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LEAD USE IN HUNTING

Chemical compositional standards for non-lead hunting ammunition and fishing weights

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Abstract The chemical composition of non-lead, non-toxic, gunshot used for hunting waterfowl is regulated only in Canada and the USA. No nation regulates the composition of non-lead fishing weights, rifle bullets, and gunshot used for upland game hunting. Compositional criteria for these non-lead products are proposed here, based on established experimental toxicity protocols. Because of the demonstrated acute toxicity of ingested zinc shot to birds, fishing weights and gunshot should never be made of this pure metal. Nickel should be avoided as an incidental component of gunshot because of potential carcinogenicity concerns about such embedded shot in birds and other animals. These compositional criteria could be adopted by all nations undertaking the transition to non-lead fishing weights and hunting ammunition. The listed criteria would facilitate production and international trade in non-lead products, and promote easier enforcement and user compliance with non-lead standards.

Keywords Bullets · Fishing gear · Regulations · Shot · Sinkers

INTRODUCTION

For centuries, metallic lead has been used in ammunition and fishing weights[1] because of its availability and physical properties. The over two centuries of game shooting, especially with shotguns, has resulted in an enormous global accumulation of spent gunshot, estimated to be around 40,000 tonnes annually (Hansen et al. 2004). Spent lead gunshot and lost lead fishing weights remain in the environment, and resist corrosion for many years. A large body of scientific evidence shows that, globally, ingestion of spent leaded gunshot, bullet fragments, and fishing weights causes chronic and acute lead poisoning of both wildlife and humans (Franson et al. 2003; Watson et al. 2009; Delahay and Spray 2015; Arnemo et al. 2016; Grade et al. 2018). The toxicological impacts upon wild birds and the health impacts on humans who consume hunted game have caused hunting and fishing with lead products to be viewed as unsustainable (Kanstrup et al. 2018), and has led to the development of substitutes for both hunting ammunition and fishing weights. A transition to the use of non-lead[2] products in wetlands is underway in 33 countries (23 total, and 10 partial bans) (Stroud 2015). This number may increase if the recommendation of the European Chemicals Agency of the European Commission (ECHA) that a transition to the use of non-lead ammunition for hunting in European wetlands becomes law. The Committee for Socio-Economic Analysis of the ECHA adopted, in June 2018, its final opinion to restrict use of lead-based gunshot in wetlands and wetland shot fall-out zones (SEAC 2018).

Many companies are involved with the manufacture and trade in shotgun and rifle ammunition and fishing weights, especially in Europe and the USA, and a growing number are involved with producing non-lead products. However, there is no international agreement on the chemical composition of non-lead products to ensure that they are non-toxic to animals that ingest them, and to the general environment into which they ultimately fall and remain. Only the USA and Canada have national legislation whose regulations require that candidate non-lead shot designed for waterfowl and coot hunting be tested scientifically to assess its toxicity to wildlife and other ecosystem

[1] The term "fishing weights" includes split shot, sinkers, worm weights, trolling weights, jigheads, and fishing gear or tackle.

[2] Non-lead means, currently, containing less than 1% lead by mass. This term is used synonymously with "lead-free."

components (USFWS 1997, 2013). There is no requirement for fishing weights, rifle bullets, and shotgun shot used for hunting non-wetland/non-waterfowl species to conform with that same toxicity testing in any nation, including the USA and Canada. By default, the only compositional criterion is that non-lead ammunition must contain less than 1% lead by mass, a condition of the US federal regulations (USFWS 1997).

There is no biochemical difference in the nature of lead toxicity in animals, whether the source of lead is gunshot, bullets, or fishing weights. However, a product that is "lead-free" may not be non-toxic when ingested. Thus, a common set of standards, applicable to ammunition and fishing weights, and internationally acceptable, would facilitate a transition to non-lead products at the manufacturing and enforcement levels. Much testing of the toxicity of the principal substitutes for lead gunshot has already occurred in the USA under federal regulation. This paper proposes using those and other published toxicity studies for the creation of compositional standards that can be applied readily to shot, bullets, and fishing weights, and be reflected in new regulation.

