Report synthesising the existing and potential uses of shells as by-products of the aquaculture industry

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WP6: MOLLUSC SHELL PRODUCTION AS A MODEL FOR SUSTAINABLE BIOMINERALS.

D6.3: REPORT SYNTHESISING THE EXISTING AND POTENTIAL USES OF SHELLS AS BY-PRODUCTS OF THE AQUACULTURE INDUSTRY

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This report is an expanded text based on the following peer-reviewed and published articles by the principle author:

- Morris JP, Wang Y, Backeljau T, Chapelle G (2016) Biomimetic and bio-inspired uses of mollusc shells. *Marine Genomics* 27:85-90. DOI: 10.1016/j.margen.2016.04.001
- Morris JP, Backeljau T, Chapelle G (*in press*) Shells from aquaculture: a useful biomaterial, not a nuisance waste product. *Reviews in Aquaculture* DOI: 10.1111/raq.12225

1. Introduction & Rationale

World aquaculture production is growing rapidly as seafood demand increases and marine fisheries production plateaus (FAO, 2014). Commercial shelled molluscs (referred to herein as molluscs or shellfish) 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, 2015, 2014). The distribution of the world's top 10 mollusc producing countries is highlighted in figure 1. Although global aquaculture production is currently dominated by East Asia, the EU, for example, hosts a high value industry. In 2012, first sale value from aquaculture totalled €4.76 billion in the EU: of this, molluscs made up 28 % of the total value (Bostock et al., 2016). Practiced responsibly, mollusc aquaculture can be one of the lowest-impact (environmentally and in terms of energy consumption) and most sustainable proteinaceous food sources currently available (Bostock et al., 2016; Klinger and Naylor, 2012; Shumway et al., 2003). Both global aquaculture (freshwater and marine) and its shellfish component are likely to be of increasing importance to the food industry in 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 farming, and farming as part of an integrated multi-trophic aquaculture (IMTA) approach (reviewed by: (Chopin et al., 2012; Granada et al., 2015)). The refinement of these techniques may further improve the productivity (and sustainability) of the global aquaculture sector. In addition, 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 and Luckenbach, 2000) and natural coastal protection (Ridge et al., 2015; Walles et al., 2016). Thus, diversification of aquaculture away from simply a food source into an ecosystem service may further expand its value.

One key aspect of shellfish aquaculture and food production that remains a barrier to its continued sustainable growth is waste management: particularly the issue of calcareous 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: used as far back as 100,000 years ago by the Neanderthals (Douka and 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 95-99.9% 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 replicated beyond the nano-scale in research laboratories (Nudelman and 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, 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). They are also 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 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 large shell enterprises, and many small-scale localised initiatives (as described below), the majority of shells from aquaculture processing remain a waste product. This report highlights historical uses of shells, issues surrounding modern shell valorisation, the current shell market, and, finally, 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, innovation, or whether shells have more value simply being returned to the marine environment.

China	83.4 %
Japan	2.2 %
Republic of Korea	1.9 %
Chile	1.7 %
Thailand	1.4 %
Vietnam	1.2 %
Spain	1.1 %
USA	1.1 %
France	1 %
Italy	0.7 %

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: Abalones, clams, cockles, conchs, freshwater gastropods, freshwater mussels, mussels, oysters, scallops, and winkles (Morris et al. *in press*).

2. History of shell use

The variety of examples of shell use across the globe throughout human history stands testament to the importance of shells in human culture. As technology developed and allowed for the production of synthetic materials, society moved away from its reliance on natural biomaterials. However, in recent years, with the growth in interest of biomimicry and circular economy principles, researchers are, once again, turning to biomaterials for inspiration, and re-appraising historical uses for such materials to inform current and future circular economy ideas of recycling. The following sections provide documented examples of mollusc shell use in human history. A comprehensive list of publications relevant to Section 2 is available in Appendix I.

