Mass Mortality of marine species along N.E coast of England:

(2nd Report)

Up-dated Review of relevant data provided by DEFRA Agencies and others

Briefing Paper to Whitby Commercial Fishing Association

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Introduction:

I*n January 2022 I was commissioned by the Whitby Commercial Fishing Association (WCFA)to write a "Preliminary" report" on the Mass Mortality (MM) of marine species including crabs and lobsters, along the N.E. coast of England. The purpose of that Report was to review relevant environmental data made available by DEFRA Agencies (Environment Agency, CEFAS, Marine Management Organisation) in response to a number of FoI submissions.*

The FoI responses consisted of chemical analyses of crab flesh samples and data, introduced in support of the DEFRA hypothesis that the MM had been caused by a toxic HAB (Harmful Algal Bloom). The DEFRA hypothesis postulated that HAB had either inflicted direct toxic impacts on marine life, or had caused secondary lethal impacts as a result of hypoxic (depleted oxygen) conditions generated by the eventual "die off" of the algal bloom.

The WCFA report concluded that the HAB hypothesis was NOT supported by significant empirical evidence and that, unless supporting empirical evidence was forthcoming, it remained an un-evidenced hypothesis.

The WCFA report noted that DEFRA agency chemical analyses of crab flesh had reported the presence of elevated concentrations of the presence of the toxic chemical Pyridine in N.E. coastal water crab samples (max 430 mgs/kg), relative to low concentrations in "control samples" from Penzance (5 mg/kg). The WCFA report provided additional scientific material about Pyridine toxicology and environmental behaviour and concluded that, on the basis of the available empirical evidence, the toxic chemical Pyridine represented the more likely causative factor for the MM.

Following the publication of the WCFA report, DEFRA has continued to promulgate its HAB hypothesis and briefed regional MP and media on the matter while ignoring or "down playing" the WCFA commentary on the toxic chemical Pyridine.

In response, and on behalf of WCFA, an additional series of FoI submissions have been made to DEFRA agencies and others requesting the supply of additional information relating to both the un-evidenced DEFRA HAB hypothesis and supporting the body of empirical evidence supporting WCFA identification of as a likely causative factor.

It is in the context of responses to that second round of FoI submissions, and further scientific desk reviews carried out on behalf of the WCFA, that this second, up-dated report has been compiled.

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Major Conclusions: Pyridine:

Of the multiple chemical determinands in crab flesh analysed by DEFRA agencies, only the toxic chemical Pyridine was present at the relatively very high concentrations (up to 400+ mg/kg) reported.

It is clear that crab flesh samples from within the area impacted by the NE coast Mass Mortality hold up to 80 times greater concentration of Pyridine than "control samples" collected from outside the area of the MM (Penzance)

Highly relevant is the 2013 scientific data from Pyridine toxicity tests carried out on the only marine crustacean species for which such data is available, which has reported that the initiation of Pyridine product acute toxicity, for the marine crustacean shrimp T. japonicus, occurred at concentrations as low as 6.6 micro grams (O.OO6 mg) per litre.

It is concluded, on the basis of the available empirical evidence, and in the absence of any empirical evidence to the contrary, Pyridine and its derivative compounds are currently the most likely causative factor behind the Mass Mortality of marine species along the NE coast

RECOMMENDATIONS: (It is noted that DEFRA have now committed to undertake further investigation in order to identify the cause of the Marine Mortality. This implies that DEFRA maybe reconsidering its position on HABs.)

1: It is strongly recommended that the DEFRA agencies (Environment Agency, CEFAS etc) immediately undertake follow on research in order to further, and more comprehensively clarify the in-estuary distribution of the high levels of Pyridine and its derivative compounds reported in TEES estuary sediments in 2021 (see paras above), such work would also greatly assist the identification of the most likely source of the most significant Pyridine (and derivative compounds) input to the TEES estuary.

2: It is strongly recommended that the DEFRA agencies undertake a review of ALL sources of Pyridine (and derivative compounds) discharged to the TEES estuary. As highlighted in the WCFA January Review document the Environment Agency is expected to hold a comprehensive list of all licensed/permitted discharges of these substances to the TEES estuary and it should be a straightforward task for the EA to interrogate their record and produce this information

3: It is further recommended that the DEFRA agencies undertake a wide ranging assessment of regional marine wildlife species of all trophic levels in order to identify the full range of species impacted by the Mass Mortality. This assessment should include consultation with regional Wildlife Support Groups, consider apex predator species such as seabirds and common and grey seals and review the photographic and other records of the range of species stranded on the regional shorelines during the Mass Mortality.

4: It is additionally strongly recommended that regional inshore commercial fishermen, who by virtue of their daily work experience are custodians of vitally relevant local knowledge of the marine environment, fisheries and wildlife are consulted by the DEFRA agencies in order to enhance the effectiveness of the DEFRA investigations.

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CONCLUSIONS regarding the DEFRA HAB hypothesis
It is concluded, on the basis of the current ambiguous and inconclusive evidence

submitted by DEFRA agencies in support of the claim that HAB is the cause of the Mass Mortality of NE coast marine life, there is no empirical evidence to support that claim.

***RECOMMENDATIONS*:**

1: ***It is recommended that independent academic (not DEFRA based) analysis of the TEES estuary sediments is undertaken in order to confirm whether or not the TEES estuary sediments have "similar spectral properties" to those of any algal bloom species (including Karenia mikimotoi).***

2: It is further recommended that independent academic (not DEFRA based) analysis of the PML TEES estuary satellite imagery is carried out, in order to provide empirical proof whether or not the imagery shows any indication that the "spectral properties" of TEES estuary sediments are causing "ambiguities".

