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Environmental risk assessment of accidental marine spills: A new approach combining an online dynamic Hazardous and Noxious substances database with numerical dispersion, risk and population modelling

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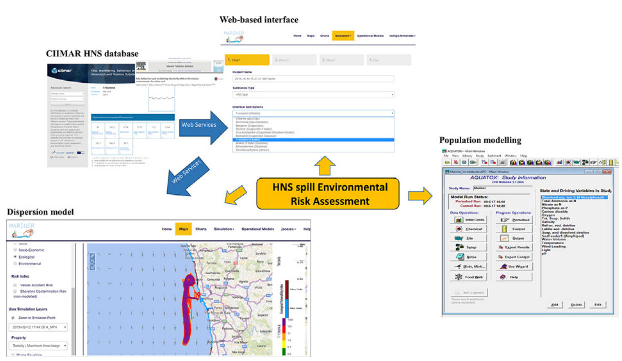
HIGHLIGHTS

- Development of a web-based tool for modelling HNS environmental impact
- Update of a physicochemical and ecotoxicological dynamic online HNS database
- Coupling of HNS numerical dispersion model with its ecotoxicological risk
- Development of a population model, foreseeing HNS ecological impacts

GRAPHICAL ABSTRACT



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ABSTRACT

The foreseen rise on maritime transportation of Hazardous and Noxious Substances (HNS) increases the likelihood of accidents, leading to a higher risk of chemical spillage that can have severe ecological impacts. Considering the lack of information on HNS spills, the response to these events is less well established than those involving oil. Moreover, a paramount knowledge of the physicochemical and ecotoxicological properties of the substance involved is required for an effective environmental risk assessment and response to an HNS spill. In the present work, a new online interface, in which a dynamic HNS database feeds a chemical numerical dispersion model, was developed with the aim to improve predictions regarding the behaviour and environmental risk of HNS spills on marine ecosystems. Potential impacts to pelagic organisms were characterized by coupling model outputs with toxicity risk ratios. Furthermore, a simple population model was developed, foreseeing impacts at the ecological level. The integration of the developed tools establishes an innovative framework, which aims to improve predictions related to HNS plumes' behaviour and potential hazards to the marine environment and associated

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Population modelling

ecosystem services. Further, this new approach fosters an improved preparedness and response to coastal pollution incidents, enhancing effective decision making and management by competent authorities.

1. Introduction

The increase in the maritime transportation of Hazardous and Noxious Substances (HNS), combined with the need for an effective acknowledgement of HNS spills, led the scientific community to create the OPCR-HNS Protocol (The Protocol on Preparedness, Response and Co-operation to Pollution Incidents by Hazardous and Noxious Substances), that aims to foster an improved response to HNS spillages (International Maritime Organization, 2000; Neuparth et al., 2012). However, many gaps still exist in the preparedness and response to HNS spills. According to the International Maritime Organization (IMO), only three of the twelve EU members that ratified the OPRC-HNS protocol have claimed to have specialized ability to respond to HNS spills (International Maritime Organization, 2000; International Maritime Organization, 2010). Furthermore, considering the paucity of available information, knowledge of the ecological hazards caused by HNS spills are still less well recognized and understood than those involving oil pollution (Neuparth et al., 2014; Cunha et al., 2015).

One of the most important potential impacts of an accidental spill of chemicals in the marine environment is the ability of the spilled compounds to elicit a toxic effect within the receiving ecosystem and, ultimately, on human health. HNS exhibits a wide range of behaviours (i.e. they can sink, float, evaporate, dissolve, adsorb to sediments, as well as display a combination of these behaviours) and, consequently, an ample spectrum of toxicity to organisms is expected (Cunha et al., 2017). Nevertheless, a fundamental information gap still exists regarding the behaviour of HNS once spilled at sea, as well as their local environmental impacts. HNS potential effects can be anticipated by investigating the toxic hazards associated with specific chemicals and through integrated risk assessment analysis. Modelling is an essential component of environmental assessment, as it can help mentor and scale the mobilization of resources, prioritize protection or mitigation actions, and support management decisions (Castanedo et al., 2006). Previously, oil spill models have proven useful in pre-planning emergency responses (Mearns et al., 2001, 2003; Neuparth et al., 2011; Spaulding, 2017) as well as in natural resource damage assessment (French McCay, 2003; French-McCay, 2004). French-McCay (2002, 2003, 2004) describes such models of coupled oil fate and effects for the evaluation of short-term oil spill impacts to habitats, wildlife and aquatic organisms. Bejarano and Mearns (2015) have integrated oil trajectory modelling with Species Sensitivity Distributions (SSDs) to facilitate the quantification of potential short-term adverse effects to entrained water column organisms (proportion of species affected).