2.1 Currency

Shells were used as a form of currency in many cultures, and at one point were the most widely used form of currency in the world. Cowrie shells (*Cypraea* sp.) were probably the first shells to be used as a currency (Figure 2). Archaeology has uncovered cowrie shells in prehistoric Stone Age sites in China (Yang, 2011). Cowries were also widely used throughout Africa (Johnson, 1970). In the 18th century it is thought that around 400 million cowries were being traded each year, however due to their finite nature, inflation was thought to be the cause of their demise as a currency (Bourquin and Mayhew, 1999). Many other shells have also been reported as being used as a means of goods trading: spiny oyster shells (*Spondylus princeps*) were traded in the Andean states of South America, and the tusk shell (*Dentalium pretiosum*) was traded in Eastern India (Bourquin and Mayhew, 1999).

Figure 2 Cowrie shell currency, with carvings to denote its value. Licence: CC-BY-SA-1.0. Credit: Trustees of the British Museum

2.2 Construction

Shells from molluscs have been used in construction in many coastal settlements around the globe. Tabby is a form of concrete made by heat-treating shells to form lime, then creating a mixture of lime, sand, water, ash and broken shells. Oyster shells have been traditionally used in this process. The origin of Tabby is disputed between North Africa, India, and Spain. The technique was also used England, and widely in the Southern states of the USA (Morris, 2014). Tabby structures are still standing in Florida, Georgia and the Carolina’s, as well as parts of Spain and Southern England. Shells have been used in construction in the Saloum Delta, Senegal as far back as 5000 years ago (Hardy et al., 2016). Islands, and their infrastructure, built entirely of shells are still present to this day, and have become a popular tourist attraction in the area (Figure 3).

Figure 3 Cemetery Island (1982) in the Saloum Delta, Senegal, made entirely of shells. Similar to its larger neighbouring island: Ile de Fadiouth. Licence: CC-BY-SA-2.0. Credit: John Atherton

2.3 Medicinal uses

In Southern Africa, in the 19th Century, wearing a shell amulet was thought to help maintain health, fertility and luck (Bourquin and Mayhew, 1999). Oyster shell amulets coated in gold, silver, or electrum found in Egypt were known to have been worn during the Middle Kingdom (1965-1920 BCE) as a form of functional jewellery that promoted good health (James and

Russmann, 2001). Powdered forms of shells have also been used for medicinal purposes and have been historically attributed with a myriad of health benefits and healing powers (Panda and Misra, 2007).

2.4 Jewellery

Mollusc shells and jewellery have been intricately linked through history. In fact, the oldest identified piece of jewellery in the world was discovered at Skhul in Israel and is made from the shells of the sea snail *Nassarius gibbosulus*. This sea snail shell jewellery dates back to between 100,000 and 135,000 years ago (Balter, 2006; Vanhaereny et al., 2006). By 50,000 years ago, during the Upper Palaeolithic, shell adornments were common across Europe and Asia (Fernandez and Joris, 2007). Further, records of shell jewellery in Middle Palaeolithic archaeological sites have been used as evidence for the paradigm shift that early modern humans in the Levant and Africa were more behaviourally, socially, and culturally advanced than had been previously thought (Bouzouggar et al., 2007; d'Errico et al., 2005; Francesco et al., 2009).

2.5 Tools

There are countless records of the use of mollusc shells as tools. Many of these applications are centred on their weight bearing potential and toughness: this is testament to mollusc shell strength and hardness which must have been clearly understood throughout modern human history. A study of a single archaeological site in Texas recovered over 3000 shell artefacts, many of which would have been used as tools for a variety of purposes including hammering, bevelling, chipping, chopping, and cutting (Dockall and Dockall, 1996). Other examples of mollusc shells as tools include the sea snail *Melo melo* whose common name is the Bailer (Baler) shell derived from its use a water bailing device in the canoes of native Australians (Bail and Poppe, 2001), the shell is thought to have been used for many other tools also (Przywolnik, 2003). These bailer shells were also as cooking pots by Australian Aboriginals (Gardiner, 2013).

3. Considerations for modern shell use

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 (FitzGerald, 2007; Morris et al., 2016; Yao et al., 2014). The proceeding 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 wide-spread applications. Intentionally split from other 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 reasons why we may benefit from such activities. A systematic review of published literature was performed, and is described in figure 4 (full literature database is available in appendix I).

