Article

Plastic litter from shotgun ammunition in marine ecosystems – problems and solutions

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Abstract: Parts of shotgun cartridges are a significant source of plastic litter in the marine environment. Empty cartridge shells may not be picked up by the hunter who fired them, and plastic wads that serve to separate the propellant from the shot load, are lost down-range when a shot is fired. Such litter items constitute a cosmetic and aesthetic problem on coastlines and may cause harm to marine animals and in the later stages of decomposition break down into harmful micro plastic particles. There exists no reliable estimate of the global exposure of marine ecosystems to this plastic source. However, in some countries it has been subject to closer examination, including for example, Denmark where the annual contribution of plastic wads into marine systems was estimated to 600,000 pieces (c2 tonnes), and the accumulated density of washed-up items (both wads and shells) was 3.7 items per 100 m coastline. Increasing awareness of this problem has caused scientists, hunters' communities and governments to suggest altered practice including transition to the use of biodegradable cartridge components, first and foremost wads as this item is invariable lost during hunting. Several manufacturers provide shotgun cartridges containing biodegradable wads based on different types of materials, including fibers and various types of plastics, for example PVAL (poly(vinyl alcohol)) and PHA (polyhydroxyalkanoate). In this paper, we review the most recent literature on the amounts and related environmental hazards of plastic dispersed from hunting ammunition into marine ecosystems. We summarize the market availability of shotgun cartridges with biodegradable wads and discuss chemical, technical, economical and legal aspects of a transition to the use of such products.

Keywords: Biodegradable labeling; Decomposition; Fibre; Micro plastic; PVAL; PHA; Shotgun wad

1. Introduction

Plastic litter in the environment has become a major global issue and plastic ammunition components (wads and shells) are an unwelcome addition to the problem. Regardless of the source, macro plastic items are a cosmetic and aesthetic problem that may also cause serious harm to marine animals that ingest or become entangled by them. Micro plastic particles created by the decomposition of macro plastic items are ingested by small animals and filter-feeders, then accumulate in food chains and create hazards for ecosystems, other wildlife, and potentially, human health [1, 2]. Against this background, it is imperative to find a solution and to substitute plastic with other materials e.g. degradable types of plastic with lower risk of impact on the natural environment.

Civilian use of firearms includes sport shooting and hunting as well as the associated training. While sport shooting and training mostly takes place either indoors or on closed shooting range facilities, hunting takes place in natural habitats either wet habitats (e.g. rivers, estuaries, lakes, coastal areas or sea), or in drylands (e.g. forests, mountains and arable land). When firing firearms, ammunition parts are dispersed to the surrounding environment. For rifles, this applies to rifle projectiles, which usually weigh between 5 and 11g and are predominantly made of lead and copper. Shooting with smooth barreled shotguns, which is the core of this article, causes downrange dispersal of both the shot load (c30g lead, steel or bismuth) and the wad (shot-cup) that serves to separate the propellant from the shot load. The cartridge shell that contains these ammunition parts are normally retrieved by the hunter and disposed according to local regulations (e.g. as common waste). However, they are often discarded in the hunting environment in particular when semi-automatic and pump –action guns are used and often during hunting in wet habitats, where the discarded shells are spread in a short time due to currents and wind.

Originally, wads were made from fibers (wool, hair or paper) and shells from paper inserted in a basic brass (today iron) construction holding also the primer (Figure 1).

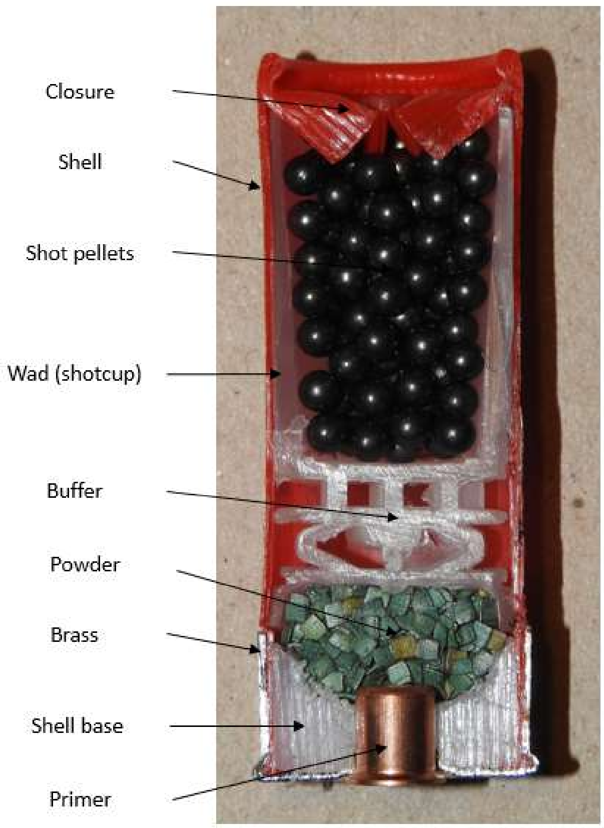

Figure 1. Construction of a modern shotgun cartridge.

Dispersal of leaded gunshot has been subject to much attention [3] and a complete phase-out is at present considered within the European Union. Hence, it will not be covered further in this paper. The main focus here is on the plastic based components of ammunition - first and foremost the wad. The main function of the wad is to provide a gas packing between gunpowder and shot load. Modern plastic wads are constructed to contain the shot load in a cup to prevent contact between shot pellets and the gun barrel. In cartridges with soft shots (e.g. lead and bismuth) such contact may cause an undesirable damage to pellets (degrading the external ballistic, i.e. the pattern). In cartridges with hard shot pellets (e.g. steel) the cup prevents the barrel from been damaged by the shot. Until recently plastic components in shotgun cartridges have almost exclusively been made from low density polyethylene (PE-LD) or high density polyethylene (PE-HD), which are a non-degradable plastics.

