REVIEWS IN Aquaculture

Reviews in Aquaculture (2019) **11**, 42–57 doi: 10.1111/raq.12225

Shells from aquaculture: a valuable biomaterial, not a nuisance waste product

James P. Morris[1], Thierry Backeljau[1,2] and Gauthier Chapelle[3]

1 OD Taxonomy and Phylogeny, Royal Belgian Institute of Natural Sciences, Brussels, Belgium
2 Evolutionary Ecology Group, University of Antwerp, Antwerp, Belgium
3 Independent researcher, Brussels, Belgium

Correspondence
James P. Morris, Royal Belgian Institute of Natural Sciences, Rue Vautier 29, 1000 Brussels, Belgium.
Email: jmorris@naturalsciences.be

Received 1 June 2017; accepted 2 October 2017.

Abstract

Mollusc aquaculture is advocated as a highly sustainable food source and may play an important role in future food security globally. With production increasing worldwide, it is timely to appraise all aspects of aquaculture when considering its expanding role as a food source. In this regard, one regularly overlooked aspect of mollusc aquaculture is waste generation: namely the production of calcareous shells. Shells from the aquaculture industry are widely regarded as a nuisance waste product, yet at the same time, calcium carbonate is mined in the form of limestone and viewed as a valuable commodity. In a time of increased awareness of the need for a circular economy, the aquaculture and seafood industry should consider shells as a valuable biomaterial that can be reused for both environmental and economic benefit. This review discusses the current waste shell issue and identifies large-scale shell applications that are already in place. Further, it highlights proposed applications that have the potential to be scaled up to address the problem of waste shell accumulations and reduce our reliance on environmentally damaging incineration and landfill disposal. Of the plethora of shell valorisation techniques proposed in the scientific literature, this review will focus only on those that can incorporate large-scale shell utilisation, and do not require high-energy processing, and are thus; simple, sustainable and potentially economically viable. Further, this review questions whether, in many cases, shells can provide more inherent value being returned to the marine environment rather than being used in land-based applications.

Key words: aquaculture, biomimicry, mollusc shell, sustainability, waste valorisation.

Introduction

World aquaculture production is increasing rapidly as seafood demand grows and marine capture production stalls (FAO 2014). Commercial shelled molluscs (referred to herein as molluscs or shellfish) are an important component of the global aquaculture industry and account for ~23% (or ~15 million tonnes) of the total production by live weight (FAO 2014). There are a number of regions across the globe where mollusc aquaculture is particularly prevalent. Eastern Asia, particularly China, dominates by live production weight. However, Western Europe, Chile and the USA also host significant mollusc aquaculture operations (FAO 2014, 2015). The distribution of the world's top 10 mollusc-producing countries is highlighted in Figure 1. Practiced responsibly, mollusc aquaculture can be one of the lowest impacts (environmentally, and in terms of energy consumption) and most sustainable proteinaceous and nutritious food sources currently available (Shumway *et al.* 2003; Klinger & Naylor 2012; Bostock *et al.* 2016). Both global aquaculture (freshwater and marine) and its shellfish component are likely to be of increasing importance to the food industry in the light of impending freshwater shortages, energy security worries and an increasing human population (Bogardi *et al.* 2012; Ozturk *et al.* 2013). Recent technological and scientific advances have allowed for the development of offshore mollusc farming, and farming as part of an integrated multitrophic aquaculture (IMTA) approach (reviewed by: Chopin *et al.* 2012; Granada *et al.* 2015). The refinement of these techniques may further improve the sustainability and productivity of the global aquaculture sector. Further, attention has been brought to the idea that mollusc culture, in particular, can provide ecosystem services such as anthropogenic eutrophication control (Lindahl *et al.* 2005), and reef growth for biodiversity maintenance (Coen & Luckenbach 2000) and natural coastal protection (Ridge *et al.* 2015; Walles *et al.* 2016).

One key aspect of shellfish aquaculture and food production that remains a barrier to its continued sustainable growth is the issue of shells. Shell waste can be a big problem for shellfish producers, sellers and consumers, both practically and financially. Species dependent, shells can account for up to 75% of the total organismal weight (Tokeshi *et al.* 2000). Consequently, a large proportion of production is considered by the shellfish industry as a nuisance waste product. In parts of the UK, for instance, the proper disposal of shells at a landfill site could cost over £80 per tonne (HM Revenue and Customs standard rate landfill tax as of 1st April 2016), a sizeable figure for a small or medium enterprise. Shell piles are common around the world as an unregulated disposal procedure and can be an eyesore, creating strong noxious smells and contaminating the local environment if uncontrolled (Mohamed *et al.* 2012). When promoting mollusc aquaculture as a low-impact food source, all aspects of production must be considered. Further, if suggesting that increased shellfish aquaculture production could be an important component in a shift away from many of the unsustainable food sources we currently rely on, then by-products of that industry should be a prime consideration.

Historically, shells have been an important part of human culture: acting as a globally traded currency (Johnson 1970) peaking in the mid-19th century, and as primitive tools dating as far back as 100 000 years ago, used by the Neanderthals for example (Douka & Spinapolice 2012). Shells still capture the imagination of adults and children alike, and the global ornamental shell trade remains strong (Nijman *et al.* 2015). Scientists have long understood the impressive attributes of shells: made from 95 to 99.9% calcium carbonate, with a small amount of organic matrix (Currey 1999; Harper 2000). Despite many positing that major innovations may arise from the synthetic replication of shell structures and properties, their remarkable structural and mechanical attributes are yet to be copied beyond the microscale in research laboratories (Nudelman & Sommerdijk 2012).

Calcium carbonate ($CaCO_3$) from limestone is one of the most heavily exploited minerals on the planet (USGS 2016). It is mined in huge quantities across the globe as 'ground calcium carbonate' (GCC) for a myriad of applications, including cement production. Other applications,

Figure 1 Distribution of the top 10 countries in freshwater and marine mollusc aquaculture production, representing 95.7% of the total global production by live weight. The area of each circle represents that countries percentage share of the ~15 million tonnes of global production. The adjoining table provides the figures from FishstatJ and FAO (2015). The data include the following: Abalones, clams, cockles, conchs, freshwater gastropods, freshwater mussels, mussels, oysters, scallops and winkles.

such as filling and whitening agents in paper manufacture, require higher-grade synthetically produced 'precipitated calcium carbonate' (PCC), which requires additional processing of high-grade mined limestone. GCC and PCC have significant environmental costs associated with their production, both in terms of the energy intensive and ecologically damaging nature of resource mining (Smil 2013), and also as a significant CO_2 source during the various stages of processing: cement production accounted for ~8% of the global CO_2 emissions in 2012 (Olivier *et al.* 2012). Herein lies the incongruity: by one sector, $CaCO_3$ is mined and processed in vast quantities for numerous and varied applications, whilst in another industry, $CaCO_3$ is produced as a by-product and viewed as a nuisance waste. It is important to note that the scale of $CaCO_3$ production by the aquaculture industry is orders of magnitude smaller than that of the mining industry, but nevertheless the stark contrast in the way the two $CaCO_3$ sources are viewed is striking.

Over the past couple of decades, numerous articles have been published on the subject of shell valorisation, citing a variety of potential applications that could alleviate the burden of waste shells on aquaculture and food producers, and in some cases, present economic as well as environmental incentives to do so. Further, understanding has recently grown of the importance of shellfish and mollusc shells on the healthy functioning of a variety of complex ecosystems. In the light of such research, a growing understanding of the unsustainable nature of many current human exploits and a concerted drive towards a more circular economy, it might be expected that shell valorisation is already commonplace in areas of intense aquaculture. However, this is not the case. Aside from a few shell enterprises, and many small-scale localised initiatives (as described below), the majority of shells from aquaculture processing remain a waste product. This article highlights the current shell market and discusses the feasibility of other potential shell applications. Further, it discusses whether the focus of shell valorisation should be towards economically beneficial uses, environmentally centred applications or whether shells have more value simply being returned to the marine environment.

Shell valorisation

Valorisation is the principle of assigning value, or greater value, to something: where value can be seen from an economic, social or environmental perspective. Valorisation is a particularly pertinent concept with the recent drive towards recycling, zero waste industries and a more circular economic system (European Commission 2015). Mollusc shells, as a by-product of the aquaculture industry, can be given value in numerous ways (Morris *et al.* 2016). The following sections will introduce and review current, potential and unexplored valorisation strategies. The current applications section includes those that are well established, widely exploited or large-scale and sustainable. The potential and unrealised applications section includes those that have been discussed in academic literature or elsewhere, have been advocated as feasible or have been trialled, but have not become established or widespread applications. The final section will discuss the value of returning shells to the marine environment, highlighting current projects that are returning shells to the water, the rationale behind such projects, and discussing further benefits of such activities.

One key consideration regarding shell waste in the aquaculture and food industries is the point at which the waste is produced. Unlike many other food sources where a single process is ubiquitous, shells can be removed by the aquaculture producers, by a processing company, by restaurateurs or by consumers (Fig. 2). Waste production can depend on the species as well as the type of product. For instance, in Europe, mussels are sold and served in full shell or processed and canned/frozen without shell. Oysters are commonly provided to restaurants in full shell and consumed in half-shell. Scallops on the other hand are more generally processed and sold with no shell. As such, shell waste is produced in potentially many different locations, making large-scale valorisation more difficult. Yet, as the following examples show, valorisation is still possible. Further, if shellfish aquaculture is one component in a global movement towards a more sustainable food sector, then the way we eat shellfish in many parts of the world may need to adapt also: in part moving away from a luxury items, served in shell for aesthetics, towards a more commonplace protein source, preprocessed to remove shells. In such a scenario, more shell waste would be generated in single locations, and thus, the opportunities and motivation for large-scale shell valorisation would also be greater. In contrast to European mollusc consumption, in Asia (particularly China), the majority of products are processed, and shells are removed at the point of harvest and regularly discarded back into the water, or along the coastline (*pers. observ.*; *pers. comms.*). This combined with the scale of production means that shell waste issues are of greater concern than in Europe, for instance. This also means that the opportunities for shell valorisation projects are greater.

