

Marine Pollution: In-situ monitoring of nutrients – article written by Richard Burt, Chelsea Instruments for the Guide to the UK Environment Industry, January 2000.

Pollution of the World's water poses a major threat to the health and well being of millions of people and global eco-systems. Loss of biodiversity through the extinction of certain species caused by anthropogenic activities has given rise to governmental and regulatory bodies taking action. To achieve this, there is a need for a greater understanding of the various background environmental processes for which the means of conducting continuous in situ studies are essential.

In-Situ Monitoring

Quantitative knowledge of nutrients and primary production is essential for investigating the ecology and biogeochemistry of aquatic ecosystems. Until recently, the only way to monitor nutrient levels has been to collect discrete samples or use research vessels with onboard laboratory facilities to steam through a particular area of study. Collected samples are either analysed at the collection site if convenient or transported to a central laboratory to be analysed later. Monitoring schemes such as these may not detect short-term changes such as storm events or point discharges between sampling events. Weather conditions and the high cost and logistics of using research vessels for routine studies may not allow complete data sets to be compiled. There is also considerable evidence to suggest many of the sample preservation techniques introduce some level of variance into nutrient determinations. Consequently, significant errors may be introduced into preserved samples and in both cases the cost and logistics of continuously monitoring a particular environment would generally be prohibitive.



Advances in analytical chemistry have now made it feasible to perform a wide range of chemical determinations *in-situ* and the development of remotely deployable instrumentation has been particularly important in this respect. For example, Chelsea Instruments' advanced nutrient & chemical monitoring system, Aqua^{sensor} enables *in situ* micronutrient determinations to be carried out in fresh, estuarine, coastal and ocean waters to depths of 25 metres for periods of 30 + days.

The instrument is based on laboratory Flow Injection Analysis techniques that are familiar to many working in the area of environmental analysis. This approach has produced a very flexible field instrument as it allows different chemical species to be determined by simply changing the chemical manifold and reagent set. This particular instrument is unique in that it can also be used as a bench instrument, which allows the appropriate methodology to be validated in the laboratory against accredited standard materials and methods prior to field deployments. Thus eliminating the problem of how to determine the actual performance of field instruments which has always given cause for debate amongst organisations who wish to use *in situ* instruments. The Aqua^{sensor} has been designed to operate autonomously with its own data logger and internal battery pack. It is ideally suited for installation into a buoy or fixed monitoring station. A network of Aqua^{sensors} in a region will provide a synoptic picture and early warning of eutrophication beyond that of traditional monitoring methods.

The Role of Nutrients in the Marine Environment

Seawater contains a complex, delicately balanced mix of organisms that all interact and play an important role in the marine life cycle. At the start of the marine *Food Chain* are the photosynthetic plant organisms, phytoplankton. Their growth, or *Primary Production*, is the photosynthetic conversion of inorganic micronutrient elements into energy-rich organic compounds such as proteins, fats and carbohydrates. Herbivorous zooplankton graze on the phytoplankton, converting it to animal tissue, which is the *Secondary Production* stage. The herbivore zooplankton are in turn grazed upon by carnivorous zooplankton and fish predators and this is the *Tertiary Production* stage.

In common with terrestrial plants, marine phytoplankton require nutrients for growth. The most important of the micronutrient elements are nitrogen and phosphorus, which are considered to be growth limiting. Organisms such as diatoms with siliceous frustiles also require a source of silicon. Trace concentrations of elements such as manganese, iron, molybdenum, copper, vanadium and zinc are also required for healthy growth.

There is a fine balance however, between sufficient nutrients to promote healthy but controlled phytoplankton growth and excess, which is likely to cause excessive algal blooms.

Eutrophication

Nutrient enrichment or *eutrophication* of natural waters can ultimately result in a simplification of the aquatic ecosystem where the higher-order plant species decline and the lower organisms such as algae proliferate. Some such organisms are just unsightly, some are toxic to shellfish and fish and some may be harmful to mammals, e.g. *aphanizomenon flos-aquae* Blue-Green Algae.