There is no precise estimation of the total amounts of plastic that are dispersed Worldwide or within the EU from ammunition. Based on the mass of a wad (c. 3g for a standard cartridge type) and the estimated annual consumption of cartridges, data from Denmark indicate a dispersal of plastic wads during hunting in coastal habitats of some 1,860 kg per annum [4]. The same study demonstrated that hunting litter in coastal areas is one of the single most common sources of macro pollution into the environment, suggesting that a substantial quantity of plastic ammunition litter will expose coastal habitats to an un-welcome source of pollution for many years to come. The total annual dispersal of plastic from hunting ammunition in Denmark was estimated at 23-30 tonnes in 2018 [5]. In the UK, the annual disposition of waste plastic to the countryside from this source was estimated at 500 tonnes, if all hunting cartridges fired contained plastic wads (equivalent to app. 160 mil. rounds). A more recent estimate suggested that if all the cartridges used for shooting ducks and geese contained plastic wads, the dispersal of waste plastic wadding might be some 6 tonnes in and around UK wetlands . Based on a 2016 beach litter data set, Addamo et al. (2017) [6] identified 2,263 shotgun cartridges out of a total of 355,671 marine litter items that were recorded during 679 surveys on 276 European beaches. This corresponds to 0.64% and make such items rank at a place 27 out of 238 identified items. Based on figures for the annual use of shotgun ammunition in Europe, at least 2,100 tonnes of wad material are annually dispersed into natural systems the majority hereof being PE. According to the Virginia Institute of Marine Service , the Worldwide annual production of plastic wads is in the billions and production has lasted for at least 50 years. The OSPAR Commission which is a mechanism by which 15 Governments and the EU cooperate to protect the marine environment of the North-East Atlantic provides frequent reports on plastic pollution including cartridge shells and wads (OSPAR Code 43 = "shotgun cartridges"). Based on 2015 figures, this type was among the top ten items in the North Sea/Skagerrak and the Baltic Sea/Inner Danish waters [7]. Non-governmental bodies also engage in mapping of plastic debris in marine systems, e.g. the American Surfrider Foundation providing a platform for online registration of shotgun wads worldwide .

Just as other plastic litter items, hunting debris is a source of pollution that must be regarded in an international context because items float and move over large distances. Kanstrup and Balsby [4] suggested cross-Atlantic movements based on high densities of ammunition parts found on Shetland Island coasts that could not be explained by local or regional dispersal.

Over the last years, wads that decompose, dissolve or bind to soil colloids in nature have been introduced to the European and North American markets. However, the range of biodegradable products is still limited in terms of both materials and coverage of gun calibers. The market is developing at a rapid pace and new products are constantly being introduced some of which do not necessarily comply with existing regulations. Many of these products claim biodegradability although they are not certified according to common standards. Some countries plan to impose special regulations to minimize shotgun wads as a source of plastic pollution of natural ecosystems. Some hunters and hunting outfitters demand such products and manufacturers request clear specifications to ensure relevant requirements are fulfilled by these new products.

Against this background, the aim of this paper is to provide an updated review of shotgun ammunition litter as a source of plastic in natural systems and provide analysis of the ongoing initiative to replace non-degradable plastic type biodegradable types - all with the main focus on marine ecosystems. We screen market availability of biodegradable alternatives to polyethylene (PE) and evaluate such products against their actual ability to biodegrade in relevant environments and their practical use. Furthermore, we evaluate products against legislative provisions and suggest tools to be used for screening of biodegradability of materials intended for the production of biodegradable wads. The paper is based on research programs initiated in 2018 by Aarhus University, The Danish Academy of Hunting and The Danish Hunters' Association and a consultancy work carried out in 2020 by Technological Institute for the Danish Agency for the Protection of the Environment [8].

2. Biodegradable wads on the market

To map the market of shotgun cartridges with wads promoted as biodegradable, we sent an electronic questionnaire to 110 Danish traders of hunting ammunition (i.e. gun stores and importers). Following this, we made follow-up interviews by phone or in person with selected traders, performed an internet search on Danish and European platforms, and consulted key NGOs, i.e. the Danish Hunters' Association, the Danish Gun Trading Organization and the British Association for Shooting and Conservation. The response to the questionnaire was very poor and data were not suited for quantitative analysis. However, responses by telephone and follow-up consultation in person gave valuable qualitative information which in some cases extended the communication to manufacturers, e.g. in Spain.

An overall observation from this part of the study was that the market for shotgun ammunition is complicated, as cartridges with identical components and charges are marketed under different names in some cases the name of the manufacturer and in other cases the name of the importer or, eventually, national chains of distribution.

The internet search revealed that at least 13 different brands of shotgun cartridges for hunting and sport shooting were available in Denmark with wads described as "biodegradable". All identified products were purchased by the project and subject to analysis and inspection of single components and for a majority also field testing (see later). Based on information from the manufacturers and initial inspection we made the following three categories: Fiber (paper, 3 brands), solid (5 brands), and water-soluble (5 brands) (Table 1).

The range of biodegradable products was very limited in terms of coverage of calibers, where 12/70 by far was the most widespread as it is the most commonly caliber used by Danish and European hunters. As the survey was performed during the hunting season, most of the marketed products were typical hunting cartridges (shot size 3-3.5 mm). However, a single clay shooting cartridge was included (shot size 2.5 mm). We only included steel shot cartridges in the survey.