A key consideration in shell valorisation is the proximity of shell waste production to suitable processing facilities, as well as proximity to regions in which potential shell applications have a market. A recently conducted a life cycle assessment (LCA) on oyster shell waste (*Crassostrea gigas*) in Brazil, incorporating distance between shell source and the processing facility, found that a distance >323 km between the two yielded no environmental benefit of shell valorisation over landfill disposal (de Alvarenga *et al.*

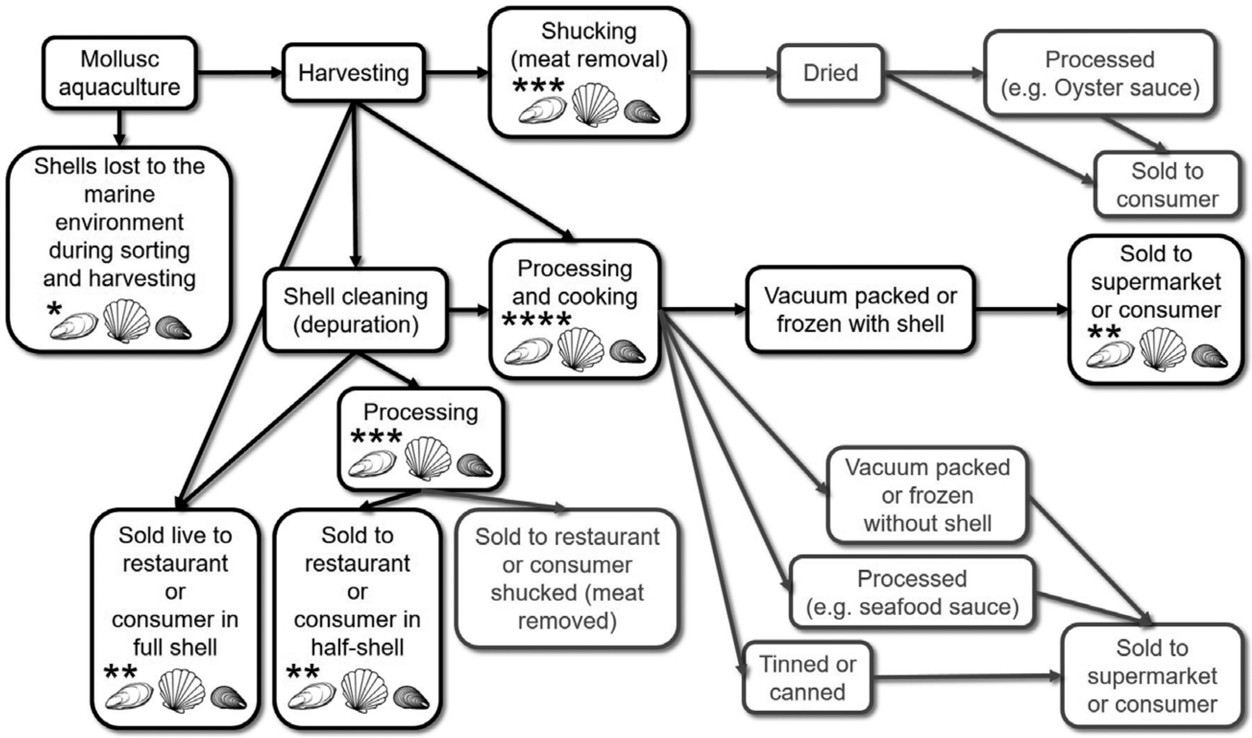

Figure 2 Conceptual diagram describing some of the key processes undertaken during the delivery of commercial bivalves, such as oysters and mussels, from aquaculture to consumers, highlighting the points at which shell waste may be produced. Black boxes represent stages where shells are still attached, and grey squares represent stages where shells have been removed. Shell cartoons highlight at which stages shell waste is produced: * living individuals can become detached from growing ropes, rafts or bags in adverse conditions, and also during processing stages such as size sorting or harvesting. Organic material decays or is eaten, but shell hash remains and is commonly observed below aquaculture installations. The 'shells returned to the marine environment' section below describes how shell accumulation can, in some cases, have positive ecosystem service effects. ** Once harvested, the product can be sold directly (live) to consumers and restaurants or cleaned processed and cooked with shells. In these cases, shell waste is spread to the consumer and is hard to recover and aggregate in large quantities. *** Some products require further processing (shucking or half-shell removal, resulting in clean raw shells being accumulated at processing facilities). **** Processing that requires cooking is usually carried out with shells attached, subsequent products, such as tinned mollusc meat, where shells are removed, results in cooked and cleaned shell waste. This form of shell waste is most easily applicable to reuse because of prior cleaning and cooking.

2012), highlighting that consideration must be given to the potential distances between source and application. Aside from environmental benefits, economic benefits of shell valorisation are also very dependent on distance.

Finally, there is a plethora of published research on shell valorisation where shells, in various states, are converted to calcium oxide (CaO) prior to their use in the described applications (e.g. Viriya-empikul *et al.* 2010; Hu *et al.* 2011). This conversion is carried out via the process of calcination: heating to high temperatures in air or an oxygen-enriched environment. For limestone, the conversion of $CaCO_3$ to CaO requires heating to ~800°C, and produces CO_2 in the process. This article concerns the sustainable valorisation of shell waste, and as such, those applications that require calcination, or other high-energy and CO_2-yielding pretreatment processes do not, in the authors' opinion, provide scalable and sustainable solutions to shell waste at present. As an example, calcined shells have been advocated as a potential CaO source in CO_2 sorbents. Wang *et al.* (2014) performed a LCA on CaO derived from waste oyster shells from oyster farms in Eastern Taiwan (*Crassostrea angulate*). As a CO_2 sorbent, waste shells were determined to be a more sustainable starting medium in CaO production when compared to mined limestone in terms of CO_2 emissions. Although waste reutilisation is a step in the right direction in any process, $CaCO_3$ calcination will remain an inherently unsustainable process regardless of the $CaCO_3$ source. Processes such as these may hold future value in solid carbon storage techniques, but at present, high-energy conversion of $CaCO_3$ to CaO limits such avenues. Still, CaO is necessary in many industries; however, as will be highlighted below, shells can be reused in a variety of ways that present more simplified and more sustainable applications.

There is also a plethora of potential small-scale shell valorisation techniques. Although such applications are interesting in the discussion of innovation in waste reuse, these techniques, such as the use of shell powder in biomedical techniques (as highlighted by Green *et al.* (2015)) or in functional cosmetics (Latire *et al.* 2014), will not provide solutions to large-scale shell waste issues, which is the focus of this article. Previous articles have reviewed aquaculture and shell waste valorisation from a more generalised perspective without specific considerations for scalability or sustainability (Ferraro *et al.* 2010; Yao *et al.* 2014). As such, the following sections will concentrate on those applications that do not require high-energy processing, and on those that have the potential to significantly impact global- and regional-scale waste shell problems.

Current market for mollusc shells

There are several large-scale shell valorisation strategies that are currently exploited. Generally, these applications have been established in areas that generate large amounts of shell waste, and where mutually beneficial partnerships have been established between shell producers and other industries. An example of this is the historic and continued use of mussel shells (*Mytilus galloprovincialis*) as a soil liming agent in agriculture in Galicia, Northern Spain (as described below). Further, there is also an online market for shells, promoted for a variety of applications, as highlighted in Table 1 (and Appendix). The following sections will highlight the major shell applications currently exploited.

Livestock feed supplement

Calcium supplementation is used to improve the health of livestock, particularly bone health, but also in laying birds as a supplement to improve the quality and strength of eggshells (Suttle 2010). Calcium supplementation has been used widely in laying hen farming over the past several decades where $CaCO_3$ sourced from mined limestone is commonly used. Several studies have tested the effect of oyster shell-derived $CaCO_3$ in comparison with a more standard limestone-enriched diet, on poultry, and found that as well as being a potentially cheaper source of $CaCO_3$, crushed oyster shell at optimal dosage can perform equally to limestone as a form of calcium supplementation across a number of tested parameters. In 1971, Scott and colleagues found that partially substituting oyster shells for limestone both increased the egg production rate and eggshell strength of laying hen eggs (Scott *et al.* 1971). Quisenberry and Walker (1970) observed similar results with oyster shell supplementation, showing increased eggshell weight and thickness (Quisenberry & Walker 1970). A later study found no significant differences between oyster shells, clam shells (*Spisula solidissima*), limestone, aragonite or eggs shell supplementation across a number of hen and egg performance indices (Muir *et al.* 1976). In 1990, studies suggested that oyster shells were both a cheaper and more effective calcium supplement than limestone in cottonseed cake (CSC) feed mix for broiler chickens (Aletor & Aturamu 1990; Aletor & Onibi 1990). Chickens fed on an oyster shell-enriched CSC diet showed higher weight gain capacity than those fed on an unenriched CSC diet (Aletor & Onibi 1990). However, another study found that calcium source had no appreciable effect on calcium utilisation and chick performance when comparing bivalve shells, oyster shells and limestone sources (Guinotte *et al.* 1991). Further, Ajakaiye *et al.* (2003) found no significant difference between marine shell-derived $CaCO_3$ and mined $CaCO_3$ sources, having tested bivalve, periwinkle and oyster shells (Ajakaiye *et al.* 2003). However, more recently, and with more modern feed mixes, it has been shown that the addition of shells (*Venus gallina*) to a limestone supplement significantly improved the egg production performance of laying hens (Çath *et al.* 2012). Another recent study, again, found that oyster shell alone performed better than snail shell, wood ash or limestone as a calcium supplement in terms of growth response (weight gain and feed intake; Oso *et al.* 2011). Further, it has even been suggested that nuisance invasive molluscs, such as the zebra mussel (*Dreissena polymorpha*), could be used as a feed and calcium supplement for chickens rather than having them disposed