Only when such work has been completed can it be empirically confirmed that the PML satellite imagery has not been mis-interpreted as a "false positive" identification of a Karenia spp Harmful Algal Bloom, when it may have been imagery of some other algal bloom or suspended sediment.

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PYRIDINE: The original FoI submission requested details of regional crab analyses, Blue Mussel analysis, water and sediment analysis. Following an extensive in-depth review of the data supplied by Env' Agency, supported by a search for and review of relevant academic literature, this Consultancy concluded that the Crab (chemical) analyses best represented the issue under investigation because regional crustaceans were one of the most impacted species groups and the analyses were carried out for a very wide range and number of chemical subjects.

The chemical analyses of regional inshore waters Crab samples from Seaton (Tees mouth), Bran Sands (Tees mouth), Saltburn (approx. 20 kms south east of Tees mouth), Runswick (approx. 55 kms south east of Tees mouth), St Mary's Lighthouse (approx. 55 kms north of Tees mouth) and "Eastern IFCA" were collected and analysed for a large number of chemical determinands.

Control samples of Crab obtained from a Penzance (Cornwall) fish merchant were also analysed and the outcomes presented for comparison purposes.

Review of the details of these chemical analyses reveals that the very great majority of samples were shown to hold very low levels (fractions of mg/Kg). A few determinands were shown to be present in some samples at concentrations of up to 10 mg/Kg.

However, this Review reports that the most outstanding analytical data outcomes were those detailing the generally very high concentrations of Pyridine in regional Crab samples compared to the control samples from Cornwall; as tabulated below:

Pyridine in Crab samples:

Site	Pyridine concentrations
Penzance (control)	**5.929 mg/Kg**
Seaton	**203.765 mg/Kg**
Bran Sands	**255.700 mg/kg**
Saltburn	**439.611 mg/Kg**
Runswick	**20.0710 mg/Kg**
St Mary's Lighthouse	**77.917 mg/K**
"Eastern" IFCA 3	**194.600 mg/Kg**

In the context of the relatively very high concentrations in NE coast crab samples it is both unusual, and surprising, that no further investigation of Pyridine in the environment has been carried out by the DEFRA agencies.

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Review of PYRIDINE marine environmental data: Pyridine is a chemical compound which is structurally related to highly toxic long lived poly aromatic hydrocarbons (PAHs). Very low(trace) levels of Pyridine can be found in some plant and animal products, but it is not naturally abundant (see Penzance control levels of Pyridine). In the environment, concentrations of Pyridine elevated above "trace levels" are consensually agreed to be derived from human activity.

Pyridine is widely reported as very dangerous to humans. The fate/behaviour of Pyridine in marine environments and the toxic impacts to marine species is relatively uncommon and it is clear that, compared to many other chemicals, these parameters for Pyridine have been poorly studied.

Sources to the Environment: pyridine is released into the environment as a waste product discharged from industrial processes such as steel manufacture, processing of oil shale, coal gas production, coking plants and incinerators and from marine antifouling and anticorrosion applications. Pyridine and its derivatives occur in many compounds used in industry, agriculture and the maritime industries. Historically Pyridine has been intentionally produced from coal tar or as a by-product of coal gasification, but is now manufactured by a number of chemical industry processes.

No data on the quantities of Pyridine produced in the UK as a waste product or by deliberate manufacture, or of the volumes of Pyridine (and derivatives) permitted for discharged to UK water courses has been identified.

U.S. industrial releases of Pyridine to surface water and groundwater (underground injection) reported in 1987 were estimated to be 4,630 pounds and 303,650 pounds, respectively. In addition, 209,880 pounds of pyridine were disposed of in publicly owned treatment works in 1987. Some fraction of the quantity treated at POTWs is probably released to the environment. Pyridine was detected in one of two oil shale processing effluents at a concentration of 152 µg/L (ppb), but not in coal gasification plant effluents. Pyridine was also detected in effluents from coke-oven quenching operations at 11mg/L and detected, but not quantified, in four industrial effluents. Pyridine was also found in oil-shale retort water in Australia at a concentration of about 5 mg/L.

Uses: Pyridine is a precursor/base of a number of agrichemicals (including insecticides, fungicides and herbicides used in both terrestrial and marine applications), it is highly recommended as an anticorrosion treatment for marine structures such as those in the offshore hydrocarbon industry. It is also an industrial solvent, a water proofing agent, and a constituent of many dyes and disinfectants.

Marine environmental behaviour and fate: Pyridine mixes well with water. However, when discharged to water courses, Pyridine rapidly sequesters into marine intertidal and seabed sediments by adsorption to the outer surfaces of sedimentary particles, especially those suspended in the marine water column. Under the influence of flocculation processes in estuarine environments, such particles agglomerate, become heavier and are deposited out into estuarine intertidal and subtidal sedimentary deposits. The process reduces water column bio-availability of Pyridine but significantly increases concentrations in the deposited sediment.

Pyridine is persistent and non-bio-degradable in anoxic (oxygen depleted and typical of industrial/urban estuaries) marine sediments over extended time scales. Marine sediments collected from estuarine environments are shown to degrade Pyridine at varying rates depending on the ambient salinity. **(REFs: Kuo CE et al: Chemosphere 33: 771-81. 1996. & Liu SM et al': Chemosphere 36; 2345-57. 1998)**

Bio-degradability of Pyridine in marine intertidal and subtidal sediments is, in common with many other chemical pollutants, also reduced by non-exposure to UV (sunlight) and/or elevated sea surface temperatures.

Concentrations of Pyridine will significantly increase in "industrial" estuaries if inputs continue over the long term at rates greater than the degradation rates. Since estuaries heavily polluted with urban/municipal and industrial wastes generally suffer from highly depleted oxygen and UV and lower temperatures, reduced bio-degradability of Pyridine is to be expected.