Table 1. Thirteen brands of shotgun cartridges with biodegradable wads identified by internet search, questionnaires and visits to ammunition stores. All data were anonymized.

Wad type	Cartridge production country	Shot load (g)	Shot size (mm)	Price (Euro per 25 pc.)	Information on cartridge box
Fiber	UK	28	3	19	Biowad
	France	28	3.2	16	Biodegradable wad
	UK	28	3.2	19	Biowad
Solid	Spain	32	3	16	Biopolymers used (both wad and shell) are biodegradable and compostable
	Spain	24	2.5	13	Biopolymers used (both wad and shell) are biodegradable and compostable
	Italy	28	3	12	Biowad
	France	28	3.2	17	Biodegradable wad and obturator
	UK	32	3.5	no information	Biowad
Water soluble	Italy	32	3.5	15	Water soluble wad
	Spain	28	3.2	16	Wad is non-toxic, water soluble and compostable according to EN3432
	Spain	32	3.2	16	100% biodegradable
	Spain	24	3.2	17	Wad is non-toxic, water soluble and compostable according to EN3432
	Spain	28	3.2	15	100% biodegradable water soluble wad

Judging from the information given by the gun stores and with the purchased products (brochures, printed text on cartridge boxes, inserted instructions etc.), we noted that fairly limited data was available on the properties of the biodegradable wads, including degradation time and material composition. Some products referred to European standards for biodegradability relevant for the material type of the product in question. The project team established contact to some manufacturers and achieved additional information in these cases. However, detailed information of basic properties of the products was very limited (apart from being "biodegradable") and therefore insufficient for the customer to judge the product appropriately. In other words, most products did not provide data to substantiate their claims of biodegradability.

Cartridge products with wads marketed as biodegradable were sold at slightly higher prices than traditional types. Here we found an average price at 16 Euros (per 25 pc.) of the 13 identified products whereas the average price of three equivalent cartridges with traditional PE-wads was around 13 Euros. Kanstrup and Thomas [9] found an average price of traditional steel shot cartridges to be 11.90 Euro (per 25 pc.) in the range between 7.50-25.25 Euros. However, in the present survey we found some products with degradable wads that were offered at the same price as traditional types and we therefore assume that the price alone will not prevent the average cartridge customer from buying the biodegradable products.

There is undeniably an increase in the interest for biodegradable wads among both consumers and retailers. One Danish retailer suggested that the sale of cartridges with biodegradable wads in his region would reach 80% of the total sale in the 2020 hunting season and that PE plastic wads would probably phase completely out in forthcoming seasons. However, there is much uncertainty regarding the labeling of the products, as there are no accepted standards and information provided by the producer is often insubstantial. Thus, there is an apparent need among the targeted stakeholders for clarification of terms as well as specification requirements for the products. In conclusion, there is obvious support in the industry for a shift towards more environmentally friendly solutions, but there is a lack of knowledge regarding necessary requirements, including crucial legal requirements.

Provisions for biodegradability of wads

Because wads from hunting ammunition cannot be retrieved and recycled after discharge, biodegradability (used here as an overall term for the ability of materials to decompose, dissolve or bind to soil colloids) is a central element in an environmental adaptation of wads dispersed from hunting and shooting. However, provisions for biodegradability of wads are not clear. Plastic materials that could potentially be used to make wads are subject to the same legislation whether they are biodegradable or not. The EU Commission's disposable plastic directive 2019/904 focuses on the 10 most frequently found disposable plastic articles as well as plastic fishing gear, which together make up approx. 70% of the waste found on European beaches. Wads are not included in the Directive's list of restrictions unless they are made of oxo-degradable plastic in which case Member States, according to the Directive, shall prohibit the placing on the market of such wads. For specific claims of biodegradability, products must be certified according to the harmonized standard EN 13432 / EN 14995, which must be carried out by an independent third-party laboratory. However, the high temperatures (58 °C) used in this biodegradability protocol do not reflect the conditions found outdoors in temperate Europe, hence the protocol seems not to be suited to assess to what degree plastic wads in reality decompose under such climate conditions. However, there exists a number of certification schemes and labels relevant for plastic wads, where the test conditions in the associated standards do not use accelerated tests at elevated temperatures. In particular, TÜV Austria's label "OK Biodegradable" uses experimental conditions that are relevant for wads dispersed in temperate European environments. From this labeling scheme, "Biodegradable Soil" (ISO 17556) and "Biodegradable water" (EN 14987) are particularly relevant, as operation temperatures are 20-25°C, which to a large extent reflects the climatic conditions in temperate Europe during the summer months. For wads dispersed in marine environments "Biodegradable marine" is of relevance although the related testing takes place at temperatures (30 ± 2°C) slightly higher than typical marine water temperatures in Europe. Degradation of wads in marine environment will be significantly influenced by the density of the material, as lighter materials will float and therefore be exposed to UV-light from the sun, which accelerates degradation. On the contrary, heavier materials will not float and thus typically be subjected to lower temperatures and no radiation, resulting in slower degradation.

