MARINE ORGANISMS AS FOOD, FORAGE, INDUSTRIAL, AND MEDICAL PRODUCTS

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Fish have always been an important part of the human diet. Fishing is one of the oldest occupations and industries, and international trade in fishery products for food and non-food uses has been going on for some thousands of years. A historical perspective from early to recent times introduces the utilization of marine organisms for food and non-food purposes and follows the emergence and progress of the major preservation methods. World fisheries have expanded 30-fold from 1900 to 1996, reaching some 120 million tonnes and generating about US$110 billion in international trade. Since the 1980s, the major opportunities for increased supplies from marine resources for food have come from increased aquaculture of fish, shellfish and seaweeds. This article describes the major preservation methods for seafood—chilled, frozen, cured and canned, and the non-food uses from fisheries for reduction to meal and oil, and for silage and hydrolysates, as well as other nutritional and industrial uses. The contributions of marine invertebrates, crustacean wastes, seaweeds, and microorganisms, to the growing quest for new functional food ingredients and cosmetics, for novel applications across the industrial sector, for materials to aid research and analysis to develop new applications in medicine, nutrition and health, are described. The potential value of compounds isolated from marine organisms in screening for new drugs for use as antimicrobial, antiviral, antitumor and antiinflammatory agents by exploitation of novel biopolymers, secondary metabolites and thermostable enzymes, is described. These exciting developments are likely to exceed rapidly the present value of production and international trade in fishery products for food and feed.

1. Historical Perspective

1.1 Food Use

1.1.1 Early to Classical Times

Fish have long been an important part of the human diet. Fishing is one of the oldest industries, and international trade in fish products has been going on for some thousands of years. Like their forebears, humans have made use of living marine resources for food since the emergence of anatomically modern *Homo sapiens* over 120 000 years ago. Coastal caves in South Africa used by hunter-gatherers well over 60 000 years ago show evidence of mussel shells, the bones of large reef fish, as well as the ashes from hearths in the deposits, and the deposits from 20 000 years ago are filled with fish bones. These peoples not only cooked but also may have smoke-dried their seafood. They would have known that fresh fish does not last very long and becomes putrid much more quickly than meat. The bones of sea fish are also found in cave deposits from 40 000 years ago in the Dordogne (France), but there is no evidence of how the fish were preserved. Fresh fish and shellfish were an important source of animal protein for those communities that settled close to the coast as a consequence of societal evolution. In time, simple methods of preserving fish and other foods by drying became well established in order to provide some protection against shortages by preserving day-to-day and seasonal surpluses. In different climates, conditions and communities, sun-drying, air-drying and drying and smoking over fire were used. Preservation with salt is thought to have developed in the Neolithic period, which was characterized by great advances in food production as the human lifestyle changed from nomadic to agrarian. Indeed, curing of food (defined as the preservation of food by salting, smoking, drying, fermenting, acid-curing or any combinations of these) was critical to the survival of early humankind and led to a flourishing trade in cured fish. Fresh sea fish were eaten only by those within easy reach of the coast. In Mesopotamia, as early as 3500 BC, fish in dried, smoked and salted forms were eaten on quite a large scale compared with only small amounts of meat.

A trade in dried fish developed with settlements on the Persian Gulf, and fish from the Arabian Sea were traded with the Indus valley peoples. Salt too had become an important commodity. Carvings in Egyptian tombs, circa 2500 BC, show fish being split and salted to dry more quickly in the heat of the sun. It is thought that the filleting of fish first began in Greek culture. Fishing and production of salted and dried fish was a major activity among the coastal colonies of the Mediterranean and the Black Sea, established from Phoenician (circa 1250 BC) to Roman times.

The enterprising Carthaginians also fished the Atlantic for whales, seals, sharks and other species, and salted the catch at sea. However, salted tuna seems to have been the most important sea fish for food in the classical world. Roman rules required the rapid sale of fresh fish because it spoiled so quickly, and elaborate saltwater (and freshwater) fish-ponds were built to keep live fish to ensure the availability of fresh fish for the very rich. For most people, only salted or brined fish, or fish pickled in vinegar, were available. As early as 100 BC, dugout food stores, chilled by ice-cold water or snow and ice brought from the mountains, were used in Rome, and may have been used for fresh fish. In the fourth century, Rome decreed days of the year on which only salt fish could be eaten.