Table 1 Examples of the current online bulk mollusc shell market, quantity sold and € price per kg for each application type (reference links provided in Appendix)

Type of application	Processing required	Quantity sold	Selling price (as of June 2017)	Appendix references
Poultry feed	Heat treated, crushed	1–25 kg	0.4€–3€ per kg	1–7
Pet bird nutrition	Heat treated, crushed	440 g–2.5 kg	0.6€–7€ per kg	8–10
Biofilter medium	Heat treated, crushed	600–1000 kg	0.4€–0.5€ per kg	11, 12
Aquarium/pond pH buffer	Heat treated, crushed, chlorine washed	5 kg	4€ per kg	13, 14
Soil liming	Heat treated, powdered	22.7 kg	0.4€–0.6€ per kg	15–18
Shell aggregates	Whole shell, dried	250–1000 kg	0.3€–0.9€ per kg	19–21
	Dried, crushed	15–1000 kg	0.3€–3€ per kg	22–24

Reviews in Aquaculture (2019) **11**, 42–57

of at landfill (McLaughlan *et al.* 2014). McLaughlin found that the zebra mussel meal (meat and shell) was palatable for chickens, and despite lower than expected protein and energy levels in the feed, they concluded that zebra mussel feed could still be utilised as a calcium supplement on account of the $CaCO_3$ shells (McLaughlan *et al.* 2014).

The above summarises some of the key published scientific literature on shells as a calcium supplement for livestock. It is clear that shells are, at least, comparable to commonly used limestone as a source of calcium for livestock, with several studies suggesting shell-derived $CaCO_3$ can outperform limestone in this regard. In 2011, there was a population of 363 million laying hens in the EU-27 group (Eurostat 2011). Of those, France was the biggest egg producer, at 924 000 tonnes in 2011 (Eurostat 2011). Laying hens require ~2.5 g of daily calcium, and with a retention rate of ~50% that would equate to 4.0–4.5 g of calcium (Dale 1994), or ~10 g of crushed shell $CaCO_3$ (taking into account a ~40% calcium content of shell-derived $CaCO_3$). To a lesser extent, broiler chickens also benefit from calcium supplementation in their diet. As such, there is certainly a considerable demand for calcium carbonate by the livestock industry. However, the expansion of the use of mollusc shells maybe limited by the costs associated with aggregating enough mass of shells at a single location for the sort of continued and reliable source that large livestock producers expect.

For the EU, as outlined in Regulation (EC) No 1069/2009, shells can be used for supplementation as long as they meet a free-from-flesh standard, with which they are then exempt from animal by-product classification. Each member states relevant competent authority controls the designation of free-from-flesh standards. Finally, distance between shell production and each farm must be considered. From both an environmental and economic perspective, only farms in close proximity to a large shell-producing operation are likely to be candidates for this type of shell valorisation.

Agricultural liming agent

The second major market for shells is, again, in the agricultural sector, but involving the neutralisation of acidic and metal contaminated soils. Generally referred to as liming, the practice involves treating soil or water with lime (or a similar substance) in order to reduce acidity and improve fertility and oxygen levels. Liming, reportedly, dates back to the first and second centuries B.C. and has subsequently been prevalent in many societies since then, as reviewed by Barber (1984). The practice of liming is well known as having numerous positive effects on the productivity of agricultural crop yields and can also have longer term positive effects on soil quality and structure as reviewed by Haynes and Naidu (1998). Further, although still unresolved, it has been suggested that under certain conditions, the application of a liming agent to agricultural land can act as a net carbon sink mechanism (Hamilton *et al.* 2007).

Crushed mollusc shells from the aquaculture industry can be a viable replacement for more commonly used mined-$CaCO_3$, such as limestone. A number of studies have quantified various effects of the application of crushed mollusc shells to agricultural land. In Korea, crushed oyster shells were applied to two acidic soil types at a variety of rates, and assessments of Chinese cabbage yield, and soil pH and nutrient metrics, were analysed. The study found that the crushed oyster shell meal significantly increased soil pH, improved soil nutritional status metrics including available phosphate and organic matter mass (Lee *et al.* 2008). Previous concerns regarding elevated salt levels (NaCL) were tested, and despite a slight increase in soil Na concentrations, no signs of toxicity damage were observed in the cabbage. Further, improved soil status promoted microbial populations, increasing nutrient cycling. Each of the above likely contributed to significantly increased cabbage productivity in both soil types with the application of crushed oyster shells. Highest productivity was achieved under the application of 8 Mg ha^{-1} of crushed oyster shells (Lee *et al.* 2008). In Galicia (Spain), mussel shells (*Mytilus galloprovincialis*) have been used as a liming agent on soils. In 1997, a study found that 9 t ha^{-1} of mussel shell had a comparable short-term positive effect on soil acidity as conventionally used magnesium limestone (Iglesia Teixeira *et al.* 1997). However, in the longer term, mussel shell was found to be less effective than mined liming agents in terms of soil fertility (Iglesia Teixeira *et al.* 1997). More recently, Garrido-Rodríguez *et al.* (2013) studied the effect of mussel shell treatment on the ability of soils to ameliorate the detrimental effects of copper addition. They found the mussel shell-treated soils had a higher desorption rate than untreated soils and concluded that mussel shell addition could help reduce the potential threat of copper-enriched soils under acidification events (Garrido-Rodríguez *et al.* 2013). Another study in Galicia (Spain) found that the application 24 Mg ha^{1} of ground mussel shell increased the adsorption and decreased the desorption of arsenic in both forest and vineyard soils, thus reducing the risk of arsenic soil pollution in these areas (Osorio-López *et al.* 2014).

Acidic soil that could benefit from the application of a liming agent is prevalent across large areas of Europe, particularly in more northern regions (Fabian *et al.* 2014). On a large scale, Galicia is the major region in Europe currently utilising shell waste as a liming agent. This is both because of the proximity of agricultural land to large shellfish aquaculture sites, and because of the presence of a large shell processing facility.

On a smaller scale, there is also interest amongst gardeners and landscapers regarding the use of shells as a decorative topsoil or mulch (Table 1). In such cases shells are sold mainly for decorative purposes but with the added potential functionality of acting as a liming agent/pH buffer.

The use of sufficiently clean, cooked, shells is determined in the EU by each member states' competent authority, as outlined in Regulation (EC) No 1069/2009. In England, for instance, the use of cooked and cleaned shells, in crushed form, is allowed for use as organic fertiliser or soil improver as laid out in the Department for Environment, Food and Rural Affairs (DEFRA) authorisation B6 (DEFRA 2017). Other EU member states and non-EU countries may have further restrictions or exemptions. Additionally, entirely free-from-flesh shells are exempt from animal by-product classification in the EU, as outlined in Regulation (EC) No 1069/2009 and could be used without any restrictions.

Shell aggregates

There are many examples of shells being used as a simple material for construction or incorporated into aggregate and mortar mixes. Shell waste has many characteristics that might make it suitable for certain construction aggregates. However, care must be taken in such propositions though, as many construction materials are highly regulated for performance and safety purposes (as outlined in; EU Regulation No. 305/2011). The concept of shell use in construction is by no means a new one: there are many historical examples of shells in construction, much of which is known as 'Tabby'. Florida (USA) has a particularly rich history of incorporating whole oyster shells into the walls of houses, being of likeness to a modern day poured concrete structure (Sickels-taves 2016). There are ongoing projects to incorporate shell waste into aggregate mixes. In Spain, Galician mussel shells have been tested for their suitability in aggregate mixes (project website: https://proyectobiovalvo.wordpress.com, accessed: 20/09/2017). Whole oyster shells are used for simple wall structures in coastal villages associated with oyster aquaculture in China, and crushed scallop shells have been used as a simple path aggregate on the Isle of Mull, Scotland (*pers. observ.*). Undoubtedly, many other examples exist of this pragmatic use of waste shells, but, in order for these applications to become more established, they must be science-backed and controlled, in order to meet regulations. At this time, shell incorporation in aggregates and mortars is largely primitive, and thus, the discussion of the scientific literature in this area is included below, under potential and unrealised applications, rather than being discussed here as an established market.

Biofilter medium

There is a significant body of research on the use of mollusc shells as biofiltration medium for treating wastewaters. However, a large proportion of that research does not use shells directly, but pretreats them via calcination or pyrolisation, forming CaO. This adjusted product is then found to be a good filter medium (Kwon *et al.* 2004; Ma & Teng 2010; Castilho *et al.* 2013; Chiou *et al.* 2014). However, as stated above, high-energy conversion of shells is not deemed a sustainable or scalable solution to the issue of large-scale shell waste at present. As such, only literature that tests the suitability of uncalcined/unpyrolysed shells as biofilter mediums has been considered, representing both the current market for shells sold as biofilter media and also a more feasible large-scale potential valorisation strategy moving forwards.