Concerning HNS spills, immediate decisions regarding the safety, containment and recovery of the chemical spill, as well as medium- and long-term decisions related to HNS environmental impact need to be well-founded. Chemical dispersion models, although scarcer than oil spill models, have also been developed. For example, CHEMMAP, developed by Applied Science Associates, predicts the trajectory and fate of a wide variety of chemicals products, forecasting expected water concentrations and atmospheric flux for real events (French MacCkay, 2001). Stochastic applications for ecological risk assessment of chemical spills are also included in CHEMMAP (French MacCkay, 2001). In this case, concentrations are compared to ecological endpoints to determine areas of potential ecological impact, considering acute toxicity data (French McCkay et al., 2006).

While thus far discussions have focused on potential acute toxicity (mortality) to aquatic species, it is important to recognize that chemical spills, generally, involve large volumes of substances, and can last from few days to several weeks, highlighting the importance of considering chronic sublethal toxicity (e.g. growth, reproduction), especially for species with short life-cycles (few days), which usually constitute the basis of the food web chains. In these cases, potential effects at traits with outcomes at the population level could occur, highlighting the importance of chronic toxicity data.

In the present work, CIIMAR and Bentley Systems, in the frame of MARINER project, developed a web-based platform to improve the prediction of chemical dispersion integrated with ecotoxicological risk, considering not only the direct impacts in the short-term (acute toxicity), but also sublethal long-term contamination (chronic toxicity). Furthermore, a simple ecological model was also implemented, aiming at foreseeing HNS ecological impacts at the population level. The linkage of the developed tools into a unique framework innovatively fosters spill preparedness and decision-making, contributing to an effective HNS spill response and management.

2. Material and methods

2.1. Physicochemical and ecotoxicological HNS database

Having identified that for many HNS there was no basic information about their behaviour or effects on the environment, CIIMAR, under the EU projects ARCOPOL platform and MARINER, has developed an online database designated “Fate, weathering, behaviour and toxicity of priority Hazardous and Noxious Substances” (Cunha et al., 2016), which can be consulted at https://www.ciimar.up.pt/hns/substances.php.

Based on a weigh-of-evidence approach, twenty-four priority HNS were identified (Neuparth et al., 2011) and the parameters that rule the chemicals behaviour in water (e.g. physical state, relative molecular mass, density, vapour pressure, water solubility, melting and boiling points) and those that determine their distribution and persistence in the environment, such as fugacity, physicochemical degradation, biodegradation and bioaccumulation/biotransformation were provided in the database (Cunha et al., 2016).

At the present work, the HNS database was further upgraded with literature data regarding HNS toxicity and ecotoxicity criteria were derived as a proxy to improve HNS Environmental Risk Assessment (ERA). A new web service (described in Section 2.1.1) was also associated to this database, to facilitate the linkage to online systems.

ERA, as described in EU Technical Guidance Documents (European Commission, 2003; European Chemicals Agency, 2008), is a process of predicting whether there may be a risk of adverse effects on the environment caused by a chemical substance. This involves: i) determining a predicted no-effect concentration (PNEC), derived from ecotoxicity data and the application of assessment factors (AF) (effects assessment); ii) the calculation of a predicted exposure concentration (PEC) (exposure assessment) and iii) risk characterisation, which involves the calculation of a quotient - the PEC/PNEC ratio, herein RQ (risk quotient). Regarding the aquatic compartment, ERA implies a base dataset that encompasses test results, representing acute and chronic aquatic toxicity, of at least three trophic levels represented by algae (primary producers), invertebrates (primary consumers) and fish (higher level consumers and predators). In acute (short-term) tests, the 96 h LC_{50} (the concentration that causes 50% mortality of the test species) is usually determined for fish and crustaceans, the 48 h EC_{50} (the concentration of a substance which produces a 50% response in the defined endpoint) is determined for the commonly used freshwater crustacean *Daphnia sp*. (based on immobility), while the 72/96 h