1.1.2 Middle Ages to the Twentieth Century

The benefits of preserving whole fish by autolysis in concentrated brine were noted in China in the seventh century. Since then there has been widespread use of fermented fish sauces in cooking and flavoring in Southeast Asia. Salting became the staple method of preservation in medieval Europe, either combined with drying or smoking, or as a wet curing or pickling process, and in the west, the focus of large-scale sea fishing shifted to the more prolific North Sea.

Fatty fish like herring that were seasonally abundant in the coastal fisheries of Scandinavia, the British Isles and northern Europe could not be dried in the open because they quickly became rancid, due to oxidation of the fat. Instead, these fish were salted and heavily smoked and dried for some weeks, a product known as “red herring.” Alternatively, the fish were eviscerated, pickled in salt and packed tightly in barrels, which were topped up with brine and closed.

These products were important developments of the Middle Ages, and in Britain and other countries, strict regulations governed the sale of fish. There are many recorded cases of traders who were punished for selling poor quality fish. Salt herring became the primary mass-produced food of the late Middle Ages. Herring was such an important source of food and trade in northern Europe that wars were fought over fishing rights. Marine aquaculture was also established; the culture of mussels along the French coast dates back to the thirteenth century.

In the early fifteenth century, the English and others sailed to Iceland to increase supplies of cod and other lean, so-called, "white fish" species. These were either dried in the sun and wind to produce "stockfish" (produced in Norway over 1000 years ago), or salted and dried to produce "salt fish." In the early sixteenth century, Portuguese, Spanish and French fishermen (and later the English) extended their voyages to harvest, salt and dry cod from the plentiful fisheries off Newfoundland. These basic methods of preservation for fish still remain in use. In fact, until the advent of the railways from about 1840, which enabled the rapid and cheap distribution of fish, sea fish were preserved mostly by drying, salting or smoking.

Records suggest that throughout the ages most people, given the choice, preferred fresh fish to salted, smoked or dried fish. Indeed, the development of the fishing industry in modern times can be seen as a succession of attempts to keep fish fresh between catching and consumption. The landing of live fish from "well-vessels" developed into a large-scale industry in the North Sea in the eighteenth and nineteenth centuries. The live fish trade remains important in Asia and parts of Scandinavia, and for the transport of crustaceans and mollusks

Investigation of chilling has been attributed to Francis Bacon in the seventeenth century, who experimented with chicken buried in the snow to see how much longer it would remain edible. Chilling of fish with natural ice was in common use in China in the eighteenth century. This practice was introduced into Scotland in 1786 to chill Atlantic salmon for transport to the London market. It became common in the fresh fish trade by 1820 and was systematically introduced for preservation of fish at sea in about 1850. In this period, the plentiful supplies of small fish from trawling provided the raw material for the origin in London of the fried fish trade.

Fish and chip shops still accounted for 25% of the white fish consumed in Britain in 1999. By 1900, artificial ice plants had been erected at the ports, enabling the steam powered fishing vessels to sail to more distant grounds and return with fresh fish, although there always was a compromise between the amounts of coal and ice carried for the voyage. The fish industries of the world grew rapidly in the nineteenth century, providing a good protein food that was cheaper than meat and one that the working poor could afford. By 1900, the world fish catch was estimated to be four million tonnes. Canning of food began commercially early in the nineteenth century and large-scale canning of fish, such as Pacific salmon species and sardines, began in the second half of the century

Natural freezing in countries with suitably cold climates was known for centuries as a way of longer-term preservation of fish. Initially, it probably began for domestic purposes to help protect food supplies for the winter, and for bait. However, attempts to distribute naturally frozen fish commercially to more distant markets produced a very poor product. The first patent in the US for freezing fish was granted in 1861. Fish were frozen in pans using an ice-salt mixture, glazed, and stored in insulated chambers cooled by metal tubes containing the freezing mixture. These products were of rather poor quality. In 1868, the authors of "Wholesome Fare" wrote:-

Frozen fish is neither good for soups nor for anything else. The northern nations eat it out of necessity, not choice. The convenience of transport gained is more than outbalanced by the deterioration of quality. The effects of frost are to rend the tissues and to reduce them to a tasteless pulp, whose very wholesomeness is questionable. If such is the case with the most substantial meats, it is still more so with delicate muscle, like that of fish. Meat and fish, once frozen, soon putrefy after thawing; they should be used immediately or not at all. Refrozen it is difficult to ascertain their actual condition and their consumption may cause serious derangement to health.

