Running title: Passive sampling naphthenic acids in produced water

SUBMITTED AS SHORT COMMUNICATION

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SHORT COMMUNICATION

MEASUREMENT OF NAPHTHENIC ACIDS IN THE RECEIVING WATERS AROUND AN OFFSHORE OIL PLATFORM BY PASSIVE SAMPLING

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Abstract

Polar organic chemical integrative samplers (POCIS) were deployed in the vicinity of an offshore oil installation and analysed for naphthenic acids (NA). POCIS accumulated a range of mono to tetracyclic NA, with different degrees of alkylation, with monocyclic acids being the most abundant. POCIS or similar polar samplers may currently be the only way to measure exposure to NA from offshore discharges in situ. In addition they may be a valuable tool for monitoring similar organic acids in general.

Keywords

North Sea, POCIS, Produced Water, Marine Pollution

INTRODUCTION AND BACKGROUND

Produced water (PW) is the largest discharge to the marine environment by the offshore oil and gas industry. As such considerable effort has been directed to studying the potential for long-term biological effects of PW, both in the laboratory (e.g. Holth et al. [1]) and in situ [2, 3]. Risk assessment of PW has largely focussed on the biological effects of only two groups of organic compounds; polycyclic aromatic hydrocarbons (PAH) and alkylated phenols (AP) [4]. This is despite the fact that PW is a highly complex mixture containing many unresolved toxic components, potentially at higher concentrations than PAH or AP. For example in 2010 the total amount of organic acids released in the Norwegian sector from PW discharges was 22,000 tonnes compared to 298 tonnes of AP (C_1-C_3) and 1.5 tonnes of PAHs (EPA16 minus naphthalene) [5]. The majority of the acids discharged consist of simple low molecular weight carboxylic acids such as formic, acetic, propanoic, butanoic and pentanoic acids [6], which likely do not pose much of an environmental problem. However, significant quantities of naphthenic acids (NA) may also be present [7], at similar concentrations to those of PAH and AP. The NA present are a highly complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids. They are described by the general chemical formula $C_nH_{2n\ z}O_2$ where *n* indicates the number of carbons and *Z* equates to a homologous series through hydrogen deficiency [8]. Various toxicological responses have been attributed to NA and recently it was suggested that they represent a large fraction of the oestrogen receptor agonist activity found in PW [9]. However, determining concentrations of organic constituents (including NA) in the receiving waters around oil installations is challenging not least due to the rapid dilution of the discharges [2]. In addition biological methods for determining exposure are currently lacking or unsuitable, not least due to low bioaccumulation of polar or medium polar

compounds such as NA [10]. Thus whilst the in vitro toxicity of NA has been demonstrated in the laboratory [9], determining the exposure and subsequent risk of NA to the environment, is not straightforward.

Passive sampling devices typically provide low detection limits and have successfully been shown to accumulate PW originating PAH and AP in discharge receiving waters [10,11]. The principle of passive sampling is the placement of a device in the environment for a fixed period of time, where it is left unattended to accumulate contaminants by diffusive and sorptive processes [12]. Such devices offer sensitive, time-averaged sampling without confounding factors, which may occur when using bio-monitoring organisms. In the present work they were used as a support parameter in a biological effects monitoring programme, to measure exposure of organisms to groups of chemicals where suitable biological methods for measuring exposure (not effects) are lacking, as mentioned above. The chosen passive sampling device was the polar organic chemical integrative sampler (POCIS), which has been successfully applied for measuring a wide range of over 300 polar-medium polar contaminants, see reviews by Harman et al., and Morin et al., [13,14]. Thus the aim of the present work was to determine the ability of POCIS to accumulate PW discharge originating NA from the receiving waters around offshore oil platforms, as a first step towards developing a quantitative technique for exposure assessment.

MATERIALS AND METHODS

Sampler deployment

Standard POCIS, with a surface area per mass of sorbent ratio of ca. 180 cm^2/g [15] were obtained from ExposMeter . The configuration used contained Oasis® HLB sorbent between two discs of polyethersulphone (PES) membrane. Samplers were deployed in

duplicate, using commercially available stainless steel canisters (Environmental Sampling Technologies) which were attached directly to the main rope of a sampling rig at roughly 15m depth, alongside netted blue mussels (see Harman et al. [16]) which were analysed for a suite of biomarkers as described elsewhere [17]. Deployment lasted for 6 wk (April-May, 2011), with locations chosen to represent a gradient away from the PW discharge point, and in the direction of prevailing currents, at Gullfaks C, an oil platform in the North Sea (Figure 1). After retrieval samplers were kept frozen under transport and until analysis (-20 °C).

