagen und Verfahren standortbezogener Leistungsschätzung - mit Fichten-Leistungstafeln für einige Standorteinheiten in Mittelschwaben	7,50 €
1	1971	A. Schmidt	Wachstum und Ertrag der Kiefer auf wirtschaftlich wichtigen Standorteinheiten der Oberpfalz	7,50 €