The use of mollusc shells as a treatment for heavy metal contaminated wastewaters was explored using both aragonite-rich razor clam shells and calcite-rich oyster shells. It was found that both shell-derived powders had similar Zn^{2+} sorption capacities. However, the calcitic oyster powder proved a better Pb^{2+} sorbent, whilst the aragonitic clam powder had a better capacity for Cd^{2+} sorption (Du *et al.* 2011). Because geological $CaCO_3$ is more prevalent in calcite form, the authors suggest that aragonite-rich shells maybe of particularly use in wastewater treatment facilities. However, the mix of both calcite and aragonite is needed to optimise heavy metal removal from wastewaters. Further, as the shell preparation technique was simple (washed, air-dried and pulverised), in areas where waste shells are generated, the use of shell powder may be an economically viable sorbent for inclusion in wastewater treatment facilities using this technique (Du *et al.* 2011). Another study, conducted in India, showed that similarly treated shell dust from the invasive freshwater snail (*Physa acuta*) was an efficient Cd^{2+} sorbent from an aqueous solution (Hossain & Aditya 2013). Further, a report commission by the Auckland regional council in 2010 (New Zealand) highlighted the potential of mussel shell waste as a replacement for graded sands in the sand filters conventionally used in storm water treatment facilities (Craggs *et al.* 2010).

There is also a small market for shells as a filtration and pH buffering medium in ponds and aquaria (Table 1). The potential biofiltration capacity of shells is described above, and the pH buffering capacity of $CaCO_3$ is well known in scientific literature. Ponds and aquaria vary in pH according to day/night cycles due to the presence of algae/plants and respiring organisms, and the concomitant variation in dissolved CO_2. However, the maintenance of a steady pH flux is important for healthy ponds and aquaria. Crushed shells are sold as simple pH buffering substrates to prevent dramatic acidification. They are also sold for inclusion in trickle and biological filtration systems for their ability to remove unwanted water contaminants, such as heavy metals in addition to their pH buffering capacity.

Potential and unrealised applications of mollusc shells

The applications of shells described in the section above all have some current and sustainable market value. This section will describe potential and as yet unrealised applications of shells. Such applications may have been theoretically discussed, tested in a laboratory setting or used in real-world scenarios, but have yet to attain a market value, or become an established valorisation strategy. As before, many potential shell valorisation techniques described in the scientific literature require high-energy processing, in many cases to convert the shell $CaCO_3$ to CaO. The following potential applications are those that could prove viable economically whilst also being environmentally benign.

De-icer grit

Paved and tarmacked surfaces can become impassable with even a small amount of snow, ice or frost. A common strategy in many developed countries is to spread de-icing and anti-icing substances. These act to either remove snow, ice or frost (de-icer) or delay their formation (anti-icer). Both also aid the mechanical removal of snow, ice or frost once established. Excluding airports, the most common de-icing substances are chlorine-based, such as rock salt (NaCl). De-icer and anti-icing are sometimes collectively referred to as road grit. Road grit is inexpensive and usually available in large quantities; however, in recent years, the UK and Europe have experiences numerous localised shortages during cold periods due to a lack of stockpiling and uncertainty of demand. It is well known that chlorine-based road grits can be detrimental to both the urban environment and the natural environment: road grit is specifically not used in airports because of the corrosive effect it can have on aeroplanes. Research has shown that road grits can have negative effects on the natural environment in close proximity to its use (as reviewed by: Fay & Shi 2012), and Forest Research (the research agency of the Forestry Commission, UK) reports a variety of detrimental effects of salt contamination and spreading techniques on a number of common UK tree species (Webber & Rose 2011).

One potential environmental-friendly road grit not containing chlorine is calcium magnesium acetate (CMA) or any calcium acetate derivative. There have been a number of publications regarding CMA as an alternative to chlorine-based de-icers over the past few decades. Most have concentrated on the use of waste products as acetate donors, for instance: vegetable waste (Jin *et al.* 2010), cheese whey (Yang *et al.* 1992), bamboo vinegar (Jiang *et al.* 2010), as well as wood and paper waste biomass (Wise & Augenstein 1988). There is little discussion of the potential use of waste $CaCO_3$ from the aquaculture industry as the calcium donor in the formation of calcium acetates. There are, however, reports of the use of scallop shells mixed with apple pomace waste from two industries local to the Aomori Prefecture in Northern Japan being combined to form a calcium acetate de-icer substance for use on local roads.

The formation of an eco-friendly de-icer substance from the waste shells of shellfish aquaculture, mixed with a mild acetate waste substance from another industry such as those listed above could prove an environmentally beneficial use of shells, and with the recent localised shortfall in de-icer substances across Europe during cold periods, there is potentially a market for alternatives to road grit as de-icing agents. Biochemical oxygen demand (BOD) is an important consideration for this potential application (as highlighted by FitzGerald 2007). BOD is the amount of dissolved oxygen required for the biological breakdown of organic material within a given water sample and is used as a proxy for organic pollution. It stands that de-icer substances of organic origin may produce greater BOD load to localised water. This should be tested, and the impact weighed against the known impact of chlorine-based road grits on the localised environment.

Green roofing substrate

Green roofs, also known as living roofs, have seen a surge in popularity in the last decade, particularly in urban areas, as there is a growing conscience of the importance of green spaces on environmental health. Green roofs can have a number of beneficial effects: increasing habitat space for wildlife (Brenneisen 2003), mitigating urban heat island effects (Santamouris 2014), providing building insulation (Niachou *et al.* 2001), providing rainwater absorption and improved wastewater management (Berndtsson 2010), as well as potentially providing a stress-reducing and attention-increasing environment for those in proximity (Lee *et al.* 2015). Green roofs typically come in two forms: extensive and intensive. The two are differentiated according to the depth of planting medium used and the need for maintenance: type 1 extensive roofs having 10–25% of the growing medium of type 2 – intensive roofs. Extensive roofs are designed for minimal maintenance, whereas intensive roofs can be more versatile but require maintenance as a garden would. Both types of roof are designed with the same principle layers: vegetation, growing medium, filter membrane, drainage layer, root barrier and waterproofing membrane (Weiler & Scholz-Barth 2009).

Another potential use of waste mollusc shells is as the drainage layer in green roofing structures. The drainage layer is important in carrying away excess water from the roof. It is a 3D structure between the filter layer and the waterproof membrane (Weiler & Scholz-Barth 2009). Whole shells may be ideal for such structures, as when heaped they provide a complex 3D structure to aid drainage. In addition, $CaCO_3$ shells incorporated into green roofing structures may help with the neutralisation of acid rain, and the reduction in heavy metal contamination in the resultant drainage water. Shells could also be incorporated into the filtration and topsoil layers of a green roof for their bioremediation potential. Green roofing has many ecological and environmental benefits, and those interested in green roof structures may also be inclined to the idea of incorporating waste products into such structures. Weight is a primary concern of any potential green roof layering material, and various shell types must undergo water-saturated weight tests to determine their feasibility in specific projects.

Raw shell biofilter

Although included in the previous section with examples of shells already being used and sold as a biofilter substrate, there are many more avenues that are yet to be fully exploited for this potentially simple valorisation strategy. As highlighted in the section 'Biofilter medium', uncalcined, variously graded calcareous shells can be used as: heavy metal, nitrate, sulphate and phosphate sorbents, as well as a pH buffering substrate and an oxidation substrate (reduction in biochemical oxygen demand). Shell valorisation of this kind has, as yet, been restricted to private enterprises and farms, with only the example of Auckland regional council (New Zealand) commissioning a study into the use of shells in public infrastructure (Craggs *et al.* 2010). Because of the simplicity of this valorisation strategy, the lack of high-energy processing of shells and the ubiquity of wastewater treatment needs in both urban and rural areas, the potential for shells to be used as biofilters is much greater than its current exploitation.

Construction aggregates

There is a small body of research concerning the use of calcareous shells in aggregates and mortar mixes, and examples of projects incorporating shells into certain aggregate mixes (as discussed above). This avenue of shell valorisation does hold further promise for aggregates and mortars that are not tightly regulated.

In 2004, a study addressed both the growing issue of oyster shell waste associated with aquaculture in South Korea and the need for aggregate substitutes because of dwindling aggregate sands. The study tested large and small particulate crushed oyster shell mixes to conventional sand mixes as a mortar. It was found that small oyster shell particles (2–0.074 mm) were a potentially viable substitute to conventional mortar sands in terms of compressive strength. Further, the strength of the small oyster shell particle mix was improved with the addition of fly ash (a common by-product of coal burning, and regularly added to Portland cement mixes; Yoon *et al.* 2004). Another study, investigating the incorporation of mussel shell waste in Spain into mortars, found that differences in particle microstructure between quarried limestone (rounded particles) and mussel waste $CaCO_3$ (elongated prismatic particles) resulted in mussel waste-derived mortars showing improved setting times and final strength (Ballester *et al.* 2007). The authors concluded that ground mussel shell waste could be incorporated into cement mixes, reducing the cement mix cost as well as the providing environmental benefits of reduced quarried limestone reliance. In France, a study investigated the incorporation of crushed *Crepidula* sp. (slipper limpet) shells into pervious concrete mixes and concluded that shell incorporation did not have an adverse effect on the concretes mechanical strength and increased porosity allowed for better water permeability, an important characteristic of pervious concretes (Nguyen *et al.* 2013). Further studies have found similar viability of shell incorporation in various aggregate mixes (Yang *et al.* 2010; Lertwattanaruk *et al.* 2012; Kuo *et al.* 2013; Nor Hazurina Othman *et al.* 2013).

Shells returned to the marine environment

The preceding sections have shown that shells are already being utilised for various purposes and highlight that there are further sustainable applications for shells that have yet to be exploited. There is, however, a growing body of evidence in scientific literature to suggest that shells are a valuable material from a biological perspective within the marine environment and may provide and promote a variety of ecosystem services that could be of similar or greater value than those previously described. Further, there are an increasing number of organisations, charities and research groups that are already returning shells to the marine environment for conservation reasons. This section will highlight the potential ecosystem service that waste shells from aquaculture could provide being returned to the marine environment by various methods and address the question of whether we should be seeking economic value from shells in the ways described in the preceding sections, or whether shells have more inherent and enduring value being returned to the marine environment.