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 (Figure 5). 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, with high-end products served in 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 have to adapt also: in part moving away from a luxury items, served in shell for aesthetics, towards a more commonplace protein sauce, pre-processed 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 this regard, a key consideration in shell valorisation is the proximity of shell waste production to shell processing facilities as well as proximity to regions in which potential shell applications are suitable or beneficial. 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

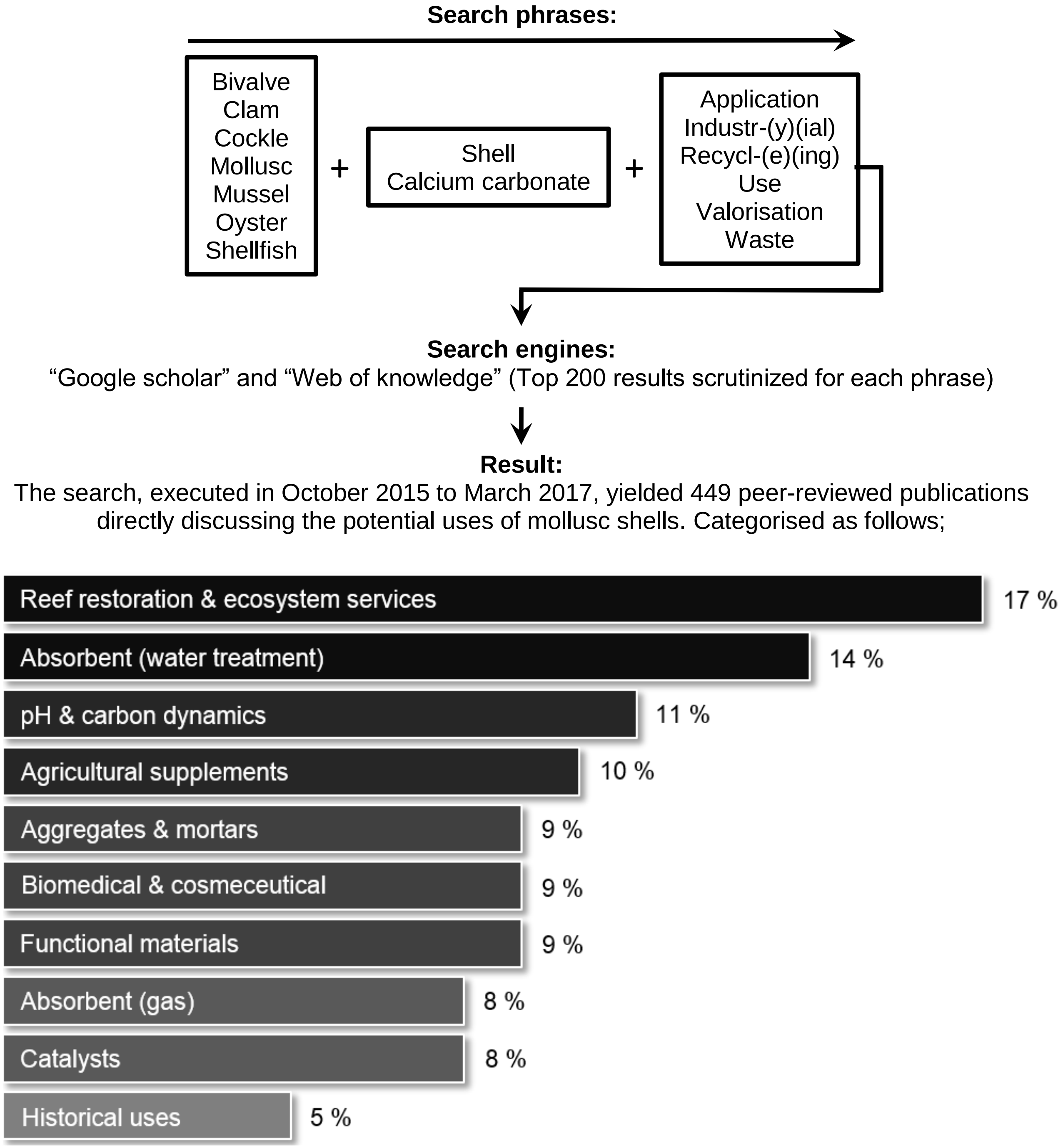

Figure 4. A schematic detailing the method and results of a generalised abbreviated search elucidating the discussed potential uses of waste mollusc shells. The schematic shows the derivation of non-biased search terms and the search engines and result cut-offs used. Results were grouped into broad application categories, and the percentages represent the proportion of each group in the overall analysis of waste shell use.

greater than 323 km between the two yielded no environmental benefit of shell valorisation over landfill disposal (de Alvarenga et al., 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, both will be considered in the discussions below.