EC_{50} (reproduction and/or growth) generally applies to microalgae (GESAMP (IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection), 2014). The same process is used to "classify" sublethal chronic toxicity, which addresses the impact of long-term effects exposure (generally, 21–28 days (d), or even 60 d depending on the species, life stage and assessed endpoints) of aquatic organisms. Chronic toxicity is represented by the NOEC (no observed effect concentration) or equivalent effective concentration, generally, EC_{10}. Nevertheless, life-cycle studies reporting NOEC values are still scarce. In some studies, only LOEC (lowest observed effect concentration) can be obtained, in which case NOEC can be calculated as LOEC/2. The lowest of the available toxicity values ($LC(E)_{50}$ or NOEC) within and between the different trophic levels is used as the ecotoxicological dose descriptor that through division by an AF allows PNEC derivation utilized in hazard assessment (PNEC = lowest ecotoxicological dose descriptor / AF). The AF reflects the degree of uncertainty in extrapolation data from laboratory tests for a small number of species to the actual ecosystem scenario. Taking in consideration saltwater, to which available biological data are meagre comparing to freshwater, when only short-term toxicity data are available, an AF of 10.000 is applied on the lowest $L(E)C_{50}$ of the relevant available toxicity data, irrespectively of whether or not the species tested is a standard test organism. A lower AF of 10 is applied on the lowest EC_{10} or NOEC derived in long-term tests with relevant test organisms of three different trophic levels and two additional marine taxonomic groups (European Chemicals Agency, 2008). AF applied for long-term tests are smaller as the uncertainty of the extrapolation from laboratory data to the natural environment is reduced and for this reason, long-term data are preferred to short-term data (European Commission, 2003). Furthermore, if a large data set from long-term tests for different taxonomic groups is available statistical extrapolation methods may be used to derive a PNEC, e.g. use of SSDs. In this case the PNEC is calculated as: *PNEC = 5% SSD (50% confidence interval) / AF*. An AF between 5 and 1 is used, reflecting the further uncertainties on the basic considerations and minimum requirements defined when using the SSD (e.g. input data, taxonomic groups, minimal sample size, fit to a distribution, estimated parameter) (European Commission, 2003). An asset of this method is that it utilizes the bulk sensitivity distribution of species in an ecosystem to derive a PNEC rather than ever choosing the lowest long-term NOEC. Nevertheless, prevailing drawbacks are the lack of transparency by using this method related to the standard approach, the question of representativeness of the elected test species, the comparability of distinct endpoints, the discretionary selection of a specific percentile and a statistical confidence level (European Commission, 2003). The outstanding species diversity in the marine environment, compared to freshwaters, including the existence of diverse taxa that occur entirely in that environment, may signify that the distribution of sensitivities of species is broader, reflecting a greater uncertainty in the extrapolation. At the present work, which is based on the application of ERA in the marine context, the choice of the most sensitivity species is used as precautionary approach since in most cases insufficiency of data for further taxonomic groups (e.g. rotifers, echinoderms or molluscs) rises the unpredictability in the extrapolations. Thus, it is assumed that the ecosystem sensitivity depends on the most sensitive species and that protecting ecosystem structure protects community function as well (European Commission, 2003). A leverage of the conferred approach is that it is exhaustively supported by quantitative data of reliable studies (assessed on EU reports), widening the confidence of the environmental assessments.

Furthermore, data from freshwater aquatic toxicity tests are acceptable for evaluation in the case of absence of marine data since the molecular processes governing bioaccumulation and non-specific "baseline toxicity" effects are usually the same for marine and freshwater organisms (GESAMP (IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection), 2014), at least for the typical aquatic taxa (i.e., fish, crustacea, algae). Where discrepancies in the probable sensitivity of freshwater and marine biota were observed for individual compounds, such differences were consistently within a factor of 10 (European Commission, 2003). In such circumstances, the utilization of pooled data is recommended and PNECs should be derived from the most sensitive endpoint disregarding of the medium. Noteworthy, a lower/higher factor may be considered according to the knowledge of the substance's mode of action (e.g. non-specific mode of action or, on the other hand, indications of bioaccumulation potential or other adverse effects according toxicity studies, such as endocrine disorders, etc.).