PREVAILING METALS AND MATERIALS USED IN LEAD SUBSTITUTES

The metals used in place of lead are selected according to their availability, density and other physical properties, ballistic suitability, ease of manufacture, and costs, and demonstrated non-toxicity to animals under specified conditions. These comprise iron (Fe), tungsten (W), bismuth (Bi), tin (Sn), and copper (Cu). Steel shot is widely used as a substitute for lead gunshot and is annealed soft iron that may contain approximately 1% or less carbon. Tungsten can be made into shot either as a mixture of powdered metal mixed with a high-density plastic polymer (95%W + 5% polymer), or as a composite mixed (sintered or alloyed) with other metals. Powdered tungsten can be mixed with a soft polymer putty that can be squeezed around fishing lines, and then be removed and re-used later. Tungsten powder can also be mixed with hard plastic polymers and shaped into many forms designed for use as fishing weights. Bismuth is alloyed with 3–6% tin to reduce the frangibility of the bismuth, whether used as shot or fishing weights. Pure tin has been used for small fishing weights, its malleability enabling it to be clamped repeatedly on and off fishing lines. Its low density (7.31 g/cm^3 vs. 11.3 g/cm^3 for lead) does not predispose it to use as gunshot or bullets. Pure copper (density 8.96 g/cm^3) is used in hunting bullets and slugs fired from shotguns. Copper can be alloyed with approximately 5% zinc to make similar non-lead bullets. Bronze is an alloy of approximately 90% copper and 10% tin. Powdered bronze can be sintered with tungsten powder to make a hard, high-density tungsten-bronze gunshot.

The list of lead substitutes for gunshot has not changed in the past decade. This is because the most likely substitute materials and their suitability for gunshot have already been proposed and evaluated in North America. The same materials can be used for fishing weights, as can other materials which have not undergone any evaluation. Rifle bullet composition has not been subject to any regulation, other than the US default position that it contains less than 1% lead.

LISTING OF APPROVED NON-LEAD, NON-TOXIC, SHOT FORMULAE

Eleven distinct shot types have been given unconditional approval in the USA for hunting waterfowl (USFWS 2006) (Table 1). Presently, not all of these shot types are in commercial production. The North American and European markets are dominated by steel shot use because of price and availability. Other less-common types of non-lead shot include bismuth-tin shot, Tungsten-Matrix® shot, and Hevi® shot made from tungsten and other metals. High world market prices for tungsten are reflected in the highest

Table 1 List of shot formulations unconditionally approved for hunting waterfowl and coots by U.S Fish and Wildlife Service (USFWS 2006)

Approved shot types	Composition by weight
Bismuth-tin	97% bismuth and 3% tin
Iron (steel)	Iron and carbon
Iron-tungsten	Any proportion of tungsten and ≥ 1% iron
Iron-tungsten-nickel	≥ 1% iron, any proportion of tungsten, up to 40% nickel
Tungsten-bronze	51.1% tungsten, 44.4% copper, 3.9% tin, and 0.6% iron
	and 60% tungsten, 35.1% copper, 3.9% tin, and 1% iron
Tungsten-iron-copper-nickel	40–76% tungsten, 10–37% iron, 9–16% copper, and 5–7% nickel
Tungsten-matrix	95.9% tungsten and 4.1% polymer
Tungsten-polymer	95.5% tungsten and 4.5% Nylon 6 or 11
Tungsten-tin-iron	Any proportions of tungsten and tin and ≥ 1% iron
Tungsten-tin-bismuth	Any proportions of tungsten, tin, and bismuth
Tungsten-tin-iron-nickel	65% tungsten, 21.8% tin, 10.4% iron, and 2.8% nickel

This includes steel shot coated with a thin layer of copper or zinc prices of loaded cartridges. Bismuth and tin also cost more than iron, this also being reflected in higher prices than for steel shot cartridges (Thomas 2015a). However, mechanisms other than the cost of single cartridge components, including production volume and demand, influence the price of the final product.