There are two generalised reasons for developing or implementing shell valorisation techniques: 1) to impact local, regional, or global-level shell waste issues, or 2) to drive innovation in waste management and circular economy principles. Depending on which rationale is driving development, certain applications will be more or less applicable. For instance, if a company’s focus is on the long-term management of shell waste in their region, then scalability, sustainability, and economic feasibility of applications is of prime concern. In contrast, if the focus is on circular economy innovation then more niche, high-risk, exploratory applications (that are not constrained by sustainability or scalability demands) may be of interest. As this report is directed at the re-use of shell waste from the aquaculture industry primarily from a sustainability standpoint, the applications discussed are focussed accordingly.

However, 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. This conversion is done via the process of calcination: heating to high temperatures in air or oxygen. The conversion of $CaCO_3$ to CaO requires heating to ~800°C, and produces CO_2 in the process. Such applications do not, in the authors’ opinion, provide scalable and sustainable solutions to shell waste. Calcined shells have been advocated as potential CO_2 sorbents. Wang et al. (2014) performed a LCA on CaO-derived from waste oyster shells from 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 reutilization is a step in the right direction in any process, the calcination process itself was not considered, and it is the authors’ opinion that $CaCO_3$ calcination will remain an inherently unsustainable process regardless of the $CaCO_3$ source. Further, there is also a plethora of potential shell valorisation techniques only require a small amount of shell waste. Techniques requiring calcination, or those that only require a small amount of shell waste input will be considered separately from other applications, and will be discussed in the “potential niche shell uses” section. As such, the following sections will concentrate on those applications that do not require high-energy processing and thus represent truly sustainable valorisation methods, and also on those that have the potential to significantly impact the global waste shell problem. Interestingly, as described in the following section, applications with a current market value are those that require little pre-processing, suggesting that high-energy processing may not represent an economically viable strategy for shell valorisation in any case, regardless of its environmentally unsustainable nature. A comprehensive list of publications relevant to the general concept of shell re-use is available in Appendix I.