During the step of effects assessment, it is very important to evaluate data regarding their adequacy and completeness. In this work, $LC(E)_{50}$ and NOEC data were identified from peer-review valid studies relating to the reliability of the available data and the relevance of that data for ERA. Preference was given to studies carried out according to good laboratory practices (GLP) and internationally validated standard test guidelines, such as those provided by the Organization for Economic Co-operation and Development (OECD), the International Organization for Standardization (ISO), the US Environmental Protection Agency (USEPA) and the American Society for Testing and Materials (ASTM) for each trophic level (algae, invertebrates and fish). When ecotoxicological data for a specific HNS were missing, those were predicted using ECOSAR (Ecological Structure Activity Relationships model, U.S. EPA), which predicts the potential toxicity of chemicals to aquatic organisms. The model uses measured data to predict the toxicity of chemicals for which no data exist, using Structure Activity Relationships (SARs) and Quantitative Structure Activity Relationships (QSARs) (Mayo-Bean et al., 2017). The PNECs were then derived from the lowest ecotoxicological dose descriptor divided by the respective AF, privileging NOEC values whenever available, for each of the twenty-four priority HNS. Apart from the majority of the published works, which focus on potential acute toxicity of chemical spills, this work has given preference to chronic aquatic toxicity data since, as previously mentioned, long-term toxicity tests values reduce the ambiguity of the extrapolation between laboratory and real environmental data. Also, chronic toxicity is a crucial component of aquatic hazard evaluation, as it considers the influence of: i) operational discharges from ships in heavily used shipping lanes, particularly near specially protected marine areas; and ii) accidental spills from ships where the timescales involved may be longer than expected, bearing in mind the potentially large volumes involved (GESAMP (IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection), 2014).

In several situations, chemical discharges are discontinuous in time and/or occasional, i.e. released to the environment from industrial sources as a result of batch, which means that environmental exposure will be temporally constrained. At least for dynamic systems such as estuaries, the probability of long-term effects emerge in such cases is minor, the principal risk being that of short-term toxic effects. Thus, the lowest $L(E)C_{50}$ of at least three short-term tests from three trophic is used to derive a $PNEC_{water,intermittent}$, through application of an AF of 100 (European Chemicals Agency, 2008). This extrapolation should be carried out with care as substances may be taken up rapidly by aquatic organisms, leading to delayed effects even after exposure has ceased. This will generally be considered by the assessment factor of 100 but there may be occasions when a higher (e.g. chemicals with potential to accumulate) or lower AF (e.g. substances with a known non-specific mode of action) would be appropriate (European Commission, 2003).

The updated HNS database was then dynamically linked to a new web-based interface (described in the next Section 2.1.1) to facilitate the linkage to online systems, specifically a numerical dispersion model for HNS, providing by this way the physicochemical characteristics of the compounds, which affect their behaviour in the water, and the HNS ecotoxicity data. As it is, any new update on the HNS database (i.e., any field modification or new chemical products included) become automatically available for selection in the web-based interface for spill simulation.

2.1.1. Web-based tool for modelling HNS environmental impact

A novel and integrative online interface was designed in a responsive and cross-platform fashion, supported by commonly used interoperational web services and standards, like OGC (Open Geospatial Consortium) and REST API (Representational State Transfer Application Programming Interface). The REST API established for the platform represents a web service that allows to query database data from the backend servers. In the platform the on-demand simulations are saved in backend database and their results and location (e.g. oil, chemical and toxicological properties for each instant) are retrieved to the online platform, via the REST API, so it can be plotted on map and chart formats.

The web-based tools provide an interactive way to i) predict, in real time, the fate and behaviour of a user-defined chemical (from the dynamic HNS database) during the spill and its associated ecotoxicological risks; ii) depict the current and forecast results for the next hours-days for meteorology and meteocean conditions, and specific indices with high-resolution coastal sensitivity; and to iii) run on-demand pre-established spill scenarios, and verify their evolution and impact in time, which is essential for spill preparedness. Three different sensitivity indices were included: a socio-economic index (related with the potential social and economic consequences), an ecological index (related with potential damage to highly significant biological and ecological resources), and an environmental (coastal) index (related with the generic shoreline environmental vulnerability to oiling and easiness of clean-up and restore operations, mainly influenced by geomorphologic and morphodynamical aspects of the shore). These indices were developed and updated in different projects, including EU R&D projects EROCIPS and ARCOPOL platform (Fernandes and Santos, 2018). The drift and behaviour components were developed prior to this project (Fernandes, 2014; Fernandes et al., 2016), while the risk assessment was fully implemented in the course of MARINER. The platform can be consulted at http://mariner.actionmodulers.com/, where both maps, charts and on-demand components of the web-based tools are explained and exemplified with video tutorials. Access to spill modulations were decided to be restricted by the MARINER project consortium to the competent authorities, such as the Portuguese Maritime Authority, port authorities and others, for emergency management and preparedness. Public access is presently restricted to avoid an alarming overrate and circulation of misleading information in a situation of crisis by the general public and/or media. However, access can be requested by the general public, and the request evaluated by the consortium before granting it for a limit period.