Natural conditions vary according to the types of habitats, where shotgun hunting takes place. For most European countries, a distinction can be made between "Arable land", "Forest", "Dry grassland", "Wet grassland", "Inland waters", "Shallow brackish waters" and "Marine". Regarding current certifications for biodegradability, these can be translated into the three classes "Biodegradable Soil", "Biodegradable Water" and "Biodegradable Marine" (see table 2). As an example, we estimated the distribution of dispersal of wads from hunting in different Danish habitats. This was based on reported game bags and the estimated quantity of fired shots indicating that more than 1/3 of wads are dispersed on arable land, where certification according to "Biodegradable Soil" is relevant. The same applies to almost 1/3 that are dispersed in forests and grassland. The remaining approx. 1/3 of wads are dispersed in or near lakes, streams, shallow fjords, and in marine areas where certification according to "Biodegradable Water" and "Biodegradable Marine", respectively, is of relevance. This distribution may be different in more continental countries with less hunting taking place in coastal areas than is the case for Denmark.

Table 2. Labeling schemes are relevant for the decomposition of wads in temperate region nature.

Certification	Biodegradability class	Test standard	Test conditions	Degradability	Typical natural conditions temperate regions	Recipient
SOIL OK biodegradable TÜV AUSTRIA SOIL	Soil	ISO 17556	20-25 °C	90 % in 2 years	Plant cover (DS/EN 17033:2018, 2018) 3-20 °C	Arable land, forest, grassland
WATER OK biodegradable TÜV AUSTRIA WATER	Water	EN 14987	20-25 °C	90 % in 56 days	5-20 °C. (mean 8.5 °C)	Freshwater
MARINE OK biodegradable TÜV AUSTRIA MARINE	Marine	ASTM D 708 1 (withdrawn) ISO 22403:2020	30 ± 2 °C	90 % in 6 months	Mean temperature 10 °C	Marine

Table 2 indicates which labeling schemes are relevant for the decomposition of wads in temperate regions. In contrast to standardized tests, however, the degradation time will be significantly longer in nature than in a controlled environment in the laboratory, due to higher temperatures, fluctuations in the environment, nutrients, water and oxygen availability. Thus, a material that lives up to the degradation rate of the standard cannot be expected to degrade under natural conditions within the set time limits.

Of the wads examined in this study, none were certified according to any of the above mentioned biodegradability classes, most likely because a certification would be difficult to obtain for a wad as a product due to the relatively large thickness of the final product shape. Biodegradability is claimed with reference to the properties of the material used. Typically, the biodegradability of a material will be certified for a relatively thin film. Shotgun wads having solid bases and thick "walls" thus will have a significantly slower degradation than a foil of the same material. It will therefore be difficult to obtain a certification for wads without adjustment of the requirements established for the three mentioned classes. A material or foil that decomposes in a standard laboratory test related to the mentioned certification classes will also decompose in a natural European environment. However, this decomposition will take place more slowly due to fluctuations in the annual temperature. It is estimated that the fluctuations in annual temperature reduce the decomposition rate 4-5 times under climate conditions in Denmark [8].

In this study we aimed at assessing biodegradability of representative samples of the identified wad products. However, a complete material analysis of all sampled wads was not possible within the scope of the project. Hence, FT-IR analysis (Fourier-transform infrared spectroscopy) of the samples was performed at the Danish Technological Institute to ensure different chemical composition of the samples selected for the biodegradability tests. The following materials were found by FT-IR analysis of nine of the products: (i) PVAL in a soft injection mold quality, (ii) PHA, and (iii) paper with PE liner. In addition (iv) a PE wad was chosen as reference (Figure 2).

Figure 2. Wads made from biodegradable materials are available at the European marked and selected for testing of biodegradability: (i) PVAL, (ii) PHA, and (iii) fiber with a liner. Also shown is (iv) a traditional wad made from LDPE. All originate from shotgun cartridges caliber 12/70 (the most commonly used).

A sample from each category was selected for biodegradability testing in soil with a test run adapted to the standards ISO14855 / ISO17556 and OECD301B to detect biodegradability within a short time. To accelerate the degradation, the wads were milled to <2 mm yielding a larger surface area thereby accelerating the degradation. 50 g sample was mixed with 536 g compost soil screened to <4 mm, and water added to adjust the moisture to 54%. The mixed compost was aerated with 200 ml/min CO2-free air removed by a 10 M NaOH scrubber. To determine the amount of CO2 evolved, the effluent gas was captured in 0.5 M NaOH and titrated against 0.5 M HCl. The rate of biodegradation was determined as the CO2 evolved versus the theoretical limit based on an elemental carbon analysis of the wad samples. A negative control was used to subtract the CO2 evolved from the compost soil alone. The experiments were carried out at 5 and 21 °C, respectively. Four wads of different materials were tested: PE (reference), PVAL, PHA and paper fibers with a PE liner.

Results after 28 days showed degradation of PVAL to be similar to the reference cellulose material at standard temperature (21 °C). Degradation of paper-based wad material is at a slightly lower but comparable level, while only very low degradation of PHA was found. At 5°C the same trend was seen, but the degree of degradation is reduced by a factor of 2.4-4.6.

Based on literature as well as the obtained results it is concluded that PVAL wads will decompose in all types of environments typical for shotgun hunting but not necessarily completely under all conditions. However, there is only a small risk that toxic intermediates are formed during the degradation of PVAL. Furthermore, PVAL is not classified as toxic. Of special interest for shotgun wads used in the marine environment, the test showed that decomposition of PVAL wads takes only a few hours in aquatic habitats whereas decomposition is slower (a few weeks) in dryer upland habitats. The study indicated the same possibility for paper-fiber wads, whereas this was not the case for the specific PHA-based wad of the study.

Hunting takes place mainly from autumn to the end of January. Therefore, biodegradation will typically be limited before the subsequent summer period. During biodegradation plastic fragments that can be characterized as microplastic will almost certainly be formed for all types of biodegradable plastic. In particular, plastics of the types PHA (including PHB (polyhydroxybutyrate) and PHBV (polyhydroxybutyrate-co-valerate)) as well as TPS (thermoplastic starch) meet the requirements for one of the three certifications. All these three types of plastic are available in a quality that can be used to make wads by injection molding.