Ocean alkalinisation has been proposed as a method of limiting atmospheric CO_2 increases and ocean acidification through pH buffering (Ilyina *et al.* 2013). In the published literature, limestone is regularly cited as a potential liming agent (Harvey 2008). The efficacy of ocean alkalinisation techniques is debated, however, due to the volume/mass of buffering agent required. $CaCO_3$-based buffers such as limestone are unlikely to be practical at large scale in the near future, with minerals such as olivine $(Mg^{+2}, Fe^{+2})_2SiO_4$ holding greater potential (Köhler *et al.* 2013). However, more localised and confined systems that are affected by acidity could be treated in a simple and cost-effective way by the addition of $CaCO_3$. Korfali and Davies (2004) have shown that rivers under the influence of limestone showed high metal self-purification processes and increased alkalinity. Liming has also been shown to facilitate the recovery of species lost during temporal acidification events (Raddum & Fjellheim 2003). Similar to the effects described in the 'biofilter medium' section, $CaCO_3$ can have many positive influences on local watercourses and systems. The practice of liming rivers with limestone is not new (Olem 1990). However, there is little evidence of the use of powdered, crushed or whole waste shells as the calcium carbonate source. If significant shell waste is produced in areas where local water systems would benefit from liming practices, it could be a mutually beneficial practice, alleviating both acid water problems and the cost and environmental strain of dumping waste shells at landfill.

Waste shells can also have many positive influences from a more biological perspective. Oyster populations rely on a suitable substrate for larval settlement and attachment. In many cases, in natural systems, existing adult shells provide such a substrate, resulting in oyster reefs (Gutierrez *et al.* 2003). Many potential substrates can act as sites for larval settlement: granite, concrete, steel, plastics, etc. (Tamburri *et al.* 2009). However, research has shown that oyster larvae have an affinity for biogenic materials such as shells (Nestlerode *et al.* 2007; Kuykendall *et al.* 2015), and particularly to the tissue extracts and shells of their parent species (Crisp 1967; Devakie & Ali 2002; Su *et al.* 2007). In recent decades, there have been numerous examples around the globe of declining oyster populations. Alongside worsening water quality, and diseases and parasites, overfishing and loss of shell reef structures are regularly cited as major causes of population crashes (Brumbaugh & Coen 2009; Beck *et al.* 2011). Population declines have been observed on both the east and west coast of the USA (Rothschild *et al.* 1994; Brumbaugh & Coen 2009), on the south coast of the UK (Kamphausen *et al.* 2011), in Tasmania, Australia (Edgar & Samson 2004), and in China (Mackenzie 2007) as examples.

With a developing understanding of the importance of ecosystem preservation and the services that healthy ecosystems can provide, there have been a growing number of oyster reef restoration projects initiated and a concurrent increase in research articles studying the variety of potential ecosystem services that they provide (Beck *et al.* 2011; Baggett *et al.* 2015). Restoration programmes and research typically use dredged shells or calcium carbonate-based structures (concrete reef balls, for instance) to create a suitable settlement site for oyster larvae, then either let the natural larval stock settle if present or seed the reef structures from hatchery stock. These programmes are proliferating in the USA (Piazza *et al.* 2005; Coen *et al.* 2007; Glausiusz 2010), but also in Europe (Sawusdee *et al.* 2015; Walles *et al.* 2016). Because of shell-cleaning issues and legislation, very few of these projects use waste shells from the aquaculture industry as reef restoration substrates. The Billion Oyster Project on Governors Island in New York is one project that links a waste shell collection service around Manhattan restaurants with a reef restoration programme using those collected shells once cleaned and dried (www.billionoysterproject.org – accessed 01/06/2017). Healthy oyster reefs are now well known to promote biodiversity through complex habitat formation (Grabowski & Powers 2004; Soniat *et al.* 2004; Coen *et al.* 2007; Kochmann *et al.* 2008), counteract of eutrophication and other adverse nutrient conditions (Kirby & Miller 2005; Higgins *et al.* 2011; Kellogg *et al.* 2013), protect against sea level rise and coastal erosion (Piazza *et al.* 2005; Walles *et al.* 2015, 2016). These ecosystem services are not limited to reef building oyster species however. For instance, a study in Sweden has modelled the bioremediatory effects of mussel farming on the west coast of Sweden, suggesting the promotion of mussel populations for the purpose of nutrient and biotoxin assimilation, via a nutrient trading system (Lindahl *et al.* 2005). Shells, and the complex habitats they form, provide not only a substrate for oyster larvae settlement, but also a hard surface for the attachment of other shelled mollusc species such as mussels and scallops (Ceccherelli & Rossi 1984; Gutierrez *et al.* 2003; Guay & Himmelman 2004; Diederich 2005). It is also important to consider the role of shell- and living mollusc ecosystem service provision in the context of climate change and ocean acidification (OA), as reviewed by Lemasson *et al.* (2017). The effects of climate change and OA on the ecosystem services provided by molluscs and shells are likely complex. There are, however, several well-studied negative implications of climate change that could affect ecosystem service provision, including; reduced calcification (Wright *et al.* 2014), increased shell dissolution (Waldbusser *et al.* 2011) and impaired filtration rates and feeding (Dove & Sammut 2007), for example. Ecosystem services of molluscs are likely to become more valuable under climate change, and considering that their ability to provide such services maybe be impaired, there should be even greater emphasis on the need to protect and promote shell and biogenic reefs.

Whole waste shells from aquaculture and food industries could provide a suitable substrate for the promotion of bivalve populations, which could then provide a myriad of ecosystem services. The majority of initiatives and studies currently using shell material for ecosystem service provision, however, use trawled shells rather than shells from the aquaculture industry. We suggest the promotion of cleaned waste shell usage in the establishment or re-establishment of shell substrates in coastal and estuarine waters that could benefit from the ecosystem services that $CaCO_3$ shells and healthy bivalve populations provide. In doing so, linking waste valorisation with ecosystem restoration, the sustainability of related aquaculture and food industries can be improved using core circular economy and biomimetic principles.

Summary

In mollusc aquaculture, shell waste remains a barrier to sustainable growth. Shells are majority calcium carbonate, with a small amount of organic matrix. Limestone which is also calcium carbonate is mined in huge quantities globally and refined for numerous purposes, from cement to paper whitening. As such, it might be expected that shells have simple valorisation routes; however, this is not regularly the case. Shell waste aggregation, cleaning and preparation, distance from potential application sites and complex regulations all contribute to difficulties in the valorisation of shell waste from aquaculture. Despite this, there are already a number of well-established markets for shells, as described above: ranging from calcium supplementation in poultry farming, to pH regulation in hobbyist aquarium systems. In addition, there are a number of potential valorisation techniques that have been discussed in scientific literature and beyond, but that have yet to be realised at a viable scale. From the use of shells in eco-friendly road deicer substances, to their use in green roofing structures as a functional drainage layer, it is clear that there are many potential waste shell uses that do not require high-energy processing such as pyrolysis. In the scientific literature, there is a plethora of research suggesting uses for waste shells that requires they undergo calcination. This, however, would require a significant amount of energy input that, given the need for sustainable solutions to waste production, would not fit with this principle, and thus have not been addressed in this article. In a different capacity, it is well known that shells are important component of many marine ecosystems, and it is likely that loss of shells structures has contributed to the loss of important ecosystems globally. With this in mind, this article has addressed the question of whether, in some cases, shells might have more inherent value simply being cleaned and returned to the marine environment rather than processed for more economically targeted reasons. Shells have been utilised in the restoration of natural reef building oyster populations, which then provide a host of ecosystem services including complex habitat and ecosystem promotion, and eutrophication control. Shells can also be used in powdered form to contribute to local alkalinisation techniques, improving the water quality of lakes and small river systems, as well as promoting biodiversity.

It is clear that shells are a potentially valuable commodity and do not require high-energy processing to give them value. Where shells are produced in a significant volume, it should be possible to find an appropriate valorisation strategy for them within a close-enough proximity to make it both sustainably and economically viable. In addition, with the significant cost of proper landfill disposal in many parts of the world, cleaned shells which cannot be used for any applications could be returned to the marine environment in a directed manner, where they can have a myriad of positive effects on the environment. Where regulations control the use of the shell waste, exemptions could be made allow to easier shell utilisation. In the EU, for instance, exemptions have already been applied to their animal by-products regulations for certain well-established shell valorisation techniques such as the use of crushed, cooked and shells in agricultural liming. If mollusc aquaculture is to play an increasingly significant role in the global provision of protein, then it can be expected that there will be a diversification of mollusc products, with more sold in processed form where shells are removed during processing. In such a scenario, shell waste valorisation will be a key concern. In areas of high mollusc production, such as China, shell waste is already an issue, with shell dumps providing an unsightly and odorous nuisance. Therefore, it is important that the way we view shells changes from a nuisance waste product, to a valuable commodity that could provide economic and environmental benefits if utilised correctly.

Acknowledgments

This work is funded as part of the European Union Seventh Framework Programme – Grant No. 605051 – Marie Curie Initial Training Network ‘Calcium in a Changing Environment’ http://www.cache-itn.eu/. The authors would like to thank two anonymous reviews for their comments and suggestions.

References

Ajakaiye A, Atteh JO, Leeson S (2003) Biological availability of calcium in broiler chicks from different calcium sources found in Nigeria. *Animal Feed Science and Technology* **104**: 209–214.

Aletor VA, Aturamu OA (1990) Use of oyster shell as calcium supplement. Part 2. An assessment of the responses of hepatic and serum enzymes, relative organ weights, and bone mineralisation in the broiler chicken fed gossypol-containing cottonseed cake supplemented with oyster shell. *Molecular Nutrition and Food Research* **34**: 319–324.