2.1.2. HNS drift, behaviour and risk numerical model

The chemical spill modelling software used is the chemical spill component of the MOHID modelling suite. MOHID is a public-domain open-source system, developed following a modular structure combined with object-oriented programming (Neves, 2013). The model is freely available for public access, following a FOSS (free/open source software) strategy. MOHID has been applied to different study cases, as coastal and estuarine areas, as well as oceanic processes and reservoirs, and it has shown its ability to simulate complex features of the flows (Ascione Kenov et al., 2014). For example, MOHID lagrangian module has been widely used not only in oil spills (Fernandes and Santos, 2018; Balseiro et al., 2003; Janeiro et al., 2008; Mateus and Fernandes, 2008; Fernandes et al., 2012), but also in sediments transport, harmful algal blooms (Mateus et al., 2012), fish larvae (Nogueira et al., 2013), residence time in estuaries (Braunschweig et al., 2003), faecal contamination in bathing waters and plume diffusion and dispersion (near and far field) in the water column from submarine outfalls or rivers (Miranda et al., 1999; Viegas et al., 2012). Input data and algorithms are according to the existing bibliography from different models and the approach is quite similar to the methodology adopted from other models. i.e. RPS, ASA, CHEMMAP. Documentation on detailed equations for this model can be found on software manuals (which are not available for public), as well as (French McCay, 2003; French-McCay, 2004; French-McCay, 2002; French MacCkay, 2001; French McCkay et al., 2006). MOHID chemical spill module is a recent implementation inside MOHID (Fernandes, 2014; Fernandes, 2017). Integrated in the lagrangian component of the model (Ascione Kenov et al., 2014), the spilled mass is tracked through phase changes and transport, with all reaction products assumed to move together – chemical reactions are not specifically addressed in the model. The loss of chemical by reaction to some other form no longer of concern is included in degradation, which is estimated assuming a constant rate of "decay" specific to the environment where the mass exists (i.e., atmosphere, water columns or sediment). The model estimates the distribution of chemical (as mass and concentrations) on the water surface, on shorelines, in the water column, at the bottom and in sediments. The model tracks separately surface floating chemical, entrained droplets or suspended particles of pure chemical, chemical adsorbed to suspended particulates, and dissolved chemical. The phase changes are computed independently for each particle every time-step, and the probabilities of one particle changing from one phase to another (e.g. entrained to dissolved) is (pseudo-)randomly obtained, based on the algorithms that quantify the mass balances in the different processes. Therefore, a correct modelling using this kind of approach requires a great number of particles in the simulation, in order to properly reproduce phase changes when slow processes/small mass transfers are involved.

Chemical mass is transported in 3D space and time. The horizontal movement is controlled by currents, wave-induced velocity (Stokes Drift), wind-drift velocity in the surface layer (for floating substances), spreading, and horizontal turbulence. The vertical movement is estimated in accordance with vertical advection from currents, rising velocity, sinking velocity, and turbulent dispersion. Full details can be found in (Fernandes, 2014; Fernandes, 2017). A calibration was made with CHEMMAP (Fernandes, 2014) and results have shown good agreement.

Effects to the water-column organisms were assessed taking into consideration a time-varying approach, in which predicted chemical concentrations (PEC) at each time post-spill release were compared to specific time toxicity data. This approach considers the expected spatial and temporal chemicals fate and weathering, considering in real-time high resolution meteocean conditions (e.g. wind and current variations), being environmentally realistic. Regarding ERA modelling, the RQ (PEC/PNEC ratio), is calculated to measure the scale of risk: a value above 1 indicates risk. Different conclusions may apply on the basis of the risk characterisation: $RQ \leq 1$ presently there is no risk, while a $RQ > 1$ may indicate that there is need for further information and/or testing, or that risk reduction measures are necessary (European Commission, 2003). This scale of risk can be classified as such: between 1 and 10 risk is of lower concern, between 10 and 100 additional data are needed, over 100 is of major concern, and measures to minimize the risk to the environment should be demanded.

2.2. Population modelling

Aiming a higher tier risk assessment approach and a better projection of HNS ecological effects, a population model was developed for the amphipod *Gammarus locusta*, which was selected due to its ecological relevance in the EU Atlantic coast. This epibenthic species has a wide geographical distribution along the northeast Atlantic, being among the main preys of several invertebrates, fish and birds (Neuparth et al., 2014). Furthermore, *G. locusta* is recognized as a relevant test organism in ecotoxicological studies due to its sensitivity to a wide variety of contaminants, while essential ecotoxicological data is available in the literature (Neuparth et al., 2014; Barros et al., 2017). Notably, epibenthic amphipods are sensitive to contamination both in the sediments and overlying water which is advantageous. Furthermore, standardized water tests exist for *Gammarus spp*. (Péry et al., 2005; U.S. Environmental Protection Agency, 2016).