It is clear that any resuspension of Pyridine contaminated sediments, by dredging and dredge disposal activity, will generate the creation of Pyridine enriched dredge plumes capable of re-distributing the previously sequestered Pyridine and giving rise to abnormal and markedly enhanced bio-availability of Pyridine.

Environmental impacts: Under normal conditions bio-concentration of Pyridine has been observed in aquatic species. **(REFS: Franke C et al'. Chemosphere 29. 1501-14. 1994. &: de Voogt P et al': Aquatic Toxicology, 169-194.1991)**

Academic research of the quantification of the degree of bio-concentrations in a representative range of marine species has not been identified to date and appears to be very limited, and perhaps non-existent.

Pyridine is defined as "Very toxic to aquatic life. Warning Hazardous to the aquatic environment, acute hazard]. H410: Very toxic to aquatic life with long lasting effects [Warning Hazardous to the aquatic environment, long-term hazard] ."
(REF: https://webwiser.nlm.nih.gov/substance?substanceId=173&catId=242)

N.B. LC/50 tests quantify the amount of substance required to kill 50% of test animals. EC50 tests quantify the amount of substance require to initiate malfunction (not mortality) of 50% of test animals.

This report confirms that there is a major absence of E50 and LC50 Pyridine test data on marine species and that the great majority such testing has been carried out on mammalian and freshwater species. Additionally, the majority of the available LC50/EC50 data for Pyridine products was reported in the 1980s and 1990s. Information on the toxicity of Pyridine and its derivative compounds to aquatic organisms derived from these few earlier studies, are now considered insufficient to assess the hazards of Pyridine.

E:G… Pyridine LC50 tests for freshwater fish conducted in the 1980s found that the LC50 for Fathead Minnows was 99 mg/L **REF: "Acute toxicology of organic chemical mixtures to the fathead minnow" Broderius SJ & Kahl MD. Aquatic Toxicology 6: 307-322. 1985**

By contrast, more recent improved analytical techniques fid the following:

Fathead minnow 96 hour Pyridine LC50 = 73.6 mg/l

European carp 96 hour Pyridine LC50 = 26 mg/l

Rainbow trout 96 hour Pyridine LC50 = 4.6 mg/l

REF: "Safety Data Sheet (PYRIDINE): ThermoFisher Scientific". Creation Date 02-0ct-2009.

Even more recent academic research published in 2013, on the toxicity of Pyridine based anti-foulings, has reported that the degradation products of Pyridine antifoulings may have an influence on marine organisms, at concentrations lower than the previously reported toxic values.

The 2013 study reported that initiation of Pyridine product acute toxicity, measured by 24hour EC50, for the marine crustacean shrimp T. japonicus, occurred at concentrations as low as 6.6 micro grams (O.OO6 mg) per litre.
REF: "Toxicity of Degradation Products of the Antifouling Biocide Pyridine Triphenylborane to Marine Organisms." Toshimitsu Onduka et al'. Arch' Environ' Contam' Toxicol'. (2013) 65:724–732 (table 2 p.728)

Chronic toxicity occurs at lower environmental concentration but longer term effects, often following the acute stage. Both acute and chronic toxicity also manifest as a group of symptoms including central nervous system damage, tremor, intoxication, weakness and fatigue similar to the reported behaviour of crustaceans. As a result of these symptoms mortality may occur.

As noted above, there is a consensus that bio-concentration of Pyridine and its derivatives has been observed. However, to date no research has been found on the potential for, or quantification of Pyridine (and derivatives) to bio-accumulate or bio-magnify in individual marine animals or through marine food chains. These issues will be of major relevance to NE coast crustacean stocks since both crabs and lobsters are recognised to be omnivores, with crabs consuming smaller items (worms, small molluscs, bacteria and algae) while lobster consume larger prey (mussels, sea urchins and other crustaceans).

Conclusion: It is clear that Crab samples from sites within the area of mass mortality along the NE cost of England show concentrations of Pyridine far in excess of those demonstrated to cause both mortality and acute and chronic Pyridine generated outcomes.

Inhalation of Pyridine vapour is a dose pathway leading to vomiting and fatigue etc: (and may be implicated in the widely reported health impacts reported for dogs on beaches). Pyridine is reported to be carcinogenic to animals but no dose data has been identified to date.

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Sources of Pyridine and derivatives to the marine environment of N.E. England.

Pyridine and its derivatives occur in many compounds used in industry, agriculture and the maritime industries. Historically Pyridine has been intentionally produced from coal tar or as a by-product of coal gasification, more recently it has been manufactured by a variety of processes and is also discharged to the environment as a waste product from a number of industrial activities.

It is evident that the urban, industrial, chemical and maritime industrial activities carried on around the Tees estuary, some of them longstanding over a century or more, will have been a major source of both Pyridine and Pyridine degradation products. A number of Tees side chemical works are believed to have been involved in the manufacture of Pyridine and its derivatives. Other sites, such as ship and marine structures breakers may have discharged Pyridine and derivatives waste products into the Tees estuary environment.

It is certain that, over the operating lifetime of these industries, the work will have involved the release of large quantities of Pyridine and its derivatives in both particulate and dissolved form. There is no evidence for long term chemical analyses of Tees Estuary/Seaton Channel sediment or marine organism analysis for Pyridine, nor of any attempt to quantify Pyridine inputs to the Tees estuary.

Despite the failure to collect, quantify and publicise relevant Pyridine data it is expected that much of that material, in liquid or particulate form, has been discharged, under permit from DEFRA Agencies, into the estuarine waters or has entered the estuary by way of un-planned “runoff” from contaminated land surfaces.