At the Great International Fisheries Exhibition held in London in 1883, one exhibitor advertised refrigerating machinery for a steam carrier vessel, and a refrigerator connected to a freezing chamber or cold store for a fishing boat. It was recognized that freezing might offer a solution to the many problems raised by surplus and scarcity in fishing. In the late 1880s, some frozen fish from the US were marketed in Hamburg (Germany). However, these early and subsequent attempts to freeze fish at sea and on-shore by mechanical refrigeration produced such a poor quality product that frozen fish developed a bad reputation.

This dogged technical and practical progress until research in the 1920s and 1930s demonstrated that properly frozen fish had to be stored at a lower temperature than that considered commercially acceptable for meat and other foods. However, industry in general did not begin to accept this principle until after 1945. In the meantime, the advantages and feasibility of freezing to preserve fresh fish and extend distribution lines were being pursued commercially by Clarence Birdseye. In the 1940s, the technical emphasis changed from brine immersion freezing (only used successfully for freezing tuna, mostly destined for canning) to air-blast and plate contact freezing. A significant expansion of international trade in frozen fish began with white fish from Canada, Scandinavia and Europe to the US, and herring from western Europe and Scandinavia to eastern Europe and the Soviet Union. Successful development of the vertical plate freezer in 1953, by Torry Research Station in Scotland, enabled fish to be frozen at sea. Excellent quality frozen fish began to become available in quantity from the 1960s with the introduction of freezer trawlers. From its introduction into the US in the early 1950s, the frozen, breaded, fish stick (or fish finger as it was known in the UK when launched in the mid-1950s) was progressing to become the single most successful fish product of modern times. By 1970, there were about 900 freezer trawler and factory vessels operating on the world's fisheries. Notwithstanding these successful developments, the debate about the relative merits of fresh and frozen fish is still sometimes heard today.

Other types of fish product are worth mention—essentially those produced from minced fish flesh. "Kamaboko," a steamed and molded fish paste (also known as "fish jelly") is recorded in Japanese history at least from the sixteenth century, and from the mid-1850s, the variety of such products increased as the "cottage" industry developed. Mechanization to expand the scale of the industry, which included the development of machines to separate flesh from skin and bones, was introduced in the 1950s and kamaboko-like fish sausage analogues of meat products were developed. These techniques were continuously refined, and eventually formed the basis for the range of sophisticated products developed in Japan to simulate crab, scallop and lobster meat (so-called “seafood analogue products”) and now available in western markets. These developments also provided pointers for the strong research interest which developed in the West in the 1960s, following the leads of Japan and the Soviet Union, to recover and utilize for food the significant amount of waste fish flesh generated during the processing of traditional products, and to explore the possibilities of utilizing for food, the so-called “under-utilized resources.” The recovered fish flesh is often called minced fish. Traditional Scandinavian fish balls and fish soups can be seen as the forerunners of the wide variety of ready-prepared canned, frozen and fresh food products made with fish which are readily available for the consumer in the sophisticated market of today

The most serious attempt to use an unexploited and unconventional resource began in the 1960s with research initiated by the Soviet Union, followed by Japan, into the potential for food of the large krill resource. Krill are small shrimp-like euphausids, usually less than 50 mm in size and comprising some 100 or more species; they are particularly abundant in the Antarctic (see *Shrimps and Krill*). The chemical composition is similar to that of crustaceans, but is lower in protein and higher in fat, and is well balanced for human nutrition. The chitin content of whole raw krill is about one percent. The most serious problems are that krill are very perishable and delicate to handle and must be processed for food within 3 to 4 hours of catching, and for meal within 8 to 12 hours;; therefore, they have to be fished by ocean-going factory trawlers. Products researched included: frozen whole krill for processing on-shore; frozen peeled meat; soups; canned krill meat (which was probably the most successful product to come out of the Soviet work and into the food chain); squid stuffed with krill meat; krill balls; surimi derived from krill; and protein concentrates and paste. However, most of the catch was converted to meal. Catches peaked at about 0.5 million tonnes in 1982, and research persisted well into the 1980s, but the problems and economics of processing to food products on a large scale were not solved and catches fell to about half by the beginning of the 1990s.