The present model is a simple and theoretical approach developed with the main aims of to assess the effects of three concentration levels (low, medium and high) of a priority HNS on an amphipod population and to predict its recovery time under the different scenarios, without resource limitation (non-limited).

The model was implemented with AQUATOX release 3.1 plus developed by the U.S. EPA. AQUATOX is a simulation model for aquatic systems, capable of describing the fate and effects of various compounds (e.g. nutrients, organic chemicals, etc.) on the ecosystem (Clough, 2014; Park and Clough, 2014). The modelled site was a costal marine cell with a surface area of 1×10^4 m^2 and a volume of 1×10^5 m^3. The model forcing functions are concentrations of the dissolved HNS, ammonia, nitrate, phosphate, carbon dioxide, oxygen, total suspended solids and detritus, as well as, salinity, temperature, pH, wind loading, light and water volume.

The variation of *G. locusta* biomass and growth depends on a set of processes (e.g. ingestion, respiration, excretion, mortality) regulated by environmental forcing functions (temperature, salinity, nutrients, pollutants, etc.). For example, the amphipod's ingestion depends on a maximum consumption rate adjusted for conditions of food, temperature, sublethal toxicant effects, and habitat preferences (see Park and Clough, 2014 for details). For simplification sake, *G. locusta* was considered to feed only on detritus and no other trophic interactions were explicitly accounted for. Model parameterization was according to environmental conditions for the northwest coast of Portugal (Supplementary data, Table A1) and whenever possible using species-specific data for *G. locusta* (Supplementary data, Table A2).

The selected HNS was 4-nonylphenol (4-NP) (CAS number 104-40-05), a priority substance in the field of water policy (Annex II of Directive 2008/105/EC (European Commission, 2008)). The model ran for 360 d, with a time step 0.1 d^{-1}. Simulations accounting for the action of HNS on the amphipod population consider the effect of 4-NP for 3 d (2 to 4th of February). The variation of *G. locusta* biomass in the control simulation (without 4-NP) was compared with simulations accounting for 4-NP at three levels of concentration: low (4.5 μg/L), medium (43 μg/L) and high (380 μg/L).

3. Results and discussion

3.1. Case study with the priority HNS 4-nonylphenol (4-NP)

The present case study describes a spill scenario of the pollutant 4-NP in the marine environment, using an improved high resolution meteocean forecasting system. Additionally, the impact of the 4-NP spill on the population growth of a marine amphipod was modelled. The aim was to demonstrate the relevance of the concept of coupling ecological modelling with HNS dispersion models and ecotoxicity data.

CIIMAR HNS database fully characterizes 4-NP. Shortly, 4-NP is a persistent floater, not readily biodegradable, with a water solubility of 0.7 mg/L (25 °C), vapour pressure of 0.0001 KPa (25 °C), dynamic viscosity of 2.5 mPa.s (20 °C), partition coefficient (log Kow) of 5.76 and a bioconcentration factor of 221. Both 4-NP acute and chronic ecotoxicity data are available for three trophic levels. The database $PNEC_{seawater} = 0.033$ μg/L was obtained by dividing the lowest chronic ecotoxicological dose descriptor from a validated study (EC_{10}*Scenedesmus subspicatus* = 3.3 μg/L) (Kopf, 1997) by a factor of 100 (European Chemicals Agency, 2008). Considering that for freshwater a 10-fold lower factor than the marine AF is recognized, the obtained $PNEC_{seawater}$ is comparable to the PNEC value for surface waters (PNEC = 0.33 μg/L) present in an EU Commission report (European Commission, 2005). Altogether, these data fed the interface of the HNS dispersion model, which was used to simulate a 100 m^3 single 4-NP spill (not continuous in time), at the North coast of Portugal, with site-specific input parameters (e.g. depth, wind speed, currents velocity, water temperature, wave properties, atmospheric pressure, etc.). Fig. 1 presents the pre-spill area and the spill occurrence with its initial dispersion point near Leixões harbour (41° 11′ 14″ N, 8° 43′ 0.5″ W), which is a socio-economic area dependent on marine resources and marine-based tourism. The spill simulation trajectory lasted for 3 d (15–17th January 2019), and an initial spill trajectory towards north can be seen, reaching approximately 10.5 km from the initial dispersion point. Afterwards (~38 h post-spill), spill dispersion trajectory inflects towards south for about 29 km. The spill trajectory reflects the predominant currents and winds at the North coast of Portugal during the simulation period. Although figures evidence spill trajectory from the moment of spill release ("0 h") to a specific time-point, momentaneous images of spill dispersion, chemical concentration and ecotoxicological risk at a specific time-point and localization (without the full trajectory) can be obtained, focusing on the specific area affected at that time-point. Nevertheless, for substances that have a potential to bioaccumulate, long-term or delayed effects are possible even if the chemical is no longer in the water and, consequently, delayed effects in the ecosystems after the absence of the chemical cannot be ruled out.