Practical use

To assess the properties of shotgun cartridges regarding the practical use under field conditions a test was carried out with a total of 11 cartridge products containing biodegradable wads. Two products with a traditional PE wad were used for comparison. The test had the following components: Inspection of shot, measurement of muzzle velocity (V1.5, 5 rounds per cartridge, Chronograph Millenium CED), pattern test (35 m, 3 rounds per cartridge). The pattern test used was a modified version of "Oberfell-Thompson" [10] recommended by Danish authorities [11] and consisted of these elements: For each round: Count of the number of shot holes in a 75 cm circle inlaid with the center in the geometric center of the shot swarm and count of the number of 12-cm circles that could be inserted into the pattern without contact with shot holes (Figure 2). Based on this we calculated shot densities (shot holes within the 75 cm in percent of the total number of shot in the cartridge), and assessed distribution based on the number of shot holes in the 75 cm circle and the number of 12 cm circles with no shot holes (Figure 2). The gun used was Miroku MK 38, barrel length: 76 cm, choke: ¼. The test did not include shooting of live quarry or clay targets and did not cover aspects of wear or damage of the used weapons or other safety issues. Results from the test are showed in Table 3.

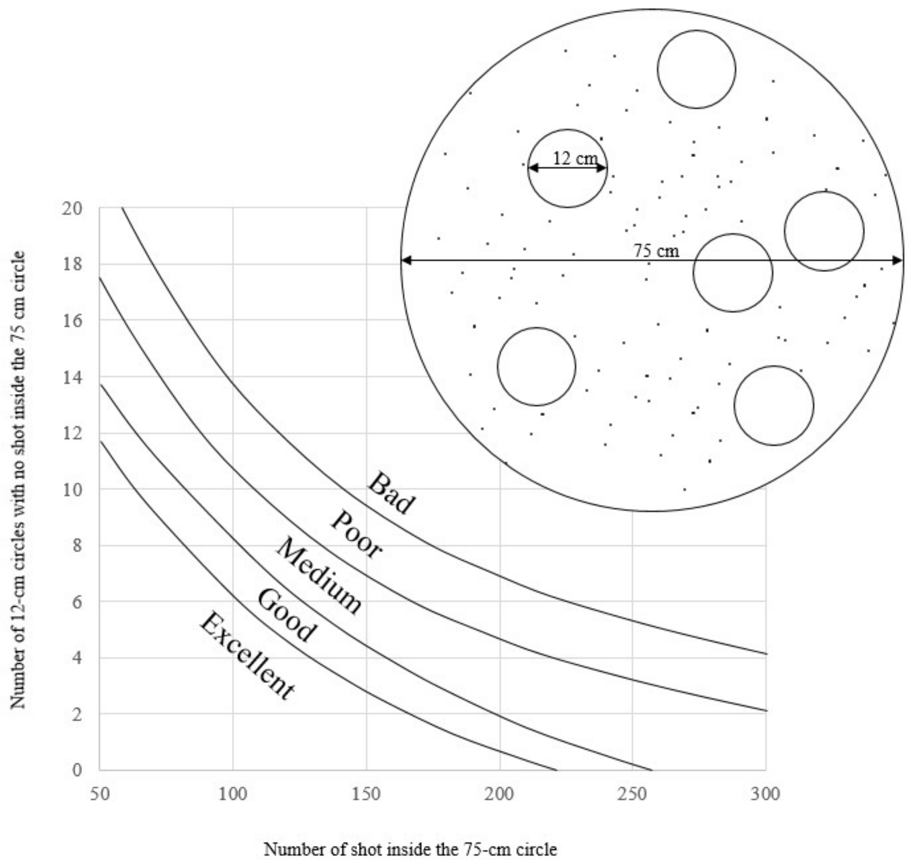

Figure 2. Tool to assess shot distribution (modified Oberfell-Thompson-model based on [10, 12]).

Table 3. Results from the practical test.

Wad type	Shot load (g)	Shot size (mm)	$V_{1.5}$ (m/s) given by manuf.	$V_{1.5}$ (m/s) measured by project	SD $V_{1.5}$ (m/s) measured
Fiber	28	3.2		390	7
Fiber	28	3.2	420	435	19
Fiber	28	3	400	365	13
PE	32	3.5	450	443	3
PE	28	3.5	430	412	3
Solid	32	3	402	378	8
Solid	24	2.7	405	392	7
Solid	28	3		417	5
Solid	28	3.2		425	8
Water soluble	32	3.5	420	398	8
Water soluble	28	3.2		376	4
Water soluble	32	3.2	410	399	6
Water soluble	28	3.2	410	407	5

Shot pellets from the tested cartridges showed high levels of uniformity and sphericity. For a single type (water soluble wad) it was observed that up to six shot pellets remained in the wad after firing. This is unacceptable both in terms of ballistics and safety, but the problem is known from other types of wads including PE types.

For most brands, the muzzle velocity seemed to achieve sufficient uniformity, but the test also showed that some types exhibited considerable variation and that fiber types had greater variation (SD column). Product development may be needed here, as the test also indicated that in some cases, the muzzle velocity did not fulfil Danish legal requirements (steel shot: min. 400 m/s) or the specifications stated by the manufacturers (column 4 in Table 3). It must be emphasized, however, that the measuring equipment used was not calibrated for standardized speed measurement, which includes specifications for temperature, humidity, choke of test weapons, etc. The test should therefore not be seen as accurate measurements of absolute velocities and should primarily be used comparatively. Nevertheless, optimizing conformity of velocity and ensuring that it is in line with legal demands must be a focus point for all manufacturers regardless of cartridge and wad type.