POCIS extraction and analysis

POCIS were opened and the sorbent washed with water (Option 3, Elga™) into an empty, solvent rinsed solid phase extraction (SPE) reservoir (International Sorbent Technologies) and dried using nitrogen. The membranes were discarded. SPE sorbents were eluted with 6 mL of methanol followed by 6 mL of acidified methanol (0.1% formic acid) before evaporation under nitrogen. 100µL aliquots were subsequently derivatisatised using 100µL N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide with 1% tert-butyldimethylchlorosilane (Sigma-Aldrich) at 60 °C for 30 mins. One µL of each sample was injected into an Agilent gas chromatograph (GC) fitted with a 30 m × 0.25 mm, 0.25 µm film thickness DB-5MScolumn (J&W Scientific) with helium as the carrier gas. The Injection was splitless at a temperature of 240 °C. The initial temperature of 60 °C was held for 2 min, followed by an increase of 5 °C/min to 300 °C, and held at this temperature for 10 min. The high-resolution time-of-flight mass spectrometer (TOF-MS, GCT Premier, Waters) was operated in full scan positive electron impact mode with a scan range of 50-1000 m/z. Accurate mass spectra to 4 decimal places was used for peak identification with an error threshold of 4 mDa, and the resolving power was >8500 at m/z 614. The NA were identified

based on the generalised formula $C_nH_{2n+z}O_2$ as described in the introduction. A more detailed description of the analytical method is provided elsewhere [9].

RESULTS AND DISCUSSION

Robust quantitative methods for analysis of NA in PW are not currently available. This is not least due to the complexity of the NA fraction, resulting in an overall inability to adequately separate and identify most compounds, despite recent progress using GC-GC methods [18]. In addition there is a lack of sampling rates for individual NA for POCIS, which prevents conversion of accumulations to time integrative water concentrations. Results are therefore presented and discussed as relative instrumental responses, and discussions of which stations appeared to show the highest levels etc. are purely descriptive. The configuration of POCIS used in the current study was shown to be able to accumulate a homologous series of C7-C14, mono to tetracyclic NA, with monocyclic acids being the most abundant. It is possible that larger, less hydrophilic NA, are less readily accumulated in POCIS. In addition they may be less present in the dissolved phase and thus less available for sampling, and may also more readily accumulate in the PES membrane. These issues need to be confirmed in laboratory studies, although the overall pattern in POCIS is highly similar to an earlier characterisation performed directly on PW extracts [9] without the potential extraction selectivity of using POCIS. The relative percent difference (n=2), between individual POCIS averaged <30% and was highest for the least abundant, larger NA, where detection limits were approached. The highest relative abundances were shown at Station 2, 500 m from the discharge point, followed by station 3, 1000 m from the discharge point (Figure 2). Lower concentrations at station 1, which was also 500 m from the discharge point suggests this station was not directly in line with the dominating plume

direction. Weather driven deviations in prevailing currents are difficult to predict and have occurred in a similar survey in 2004 [2] hence the reason for having two stations close to the discharge point (Figure 1). Relative levels at 2000 m and also at 1000 m in the opposite direction to the prevailing currents (stations 7 and 5, respectively) were noticeably lower, with fewer types of NA detected.

There was good agreement between the pattern of NA shown by POCIS and biomarker results in co-deployed blue mussels, both showing station 2 and then 3 as having the greatest exposure, and the lack of exposure at station 1 [17]. These biomarker results are summarised as an integrated biological response index (IBR), which allowed the integration of biochemical, genotoxicity and histochemcial biomarkers, and are described in detail elsewhere [17]. It is important to note here that the similarity between these results does not mean that the biological effects observed are caused by the NA. For example, whole mussel analysis for PAH also showed a similar pattern with the highest exposure at station 2 [17]. It is reassuring however that POCIS shows the same pattern of exposure relative to the PW discharge point as do the combined biological results, despite the lack of quantitative analysis and sampling rate data.