The dispersion model was used to produce outputs containing information on 4-NP trajectory, 4-NP dissolved concentrations in the water column, and the risk quotient (RQ) over space and time. The maximum time-integrated vertical dissolved concentrations (MVDC, mg/m^3) at 6, 24, 48 and 72 h post-release are presented in Fig. 2 (Supplementary data Fig. A1 presents MVDC additional 4-NP spill scenarios over time). Globally, 4-NP concentrations increased in space and time during the spill simulation, ranging from approximately 0.15 to 370 mg/m^3 (0.15–370 μg/L). Within the plume envelope, higher concentrations were registered near the spill trajectory centre, while lower values occurred with the increment in the radial distance from the spill centre (Fig. 2).

The MVDC divided by the derived PNEC allows to assess 4-NP associated dispersion RQ. Derived maximum time-integrated RQ (TMRQ) for the aquatic environment from the presence of 4-NP at the water column from the point of dispersion to its final location was, globally, of major concern (TMRQ >100) (Fig. 3) (Supplementary data Fig. A2 presents TMRQ additional 4-NP spill scenarios over time).

According to an U.S. EPA report (U.S. EPA, 2005), the most sensitive saltwater species to NP was the winter flounder, *Pleuronectes americanus* ($LC_{50} = 17$ μg/L), which was 12.3 times more sensitive than the least sensitive species, the sheepshead minnow, *Cyprinodon variegates* ($LC_{50} = 209.8$ μg/L). Acute toxicity test data (96 h LC_{50}) were also available for several invertebrates, including the marine amphipods *Leptocheirus plumulosus* ($LC_{50} = 61.6$ μg/L) and *Eohaustorius estuaries* ($EC_{50} = 138$ μg/L). Chronic toxicity values, calculated as the geometric mean of the NOEC and the LOEC, were between 5.112 and 12.02 μg/L for mysids (*Americamysis bahia*). Nevertheless, the most sensitive species to 4-NP is a freshwater alga, *Scenedesmus subspicatus* ($EC_{10} = 3.3$ μg/L). Based on model outputs, MVDC from the hypothetical spill reached and surpassed concentrations associated with 4-NP ecotoxic effects to aquatic organisms. Taken together, both MVDC range attained and the above referred ecotoxicity data, are well translated in the obtained RQ. Under the consensus approach, a 24 h exposure to 1000 mg/m^3 (1000 μg/L) of oil would be a medium to high level of concern for sensitive life stages (e.g., (Mearns et al., 2001)). Interestingly, the consensus and the highest dissolved chemical concentration observed (~370 mg/m^3) are within a factor of 2.7, with a TMRQ >100 (major concern) for the respective area.

As evidenced by the ecological vulnerability index, the coastal area of spill occurrence has zones with different ecological sensitivity. Although, 4-NP predicted impacted areas did not reach the shoreline (Figs. 2, 3), the proximity to it may suggest monitoring, especially of the areas with greatest vulnerability. The integration of meteocean plus chemical spill modelling with ecological vulnerability enhances the decision support framework, providing a more realistic approach in the assessment of shoreline impacts, raising immediate awareness