An historical perspective would be incomplete without mention of the development of fish protein concentrate (FPC) through the 1950s and 1970s, and the lessons learnt from the failure of this technology-led approach to the alleviation of world malnutrition. Considerable research effort, mostly in the US, was devoted to upgrading the fish meal product of the large industrial catch of pelagic fish (Section 1.2) directly for human nutrition. The idea was to make the food chain more efficient, emphasize the food value of industrial fish, and provide protein-rich products to alleviate malnutrition in less developed parts of the world. In the early days such products were known as “fish flour.” A fish flour was produced in Japan in the 1940s (and probably even earlier). Two main strategies for FPC emerged and were tested. First, type A—an odorless, tasteless powder, with a protein content greater than 60% and a fat content less than 0.75%, which could only be achieved by prior solvent extraction of the fish to remove the fat (the recovered oil was of inferior quality to normally produced fish oil). Second, type B—a powder with no limiting specifications for odor or flavor, produced from good quality food-grade fish by means of a redesigned, hygienic, fish meal process engineered to the highest food standards. Although FPC type A was clearly a technological success, and it had undoubted nutritional value in situations where protein deficiency was the main problem, it was not a panacea for nutritional problems. Removal of the fat made it an energy deficient product. The product was expensive and its bland nature did little to encourage its use as a food. It did not solve the problems at which it was aimed. In retrospect, the complexities of the problem and the underlying factors were not properly analyzed, understood or addressed. The less expensive FPC type B, with a composition very similar to that of fish meal and a fat content up to about 10%, has been accepted in food-aid programs in various parts of the world. However, care had to be taken to establish whether the food and social habits of a community, particularly towards fish, were likely to support acceptability. By the end of the 1970s, FPC type A was regarded as a debacle and as technological myopia. Pariser and colleagues critically reviewed the history of the projects in 1978 and wrote:

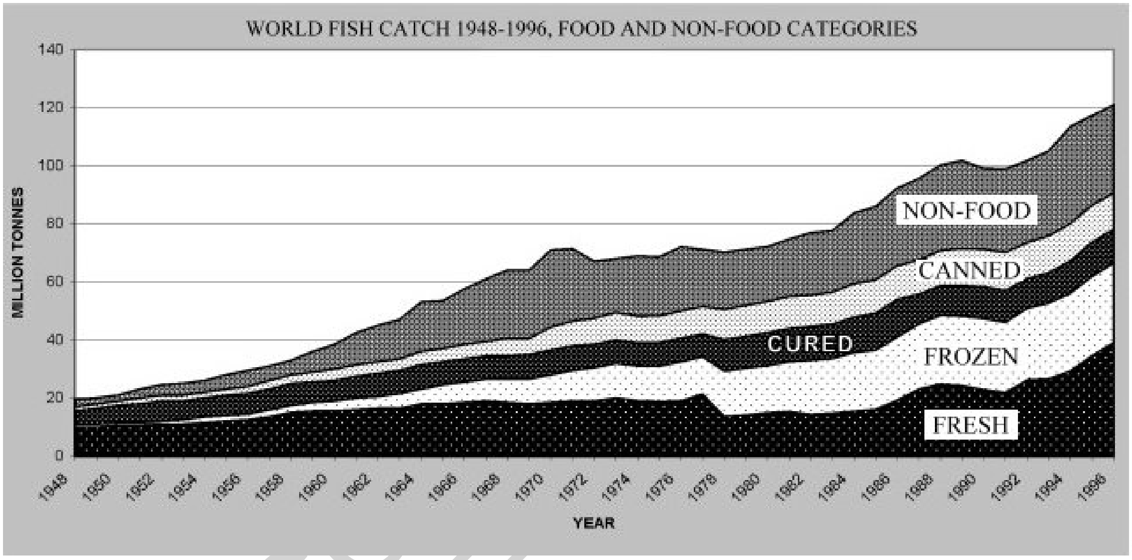

Figure 1. WORLD FISH CATCH 1948-1996, FOOD AND NON-FOOD CATEGORIES

The production of FPC is a high-technology enterprise, requiring massive inputs of capital, energy, and expertise. All these inputs are characteristically lacking in the developing world. The attempt to transfer FPC technology demonstrates that technological solutions that seem plausible in a developed context are less advantageous and usually inappropriate when transferred to a developing context.