Aletor VA, Onibi OE (1990) Use of oyster shell as calcium supplement. Part 1. Effect on the utilization of gossypol-containing cotton seed cake by the chicken. *Molecular Nutrition and Food Research* **34**: 311–318.

de Alvarenga RAF, Galindro BM, de Fátima Helpa C, Soares SR (2012) The recycling of oyster shells: an environmental analysis using life cycle assessment. *Journal of Environmental Management* **106**: 102–109.

Baggett LP, Powers SP, Brumbaugh RD, Coen LD, DeAngelis BM, Greene JK *et al.* (2015) Guidelines for evaluating performance of oyster habitat restoration. *Restoration Ecology* **23**: 737–745.

Ballester P, Mármol I, Morales J, Sánchez L (2007) Use of limestone obtained from waste of the mussel cannery industry for the production of mortars. *Cement and Concrete Research* **37**: 559–564.

Barber SA (1984) Liming materials and practices. *Soil Acidity and Liming* **12**: 171–209.

Beck MW, Brumbaugh RD, Airoldi L, Carranza A, Coen LD, Crawford C *et al.* (2011) Oyster reefs at risk and recommendations for conservation, restoration, and management. *BioScience* **61**: 107–116.

Berndtsson JC (2010) Green roof performance towards management of runoff water quantity and quality: a review. *Ecological Engineering* **36**: 351–360.

Bogardi JJ, Dudgeon D, Lawford R, Flinkerbusch E, Meyn A, Pahl-Wostl C *et al.* (2012) Water security for a planet under pressure: interconnected challenges of a changing world call for sustainable solutions. *Current Opinion in Environmental Sustainability* **4**: 35–43.

Bostock J, Lane A, Hough C, Yamamoto K (2016) An assessment of the economic contribution of EU aquaculture production and the influence of policies for its sustainable development. *Aquaculture International* **24**: 699–733.

Brenneisen S (2003) Space for urban wildlife: designing green roofs as habitats in Switzerland. *Urban Habitats* **4**: 27–36.

Brumbaugh RD, Coen LD (2009) Contemporary approaches for small-scale oyster reef restoration to address substrate versus recruitment limitation: a review and comments relevant for the Olympia oyster, *Ostrea lurida* Carpenter 1864. *Journal of Shellfish Research* **28**: 147–161.

Castilho S, Kiennemann A, Costa Pereira MF, Soares Dias AP (2013) Sorbents for CO_2 capture from biogenesis calcium wastes. *Chemical Engineering Journal* **226**: 146–153.

Çath AU, Bozkurt M, Küçkyilmaz K, Çinar M, Bintas E, Çöven F *et al.* (2012) Performance and egg quality of aged laying hens fed diets supplemented with meat and bone meal or oyster shell meal. *South African Journal of Animal Science* **42**: 74–82.

Ceccherelli VU, Rossi R (1984) Settlement, growth and production of the mussel *Mytilus galloprovincialis*. *Marine Ecology Progress Series* **16**: 173–184.

Chiou IJ, Chen CH, Li YH (2014) Using oyster-shell foamed bricks to neutralize the acidity of recycled rainwater. *Construction and Building Materials* **64**: 480–487.

Chopin T, Cooper JA, Reid G, Cross S, Moore C (2012) Open-water integrated multi-trophic aquaculture: environmental biomitigation and economic diversification of fed aquaculture by extractive aquaculture. *Reviews in Aquaculture* **4**: 209–220.

Coen LD, Luckenbach MW (2000) Developing success criteria and goals for evaluating oyster reef restoration: ecological function or resource exploitation? *Ecological Engineering* **15**: 323–343.

Coen LD, Brumbaugh RD, Bushek D, Grizzle R, Luckenbach MW, Posey MH *et al.* (2007) Ecosystem services related to oyster restoration. *Marine Ecology Progress Series* **341**: 303–307.

Craggs R, Cooke T, Mathieson T, Park J (2010) Potential of mussel shell as a biosorbent for stormwater treatment. *Auckland Regional Council Technical Report 2010/046*.

Crisp D (1967) Chemical factors inducing settlement in *Crassostrea virginica* (Gmelin). *Journal of Animal Ecology* **36**: 329–335.

Currey JD (1999) The design of mineralised hard tissues for their mechanical functions. *Journal of Experimental Biology* **202**: 3285–3294.

Dale N (1994) National research council nutrient requirements of poultry–ninth revised edition (1994). *The Journal of Applied Poultry Research* **3**: 101.

DEFRA (2017) Derogations from Animal By-Product controls under Regulation (EC) 1069/2009 and Commission Regulation (EU) 142/2011 Authorisations by the Secretary of State to enable derogations to be used in England.

Devakie MN, Ali AB (2002) Effective use of plastic sheet as substrate in enhancing tropical oyster (*Crassostrea iredalei* Faustino) larvae settlement in the hatchery. *Aquaculture* **212**: 277–287.

Diederich S (2005) Differential recruitment of introduced Pacific oysters and native mussels at the North Sea coast: coexistence possible? *Journal of Sea Research* **53**: 269–281.

Douka K, Spinapolice EE (2012) Neanderthal shell tool production: evidence from middle palaeolithic Italy and Greece. *Journal of World Prehistory* **25**: 45–79.

Dove MC, Sammut J (2007) Impacts of estuarine acidification on survival and growth of Sydney Rock Oysters *Saccostrea glomerata* (Gould 1850). *Journal of Shellfish Research* **26**: 519–527.

Du Y, Lian F, Zhu L (2011) Biosorption of divalent Pb, Cd and Zn on aragonite and calcite mollusk shells. *Environmental Pollution* **159**: 1763–1768.

Edgar GJ, Samson CR (2004) Catastrophic decline in mollusc diversity in eastern Tasmania and its concurrence with shellfish fisheries. *Conservation Biology* **18**: 1579–1588.

European Commission (2015) *Communication from the Commission to the European Parliament, The Council, the European Economic and Social Committee, and the Committee of the Regions. Closing the loop - an EU action plan for the Circular*

Economy.. [Cited 22 Dec 2017.] Available from URL: http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:52015DC0614

Eurostat (2011) *Food: from farm to fork statistics. Pocketbook*. [Cited 22 Dec 2017.] Available from URL: http://ec.europa.eu/eurostat/documents/3930297/5966590/KS-32-11-743-EN.PDF

Fabian C, Reimann C, Fabian K, Birke M, Baritz R, Haslinger E *et al.* (2014) GEMAS: spatial distribution of the pH of European agricultural and grazing land soil. *Applied Geochemistry* **48**: 207–216.

FAO (2014) *The State of World Fisheries and Aquaculture 2014*. [Cited 22 Dec 2017.] Available from URL: http://www.fao.org/resources/infographics/infographics-details/en/c/231544/

FAO (2015) Global Aquaculture Production statistics database updated to 2013: Summary information. [Cited 22 Dec 2017.] Available from URL: http://www.fao.org/fishery/statistics/global-aquaculture-production/en

Fay L, Shi X (2012) Environmental impacts of chemicals for snow and ice control: state of the knowledge. *Water, Air, and Soil Pollution* **223**: 2751–2770.

Ferraro V, Cruz IB, Jorge RF, Malcata FX, Pintado ME, Castro PML (2010) Valorisation of natural extracts from marine source focused on marine by-products: a review. *Food Research International* **43**: 2221–2233.

FitzGerald A (2007) *Shell waste in aggregates. SEAFISH technical report*. [Cited 1 June 2017.] Available from URL: http://www.seafish.org/media/Publications/SR611_use_shell_aggregates_B54.pdf

Garrido-Rodríguez B, Fernández-Calviño D, Nóvoa Muñoz JC, Arias-Estévez M, Díaz-Raviña M, Álvarez-Rodríguez E *et al.* (2013) pH-dependent copper release in acid soils treated with crushed mussel shell. *International Journal of Environmental Science and Technology* **10**: 983–994.

Glausiusz J (2010) Artificial reefs to buffer New York. *Nature* **464**: 982–983.

Grabowski JH, Powers SP (2004) Habitat complexity mitigates trophic transfer on oyster reefs. *Marine Ecology Progress Series* **277**: 291–295.

Granada L, Sousa N, Lopes S, Lemos MFL (2015) Is integrated multitrophic aquaculture the solution to the sectors' major challenges? - a review. *Reviews in Aquaculture* **6**: 1–18.

Green DW, Lee J-M, Jung H-S (2015) Marine structural biomaterials in medical biomimicry. *Tissue Engineering Part B: Reviews* **21**: 438–450.

Guay M, Himmelman JH (2004) Would adding scallop shells (*Chlamys islandica*) to the sea bottom enhance recruitment of commercial species? *Journal of Experimental Marine Biology and Ecology* **312**: 299–317.

Guinotte F, Nys Y, de Monredon F (1991) The effects of particle size and origin of calcium carbonate on performance and ossification characteristics in broiler chicks. *Poultry Science* **70**: 1908–1920.

Gutierrez JL, Jones CG, Strayer DL, Iribarne OO (2003) Mollusks as ecosystem engineers: the role of shell production in aquatic habitats. *Oikos* **101**: 79–90.

Hamilton SK, Kurzman AL, Arango C, Jin L, Robertson GP (2007) Evidence for carbon sequestration by agricultural liming. *Global Biogeochemical Cycles* **21**: 1–12.

Harper EM (2000) Are calcitic layers an effective adaptation against shell dissolution in the Bivalvia? *Journal of Zoology* **251**: 179–186.

Harvey LDD (2008) Mitigating the atmospheric CO_2 increase and ocean acidification by adding limestone powder to upwelling regions. *Journal of Geophysical Research* **113**: 21.