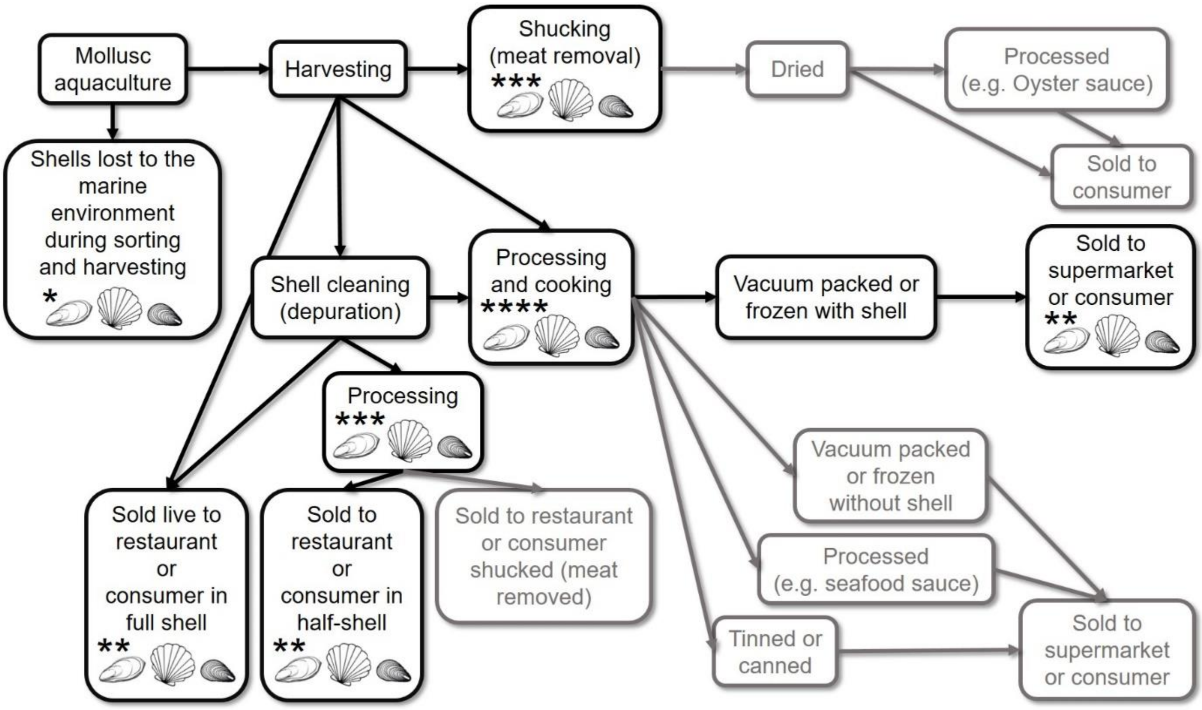

Figure 5 - Conceptual diagram describing some of the key processes undertaken during the delivery of commercial bivalves, such as oysters and mussels, from aquaculture to consumers, highlighting the points at which shell waste may be produced (Morris et al. *in press*). Black boxes represent stages where shells are still attached, 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 done 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 re-use because of prior cleaning and cooking.

4. Current shell applications

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 II. The following sections will highlight the major shell use strategies currently exploited. A comprehensive list of publications relevant to Section 4 is available in Appendix I.

4.1 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 egg shells (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 to 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 egg shell strength of laying hen eggs (Scott et al., 1971). Quisenberry and Walker (1970) observed similar results with oyster shell supplementation, showing increased egg shell weight and thickness (Quisenberry and 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 cotton-seed cake (CSC) feed mix for broiler chickens (Aletor and Aturamu, 1990; Aletor and 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 and Onibi, 1990). However, another study found that calcium source had no appreciable effect on calcium utilization and chick performance when comparing bivalve shells, oyster shells, and limestone sources (Guinotte et al., 1991). Moreover, that study found particle size was a better predictor of weight gain, feed conversion, and tibial ossification than Ca source, with finer particulate Ca performing better (Guinotte et al., 1991). 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 of at landfill (McLaughlan et al., 2014). McLaughlin found that the zebra mussel meal 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, a comparable to commonly used limestone as a source of calcium for livestock, with several studies suggesting shell derived $CaCO_3$ can out-perform 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 4.0-4.5g of calcium (Dale, 1994), or ~10g 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.

4.2 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 & 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 9t 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 only 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 top soil or mulch, or as an aggregate for pathing, for instance. There are also several mentions of the use of shells in both the topsoil. 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.

4.3 Bio-filter medium

There is a significant body of research on the use of mollusc shells as bio-filtration medium for treating wastewaters. However, a large proportion of that research does not use shells directly, but pre-treats them via calcination or pyrolization, forming CaO. This adjusted product is then found to be a good filter medium (Castilho et al., 2013; Chiou et al., 2014; Kwon et al., 2004; Ma and Teng, 2010). 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. As such, only literature that tests the suitability of un-calcined/un-pyrolysed shells as bio-filter mediums will be considered, as this represents both the current market for shells sold as bio-filter 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 waste waters 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 optimize heavy metal removal from waste waters. Further, as the shell preparation technique was simple (washed, air-dried, and pulverized), 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 and 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). In Oregon (USA), Sunmark™ Environmental currently sell storm-water filtration media, which incorporates crushed oyster shells alongside other industrial waste materials, including lumber waste (http://earth-lite.com/rain/, accessed 06/09/2016).

There is also a small market for shells as a filtration and pH buffering medium in ponds and aquaria. The potential bio-filtration 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 in order 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.

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 II).

Type of application	Processing required	Quantity sold	Selling price (as of June 2017)	Appendix II references
Poultry feed	Heat treated, crushed	1 kg – 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
Bio-filter medium	Heat treated, crushed	600 kg – 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 kg – 1000 kg	0.3€ - 0.9€ per kg	19 – 21
Shell aggregates	Dried, crushed	15 kg – 1000 kg	0.3€ - 3€ per kg	22 – 24

5. Potential large-scale shell applications

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 lab 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. A comprehensive list of publications relevant to Section 5 is available in Appendix I.

5.1 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 environmentally 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 and Augenstein, 1988). As yet no publications have discussed 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 short-fall in de-icer substances across Europe during cold periods, there is potentially a market for alternatives to road grit as de-icing agents.