The presence of iron in the composition of six of the 11 formulae is intentional. It is to make the shot slightly magnetic so it can be distinguished from lead shot in the field by conservation officers enforcing non-toxic shot regulations. U.S. regulations require that approved shot types be distinguishable from lead shot, either by a portable electronic device, or by a demonstration of positive magnetism. Tungsten-polymer shot cartridges and bismuth-tin shot cartridges are distinguishable from lead shot cartridges in an electronic meter. Several of the approved shot types in Table 1 contain nickel. This metal has not been added for ballistic reasons. Tungsten-nickel alloys are used in making military penetrators, and the metal residues from machining the penetrators are, secondarily, converted into gunshot.

Steel shot may be coated with a thin layer of copper or zinc to inhibit rusting and is permitted under US regulations (USFWS 1997). The level of uptake of copper and zinc from the dissolution of these metals in the gut of birds from such a thin layer would be defined as non-toxic under the USFWS (1997) regulations.

EVALUATION OF THE U.S. FISH AND WILDLIFE SERVICE PROTOCOL AND OTHER NON-LEAD PRODUCTS

Both the U.S and Canadian regulations for assessing the toxicity of candidate shot are based largely on results derived from experimentally ingested shot in game-farm ducks. The rigorous scientific testing of candidate shot under the Tier1, Tier 2, and Tier 3 components of the USFWS (1997, 2006) protocol means that the demonstrated non-toxicity of approved ingested shot can be largely accepted. The results of such toxicity testing have also been presented in the primary scientific literature for tungsten-based shot (Mitchell et al. 2001a, b, c) and further evaluated in Thomas et al. (2009) and Thomas (2015b). Shot made from bismuth-tin alloy is also fully approved as non-toxic (Table 1). Sanderson et al. (1997) demonstrated that ingested bismuth-tin shot did not have any toxic impact on the birds, and did not affect their reproduction.

Shotgun hunting causes many game birds and animals to be hit, but not killed (Norton and Thomas 1994; Hicklin and Barrow 2004; Falk et al. 2006), and then living with embedded shot. The issue of hunted species of animals containing embedded shot is important, because these animals, having recovered from their wounds, may live for many years with the shot material becoming solubilized and exerting potentially toxic effects. Assessing experimentally the toxicity for the target animal of such embedded shot is not part of the US and Canadian regulatory approval process. Sanderson et al. (1998) reported that shot made of bismuth-tin alloy implanted into the breast muscle of ducks did not induce toxic effects. A similar finding was reported by Kraabel et al. (1996) when shot made from tungsten-bismuth-tin was implanted into ducks. Shot made of bismuth-tin alloy was implanted into mice intra-peritoneally for extended periods of time (Pamphlett et al. 2000; Stoltenberg et al. 2003). These authors also reported that although mobilization of bismuth from the shot occurred over months, no detrimental effects on weight gain, movements, and appetite were observed. Nevertheless, these authors urged caution concerning uptake of bismuth from embedded shot.

Several shot types approved by the U.S. Fish and Wildlife Service contain varying amounts of nickel, ranging from 2.8%, 5–7%, to up to 40% nickel (Table 1). In theory, animals subject to hunting could carry embedded shot of these types in various regions of their body. Kalinich et al. (2005) demonstrated that muscle-embedded pellets of tungsten alloys containing 6% nickel caused the appearance of fatal tumors in rats within 26–38 weeks of implantation, depending on dose level. Pure nickel control pellet implants caused mortality of all rats within 30 weeks. Given that game birds and mammals would likely retain shot for greater lengths of time, the possibility arises of their generating fatal tumors from tungsten alloy shot containing up to 40% nickel (see Table 1). However, there are no case reports or studies to support this stated possibility in wild birds and mammals. A similar situation is not likely to arise in animals struck by bullets containing nickel because most hits from bullets, if not immediately fatal, would produce death within a much shorter period before signs of tumor development would appear. Thomas (2015b) urged caution in distinguishing tungsten alloys from tungsten metal (elemental W), and tungsten chemical compounds, indicating that the carcinogenic effect is often caused by another metal in the alloy, rather than the metallic tungsten with which it is alloyed (Verma et al. 2011). The issue of embedded shot also includes the element of such shot, if made from a toxic substance, to cause intoxication when the target animal eventually is consumed by predators or scavengers.