The catch from marine capture fisheries rose from four to 87 million tonnes between 1900 and 1996. Figure 1 shows the developments and the major changes in the disposal of the world production of fish into the main food and non-food categories from 1948 to 1996.

1.2 Non-food Uses—By-products

Use of fish for bait and waste fish for livestock feeding and fertilizer (particularly where large quantities were available) probably represent the oldest non-food uses for coastal communities, dating back to the change from a nomadic human existence to the development of an agrarian mode of life. Perhaps the earliest example of successful industrial use of a natural product from marine animals was the highly valued dye, Tyrian purple, extracted from mollusks and traded by the Phoenicians from circa 1600 BC. In Norway, circa 800, herring oil was recovered by primitive pressing. By the fourteenth century, cod liver oil was an important by-product for use in lamps and the dressing of leather. Fish oils had been used for centuries for medicinal purposes. Records from the Middle Ages show that cod liver oil was prescribed for rickets. The oil was produced by simply allowing the cod livers to rot. Steam heating of livers to release a better quality oil was introduced in about 1850. The unequivocal identification of vitamin A and D activities in cod liver oil is attributed to McCollum and co-workers in 1922.

During his thirteenth century travels in Asia, Marco Polo noted the common practice of feeding dried fish to animals. The current fish meal and oil industry had its origins at the beginning of the nineteenth century as the process for the production of fish body oils developed. Later, large-scale reduction plants were built, but the protein rich residue, the fish meal (or fish "guano" as it was known then), was largely used as fertilizer. Although there were reports prior to 1885 that fish guano was a dependable source of high-quality protein suitable for livestock, the potential of fish meal as an animal feed was mostly ignored. Large-scale feeding trials in Norway in 1892 led the way in confirming the suitability of fish meal for feed. This application began to grow in continental Europe, whereas in Britain and the US, its use solely as fertilizer persisted until the 1920s, when use for feed eventually became an accepted practice in these countries. Production increased substantially from 1950 (Figure 1) and, by 1960, the fish by-products industry was producing meal, so-called "solubles" (rich in B vitamins), flour (produced experimentally for human consumption), silage, hydrolysates, hormones such as insulin, adrenaline and pituitary hormones, vitamins A and D, sterols, squalene and organic fertilizers. As a proportion of the total fish catch, production peaked about 1970, when some 37% of global fish production was reduced directly to fish meal and oil, and about 50% of the fish came from the anchoveta stock off Peru, for which there was no other market.

Whales were hunted heavily from the eighteenth century but the invention of the harpoon gun in 1870 led to the near extinction of several species of whale. Most countries stopped whaling in 1986, except for Iceland, Norway, Japan and the Soviet Union. In 1992, the International Whaling Commission established a Revised Management Procedure and proposed the Southern Ocean Whale Sanctuary in 1994. Essentially, the whole animal was used. For example, the flesh was used for human consumption and pet food, or the flesh and bones were ground and used as fertilizer. Whalebone was used in corsetry and for carving for ornaments. Ambergris, a waxy substance from the guts of the sperm whale was used for making perfumes, and sperm oil from the head was used in leather making. Synthetic alternatives are used today. One of the major products was whale oil. It was plentiful in the early 1900s, but it was not much use unless it could be "hardened." The unsaturated oils tended to oxidize producing off-flavors, making them unsuitable for use in food. This could be overcome by making them more saturated (hardened). In about 1910, hardening by hydrogenation with a nickel catalyst became feasible commercially, so that hardened whale oil could be processed into margarine. In 1913, a Whale Oil Pool was set up by the leaders of the

European oils and fats industry to regulate trade in whale oil. At the end of the 1950s, hardened whale and menhaden oils were important for the margarine industries in Europe and the Soviet Union. The world production of marine oil then was about 350 000 tonnes per year and it increased to one million tonnes by the end of the 1970s; 95% of this oil was body oils, most being hardened and used almost entirely in margarines and shortenings

Chitin is a major constituent of the exoskeleton of crustaceans. Rouget, in 1859, is credited with the discovery of the polysaccharide chitosan, produced by decarboxylation of chitin by boiling it in concentrated alkali. Traditionally, the healing properties of chitin preparations were used in the Orient and elsewhere for treating abrasions and cuts. However, it was not until 1934 that patents were granted in the US for the production of chitosan and for film and fibers made from chitosan. Industrial production and applications of chitosan have increased steadily since the 1970s