Whilst it is not currently possible to derive water concentrations of NA from POCIS uptake, AP accumulated in POCIS deployed alongside those reported in the present study can be calculated, as suitable calibration data is available [19]. These results together with those from four similar monitoring surveys (2006, 2008, 2009 and 2012) at comparable locations, estimate concentrations of AP to vary between ca. 20-200 ng/L (∑C1-C9AP) at sampling points <1000 m from the discharge, with the lower substituted compounds (C2 and C3) dominating [10, 11, 16, 17]. Whilst the total organic acids discharged in all the PW

129 from the Norwegian sector is several orders of magnitude larger than that of AP (and PAH),
130 the majority of this total is made up of simple compounds such as acetic acid, as mentioned.
131 For example in 2011 the oil field in the present study was estimated to discharge 1559 tons
132 of organic acids in PW, of which 1345 were acetic acid and 17 were defined as NA. Based on
133 the total amount of PW discharged over the same period this equates to a concentration of
134 approximately 1 mg/L in the raw effluent. In comparison this was roughly 2 mg/L for AP and
135 thus it may be hypothesised that concentrations of NA in the receiving waters are also
136 roughly half those given for AP above (10-100 ng/L).

137 Process waters from other locations have shown significantly higher levels of NA, for
138 example in the range of 24-68 mg/L in the Athabasca Basin in north eastern Alberta [8].
139 Interestingly, much of the available risk assessment information concerning NA comes from
140 these areas where NA are released in large quantities to freshwater aquatic systems
141 following steam extraction of hydrocarbons from bituminous sands. Due to their high water
142 solubility (relative to the more hydrophobic components present), they are driven towards
143 the water phase and have consistently been shown to be toxic to a range of aquatic
144 organisms in the freshwater environment, including fish, zooplankton and bacteria [20].
145 Toxicity studies concerning marine organisms are largely lacking, however it was recently
146 reported that NA represent as much as 65% of the estrogen receptor (ER) agonist potency
147 in North Sea PW, while also disrupting the binding of androgen receptor (AR) agonists [9].
148 Further laboratory studies are required in order to assess the potential for these and other
149 effects of NA, at relevant concentrations. The overall effects of these compounds on the
150 environment are not known, but ongoing work is focussing on identification of the most
151 abundant compounds and their toxicity.

Improvements in cleaning technologies available offshore will continue to reduce the quantity of oil present in PW discharges and thus the concentrations of toxic and bioaccumulative hydrophobic compounds released into the environment. These technologies are however not so efficient at removing more polar contaminants such as NA and so as the overall volume of PW increases in line with the age of the wells (more water required to maintain well pressure as oil is removed), so might the quantities of polar compounds released [10]. In addition, in the Norwegian sector, prospecting and development is occurring in areas considered particularly sensitive. Thus as well as concerns surrounding the consequences of an acute oil spill, an understanding of the effects of chronic exposure to oil components is also of critical importance. In this regard it is important to take into account all of the potentially toxic components of operational discharges including NA.

CONCLUSIONS

The OASIS HLB version of POCIS was shown to be suitable for screening produced water originating NA in situ, when analysed using the described GC-TOF-MS method. Predominantly mono-cyclic NA were accumulated in POCIS deployed in the receiving waters surrounding the offshore oil installation. The pattern of exposure relative to discharge at different sites was similar between NP in POCIS and as the integrated biomarker ratio in blue mussels reported elsewhere. Thus POCIS may be used to confirm exposure to NA in similar surveys. In addition POCIS may be a useful tool for monitoring NA contamination of freshwaters in relation to non-conventional hydrocarbon extraction, such as from bituminous sands. However, POCIS calibration data and analytical method

development are required in order to achieve quantitative results, which may then be used to infer the potential for biological effects.

Acknowledgement

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240 FIGURE CAPTIONS

241

242 Figure 1. Sampling stations in relation to discharge point (X). Closed numbered circles are stations where

243 POCIS were deployed, open circles only biological sampling (reported elsewhere). Prevailing current directions

244 shown in light grey for illustration purposes. Station 9, was lost.