Dredge and dredge waste disposal plumes: As explained above, water soluble Pyridine products will quickly become adsorbed to estuarine sediments and, in that state, will deposit out in sub-tidal and inter-tidal sedimentary deposits and become sequestered in low/non degradation environments. This process means that ambient concentrations of Pyridine and its derivatives in the water column will be depleted while those found in regional sediments will be increased.

It is widely understood that, if such polluted sediments are disturbed from inter or sub tidal deposits by dredging activity, a local dredge plume of re-suspended sediment will redistribute the entrained adsorbed pollutants and rapidly, and substantially, increase the bio-availability of any chemical, heavy metal or hydrocarbon pollutants attached to the sediments. In the case of recent, current and ongoing Tees Port dredging there will be a dredge plume generated by every dredge, possibly on a daily basis. Such daily in-estuary dredge plumes will be transported by estuarine tides out of the estuary on the tidal ebb and distributed around the local marine environment.

Similarly, when the dredge hoppers are filled, the dredger will transport dredge wastes to the regional dredge waste disposal sites for dumping. Dumping of dredge wastes will then occur at some distance from the dredge site and create a second series of plumes of disposed dredge wastes, on an every-dump basis, which will impact more distant areas than the dredge plumes.

Water body movements: In addition to the effect of short term local tidal movements there are residual (non-tidal), long term single directional and relatively powerful water body movements. Authoritative sources report that the residual water body movements off the east coast of England and Scotland "are well documented" and chart the southerly flow of residual water body movements down the east coast. **REF: "Atlas of the Seas around the British Isles." Directorate of Fisheries: MAFF.1981 p2:16**

These residual current water body movements will carry dredge plume sediments and contaminants southwards from the Tees estuary while at the same time the dredge waste disposal plumes will also travel southward under the same influence.

It is proposed that the early concentration of Pyridine reported for Seaton crabs (203 mg/kg) may be a function of the in-estuary dredge plumes exiting the Tees estuary on local tides. It is proposed that the higher concentrations reported for Saltburn crabs (439.611 mg/Kg) may be a function of dredge waste disposal plumes + in-estuary dredge plumes transported southward by residual water body movements.

It is proposed that, the strong and coherent southward moving "residual" water may have the capacity to carry combined (dredge and dump) plumes, with their associated pollutants, towards Runswick and points further south exposing marine species, especially demersal "bottom" dwellers and feeders, to the pollutant contents of settling sedimentary material.

Dredging and disposal of Contaminated sediments: A 2001 report confirms that here is a broad consensus that dredged material is subject to varying degrees of contamination. A variety of harmful substances, including heavy metals, oil, PAHs, anti-fouling compounds, PCBs and pesticides, can be effectively 'locked into' the seabed sediments in ports and harbours. These contaminants can often be of historic origin and from distant sources. The dredging and disposal processes can release these contaminants into the water column, making them available to be taken up by animals and plants, with the potential to cause contamination and/or poisoning. The likelihood of this occurring depends upon the type and degree of sediment contamination, however, some remobilisation of low levels of pollutants would be expected during most dredging campaigns.

The highest levels of contaminants generally occur in silts dredged from industrialised estuaries. If contaminants are released into the water column during disposal, they may accumulate in marine animals and plants and transfer up the food chain to fish and sea mammals.

The 2001 report note that "When found in sufficient quantities in the food chain, contaminants may cause morphological or reproductive disorders in shellfish, fish and mammals" and "Generally young shellfish and crustaceans (oysters, shrimp, crab and lobsters) are much more susceptible to the toxicity of contaminants than adults".
Ref: http://ukmpa.marinebiodiversity.org/uk_sacs/activities/ports/ph5_2_5.htm

In the context of the proposal that dredging, dredge wase disposal and associated sediment "plumes" may have released and dispersed Pyridine or some other toxin, FoI requests were submitted to relevant DEFRA Agencies querying the precise timing, location and depth of dredge cuts of daily dredge activity. In particular that FoI submission has been directed to the Marine Management Organisation (MMO), the organisation responsible for licensing/permitting both dredge and dump activity and TEESPORT management, the body which has conducted and overseen the dredge and disposal activity

It is hoped that this data will assist clarification of any chronological relationship between the start of dredge and disposal plumes and the initiation of marine species mortality at successive points on the relevant coast. As of 7th March, 2022, no response has been provided.

PYRIDINE and it's derivatives in TEES ESTUARY
The Empirical evidence and data sources:
Pyridine (C5H5N) is one of a number of chemicals which are closely related and derived from similar historical sources such as coal gasification, coal tar production and oil refining, these chemicals have similar molecular structures and are widely found in a wide range of manufactured chemical compounds derivatives used in many industries. Pyridie has many derivative compounds such as Pyrene (C21H15N) which has been reported in TEES estuary sediments.?

A 2013 Report firmly placed pyridine/pyrene and their derivatives among the petrogenic and combustion product PAHs observed during analysis of samples from the INNER and OUTER TEES dredge waste disposal sites. The study further confirmed that PAH concentrations in sediments from within and outside both sites were markedly elevated relative to the majority of the other English sites sampled and analysed.
(Ref: "Polycyclic Aromatic Hydrocarbons in sediments at dredge material disposal sites around England: Concentrations in 2013 and time trend information at selected sites 2008-2013". Heather S Rumney et al'. Marine Pollution Bulletin. Vol 30. 2015)

CEFAS reporting of Tees estuary contaminated sediment dredging: Through 2014 under a contractual agreement with the MMO, CEFAS undertook a review of dredge material disposal site monitoring at a number of disposal sites around the UK coast
in order to assesses the suitability of dredged material for disposal at sea in line with the OSPAR Guidelines for the management of dredged material (OSPAR 2014). These guidelines provide generic guidance on determining the conditions under which dredged material may (or may not) be deposited at sea and involve the consideration of alternative uses, disposal sites and the suitability of the dredged material for disposal to sea including the presence and levels of contaminants in the dredged material, along with perceived impacts on any sites of conservation value in the vicinity of disposal.
(Ref: "Dredged Material Disposal Site Monitoring Around the Coast of England: Results of Sampling (2014)": SG Bolam et al'. CEFAS CONTRACT REPORT: SLAB 5.)

