Biosensors for the monitoring of harmful algal blooms

Daniel A McPartlin[1], Jonathan H Loftus[1], Aoife S Crawley[1],
Joe Silke[2], Caroline S Murphy[1] and Richard J O'Kennedy[1]

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Harmful algal blooms (HABs) are a major global concern due to their propensity to cause environmental damage, healthcare issues and economic losses. In particular, the presence of toxic phytoplankton is a cause for concern. Current HAB monitoring programs often involve laborious laboratory-based analysis at a high cost and with long turnaround times. The latter also hampers the potential to develop accurate and reliable models that can predict HAB occurrence. However, a promising solution for this issue may be in the form of remotely deployed biosensors, which can rapidly and continuously measure algal and toxin levels at the point-of-need (PON), at a low cost. This review summarises the issues HABs present, how they are difficult to monitor and recently developed biosensors that may improve HAB-monitoring challenges.

Addresses
[1] School of Biotechnology, Dublin City University, Dublin 9, Ireland
[2] Marine Institute, Rinville, Oranmore, Co. Galway, Ireland

Corresponding author: O'Kennedy, Richard J (Richard.okennedy@dcu.ie)

The current issue

Algae are microscopic phototropic uni- or multi-cellular organisms. Some algal species can form harmful algal blooms (HABs), phenomena that occur throughout the world's oceans that have led to increasing concerns for human health and environmental preservation. Additionally, severe economic implications are associated with HABs, with estimates of losses of tens of billions of US dollars annually [1•]. These concerns arise from the increasing frequency and geographic distribution of a number of toxin-producing algal species. The prevalence of these species is not fully understood, though toxicity has been suggested as a form of defence from predatory organisms [2]. Algae act as primary food sources in the aquatic food web. They are predominantly consumed by bivalve shellfish such as mussels, clams, oysters and scallops. Phycotoxins and cyanotoxins are secondary metabolites produced by marine algae and blue-green algae (cyanobacteria), respectively. These algal toxins accumulate to highly significant levels in the digestive tracts and muscles of these shellfish. Subsequent consumption by humans often results in poisoning and severe illnesses. Their presence is responsible for numerous human intoxications yearly [3]. The toxins' associated potencies are intimately linked to their chemical structure and the organs they target. They are known to cause intoxications to humans, birds and farm animals, and impact negatively on tourism.

Global populations are on the increase and so the demand for uncontaminated food sources has never been as urgent. Governments and food safety authorities now recognise the need to regulate and closely monitor toxin contamination in foods for human and animal consumption. The ability to detect, analyse and monitor these harmful algae and their associated toxins at the required limits necessary to meet legislative requirements to avoid consumer harm must be a worldwide priority.

Currently, the monitoring of HABs and their toxins relies on the use of laboratory-based methods. Light Microscopy (LM) is the principle method used for identification and enumeration of HABs species. However, accurate identification of some species can prove extremely difficult. For example, Figures 1 and 2 display data of occurrences of *Azadinium/Heterocapsa* spp. off the coasts of Cork and Galway, Ireland, respectively [4,5]. These algal genera are grouped together in this manner due to the difficulty in discerning these algae by LM. Therefore, the data shown may at times under- or over-estimate levels of harmful *Azadinium spinosum*. The use of further confirmatory methods, such as electron microscopy, is often required for further species identification. In regards to the associated algal toxins, the current detection methods involve the use of expensive chromatography-based separation methods coupled to sensitive detectors [6,7]. In addition to these issues, such laboratory-based methods require trained personnel and have an inherently long turnaround time due to sample transport and handling from the sampling site to the laboratory.

Figure 1 displays the occurrences of *Azadinium/Heterocapsa* spp. from water sample and AZA toxins extracted from shellfish from coast of Co. Cork, Ireland, from 2013 to 2014. The data show a high abundance of AZA