Toxicity assessments of over 200 blue-green algal blooms from European countries prior to 1989 revealed that 44% to 75% had produced toxins. In the case of the small number of blue-green blooms assessed in Hungary, Greece and Italy; all had produced toxins. In 1989, 60% to 70% of the blooms tested in the UK had produced toxins.

Nutrient enrichment of freshwater abstracted for drinking water is also a major concern due to the presence of toxic algal growth. In 1990, the UK's National Rivers Authority (NRA) detected blue-green algae in 90% of water supplies in their region, of which 70% of the algal strains isolated were toxic to humans.

Eutrophication permits species with high growth and reproduction rates to become dominant and this reduces the diversity of the species present in a particular area. Oxygen is also less readily available to the benthic community due to bacterial oxidation of the excess organic matter. In areas of poor tidal mixing and stratified water animals inhabiting the seabed will die as the oxygen level diminishes and in extreme conditions, organisms inhabiting the overlying water may also be killed.

Excessive algal blooms are more easily induced in warmer coastal waters because oxygen is less soluble in warm water and the bacteria have a higher metabolic rate. If anoxic conditions persist, sulphur bacteria begin to flourish. These obtain their energy by converting sulphate in organic material to sulphide ions. The dissolved sulphide forms hydrogen sulphide in the water, which can be toxic to animals.

Highly productive conditions can also lead to the over production of organisms such as *chrysochromulina polyplepis* that secrete toxins. These toxic blooms (Red Tides) can kill everything in their path. In 1988 such a bloom occurred in the Skaggerak and was carried by currents along the Norwegian coast. It killed almost every pelagic and benthic organism in its path and threatened to kill the fish stocks of the many fish farms in the area. Fish production exceeds land-based production in Norway so it was a major threat to the country's economy. Human life can also be affected if shellfish such as clams, mussels, oysters, etc. ingest and accumulate the toxins in their body tissue. Generally, the toxins do not affect the shellfish but a single clam can accumulate enough toxins to kill a human being.

Coastal Eutrophication has been identified by the Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP:1990) as being the second most serious threat to the coastal marine environment (after coastal development).

Land runoff

Nutrient levels in freshwater systems, which ultimately add to the marine nutrient load, have increased significantly in the past 50 years. This has been mainly attributed to more intensive agricultural practices that have promoted the use of nitrogenous fertilisers. For example, in 1950 the global use of nitrogen fertilisers was reported as 14 million tonnes, this figure has increased over the years to in excess of 125 million tonnes. Nitrate based fertilisers are not totally bound in the soil and therefore leach into the various inland watercourses if not taken up by plants. However, this does not always have an immediate effect and will depend on the agricultural activity and geology of a particular area. Other factors such as sewage outfalls and animal effluents have contributed to the overall increase in nitrogenous matter found in freshwater systems.

Legislation

Legislation has been introduced in an attempt to reverse the effects of increased nutrient enrichment of natural waters, and minimise the health risks thought to be associated with high nitrate levels in drinking water supplies. For example, the EC Nitrate Directive 91/676 was put in place to protect waters against pollution caused by nitrates from agricultural sources and recognises that the excessive use of fertilisers constitutes an environmental risk. This directive accepts that there is risk from both inorganic and organic fertilisers and has the necessary statutory tools to control nitrate pollution.

Previous control measures were primarily concerned with health issues but this is the first directive, which includes controls to safeguard the environment. The 91/676 nitrate directive compels member states to designate all areas which are at risk from nitrate pollution. The vulnerable zones are defined in annex 1 of the directive as:

Surface freshwaters, especially those intended for abstraction for drinking water, which either contain or could contain if protective action is not taken, more than the concentration laid down in Directive 75/440 (50 mg l⁻¹).

Freshwaters, estuaries and coastal waters that are eutrophic, or may become eutrophic in the near future if protective action is not taken.

Groundwaters which contain more than 50 mg l⁻¹ nitrate, or could contain that amount if protective action is not taken.

Conclusions

Significant advantages for monitoring are offered by Chelsea Instruments Aqua^{sensor} compared to traditional methods. A network of such sensors can provide a synoptic picture of the nutrient input and uptake within an area. To achieve this quantity of data would be unrealistic with traditional discrete sampling methods.