The density of shot here measured by the % of all shot in the cartridge that hit within the 75 cm circle ranged from 41% to 68%. This density is an expression of several ballistic conditions, where the degree of the choke of the weapon used is essential. In the method used (modified Oberfell-Thompson), the following correlations between density and choke (design of the internal dimensions of the barrel) are stated:

40% = cylinder bore

50% = improved cylinder

55% = quarter

60% = half

65% = three quarters

70% = full

With the weapon used, a density of around 55% was to be expected, which was the case for some brands. However, some showed a tendency for lower density, especially two of the fiber types (the same two that had high SD at the V1.5) showed significantly lower density percentage, while density in some of the brands with water-soluble wads were higher. There was no clear pattern in the relationship between density and wad types.

The distribution of shot (last column in Table 3) assessed on the basis of the modified Oberfell-Thompson method (Figure 2), i.e. the number of shot holes in the 75 cm circle (fourth-last column) related to the number of 12 cm circles without shot holes (penultimate column in Table 3), showed that all cartridge brands received the rating "medium" or "good". Overall, shot density and distributions of the tested products were within the generally accepted limits.

This field test was not scientific and data not sufficient for proper statistical testing. However, the methodology corresponded to the approach that has been used in Denmark in connection with e.g. campaigns to prevent wounding of game during hunting [11] and to test new types of gunshot in connection with the shift from lead shot to lead-free shot for hunting in Denmark [13]. It is therefore considered that the test gives a good indication of the performance of products of shotgun cartridges with biodegradable wads.

Regardless of the cartridge materials, a shotgun shot is technically complicated and basically a dilemma between, on the one hand, achieving necessary shot density and distribution for the prey to be hit by a sufficient number of shots, and on the other hand for the striking shot to have sufficient energy to penetrate the prey and cause lethal damage. The first part is achieved by using large charges with small shot pellets and the second on the contrary by using small charges with large shot pellets. A balance is therefore needed between the size of shot and charge to achieve the desired performance. Impact energy, regardless of shot size, can be increased with increasing velocity. In a standard caliber such as 12/70, the charge weight is limited to a maximum of approximately 32 g (steel shot) for reasons of volume. Regarding muzzle velocity, the International Commission on Arms Testing (CIP) recommends a maximum value of 430 m/s for an average of ten test shots. This is determined by inter alia safety considerations (e.g. pressure).

Within these constraints, cartridges with biodegradable wads appear to be able to live up to general standards in terms of functionality at level with cartridges with traditional wad types. Biodegradable wads some of which differ considerably in construction and solidity compared to traditionally used types do not seem to have any significant decrease in ballistic properties. The content and quality of shot did not differ from traditional types. There were no indications that the actual construction of shotgun cartridges with biodegradable wads compromised current requirements for the practical hunting use and efficiency of such cartridges. This opens up the field to a wide range of materials, where the consideration of avoiding the environmental disadvantages of spreading waste in nature can be given high weight in relation to the ballistic properties. The most crucial element seems to be to achieve an efficient gas packing between gunpowder and shot load, which apparently is obtained with the studied materials. There will also continue to be a need for a wad construction for use in classic shotguns that protects against contact between loads of hard shot (e.g. steel) and the gun barrel. It is probable, but not investigated here, that the significance of the direct contact between shot and barrel for new types of weapons with adapted and more robust types of barrel steel will diminish. Techniques to improve gun barrel steel in terms of its hardness, strength, ductility etc. may produce new generations of guns adapted to hard shots that eliminates the need to use protecting wads. Kanstrup and Hartmann (1991) [14] investigated the potential for this by firing in total 1,260 rounds of steel shot cartridges (shot size 3.4 mm) in two steel proofed shotguns. The cartridges were loaded with classical fiber wads without a cup-construction and therefore leaving full contact between the shot load and gun barrel. “Before and after” measurements showed no significant changes (diameter, scratches, bulging etc.) to the gun barrel. However, all aspects of safety and risk for damage to guns due to the use of new types of wads remains an open question and not a part of this study.

The overall finding that the wad material does not influence ballistics at any significant level was further supported by interviews and discussions with gun dealers and hunters/shooters indicating that the existing cartridges with biodegradable wads generally live up to expectations in terms of performance in both hunting and clay target shooting.

3. Results

The mass of plastic waste entering the oceans worldwide in 2010 was estimated to be 4.8- 12.7 million tonnes [15]. The amounts of plastic dispersed from hunting ammunition may seem minimal compared to the amounts of plastic waste deposited into the natural environment by the community in general. However, the hunting waste poses a different aspect of the problem, since it to a certain degree is intentional littering, resulting in plastic litter on beaches, which is both an aesthetical problem and constitutes an adverse environmental footprint from hunting. It is a source of macro-plastic that may be ingested by macro-fauna (wads have the same shape and color as small squids). Equally important, plastic wads and shells disintegrate to form micro-plastic that accumulates in ecosystems. Hence, there is a major interest in reducing plastic waste from all ammunition, regardless of the shot material used (lead, steel and other types).

The demand for ammunition with biodegradable components, in particular wads, has increased dramatically in recent years, as the concern about plastic waste from hunting cartridges has grown, driven by the general public and political concern about plastic waste in global terms , but also by aesthetic concerns relating to the effects of such waste on hunting habitats. The development is welcomed by hunters and supported by increasing demands from the sport shooting sector and some national hunting organizations [16], and from owners of hunting grounds.