5.2 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 waste-water 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, waterproofing membrane.

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. Whole shells maybe ideal for such a structure, as when heaped they provide a complex 3D structure to aid drainage. In addition to acting simply as a 3D structure to aid drainage, $CaCO_3$ shells may also provide additional benefits to green roof structures, similar to those described in the agricultural liming and waste water treatment sections: shells incorporated into green roofing structures may help with the neutralisation of acid rain, and also act as a bio-filtration medium for reducing heavy metal contamination in the resultant drainage water. Further, as described in the aforementioned sections, shells could also be incorporated into the filtration and top soil layers of a green roof. 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.

5.3 Raw shell bio-filter

Although included in the previous section with examples of shells already being used and sold as a bio-filter substrate, there are many more avenues that are yet to be fully exploited for this potentially simple valorisation strategy. As highlighted in the section “Bio-filter medium”, un-calcined, variously graded calcareous shells can be used as good: heavy metal, nitrate, sulphate, and phosphate sorbents, as well as a pH buffering substrate and an oxidation substrate (reduction of 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. Because of the simplicity of this valorisation strategy, the lack of high energy processing of shells, and the ubiquity of waste water treatment needs in both urban and rural areas, the potential for shells to be used as bio-filters is much greater than its current exploitation.

5.4 Construction aggregates

Further to the use of shells in simple path aggregates and top soil materials, shell waste has many characteristics that might make it suitable for certain construction aggregates. Care must be taken in such propositions though, as many construction materials are highly regulated for performance and safety purposes. There is, however, certainly room for the use of shell waste in certain aggregate mixes for a variety of purposes, as will be described. The concept of shell use in construction is by no means a new one: there are many historical examples of the use shells building construction, much of which is known as “Tabby”. Florida, in the 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 is a small body of research concerning the use of calcareous shells in aggregates and mortar mixes and a few examples of projects incorporation shells into certain aggregate mixes. Yet, shells have not been used in this way at anything larger than test scale at present. However, this avenue of shell valorisation does hold 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 (Kuo et al., 2013; Lertwattanaruk et al., 2012; Nor Hazurina Othman et al., 2013; Yang et al., 2010).

6. Potential niche shell uses

There are several innovative niche applications for shell waste described in the academic literature. Applications in this section include those that require high-energy processing of $CaCO_3$, or those that require only small amounts of $CaCO_3$. Such applications are not likely to impact shell waste production from the aquaculture industry, but represent innovative circular economy developments, and could provide economic benefits in the future. A comprehensive list of publications relevant to Section 6 is available in Appendix I.

6.1 Calcium oxide catalysts

Calcium oxide (CaO) is a widely used catalyst and chemical compound in a myriad of industrial applications. CaO can be formed via the calcination of $CaCO_3$: a process that requires heating $CaCO_3$ to in excess of 800 °C (sometimes in an oxygen enriched environment). Calcination results in the conversion of solid $CaCO_3$ to solid CaO, liberating gaseous CO_2 in the process.

Waste shells from aquaculture have been advocate as a low cost $CaCO_3$ source for the production of CaO for a variety of applications, particularly biodiesel production in developing countries. Fatty acid methyl esters (FAMEs) are a component of the biodiesel production, made by reacting oils and fats with an alcohol: a process called transesterification. The transesterification of oils and fats with methanol can be facilitated by a heterogeneous catalyst e.g. Calcium oxide), which provides a simplified and cheap albeit slow-reaction alternative to a homogeneous catalyst (e.g. Potassium hydroxide) (Suppes et al., 2004). Calcined oyster shells have been shown to be an effective heterogeneous catalyst in the conversion of soybean oil into biodiesel (Nakatani et al., 2009). Boey et al., (2011) calcined waste cockle shells (*Anadara granosa*) to catalyse the production of biodiesel from palm olein. Similarly, freshwater mussel shells were calcined (at 900 °C), then impregnated with deionized water and activated by heating to 600 °C, the resultant 'honeycomb-like' catalyst structure was found to be a feasible catalyst in the conversion of Chinese tallow oil to biodiesel, and was able to catalyse 7 reaction cycles (Hu et al., 2011). Finally, oyster shell-derived calcium oxide was used to modify copper-based catalysts, and compared to commercial calcium oxide sources as a hydrogenation catalyst. Results showed that oyster shell-derived CaO was a more efficient methanol synthesis catalyst, with suggestions that shell-based impurities resulted in CaO crystal defects that increased reaction surface areas, and thus reaction efficiency (Wisaijorn et al., 2017).