The CEFAS monitoring at the two Tees disposal sites, (TEES INNER and TEES OUTER), had been conducted annually for a number of years and, as such, is claimed to offer a good temporal dataset to draw upon when making contemporary assessments.
The CEFAS Report notes that "Frequent monitoring here reflects the large amounts of material being disposed (especially to the Inner site) and the high concentrations of certain contaminants of the source materials relative to those dredged around other parts of the English coast." **(Ref: "Dredged Material Disposal Site Monitoring Around the Coast of England: Results of Sampling (2014)": SG Bolam et al'. CEFAS CONTRACT REPORT: SLAB 5.**)
(page 10)

Appendix 2 of the CEFAS SLABS report to the MMO confirmed that both Inner and Outer Tees disposal sites receive "large quantities" of material dredged from the Ports of the Tees estuary, and that at the time of the investigations the Tees Inner site was the destination "of most of the 2.7 million tonnes of maintenance dredged material per year from the Tees estuary, the Seaton Channel and Hartlepool" while "material disposed to Outer Tees is usually comprised of capital dredged material" because this is a "more mobile site". Material dumped at this site is more likely to disperse out of the site and therefore to be distributed "downstream" on the long term, southward moving residual current).

The Report also noted that, by 2014, there had been a number of high profile construction and disposal at sea applications made with regard to the Tees waterways over recent years and that, in addition to the annual 2.7 million tonne of maintenance dredge disposal, permission had also been granted for the Northern Gateway container terminal which would require dredging of turning circles and deeper berthing pockets requiring an additional 2 million tonne dredge.

These "deeper berthing pockets" would seem to have required designation as Capital Dredge efforts as it would appear the dredge work was new and not definable as Maintenance dredging. In addition, a number of smaller dredge proposals had also been received.

The CEFAS report confirmed that in 2014 the TEES estuary region had "a large quantity of chemical industries which are the source of contaminants within the dredged sediments" and also noted that "dredged material from the TEES has displayed some of the highest levels of Poly Aromatic Hydrocarbons found in UK marine sediments". However, no results of analytical work were PAHs were presented.

Pages 18 & 19 of the CEFAS report summarised the methodology for analysis of PAHs and provided a list of PAH determinands to be investigated at dredge disposal sites, this list included Pyridine (C5H5N) and Pyridine derivatives.

Section 2.1.3 (page 32) of the CEFAS Report presented the results of the analysis of sediments from the two TEES disposal sites, but despite the CEFAS PAH comments reported above, did not report any analysis of TEES sediments for any of the PAH determinands, including Pyridine/Pyrene and derivatives.

N.B. It is relevant to note that at other English disposal sites covered by the CEFAS report, PAH analysis was conducted and reported in some detail. No explanation was provided for the absence of PAH analysis at the TEES site

In the context of the fate of material disposed of at TEES INNER and TEES OUTER, the CEFAS Report noted (page 29) that some results indicated that fine sediment material (silts and clays) accounted for about 66% of content, and that there were indicators that fine sediments were being dispersed out of both the TEES INNER (largely Maintenance dredge) site and the TEES OUTER (largely Capital dredge) site. However, no quantification of the extent of the dispersal of these fine sediments was provided.
(REF: "Dredged Material Disposal Site Monitoring Around the Coast of England: Results of Sampling (2014)": SG Bolam et al'. CEFAS CONTRACT REPORT: SLAB 5.)

TEESPORT SEDIMENT ANALYSIS FOR PYRIDINE DERIVATIVES: A recent response to an FoI request submitted to the TEESPORT management has supplied the data from chemical analysis of Tees Estuary sediment samples, carried out in October 2021, after an (as yet) undetermined amount of sediment had already been dredged and the dredge wastes had been disposed of at the out-of- estuary disposal sites.
Ref: TEES ESTUARY SEDIMENT CHEMICAL ANALYSES **… "MMO_RESULTS_TEMPLATE MAR 01178": SOCOTEC MARINE DEPT: Burton on TRENT**

N.B. It is not reported from what depth below the post dredge seabed surface the sediment samples were taken.
No explanation has been provided for the decision to undertake sampling in October 2021 AFTER the bulk of the dredging had been completed and significant volumes of potentially Pyridine contaminated dredge waste had been removed and disposed of.

Review of the TEESPORT data shows that a wide range of chemical determinands were analysed for, including the Pyridine derivatives "pyrene" and "ind pyr" (*indeno 1,2,3 CD pyrene).*

Page 15 of the PAH data print out reported the analysis of 11 samples for "ind pyr". The results showed that 5 of the 11 samples held over 500 micrograms per kg and that 3 of those 5 held over 1000 micrograms per kg.

Page 16 of the PAH data print out reported the analysis of 11 samples for “pyrene”. The results showed that 7 of the 11 samples held over 500 microgram per Kg and that 5 of those 7 held over 1,000 micrograms per kg, and that 3 of those 5 held over 2,000 micrograms/kg

Page 19 of the PAH data print out reported the analysis of a further11 samples for “ind pyr”. The results showed that 4 of the 11 samples held over 500 micrograms/kg and that 1 of those 4 held a concentration above 1,000 micrograms/kg.