Haynes RJ, Naidu R (1998) Influence of lime, fertilizer and manure applications on soil organic matter content and soil physical conditions: a review. *Nutrient Cycling in Agroecosystems* **51**: 123–137.

Higgins CB, Stephenson K, Brown BL (2011) Nutrient bioassimilation capacity of aquacultured oysters: quantification of an ecosystem service. *Journal of Environment Quality* **40**: 271.

Hossain A, Aditya G (2013) Cadmium biosorption potential of shell dust of the fresh water invasive snail *Physa acuta*. *Journal of Environmental Chemical Engineering* **1**: 574–580.

Hu S, Wang Y, Han H (2011) Utilization of waste freshwater mussel shell as an economic catalyst for biodiesel production. *Biomass and Bioenergy* **35**: 3627–3635.

Iglesia Teixeira B, Carral Vilarino E, Seoane Labandeira S, Lopez Mosquera ME (1997) Utilizacion de concha de mejillon como encalante en suelos acidos de Galicia. *Boletin de la Sociedad Espanola de la Ciencia del Suelo* **2**: 69–76.

Ilyina T, Wolf-gladrow D, Munhoven G, Heinze C (2013) Assessing the potential of calcium-based artificial ocean alkalinization to mitigate rising atmospheric CO_2 and ocean acidification. *Geophysical Research Letters* **40**: 5909–5914.

Jiang X, Li G, Wu Z (2010) Deicing and corrosive performances of calcium acetate deicer made from bamboo-vinegar. *World Academy of Science, Engineering and Technology* **65**: 506–511.

Jin F, Zhang G, Jin Y, Watanabe Y, Kishita A, Enomoto H (2010) A new process for producing calcium acetate from vegetable wastes for use as an environmentally friendly deicer. *Bioresource Technology* **101**: 7299–7306.

Johnson M (1970) The Cowrie currencies of West Africa part I. *The Journal of African History* **11**: 17–49.

Kamphausen L, Jensen A, Hawkins L (2011) Unusually high proportion of males in a collapsing population of commercially fished oysters (*Ostrea edulis*) in The Solent, United Kingdom. *Journal of Shellfish Research* **30**: 217–222.

Kellogg ML, Cornwell JC, Owens MS, Paynter KT (2013) Denitrification and nutrient assimilation on a restored oyster reef. *Marine Ecology Progress Series* **480**: 1–19.

Kirby MX, Miller HM (2005) Response of a benthic suspension feeder (*Crassostrea virginica* Gmelin) to three centuries of anthropogenic eutrophication in Chesapeake Bay. *Estuarine, Coastal and Shelf Science* **62**: 679–689.

Klinger D, Naylor R (2012) Searching for solutions in aquaculture: charting a sustainable course. *Annual Review of Environment and Resources* **37**: 247–276.

Kochmann J, Buschbaum C, Volkenborn N, Reise K (2008) Shift from native mussels to alien oysters: differential effects of ecosystem engineers. *Journal of Experimental Marine Biology and Ecology* **364**: 1–10.

Köhler P, Abrams JF, Völker C, Hauck J, Wolf-Gladrow DA (2013) Geoengineering impact of open ocean dissolution of olivine on atmospheric CO_2, surface ocean pH and marine biology. *Environmental Research Letters* **8**: 14009.

Korfali SI, Davies BE (2004) Speciation of metals in sediment and water in a river underlain by limestone: role of carbonate species for purification capacity of rivers. *Advances in Environmental Research* **8**: 599–612.

Kuo W-T, Wang H-Y, Shu C-Y, Su D-S (2013) Engineering properties of controlled low-strength materials containing waste oyster shells. *Construction and Building Materials* **46**: 128–133.

Kuykendall KM, Moreno P, Powell EN, Soniat TM, Colley S, Mann R *et al.* (2015) The exposed surface area to volume ratio: is shell more efficient than limestone in promoting oyster recruitment? *Journal of Shellfish Research* **34**: 217–225.

Kwon H-B, Lee C-W, Jun B-S, Yun J, Weon S-Y, Koopman B (2004) Recycling waste oyster shells for eutrophication control. *Resources, Conservation and Recycling* **41**: 75–82.

Latire T, Legendre F, Bigot N, Carduner L, Kellouche S, Bouyoucef M *et al.* (2014) Shell extracts from the marine bivalve *Pecten maximus* regulate the synthesis of extracellular matrix in primary cultured human skin fibroblasts. *PLoS One* **9**: e99931.

Lee CH, Lee DK, Ali MA, Kim PJ (2008) Effects of oyster shell on soil chemical and biological properties and cabbage productivity as a liming materials. *Waste Management* **28**: 2702–2708.

Lee KE, Williams KJH, Sargent LD, Williams NSG, Johnson KA (2015) 40-second green roof views sustain attention: the role of micro-breaks in attention restoration. *Journal of Environmental Psychology* **42**: 182–189.

Lemasson AJ, Fletcher S, Hall-Spencer JM, Knights AM (2017) Linking the biological impacts of ocean acidification on oysters to changes in ecosystem services: a review. *Journal of Experimental Marine Biology and Ecology* **492**: 49–62.

Lertwattanaruk P, Makul N, Siripattarapravat C (2012) Utilization of ground waste seashells in cement mortars for masonry and plastering. *Journal of Environmental Management* **111**: 133–141.

Lindahl O, Hart R, Hernroth B, Kollberg S, Loo LO, Olrog L *et al.* (2005) Improving marine water quality by mussel farming: a profitable solution for Swedish society. *AMBIO: A Journal of the Human Environment* **34**: 131–138.

Ma K-W, Teng H (2010) CaO powders from oyster shells for efficient CO_2 capture in multiple carbonation cycles. *Journal of the American Ceramic Society* **93**: 221–227.

Mackenzie CL (2007) Causes underlying the historical decline in Eastern Oyster (*Crassostrea Virginica* Gmelin 1791) landings. *Journal of Shellfish Research* **26**: 927–938.

McLaughlan C, Rose P, Aldridge DC (2014) Making the best of a pest: the potential for using invasive zebra mussel (*Dreissena Polymorpha*) biomass as a supplement to commercial chicken feed. *Environmental Management* **54**: 1102–1109.

Mohamed M, Yousuf S, Maitra S (2012) Decomposition study of calcium carbonate in cockle shell. *Journal of Engineering Science and Technology* **7**: 1–10.

Morris JP, Wang Y, Backeljau T, Chapelle G (2016) Biomimetic and bio-inspired uses of mollusc shells. *Marine Genomics* **27**: 85–90.

Muir FV, Harris PC, Gerry RW (1976) The comparative value of five calcium sources for laying hens. *Poultry Science* **55**: 1046–1051.

Nestlerode JA, Luckenbach MW, Beirn FXO (2007) Settlement and survival of the oyster *Crassostrea virginica* on created oyster reef habitats in Chesapeake Bay. *Restoration Ecology* **15**: 273–283.

Nguyen DH, Boutouil M, Sebaibi N, Leleyter L, Baraud F (2013) Valorization of seashell by-products in pervious concrete pavers. *Construction and Building Materials* **49**: 151–160.

Niachou A, Papakonstantinou K, Santamouris M, Tsangrassoulis A, Mihalakakou G (2001) Analysis of the green roof thermal properties and investigation of its energy performance. *Energy and Buildings* **33**: 719–729.

Nijman V, Spaan D, Nekaris KAI (2015) Large-scale trade in legally protected marine mollusc shells from Java and Bali, Indonesia. *PLoS One* **10**: 1–18.

Nudelman F, Sommerdijk NAJM (2012) Biomineralization as an inspiration for materials chemistry. *Angewandte Chemie – International Edition* **51**: 6582–6596.

Olem H (1990) *Liming Acidic Surface Waters*. Lewis Publishers, Chelsea, MI.

Olivier JGJ, Janssens-Maenhout G, Peters JAHW (2012) *Trends in Global CO_2 Emissions: 2012 Report*. PBL Netherlands Environmental Assessment Agency, The Hague.

Oso AO, Idowu AA, Niameh OT (2011) Growth response, nutrient and mineral retention, bone mineralisation and walking ability of broiler chickens fed with dietary inclusion of various unconventional mineral sources. *Journal of Animal Physiology and Animal Nutrition* **95**: 461–467.

Osorio-López C, Seco-Reigosa N, Garrido-Rodríguez B, Cutillas-Barreiro L, Arias-Estévez M, Fernández-Sanjurjo MJ *et al.* (2014) As(V) adsorption on forest and vineyard soils and pyritic material with or without mussel shell: kinetics and fractionation. *Journal of the Taiwan Institute of Chemical Engineers* **45**: 1007–1014.

Othman NH, Hisham B, Bakar A, Don MM, Johari MAM (2013) Cockle shell ash replacement for cement and filler in concrete. *Malaysian Journal of Civil Engineering* **25**: 201–211.

Ozturk S, Sozdemir A, Ulger O (2013) The real crisis waiting for the world: oil problem and energy security. *International Journal of Energy Economics and Policy* **3**: 74–79.

Piazza BP, Banks PD, La Peyre MK (2005) The potential for created oyster shell reefs as a sustainable shoreline protection strategy in Louisiana. *Restoration Ecology* **13**: 499–506.

Quisenberry JH, Walker JC (1970) Calcium sources for egg production and shell quality. *Poultry Science* **49**: 1429.

Raddum GG, Fjellheim A (2003) Liming of River Audna, Southern Norway: a large-scale experiment of benthic invertebrate recovery. *AMBIO: A Journal of the Human Environment* **32**: 230–234.

Ridge JT, Rodriguez AB, Fodrie FJ, Lindquist NL, Brodeur MC, Coleman SE *et al.* (2015) Maximizing oyster-reef growth supports green infrastructure with accelerating sea-level rise. *Scientific Reports* **5**: 1–8.