6.2 Cosmeceutical and biomedical applications

As described in the "historical uses of shells" section, shells have been used for medicinal purposes in various cultures for a variety of ailments, or for preventative measures (Herbert et al., 2003; Tong et al., 1988; Yesilada et al., 1999). Modern science has found that shells, particularly their organic protein matrix, can exhibit many properties that are of interest to the modern cosmetics and biomedical industry (Hou et al., 2016; Latire et al., 2014). The following section summarises the academic literature advocating shell-use in biomedical and cosmeceutical applications.

The most widely discussed biomedical use for shells is in bone and tissue re-engineering. Powdered shell has been shown to have osteogenic properties, likely because of its biogenic origins (Berland et al., 2002). When placed into a human bone fracture, the $CaCO_3$ powder acts as a substrate on which new osteoblasts can grow and secrete bone. In 1997, ground-breaking maxillofacial surgery was performed on eight human patients with maxillary (Jaw) defects. Nacre powder, from the oyster *Pinctada maxima*, and was found to promote bone formation, and act as a scaffold in bone reconstruction in human jaw defects (Atlan et al., 1997). More recent, research further supports the potential for shell-use (particularly nacre), in bone engineering and augmentation applications (Milthorpe et al., 2016; Niida et al., 2012; Zhang et al., 2017). Further, researchers have suggested that shell $CaCO_3$ could be converted to hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) which is the major constituent of human bones. Conversion is made via calcination of shell powder to CaO, then, conversion to calcium nitrate ($Ca(NO_3)_2$) with nitric acid, and the addition of ammonium phosphate ($(NH_4)_2HPO_4$) (Rujitanapanich et al., 2014). Shells have also been advocated in various cosmetic applications, for their anti-bacterial and anti-microbial properties (Green et al., 2015; Latire et al., 2014; Xing et al., 2013). Patents have been placed, and several companies have investigated the potential for shells as a skin exfoliator, with additional functional anti-bacterial properties (Andrade et al., 2015; Henderson and Mallet, 1983).

6.3 Functional materials

The previous paragraphs have highlighted the potential for $CaCO_3$ shells to be converted to other compounds such as calcium oxide, calcium phosphate, or hydroxyapatite, for instance. These conversions open up further potential applications, and widen the potential uses of shells in industry. Nacre, in particular, has inspired the field of nanocomposite materials for several decades due to its $CaCO_3$ - organic matrix layered arrangements (Ritchie, 2014; Sellinger et al., 1998). Whilst the field of synthetic biomimetics attempts to replicate the toughness of strength of shells via *de novo* assembly (Nudelman and Sommerdijk, 2012), there is also interest in incorporating shell waste into various functional material recipes.

There are a number of articles highlighting the potential use of waste shells from aquaculture in polypropylene and polymer composites. Waste blue mussel (*Mytilus edulis*) shells were used as a base material for $CaCO_3$ filler in polypropylene manufacture. The resulting material was found to have superior mechanical properties in comparison to a standard industrial $CaCO_3$ polypropylene mix (Li et al., 2012). Similarly, oyster and mussel shell derived-CaO was incorporated into polypropylene mixes and found to be mechanically comparable to conventional CaO sources (Hamester et al., 2012).

Green-lipped mussel shells (*Perna Canaliculus*) were used to synthesise hydroxyapatite, which was found to be of comparable quality to commercial equivalents and was advocated as a suitable photocatalyst for wastewater aqueous-pollutant treatment (Shariffuddin et al., 2013).