Page 20 of the PAH data print out reported the analysis of a further 11 samples of “pyrene”. The results showed that 9 of the 11 samples held over 500 micrograms/kg, that 6 of those 9 held over1,000 microgram/kgs, that 2 of those 6 held over 2,000 micrograms/kg and that 1 of those 2 held over 3,000 micrograms/kg of “pyrene”. **Ref:** TEES ESTUARYSEDIMENT CHEMICAL ANALYSES **… “MMO_RESULTS_TEMPLATE MAR 01178”: SOCOTEC MARINE DEPT: Burton on TRENT**

The PAH analysis data has confirmed that “pyrene” and “ind pyr” occurred at elevated concentrations (hundreds of micrograms/kg) in several areas across the TEES estuary. Areas where sediments are shown to hold over 500 micrograms/kg of “pyrene”, and/or “ind pyr”, include Seaton Channel, North Tees Berths, Navigator North Tees, Tees Dock, Phillips Terminal, Hartlepool Channel and Hartlepool Berths.

The highest reported concentrations of “pyrene” were found in and around the Hartlepool Channel and the maximum concentration of 3,630 micrograms/kg, was found in sediment samples from Hartlepool Berths (HP2).

The presence of detectable levels of Pyridine and its derivatives throughout the TEES sediments, and of Pyridine in crab flesh samples, clearly indicate that, to date, and in light of the currently available evidence, Pyridine remains the only potentially causative factor for the Mass Mortality of Crustaceans and other marine animals along the North East coast.

Conclusions (Pyridine):

Of the multiple chemical determinands in crab flesh analysed by DEFRA agencies, only the toxic chemical Pyridine was present at the relatively very high concentrations (up to 400+ mg/kg) reported.

It is clear that crab flesh samples from within the area impacted by the NE coast Mass Mortality hold up to 80 times greater concentration of Pyridine than “control samples” collected from outside the area of the MM (Penzance)

The empirical evidence of Pyridine toxicity tests on aquatic species clearly shows that low concentrations (less than 100 mg/kg) are highly toxic to aquatic species including an example of marine crustacea.

It is clear that Crab samples from sites within the area of mass mortality along the NE cost of England have concentrations of Pyridine far in excess of those demonstrated by empirical investigation to cause acute (mortality) and longer term chronic Pyridine toxicity outcomes.

It is evident that there are multiple potential sources of both historical and contemporary Pyridine and its derivative compounds in the industrial areas surrounding the TEES estuary waterways.

It is evident from data supplied by TEES ports contractors that Pyridine derivatives have been detected in sediments throughout the Tees estuary and that at a number of sites the concentrations exceed 1000 micrograms/kg (1 mg/kg) and peaked at 3600 micrograms/kg (3.6 mg/kg).

Highly relevant is the 2013 scientific data from Pyridine toxicity tests carried out on the only marine crustacean species for which such data is available which has reported that the initiation of Pyridine product acute toxicity, for the marine crustacean shrimp T. japonicus, occurred at concentrations as low as 6.6 micro grams (O.OO6 mg) per litre.

There is a consensus that Pyridine and its derivative compounds may bio-accumulate, or bio-concentrate, but there has been a lack of investigation into the quantification of the process and none for marine species.

Recommendations: It is noted that DEFRA have now committed to undertake further investigation in order to identify the cause of the Marine Mortality.

1: It is strongly recommended that the DEFRA agencies (Environment Agency, CEFAS etc) immediately undertake follow on research in order to further, and more comprehensively clarify the in-estuary distribution of the high levels of Pyridine and its derivative compounds reported in TEES estuary sediments in 2021 (see paras above), such work would also greatly assist the identification of the most likely source of the most significant Pyridine (and derivative compounds) input to the TEES estuary.

2: It is strongly recommended that the DEFRA agencies undertake a review of ALL sources of Pyridine (and derivative compounds) discharged to the TEES estuary. As highlighted in our January Review document the Environment Agency is expected to hold a comprehensive list of all licensed/permitted discharges of these substances to the TEES estuary and it should be a straightforward task for the EA to interrogate their record and produce this information

3: It is further recommended that the DEFRA agencies undertake a wide ranging assessment of regional marine wildlife species of all trophic levels in order to identify the full range of species impacted by the Mass Mortality. This assessment should include consultation with regional Wildlife Support Groups, consider apex predator species such as seabirds and common and grey seals and review the photographic and other records of the range of species stranded on the regional shorelines during the Mass Mortality.

4: It is additionally strongly recommended that regional inshore commercial fishermen, who by virtue of their daily work experience are custodians of vitally relevant local knowledge of the marine environment, fisheries and wildlife are consulted by the DEFRA agencies in order to enhance the effectiveness of the DEFRA investigations.

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The DEFRA Agency (CEFAS) hypothesised Harmful Algal Bloom (HB) causative factor:
In January 2022, having carried out parasitical/biological and chemical analysis of crab tissue in January 2022 and reported that they had found no evidence of chemical pollution impacts and thus no observed causative factor, CEFAS proposed a possible impact from a proposed Karenia mikimotoi bloom, on the basis of a reported satellite imagery observation of an algal bloom in the relevant sea area at around the relevant time. The CEFAS proposal reports identification of Karenia mikimmoi in regional water column. No report of any sampling for the concentration of Karenia spp in relevant water samples has been publicised or brought forward and it is thus concluded that no such sampling work was carried out.