1.3 Seaweeds

Seaweed has been used for centuries in coastal areas all around the world as food, as feed for animals, and as fertilizers and soil conditioners. It is thought that seaweed was first used in China directly for food. Agar is a carbohydrate colloid that can be extracted from some red seaweeds and sets to form a gel. It was known to the Japanese as "kanten" at least since the seventeenth century. In cold weather, the gel was frozen, then allowed to thaw, and the water separated; the residue was dried and stored for later use, and reconstituted to make sweet and spicy jellies. Basically, the same freeze/thaw process is still used commercially to make agar, and Japan was the major world supplier from its natural resources of *Gelidium* spp. until the Second World War. In the 1950s, it was found that *Gracilaria* spp. treated with alkali produced higher strength gels. Since *Gracilaria* can be cultivated successfully on a commercial scale, it is now used more widely. Because the gel formed is a heat resistant, and can be purified free from bacterial inhibitors, it has been used in culture media for classical bacteriological analysis since the 1880s. Seaweeds or seaweed preparations were also used as medicinal remedies or treatments for centuries. Apparently, in 1750, an English physician successfully used ash from kelp which is rich in iodine to treat goiter. Kelp was also used to treat obesity in the nineteenth century, and agar was used as a laxative. Seaweeds were used as a source of iodine, and crude extracts were used for clarification in brewing. Another hydrocolloid, carrageenan, found initially in the red seaweed *Chondrus crispus* was known in Ireland since 1810. Alginic acid, a hydrocolloid found in all brown seaweeds, was discovered first by Charles Stanford in the 1880s. Development of a large-scale alginate industry began in California and in Scotland in the late 1920s and early 1930s, respectively. *Laminaria japonica* was cultivated in China from the 1950s. The hydrocolloids have found increasing industrial and food applications (Section 2.4.6).

Apart from the few examples above and in the preceding Sections, and the isolation of fragrances from marine organisms, the serious quest for marine natural products with potential medicinal and nutritional or other industrial applications really began only in the late 1960s. Then, the strategy, particularly in the pharmaceutical industry, switched from seeking synthetic solutions for new drugs, to identifying natural products with pharmacological properties

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Biographical Sketch

K. J. Whittle graduated with PhD from the University of Liverpool in 1967, following research on the chemistry and biosynthesis of the tocochromanols in plants. He then joined the Chemistry Department at Woods Hole Oceanographic Institution (US), as an Assistant Scientist, to carry out post-doctoral research on the use of chemical cues by marine invertebrates for remote sensory perception. In 1969, he moved to Torry Research Station, Aberdeen (the UK Government laboratory concerned with all aspects of the handling, processing and preservation of fishery products and by-products) as a Senior Scientific Officer. Over the next 25 years, he developed a wide-ranging experience on the utilization of fishery resources from handling the catch on-board the fishing vessel to new product development. His special interests included factors affecting the quality of fisheries and aquaculture products, marine oil pollution problems and tainting, trace analysis of hydrocarbon contaminants in the marine environment, development of underutilized fishery resources, and algal toxins in shellfish. Besides providing expert advice to UK government departments and local authorities, he has worked with the UN Agencies, UNEP, FAO and IOC, the European Commission, commercial interests in Saudi Arabia, New Zealand, the Faroe Islands, Poland, Finland, Russia, Chile and the US, and with the International Tanker Owners Pollution Federation and International Petroleum Industry Environmental Conservation Association. In 1993, he was appointed Acting Director of Torry Research Station and, after it merged with the Central Science Laboratory, an Executive Agency of the Ministry of Agriculture, Fisheries and Food, he was Head of the re-named Food Science Laboratory, Torry, from 1994 to 1996, and also Head of the Food Quality and Microbiology Groups of the Central Science Laboratory. The Torry laboratory closed in 1996 and Dr Whittle set up a small consultancy company, Torry Research Limited, offering services in the environment, fisheries and food sectors. He became a Fellow of The Institute of Food Science and Technology of the UK (FIFST) in 1997. He is author / co-author of over 100 scientific and technical, published papers.