The availability of degradable wads seems not to be limited by production technology or costs, but mainly by uncertainty about necessary requirements, including meeting any future potential legal requirements. The present range of materials is promising as most materials in the final products marketed as biodegradable wads show the potential to decompose, dissolve or bind to sediments to a degree that is significantly higher than traditional PE. The water-soluble types are of particular interest for the use in marine ecosystems as they dissolve very rapidly when discharged to water as is the case for the PVAL-based wads. PVAL is not classified as toxic, and there is no indication of intermediate products to cause any significant risk of adverse impacts in natural ecosystems. Regarding marine systems, in particular, the dispersal of materials from shotgun wads appears to be very limited when judged against the massive volume of the recipient, hence amounts of intermediate or final products will appear in extremely low concentrations.

On this background, the present variety of materials represent a large potential for mitigating the problems associated with the dispersal of plastic from shotgun wads. However, there is a need to further evaluate possible materials. Since the introduction of injection molded wads, the material has primarily been PE-LD and to a lesser extent PE-HD. This gives an indication of some of the basic requirements, including mechanical properties (flexibility and strength) needed 1) to ensure a tight sealing between powder and shot load, 2) to provide an efficient separation of shot from the gun barrel, 3) to obtain processing properties enabling injection molding, and 4) to ensure a competitive price (for comparison, PE costs approximately 1 Euro/kg). Injection molding is the most common production method for plastic, as it is inexpensive, ensures high tolerances for dimensions, and allows for the often complex designs. The buffer part of a shotgun wad and slits are either produced through an integrated step in the injection molding or by cutting in a subsequent step. Fiber wads are produced by winding paper slides. Against this background it seems obvious to prioritize injection molding as a primary method also when materials other than those currently on the market are used.

There are a number of materials that can be used in special injection molding processes, and which are either biodegradable in nature or mineralize over time. Table 4 lists material types with the related advantages and disadvantages. All four material choices will have an innovation height. The use of natural fiber-filled plastic is considered to be the most mature and accessible process, while pulp injection molding may well be a direct route to a wad that disappears quickly in nature and is only made from materials that are already well known for their biodegradability and are otherwise considered harmless.

Table 4. Non-commercialized materials relevant for the manufacture of wads.

Material type	Production method	Price	Advantages	Disadvantages
Natural fiber-filled bio-degradable plastic.	Injection molding for fibers up to 2 mm in length. Typical filling degrees 10-40%.	Higher than for plastic, but with the addition of compounding.	Faster biodegradation than the plastic itself, as the fibers often increases the available surface area during degradation. Density can be varied.	Typically specially compounded materials. Water content in fibers is a challenge in the injection molding process. At high filling degrees, the material risks becoming brittle.
WPC (wood polymer composite) based on biodegradable thermoplastic.	Injection molding.	Lower than plastic.	Maturity.	WPC degradation in temperate environments has not been tested. Typical WPC materials are known for their durability even outdoors.
Pulp with biodegradable or soluble binder.	Pulp injection moulding.	Higher price for molds. Extremely cheap raw materials.	It may be possible to create a product that, on a short time scale, only leaves incoherent paper fibers, which then biodegrade rapidly.	Preliminary experiments have shown that the technology is difficult to handle. Significantly higher cycle times are expected. It can make production more expensive.
Clay and ceramic materials.	Ceramic injection molding.	High price for production equipment. Cheap raw materials	Raw materials are mineralized in nature.	A development phase is required to create a material that is sufficiently ductile not to damage the gun barrel and not disintegrate at the muzzle outlet.

Furthermore, biodegradable plastic with a relatively high content of short plant-based fibers may provide an alternative that would ensure rapid biodegradation and adjustable density just as a wad made by injection molding from a paper pulp with a water-soluble binder has the potential for very rapid disintegration of the wad and subsequent rapid degradation in nature.

The previous sections have mainly dealt with shotgun wads. However, shot shells are also commonly made from plastic and, thus, represent a potential source of plastic waste in the natural environment. It is a widespread practice and common shooting code that the hunter/ shooter picks up spent shells for later disposal. However, in certain circumstances shells are frequently lost in particular in the marine environment [4]. In some new cartridge brands, shells are made from PHA which over time decomposes in the natural environment. Conversely, widespread use of degradable shells could tempt hunters to leave them more often – including also the metal components of shells - in the hunting habitat. This could jeopardize the common conduct of hunters to collect shells and deposit them safely as garbage or recyclable products. We therefore recommend strategies to ensure shotgun shells made from materials with the lowest possible energetic and climate footprint and encourage the continued and reinforced efforts of hunters and shooters to retrieve and ensure recycling of shells. On this background, PE may continue to be the most widespread material for shell production for the foreseeable future. Paper is a traditional material which has, however, some disadvantages in particular for use in humid environments. We recommend an overall strategic initiative to evaluate types and materials for production of shotgun shells in order to minimize their environmental footprint.

Shotgun ammunition is just one use of plastic that pollutes the natural environment, and there is a strong focus on other uses that affect the environment. Here, too, work is being done on solutions aimed at types of plastic that decompose into environmentally neutral residual products. There is a need here for ongoing coordination and knowledge exchange in order to achieve sustainable solutions. While new solutions should seek to have the lowest possible environmental impact, the functionality of the products and inherently the safety of the hunters should not be compromised.