Rothschild B, Ault J, Goulletquer P, Heral M (1994) Decline of the Chesapeake Bay oyster population: a century of habitat destruction and overfishing. *Marine Ecology Progress Series* **111**: 29–39.

Santamouris M (2014) Cooling the cities – a review of reflective and green roof mitigation technologies to fight heat island and improve comfort in urban environments. *Solar Energy* **103**: 682–703.

Sawusdee A, Jensen AC, Collins KJ, Hauton C (2015) Improvements in the physiological performance of European flat oysters *Ostrea edulis* (Linnaeus, 1758) cultured on elevated reef structures: implications for oyster restoration. *Aquaculture* **444**: 41–48.

Scott ML, Hull SJ, Mullenhoff PA (1971) The calcium requirements of laying hens and effects of dietary oyster shell upon egg shell quality. *Poultry Science* **50**: 1055–1063.

Shumway SE, Davis C, Downey R, Karney R, Kraeuter J, Parsons J *et al.* (2003) Shellfish aquaculture — in praise of sustainable economies and environments. *World Aquaculture* **34**: 15–17.

Sickels-taves LB (2016) Understanding historic tabby structures: their history, preservation, and repair. *APT Bulletin* **28**: 22–29.

Smil V (2013) *Making the Modern World: Materials and Dematerialization*. John Wiley & Sons, Hoboken, NJ.

Soniat TM, Finelli CM, Ruiz JT (2004) Vertical structure and predator refuge mediate oyster reef development and community dynamics. *Journal of Experimental Marine Biology and Ecology* **310**: 163–182.

Su Z, Huang L, Yan Y, Li H (2007) The effect of different substrates on pearl oyster *Pinctada martensii* (Dunker) larvae settlement. *Aquaculture* **271**: 377–383.

Suttle NF (2010) *Mineral Nutrition of Livestock*. CABI, Oxford, UK.

Tamburri MN, Luckenbach MW, Breitburg D, Bonniwell SM (2009) Settlement of *Crassostrea ariakensis* larvae: effects of substrate, biofilms, sediment and adult chemical cues. *Journal of Shellfish Research* **27**: 601–608.

Tokeshi M, Ota N, Kawai T (2000) A comparative study of morphometry in shell-bearing molluscs. *Journal of Zoology* **251**: 31–38.

USGS (2016) *U.S. Gelogical Survey, Mineral Commodity Summaries, January 2016 - Stone (Crushed)*. [Cited 22 Dec 2017.] Available from URL: https://minerals.usgs.gov/minerals/pubs/mcs/2016/mcs2016.pdf

Viriya-empikul N, Krasae P, Puttasawat B, Yoosuk B, Chollacoop N, Faungnawakij K (2010) Waste shells of mollusc and egg as biodiesel production catalysts. *Bioresource Technology* **101**: 3765–3767.

Waldbusser GG, Steenson RA, Green MA (2011) Oyster shell dissolution rates in estuarine waters: effects of pH and shell legacy. *Journal of Shellfish Research* **30**: 659–669.

Walles B, Mann R, Ysebaert T, Troost K, Herman PMJ, Smaal AC (2015) Demography of the ecosystem engineer *Crassostrea gigas*, related to vertical reef accretion and reef persistence. *Estuarine, Coastal and Shelf Science* **154**: 224–233.

Walles B, Troost K, van den Ende D, Nieuwhof S, Smaal AC, Ysebaert T (2016) From artificial structures to self-sustaining oyster reefs. *Journal of Sea Research* **108**: 1–9.

Wang T, Xiao D, Huang C, Hsieh Y, Tan C, Wang C (2014) CO_2 uptake performance and life cycle assessment of CaO-based sorbents prepared from waste oyster shells blended with PMMA nanosphere scaffolds. *Journal of Hazardous Materials* **270**: 92–101.

Webber J, Rose D (2011) *Forest Research - Pathology Advisory Note No.11: De-icing salt damage to trees*. [Cited 22 Dec 2017.] Available from URL: https://www.forestry.gov.uk/pdf/pathology_note11.pdf/$file/pathology_note11.pdf

Weiler SK, Scholz-Barth K (2009) *Green Roof Systems: A Guide to the Planning, Design, and Construction of Landscapes Over Structure*. John Wiley and Sons, Hoboken, NJ.

Wise DL, Augenstein D (1988) An evaluation of the bioconversion of woody biomass to calcium acetate deicing salt. *Solar Energy* **41**: 453–463.

Wright JM, Parker LM, O'Connor W, Williams M, Kube P, Ross PM (2014) Populations of Pacific oysters *Crassostrea gigas* respond variably to elevated CO_2 and predation by *Morula marginalba*. *The Biological Bulletin* **226**: 269–281.

Yang S-T, Tang I-C, Zhu H (1992) A novel fermentation process for Calcium Magnesium Acetate (CMA) production from Cheese Whey. *Applied Biochemistry and Biotechnology* **34**(35): 569–583.

Yang E-I, Kim M-Y, Park H-G, Yi S-T (2010) Effect of partial replacement of sand with dry oyster shell on the long-term performance of concrete. *Construction and Building Materials* **24**: 758–765.

Yao Z, Xia M, Li H, Chen T, Ye Y, Zheng H (2014) Bivalve shell: not an abundant useless waste but a functional and versatile biomaterial. *Critical Reviews in Environmental Science and Technology* **44**: 2502–2530.

Yoon H, Park S, Lee K, Park J (2004) Oyster shell as substitute for aggregate in mortar. *Waste Management & Research* **22**: 158–170.

Appendix Shells from aquaculture: a valuable biomaterial, not a nuisance waste product

Market value of shells sold online in Europe and North America from Table 1 (Information correct as of June 2017).

Poultry feed

1. Jeffers Pets (USA) – 5 lb – $7.99
   https://www.jefferspet.com/products/oyster-shell-5lb
2. Valley Vet (USA) – 5 lb – $7.99
   https://www.valleyvet.com/ct_detail.html?pgguid=90a585ec-0049-4572-acf1-05f2bb5293de

3. Agrivite (EU) – 1.5 kg – £3.99
https://www.viovet.co.uk/Agrivite_Chicken_Lickin_Oystershell_Grit/c18650/
4. Mole Avon (EU) – 2.5 kg – £1.99
http://www.moleavon.co.uk/johnston-jeff-oyster-grit-25kg/p2000
5. Monster Pet Supplies (EU) – 25 kg – £16.79
https://www.monsterpetsupplies.co.uk/bird/chicken-supplies/pettex-oyster-shell-fine-25kg
6. Countrywise Supplies (EU) – 25 kg – £15.45
http://www.ebay.co.uk/itm/25kg-Oyta-Fine-Oyster-Shell-Grit-for-Chickens-Ducks-Quail-and-Caged-Birds-/141768125450
7. Leeders Animal Supplies (EU) – 25 kg – £8.99
http://leedersanimalsupplies.co.uk/index.php?route=product/product&product_id=1929&search=oyster

Pet bird nutrition

8. Petland (Ca) – 15.5 oz – CAD$3.47
https://www.petland.ca/products/hagen-bird-oyster-shell
9. Mole Avon (EU) – 2.5 kg – £1.99
http://www.moleavon.co.uk/johnston-jeff-oyster-grit-25kg/p2000
10. Viovet (EU) – 25 kg – £13.48
https://www.viovet.co.uk/Pettex_Pigeon_Grit/c13644/

Bio-filter medium

11. Dan Shell (EU) – 1000 kg – €390
http://www.danshells.dk/products/biological-filtering/
12. Specialist Aggregates (EU) – 600 kg – £229.55
http://www.specialistaggregates.com/natural-whole-cockle-filter-media-p-2049.html?osCsid=db9f22be45a98ba7c3a8c7a4127db09b

Aquarium/pond pH buffer

13. Air Aqua (EU) – 10 L – €22.95
http://www.air-aqua.nl/en/oesterschelpen-in-emmer-10-liter
14. Air Aqua (EU) – 5 kg – €19.95
http://www.air-aqua.nl/en/oesterschelpen-in-zak-5-kg

Soil liming

15. Grow Organic (USA) – 50 lb – $10.99
https://www.groworganic.com/oyster-shell-flour-50-lb.html
16. Planet Natural (USA) – 50 lb – $15.95
https://www.planetnatural.com/product/oyster-shell-lime-50-lb/
17. Murdochs (USA) – 50 lb – $15.99
http://www.murdochs.com/shop/pacific-pearl-oyster-shell/
18. Wilco farm store (USA) – 50 lb – $12.99
https://www.farmstore.com/product/pacific-pearl-oyster-shells-50-lb/

Shell aggregates

19. Specialist aggregates (EU) Whole scallop shell – 250 kg – £164.00
http://www.specialistaggregates.com/natural-whole-scallop-flats-p-1683.html
20. Specialist aggregates (EU) Whole cockle shell – 500 kg – £219.55 or 200 kg – £100.50
http://www.specialistaggregates.com/natural-whole-cockle-p-1201.html
21. Specialist aggregates (EU) – Whole Empress scallop shell – 500 kg – £219.56 or 200 kg – £100.49
http://www.specialistaggregates.com/natural-whole-empress-scallop-p-1579.html
22. Specialist aggregates (EU) – Crushed cockle shell – 15 kg – £34.50
http://www.specialistaggregates.com/barra-shell-harling-repair-p-2119.html
23. Specialist aggregates (EU) – Crushed cockle shell – 600 kg – £238.75
http://www.specialistaggregates.com/crushed-shell-natural-cockle-footpath-p-1200.html
24. Dan Shell (EU) – Crushed mussel shell – 1000 kg – €390
http://www.danshells.dk/products/biological-filtering/