7. 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 and niche 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. 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 services that waste shells from aquaculture could provide being returned to the marine environment by various methods, and address the question of whether we should solely be seeking economic value from shells, as described in the preceding sections, or whether shells also have inherent and enduring value when 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). Several projects (for example: Project Cquestrate), have attempted to apply this alkalinisation concept in scaled experiments, but have not had positive results or found workable solutions. This stands testament to the complexity of carbonate chemistry manipulation for CO_2 sequestration techniques. Despite this, several studies have shown that 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 and Fjellheim, 2003). Similar to the effects described in the ‘bio-filter medium’ section, calcium carbonate can have many positive influences on local water courses 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 (Kuykendall et al., 2015; Nestlerode et al., 2007), and particularly to the tissue extracts and shells of their parent species (Crisp, 1967; Devakie and 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 (Beck et al., 2011; Brumbaugh and Coen, 2009). Population declines have been observed on both the East and West coast of the USA (Brumbaugh and Coen, 2009; Rothschild et al., 1994), on the south coast of the UK (Kamphausen et al., 2011), in Tasmania, Australia (Edgar and 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 (Baggett et al., 2015; Beck et al., 2011). Restoration programs 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 programs are proliferating in the USA (Coen et al., 2007; Glausiusz, 2010; Piazza et al., 2005), but also in Europe (Sawusdee et al., 2015; Walles et al., 2016) (Figure 6). 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 program using those collected shells once cleaned and dried (www.billionoysterproject.org – accessed 11/01/2017). Healthy oyster reefs are now well known to promote biodiversity through complex habitat formation (Coen et al., 2007; Grabowski and Powers, 2004; Kochmann et al., 2008; Soniat et al., 2004), counteract of eutrophication and other adverse nutrient conditions (Higgins et al., 2011; Kellogg et al., 2013; Kirby and Miller, 2005), protect against sea level rise and coastal erosion (Piazza et al., 2005; Walles et al., 2016, 2015). These ecosystem services are not limited to reef building oyster species however. For instance, a study in Sweden has modelled the bio-remediatory effects of mussel farming on the west coast of

Sweden, suggesting the promotion of mussel populations for the purpose of nutrient and bio-toxin 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 and Rossi, 1984; Diederich, 2005; Guay and Himmelman, 2004; Gutierrez et al., 2003). 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 and 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. A comprehensive list of publications relevant to the concept of shell-based ecosystem services is available in Appendix I.

Figure 6 Oyster shell ecosystem services. **a.** An artificial oyster shell reef in the Oosterschelde (The Netherlands), acting as a settlement substrate for oyster larvae to promote reef growth with the secondary benefit of localised coastal erosion and sea level rise protection (Licence: Public domain, Credit: James Morris). **b.** An oyster reef constructed from oyster shell bags and shell aggregate reef balls along a segment of the North Carolina (USA) Shoreline. The reef protects the coast from erosion and promotes a healthy natural ecosystem (Licence: Public domain, Credit: Jackeline M. Perez Rivera).

8. 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 de-icer 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. Such applications are unlikely to contribute to shell waste or sustainability interests, but are of interest from an innovation and circular economy perspective and have been discussed as niche applications. 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 areas, cleaned shells, which cannot be used for any applications, could be returned to the marine environment in a co-ordinated 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 animal by-products regulations for certain well established shell valorisation techniques such as the use of crushed and cooked 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 of increasing 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 an environmentally and economically valuable commodity.

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Appendix I

Explanatory note

The following document holds links to the literature discovered through systematic review of shell-use applications. The literature cited is predominantly peer-reviewed scientific articles, but also includes patents, books and book sections, news articles, and web pages where information therein was deemed of interest and relevance to the subject. A complete list of the literature is available (“Full bibliography”), but citations have been split into application types and categories also, for ease of use.

A systematic review of available literature was performed using “Google”, “Google Scholar”, and “Web of Knowledge” with iterations of the following key words:

Group 1; “Bivalve”, “Clam”, “Cockle”, “Mollusc”, “Mussel”, “Oyster”, “Shellfish”.

Group 2; “Calcium carbonate”, “Shell”

Group 3; “Application”, “Industr-(y)(ial)”, “Recycl-(e)(ing)”, “Use”, “Valorisation”, “Waste”

Results of each search were scrutinized for relevant literature.

Link to literature database: www.cache-itn.eu/ …

Appendix II

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 (UK) - 2.5 kg - £1.99
http://www.moleavon.co.uk/johnston-jeff-oyster-grit-25kg/p2000

5. Monster Pet Supplies (UK) - 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. Leeder's 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 (UK) - 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 (UK) - 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 litres - €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/