Brief review of Karenia species blooms in UK & Irish Waters: English Channel Karenia spp bloom achieved levels of 100 micrograms per litre in sea water. North Wales Karenia spp bloom achieved 40.7 micrograms per litre. Roaring Water/Kinsale spp Karenia bloom achieved 32 micrograms per litre. Consensus that in general, algal "bloom" formation occurs at around 30 micrograms per litre.

Cape Cod (US), and multiple Irish examples of Karenia spp outbreaks occurred in sea loughs, inlets and enclosed embayments, where bottom water becomes anoxic after die off, NOT in open coastal waters. Open coastal waters are less likely to experience parameters likely to give rise to hypoxia following algal bloom die off, due to residual currents, lower sea surface temps, likelihood of more turbulent conditions in open sea than in estuaries and embayments.

Karenia blooms are reported to require high temps, fine calm weather and calm sea. US reporting of the Cape Cod incident noted that the optimal temperature range for Karenia mikimotoi is between 68 and 75 degrees Fahrenheit. Karenia mikimotoi blooms in Ireland were reported to commence in late May and die off through August.

It is concluded that end of September/early October water temps in North Sea are likely too low for Karenia spp to survive in heavy concentrations.

While toxic impacts on locally important commercial species are the major focus, Irish reports note mass mortality of multiple species in post bloom anoxic conditions as well as some possible toxic impacts. A Karenia bloom at Wexford caused reported mortalities of high numbers of lugworms, ragworms, bottom fish, rock pool fish, bi-valves echinoderms but no crustaceans. Echinoderms reported to be particularly sensitive. A dive survey of Killary Harbour noted mortality of the all of the above species but live hermit crab. Cape Cod reported similar mass mortality including Lobster and Crab.

Analysis of the DEFRA evidence for HAB: DEFRA agencies (CEFAS & Environment Agency) have proposed the hypothesis that the Mass Mortality of marine species along the north east coast has been caused by a harmful algal bloom (HAB) of Karenia mikimotoi species.The hypothesis was first introduced via the publication of a short extract from a Plymouth

Marine Laboratory (PML) paper containing satellite imagery of the regional sea surface during September and October of 2021.

Karenia input from Plymouth Marine Lab (PML): Subsequently, PML has put forward an additional short briefing paper "Analysis of Karenia mikimotoi HAB risk around Tees Estuary: (sept/oct 2021)" as a further contribution to the ongoing debate about the cause of the geographically and chronologically extended Mass Mortality (MM) of marine species (including commercial crustaceans) along the North East coast of England.

This more recent PML submission is a slightly more detailed version of the original CEFAS suggestion that a Karenia bloom was the causative factor for the MM. As was the case with the original CEFAS suggestion, the PML briefing is based on satellite imagery, but this more recent PML submission has been updated/extended by the addition of more satellite imagery which has been constructed from "7 day composite maps" of algal activity in the regional coastal waters of the N.E coast.

The PML input has not been able to supply any scientific/empirical evidence of a Karenia mikimotoi bloom. On the contrary, this Review concludes that the most recent PML input has raised further uncertainty on the DEFRA agency hypothesis.

Uncertainty of algal species identification: The PML briefing makes multiple reference to the "Karenia mikimotoi HAB risk" or "high risk" but does not provide any empirical evidence of the actual presence of any of the 12 recognised Karenia species *i.e., no evidence of sampling and/or analysis of marine algae taken from the proposed bloom. Neither PML, CEFAS or the Environment Agency reference any such sample analysis.*

However, the PML briefing does confirm that the observed algal concentrations **"may well be a dense bloom of another phyto-plankton species that resembles Karenia".**
The "may well" in this statement clearly illustrates a degree of uncertainty about the nature of the phenomenon recorded by the satellite images.

The PML submission is unusual in respect of the multiple repetition of un-evidenced, and therefore hypothetical only, phrases such as "Karenia mikimotoi HAB risk" or "high risk" compared to the strictly factual (single) admission that the observed algae "may well be a dense bloom of another phyto-plankton species that resembles Karenia".

N.B. No scientific evidence has been provided to justify the emphasis on "risk" and "high risk" in the context of the admission that there ""may well be a dense bloom of another phyto-plankton species that resembles Karenia".

Definition of algal blooming: My response to the initial CEFAS Karenia hypothesis noted that empirical, evidence based, reports of proven Karenia blooms in (Ireland, English Channel) have reported Karenia bloom densities of between 32 micrograms per litre and 100 micrograms per litre and noted that biological definitions of algal blooming quote 30 micrograms per litre as the concentration threshold usually recognised to define a "bloom".

By contrast, the most recent PML satellite imagery submission on Karenia appears to show that peak densities of algae in the proposed “bloom” off the N.E. coast are estimated at about 15 micrograms per litre.

Sea Surface Temperature parameters: My response to the initial CEFAS commentary on Karenia referenced the fact that algal blooms initiate in spring as sea surface temperatures begin to rise, and die off as sea temperatures decline in late summer/early autumn. US reporting of a Karenia caused mortality at Cape Cod (U.S) noted that the optimal temperature range for Karenia mikimotoi is between 68- and 75-degrees Fahrenheit.

In this context it is noted that the most recent PML submission does not discuss the ambient sea temperatures through the entire duration of the observation of the assumed “bloom”, and shows no satellite imagery beyond 21 October 2021.

I have not been able to I.D. precise data of day-to-day sea water temperatures along the NE coast through October, November and December 2021, but can confirm from official data that the average (Whitby) inshore sea water temperatures over recent years are: 59 degrees Fahrenheit for September, 55 Fahrenheit for October and 52 Fahrenheit for November. (This record may not be specifically correct for 2021 but I would expect that this year’s data should be available from a Whitby source.