Most of the non-lead bullets developed to replace lead are made from pure copper or copper-zinc alloy, with or without other metal jacket coatings (Paulsen et al. 2015; Thomas et al. 2016). Because there is a risk of spent bullets and their fragments being ingested by scavengers from discarded gut piles, non-retrieved killed or wounded animals, and ingestion by humans who consume bullet fragments in meat from game animals, there is need to demonstrate non-toxicity of copper-based bullets to animals. Franson et al. (2012) reported that American kestrels (*Falco sparverius*) that were dosed experimentally with copper shot exhibited no signs of copper toxicity. Paulsen et al. (2015) simulated the release of different metals from non-lead rifle bullet fragments in game meat during storage and ingestion. The release of copper and zinc from meat posed no toxic risk post-ingestion by humans, but the authors advised that the aluminum, nickel, and lead content of bullets be kept deliberately low. Irschik et al. (2013) indicated that the release of copper from shot game would not contribute much released metal to humans, concluding that the daily recommended daily intake of copper would not be exceeded, especially if bullet fragments around the entry site were removed. However, solid copper bullets do not fragment to the same extent as bonded and unbonded lead-core bullets (Hunt et al. 2009; Irschik et al. 2013; Stokke et al. 2017).

Shot made from 100% zinc[3] and 100% copper (including corrosion-inhibited copper), while made and sold in Europe, is not listed in Table 1. Ingested zinc shot are acutely toxic to waterfowl (Levengood et al. 1999, 2000), which precludes their being given approval under US federal legislation. Presumably, discarded small fishing weights made of zinc would be also toxic to waterbirds that might ingest them. Fäth et al. (2018) demonstrated high leaching rates of commercial zinc shot and copper shot in freshwater that rendered the aquatic media toxic to *Daphnia magna*, and commented on the inadvisability of zinc and copper as lead shot substitutes. Zinc, as gunshot and fishing weights should not be allowed for manufacture and use in any jurisdiction, given its potential toxic risk to animals that might ingest it and to the aquatic environment. Zinc can be alloyed with copper to make brass, which lowers the mobility of zinc in solution. Copper can be alloyed with tin to make bronze which lowers the mobility of copper in acid aqueous media (Thomas et al. 2007; Thomas and McGill 2008). Therefore, brass and bronze, whether used in bullets or fishing weights, exhibit less potential toxicity to animals which might ingest them, or to the freshwater environment where many discarded weights remain.

[3] Zinc is a commonly available, inexpensive metal that has a low melting point (419.5 °C), and can be made into shot using similar processes as for lead shot. Its density of 7.14 g/cm^3 means that it can be used as a ballistic substitute for lead shot, especially in jurisdictions lacking compositional shot regulations. While zinc shot cartridges are marketed as "lead-free" the implication that they are non-toxic is false.

It is also assumed that shot made from lead with either a thin plastic or other metal coat would not receive approval because such coatings of ingested shot would be removed quickly in avian gizzards, exposing a conventional lead core to the digestive actions of the gut. It matters little whether the shot were picked up from a marsh or ground, or from the bodies of wounded or dead birds in which it was embedded. Attempts to cover lead shot with a protective coating of non-toxic metals or other materials to prevent the degradation and uptake of lead while in the gizzard/stomach of birds have all resulted in failure to prevent lead toxicity (Friend et al. 2009).

DISCUSSION

Thomas and Guitart (2003) proposed an alternative system for evaluating the toxicity of proposed lead substitutes based on the US Fish and Wildlife Service protocol, and which relied on a more rapidly breeding avian test species. In view of the fact that no new candidate substitutes of lead shot have been unconditionally approved since 2006, it appears advisable to proceed with the already-approved list of non-toxic materials (with several considerations) for use in shot, bullets, and fishing weights. These are presented in Table 2.