Figure 1
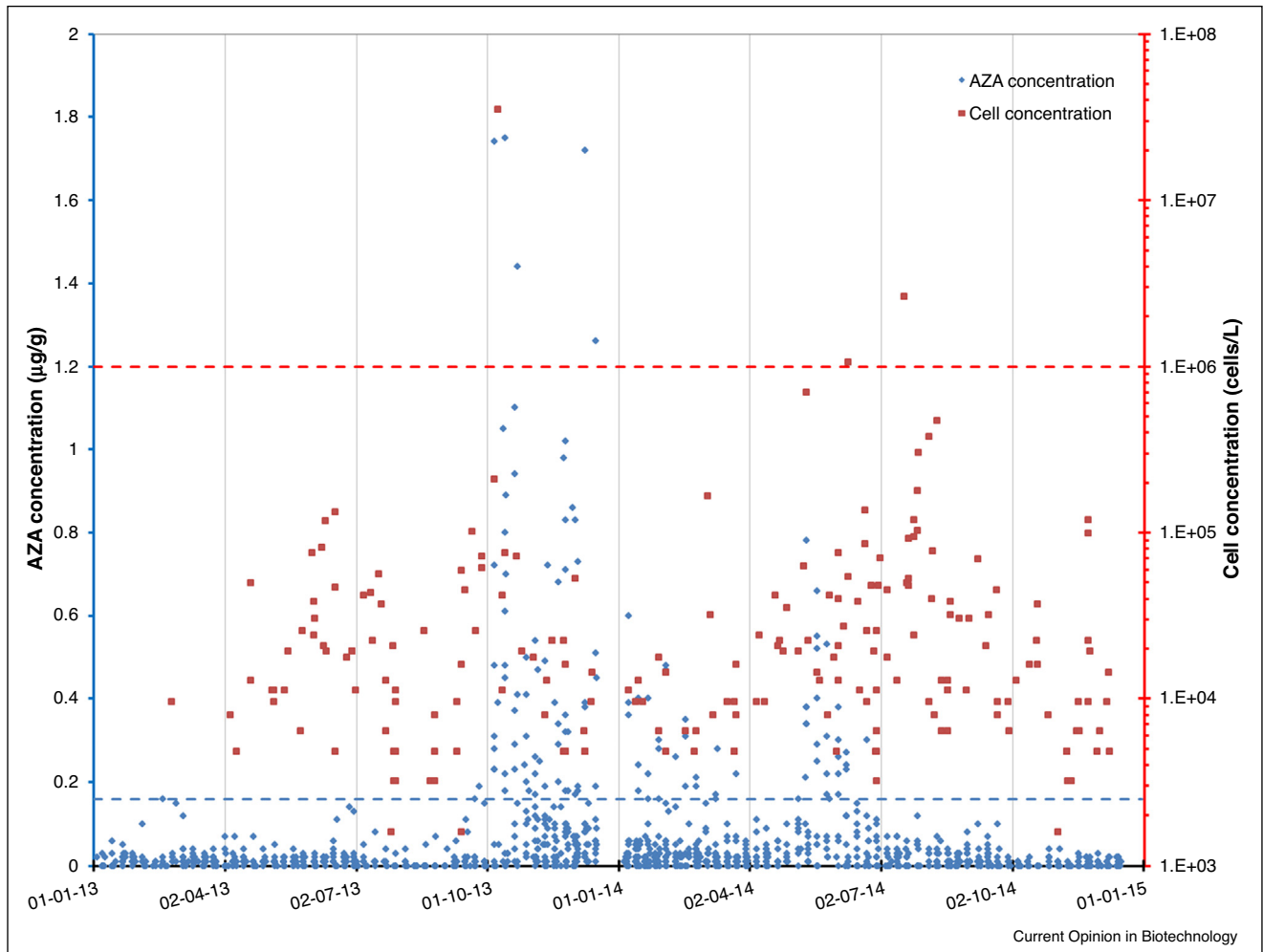
Occurrences of *Axadinium/Heterocapsa* spp. and AZA toxins (in shellfish) off the Cork coast from 2013 to 2014. Blue dashed line represents the current regulatory cut-off of AZA toxins in shellfish (0.16 µg/g). Red dashed line represents the level of a high volume algal bloom.

toxins in the Q3 of 2013. However, a very different trend was observed for 2014, with AZA toxin levels exceeding the regulatory cut-off throughout Q1 and Q2 of the year. Figure 2 displays a similar dataset but from samples acquired off the coast of Co. Galway, Ireland. Even with a geographical difference of only a few hundred kilometres, a very different trend for the occurrences of AZA toxins was observed. In 2013, Q1 experienced levels exceeding the cut-off limit, while Q3 and Q4 displayed levels up to 12-fold greater than the cut-off. In 2014, Q1 experienced AZA levels exceeding the cut-off, while the remainder of the year was largely below the cut-off. This comes despite the very high cell concentrations of *Azadinium/Heterocapsa* spp. that occurred at this time, with levels exceeding 10^6 cells/L. Such trends may give credence to the growth characteristics observed by Jauffrais *et al.*, [8], in which AZA cell quota was found to be antagonist to growth, that is cells that grew faster

had lower intracellular AZA concentrations and vice versa. These data also highlight the significant variation of cell concentration and shellfish toxin levels observed annually.

HABs present a significant monitoring challenge

HABs present a significant challenge in terms of predicting when and where a bloom may occur and the scale of a bloom. A myriad of factors play a role in influencing the dynamics of bloom growth. Physical factors include temperature [9,10], salinity, current, water level [11], turbulence, shear [12], occurrence of upwelling or downwelling winds [10], light availability [9] and biological factors, such as excystment behaviour [13], tropism and cell–cell interactions [14], among others (see graphical abstract). Human activities such as sewage-dumping and agricultural run-off are also linked closely to the occurrences of HABs.