My preliminary review report of the data provided by DEFRA agencies noted that the historical record of regional North Sea temperatures for September and October clearly indicates that they are generally far below the “optimal temperature” for Karenia blooming and thus imply that the likelihood of such an event on the NE coast is contra-indicated

N.B: the PML submission has provided no detailed evidence to indicate the presence of any presumed algal bloom at points further south than Staithes (Fig 2: Map C) let alone those points as far south as Whitby or beyond, where ongoing mortalities of crustaceans have been reported.

Geographical extent of the satellite imagery: the satellite imagery 7 day composite maps of the observed phenomenon show peak density of the imaged phenomenon centred on the TEES mouth marine area. It is clear from the available imagery that concentrations decline markedly to the south of the region imaged and that the relevant imaged area does not extend as far to the south as the reported mortalities.

Satellite imagery and the mis-identification of algal blooms: From the PML quotes above, it is evident that satellite imagery **“may well”** be unable to differentiate between algal species and specifically identify individual species of algae. It is evident that there is a considerable academic consensus that this can be an issue when attempting to interpret satellite imagery.

I have undertaken a desk review of scientific literature relevant to the interpretation of such imagery. This desk review has identified a body of peer reviewed research confirming that there is also clear scientific evidence that satellite imagery may generate false positive bloom detection, mistaking surface sediment plumes for algal blooms. Two examples of such research are summarised below.

1: On November 16, 2016, the Moderate Resolution Imaging Spectroradiometer (MODIS) on NASA's Aqua satellite captured a colour image of the Spencer Gulf of Australia which appeared to be an algal bloom. But, after a closer look at the image, the geography, and the scientific literature, ocean scientists began to formulate a different diagnosis and concluded that instead of algae, the colours in Spencer Gulf were likely to be the result of churning waters that have disturbed sea bed sediments, re-suspended them and distributed them into the surface waters of the Spencer Gulf.
REF:https://earthobservatory.nasa.gov/images/89154/algae-bloom-or-swirling-sediment (recovered 11/02/2022).

2: A 2020 peer reviewed research paper reported that typical ocean Colour Dissolved Organic Matter (CDOM) algorithms developed for open ocean waters use blue and green spectral bands to determine chlorophyll-*a* concentrations and that these algorithms were shown to confuse CDOM and sediment as chlorophyll, which can lead to "high rates of false positive bloom detection". **REF: "Current and Future Remote Sensing of Harmful Algal Blooms in the Chesapeake Bay to Support the Shellfish Industry": Jennifer L. Wolny et al'. Front. Mar. Sci., 26 May 2020**

Responding to a query from Joe Redfern (Whitby Commercial Fishermen's Association), in an email of 8/02/2022, a Plymouth Marine Laboratory scientists confirmed that "The spectral properties of sediments should be similar to the spectral properties of Karenia HAB to produce ambiguities" and also confirmed that PML "did not conduct any experiments to identify sediment composition that may lead to ambiguities."
N.B. In this context the "ambiguities" referred to by PML are "false positive" identifications of algal blooms.

A possible relationship between satellite imagery and dredging? It is relevant to note that, as reported above, algal blooms tend to initiate in spring when sea surface temperatures (SSTs) begin to rise and that they tend to die off in late summer/early autumn as SSTs decline. The pattern of the evolution of the NE coast phenomenon recorded by the satellite imagery does not accord with the normally reported season life cycle of algal blooms.

In that context it is relevant to note that there may be a "chronological fit" with the peak of the imaged phenomenon and the TEES estuary dredge and disposal activity. This cannot be confirmed, or denied, until detailed FoI requests submitted to DEFRA agencies including the Marine Management Organisation (responsible for licensing and overseeing the dredge activity) and the TEESPORT management (overseeing the dredging and disposal work) have been responded too.

CONCLUSIONS (HAB):
It is concluded that, on the basis of the current evidence submitted by DEFRA agencies in support of the claim that HAB is the cause of the Mass Mortality of NE coast marine life, there is no empirical evidence to support that claim.

It is clear that the available Plymouth Marine Laboratory submissions on the issue of HAB confirm that there are a number of "doubts" and "ambiguities", surrounding the DEFRA claims, which militate against acceptance of the DEFRA claim.

It is evident that the DEFRA hypothesis has been concocted in the absence of "spectral property" analysis of satellite imagery which would haw clarified these "ambiguities"

It is concluded that the currently available evidence advanced by DEFRA sources confirms that the current level of analysis of the satellite imagery of the Tees mouth marine area "phenomenon" is not sufficient to clarify
a: whether the observed phenomenon was an algal bloom of Karenia mikimotoi
b: whether the observed phenomenon was a bloom of any other specific algal species

And that there is sufficient academic evidence to give some credence to an alternative hypothesis regarding the "observed phenomenon":
i.e. that there is a possibility that the observed phenomenon could even be a surface plume of suspended sediment

Recommendations:
1: ***It is recommended that independent academic (not DEFRA based) analysis of the TEES estuary sediments is undertaken in order to confirm whether or not the TEES estuary sediments have "similar spectral properties" to those of any algal bloom species (including Karenia mikimotoi).***

2: It is further recommended that independent academic (not DEFRA based) analysis of the PML TEES estuary satellite imagery is carried out, in order to provide empirical proof whether or not the imagery shows any indication that the "spectral properties" of TEES estuary sediments are causing "ambiguities".

Only when such work has been completed can it be empirically confirmed that the PML satellite imagery has not been mis-interpreted as a "false positive" identification of a Karenia spp Harmful Algal Bloom, when it may have been imagery of some other algal bloom or suspended sediment.

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Tim Deere-Jones (Marine Pollution Research & Consultancy) 08/03/2022