245 Figure 2. Relative instrumental response of naphthenic acids detected in POCIS near an offshore oil

246 installation, where C = number of carbons and Z=-2 (monocyclic); -4 (bicyclic); -6 (tricyclic); -8 (tetracyclic)

247 Naphthenic Acids. Where several groups of similar compounds are shown these are distinguished by their

248 retention time. Distance of stations (ST) from the discharge point shown in m. BL= blank POCIS.

Figure 1

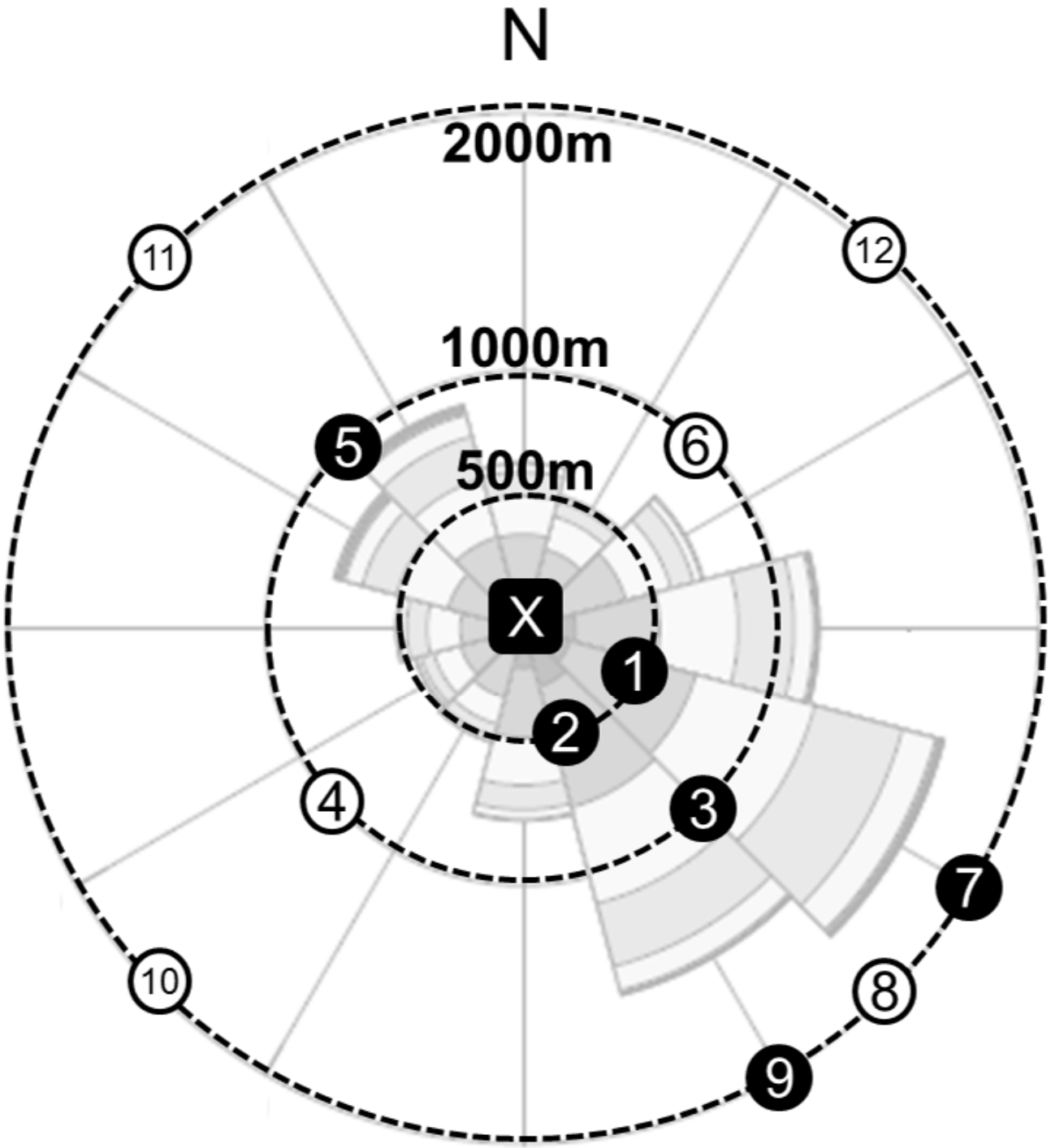
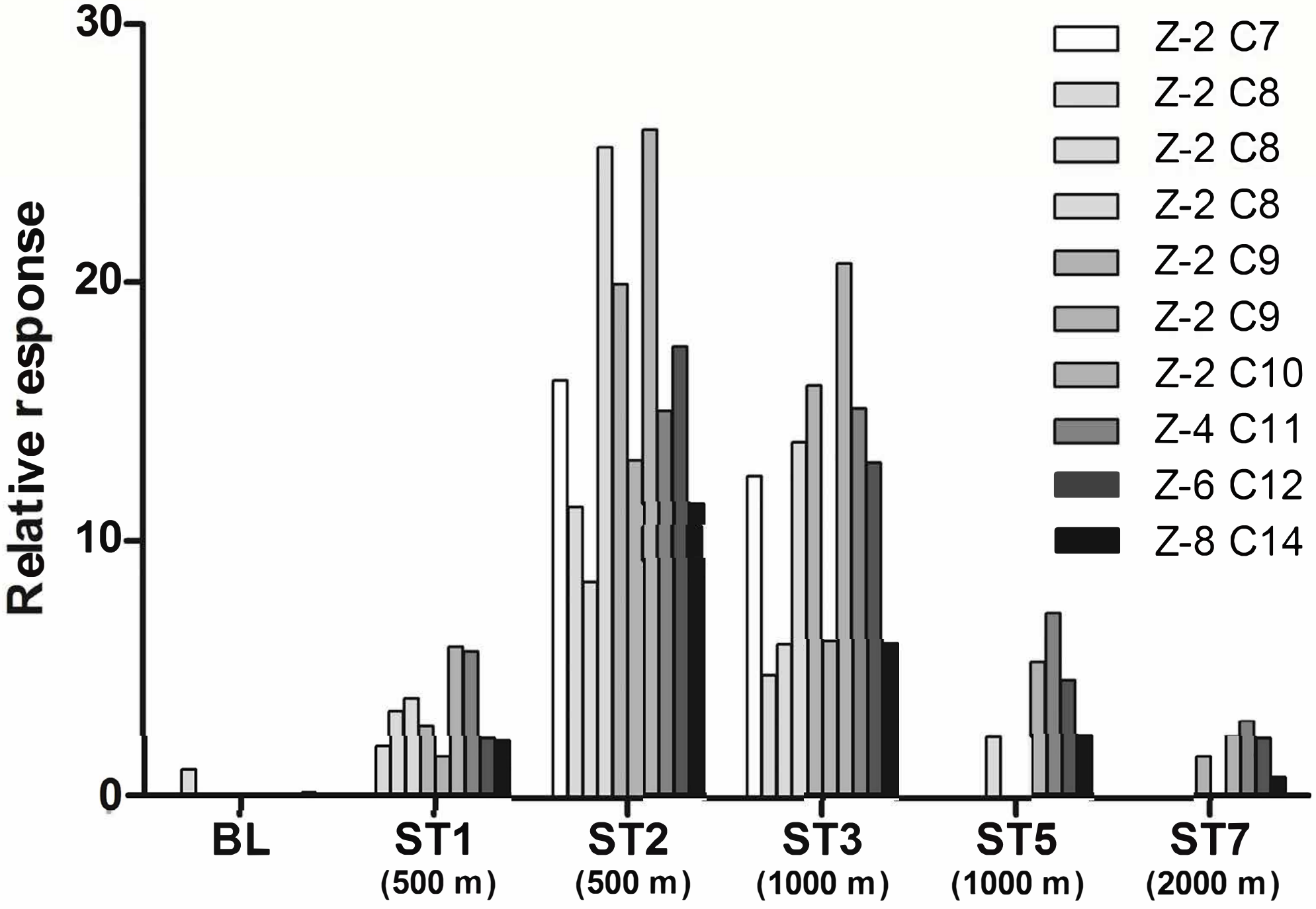


Figure 2


30
20
10
0
Relative response
Z-2 C7
Z-2 C8
Z-2 C8
Z-2 C8
Z-2 C9
Z-2 C9
Z-2 C10
Z-4 C11
Z-6 C12
Z-8 C14
BL
ST1
(500 m)
ST2
(500 m)
ST3
(1000 m)
ST5
(1000 m)
ST7
(2000 m)