5. Conclusions

The transition from conventional plastic products to more environmentally friendly alternatives is already receiving great attention both nationally and internationally - especially under the auspices of the EU. Shotgun wads are commercially available that will decompose, dissolve or bind to soil colloids in nature. Both literature studies and laboratory experiments indicate that wads made of PVAL will both decompose and dissolve in all types of environments relevant for shotgun hunting. In aquatic environments, PVAL wads are expected to dissolve completely. The literature study indicates that wads of PHA can also be degraded in temperate environments, which is furthermore applicable to TPS and paper-based wads. The accelerated degradation experiments also indicate this possibility for a paper-based wad, while this was not the case for the specific PHA-based wad of the study, however this may be the case for other types of PHA materials. A biodegradable plastic with a relatively high content of short plant-based fibers could be an alternative that can ensure rapid biodegradation and adjustable density. A wad made by injection molding from a paper pulp with a water-soluble binder has the potential for very rapid disintegration of the wad and subsequent rapid degradation in nature. New types of biodegradable wads differ in structure and solidity of the materials. However, this does not appear to have any significant influence on the ballistic properties. Thus, the range of potential materials widens and the consideration of the environmental impact of disposal in nature can be weighted higher than the ballistic properties.

Shotgun ammunition is just one use of plastic that pollutes the natural environment and there is a need for coordination and knowledge exchange in order to achieve sustainable solutions regardless of application.

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References

1. Syberg, K., Khan, F.R., Selck, H., Palmqvist, A., Banta, G.T., Daley, J., Sano, L., Duhaime, M.B. (2015). Microplastics: addressing ecological risk through lessons learned. Environmental Toxicology and Chemistry 34:945-953 doi:https://doi.org/10.1002/etc.2914
2. Galloway, T.S. (2015). Micro- and Nano-plastics and Human Health, in Marine Anthropogenic Litter, M. Bergmann, L. Gutow, and M. Klages, Editors. Springer International Publishing: Cham. p. 343-366. doi:10.1007/978-3-319-16510-3_13
3. Kanstrup, N., V.G. Thomas, and A.D. Fox (2019) (Eds.). Lead in hunting ammunition: Persistent problems and solutions. Vol. 48, Ambio: Springer. https://link.springer.com/journal/13280/volumes-and-issues/48-9
4. Kanstrup, N. and T.J.S. Balsby (2018). Plastic litter from shotgun ammunition on Danish coastlines - Amounts and provenance. Environmental Pollution. 237: p. 601-610. doi:10.1016/j.envpol.2018.02.087
5. Regeringen (2018). Plastik uden spild - Regeringen plastikhandlingsplan. Miljø- og Fødevareministeriet, 2018. https://en.mfvm.dk/fileadmin/user_upload/ENGLISH_FVM.DK/Regeringens_plastikhandlingsplan_UK.pdf
6. Addamo, A.M., Laroche, P. and Hanke, G. (2017). Top Marine Beach Litter Items in Europe. A review and synthesis based on beach litter data. JRC Technical Reports, 2017. file:///C:/Users/au85527/Downloads/technical_report_top_marine_litter_items_eur_29249_en_pdf.pdf
7. Strand, J., Tairova, Z., Danielsen, J., Hansen, J.W., Magnusson,.K., Naustvoll, L.-J., Sørensen, T.K. (2015). Marine Litter in NordicWaters. Nordic Council of Ministers http://norden.diva-portal.org/smash/get/diva2:824655/FULLTEXT01.pdf.
8. Hansen, N.M.L., , Sommer-Larsen P., Ma, N., Pallesen, B.E., Andersen, M., Vestbø, A.P., Kanstrup, N. (2021). Kortlægning af markedet for bionedbrydelige haglskåle. Miljøstyrelsen, 2021. https://www2.mst.dk/Udgiv/publikationer/2021/03/978-87-7038-281-6.pdf
9. Kanstrup, N. and V.G. Thomas (2019). Availability and prices of non-lead gunshot cartridges in the European retail market. Ambio. 48(9): p. 1039-1043. doi:10.1007/s13280-019-01151-8.
10. Oberfell, G.G. and C.E. Thompson (1957). The Mysteries of shotgun patterns. Okla. State Univ. Press.

11. Skov- og Naturstyrelsen (2002). Færre anskydninger - ja tak! - for vildtets skyld: gode råd om personlig skudstatistik / tilpasning af haglgeværet / prøveskydning af haglpatroner. Leaflet. https://www.nordisk-forum.dk/viewtopic.php?t=22602.
12. Pedersen, A.B. (1978), I våbenkammeret og udenfor. Nørhaven Bogtrykkeri, Viborg. ISBN 87-555-0598-8.
13. Kanstrup, N. and Andersen, L.T.A. (2003). Forbud mod dårlige haglpatroner. Jæger 5/2003, 2003. https://www.jaegerforbundet.dk/media/10312/j%C3%A6ger-2003-maj-forbud-mod-d%C3%A5rlige-patroner.pdf.
14. Kanstrup, N. and P. Hartmann (1991). Plastikfri jagthaglpatroner. En undersøgelse af våbenslitage, skudeffektivitet m.v. ved brug af jernhaglpatroner med filtforladning og paphylster. 1991, GameConsult April 1991.
15. Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L. (2015). Plastic waste inputs from land into the ocean. Science. 347(6223): p. 768-771. doi:10.1126/science.1260352
16. GWCT, BGA, BASC, CA, CLA, MA, NGO, SLE, SACS (2020). A joint statement on the future of shotgun ammunition for live quarry shooting. https://basc.org.uk/a-joint-statement-on-the-future-of-shotgun-ammunition-for-live-quarry-shooting/