The importance of Table 2 is that it can be used as the basis of compositional regulations used for shotgun and rifle ammunition and fishing weights, either by a single country or all member nations of the European Union or other international institutions. Listing of ammunition and sinker materials that fulfill basic criteria for non-toxicity would assist the many countries that have yet to make a transition to non-lead recreational products. The US and Canadian regulations are constrained by jurisdictional authority in that they cannot regulate anything under state/provincial authority, including fishing sinkers and hunting rifle bullets. Other countries are free from such constraints, enabling compositional standards to be set across the entire range of these products. This would be the first time that the allowable composition of sinkers and rifle bullets would be defined. Such standards would benefit the makers of ammunition and sinkers, would promote international trade in these non-lead products, and would facilitate enforcement of non-lead regulations and user compliance. Should metals not listed in Table 2 (e.g., cadmium) be made into ammunition or fishing weights, it is advisable that they undergo a toxicological examination similar to that proposed in the US Fish and Wildlife Service regulations (USFWS 1997) prior to sale.

A critical aspect of regulation is that it sets enforceable production standards, ensuring that unwanted contaminants do not enter production. Metals such as bismuth are obtained from other metal refining, and are readily

Table 2 Suggested compositional criteria for gunshot, rifle bullets, and fishing sinkers. These criteria could be incorporated into the regulations of any nation making the transition to use of non-lead products

Metal/metal alloy	Shotgun shot	Rifle bullets or shotgun slugs	Fishing sinkers
Iron, Fe	≥ 99% Fe	Not suited	Suitable as corrosion-resistant "stainless" steel for weights and jigs
Tungsten, W	95% W, with polymer	Any %W, when used as a densifier with other approved material	Any %W, when mixed with polymers, glass, or other approved material
Tin, Sn	While demonstrated to be non-toxic, and unconditionally approved in Canada, the low-density limits use as gunshot	Not suited when used alone, but can be used in conjunction with other approved materials	Suitable for use as split shot, weights, or jigs
Bismuth-tin alloy, Bi-Sn	Suitable and fully approved in USA and Canada	Not suitable, due to frangibility concerns at high-velocity impacts	Suitable as weights and jigs
Bronze, copper-tin alloy, Cu-Sn	Suitable, especially when used in conjunction with denser tungsten	Potentially suitable, but metal hardness may be problematic	Suitable as weights and jigs
Copper, Cu	Not suitable, see Fäth et al. (2018) for aquatic environmental concerns	Highly suitable, either as pure Cu, or as a 95% Cu—5% Zn alloy	Suitable as a 95% Cu—5% Zn alloy to resist corrosion
Lead, Pb	Less than 0.1% by mass	Less than 0.1% by mass	Less than 0.1% by mass
Zinc, Zn	Less than 1% by mass	Allowed only as an alloying metal	Allowed only as an alloying metal
Nickel, Ni	Less than 1% by mass	Allowed as a bullet jacket coat	Less than 1% by mass

Iron in stainless steel is unacceptable, ballistically, because of its greater hardness than annealed iron shot. This would increase pressures beyond safe limits, and be also more expensive to produce

See "Discussion" about high levels of nickel permitted in some types of approved non-toxic gunshot

contaminated by lead unless high-grade products are used. Kanstrup (2012) found that bismuth-tin shot contained up to 6,800 ppm (0.68%) lead by mass. Thus, bismuth used in shot making must be initially of high grade. The same comment regarding purity of the metal used for shot making applies to tungsten, which is available as a commercial waste material containing nickel, or as a high-grade refined product. Thus, setting the maximum allowable content of lead, zinc, or nickel at less than 1% is realistic from a production point of view, while ensuring a high level of toxic threat protection to birds that might ingest these products. The permissible lead level in gunshot is 1% for the USA and Canada, but 0.1% for Denmark, consistent with Danish criteria for lead exposure.

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