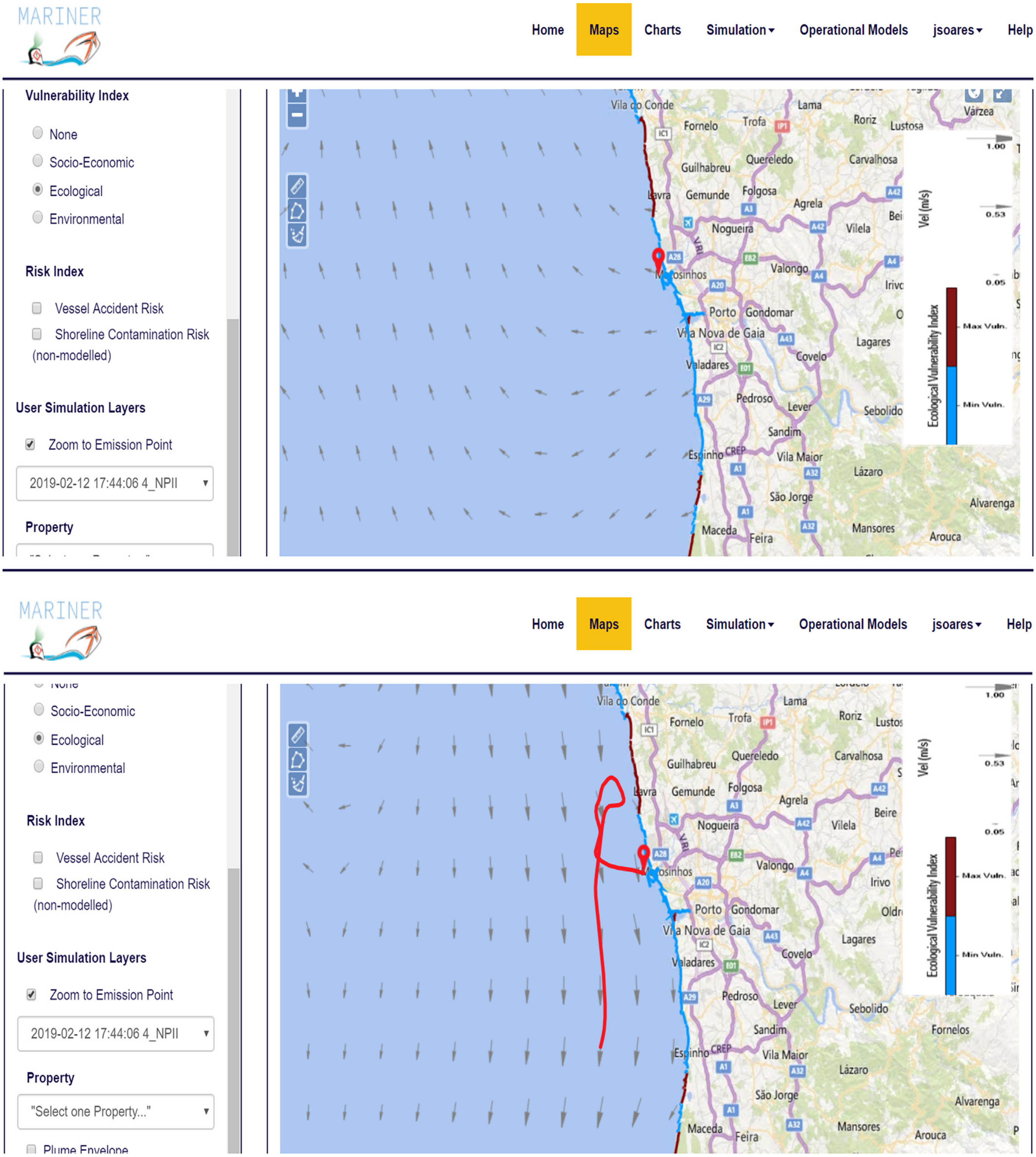

Fig. 1. Pre-spill area and spill occurrence (72 h) (top to bottom). The red circle bullet represents the spill emission point and the red solid line the plume centre trajectory during the 3 d of simulation. The ecological vulnerability index is represented in a contour along the shoreline, grey arrows represent the current velocity (m/s). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for higher risk areas and improving asset and human resources management.

In order to demonstrate the conceptual approach, 3 d simulations were implemented, linking the population model with the HNS hydrodynamic dispersion model. According to the range of 4-NP environmental levels attained after the simulated spill (Fig. 2), three range of 4-NP concentrations were selected to force the population model: low- 4.5 μg/L; medium- 43 μg/L and high- 380 μg/L. Results indicate that *G. locusta* population is not affected at 4-NP concentrations ≤4.5 μg/L and only slightly affected at 4-NP concentration of 43 μg/L (Fig. 4), which is in accordance with the mean toxicity values also found for other marine amphipods L. *plumulosus* (61.6 μg/L) and *E. estuarius* (138 μg/L), following 96 h exposures (U.S. EPA, 2005). For 4-NP concentrations of 380 μg/L, which correspond approximately to the maximum value verified at the coastal area after the spill, the amphipod population shows increased sensitivity with a significant drop in biomass and presenting very low biomass values during some days (approximately 20 d), but still being able to recover through time as 4-NP weathers (Fig. 4). In line with other authors, production losses of lower trophic levels typically are very small because of their short generation times and quick recovery after a spill (French-McCay, 2004). These results must be seen as preliminary due to the present model limitations, namely, the

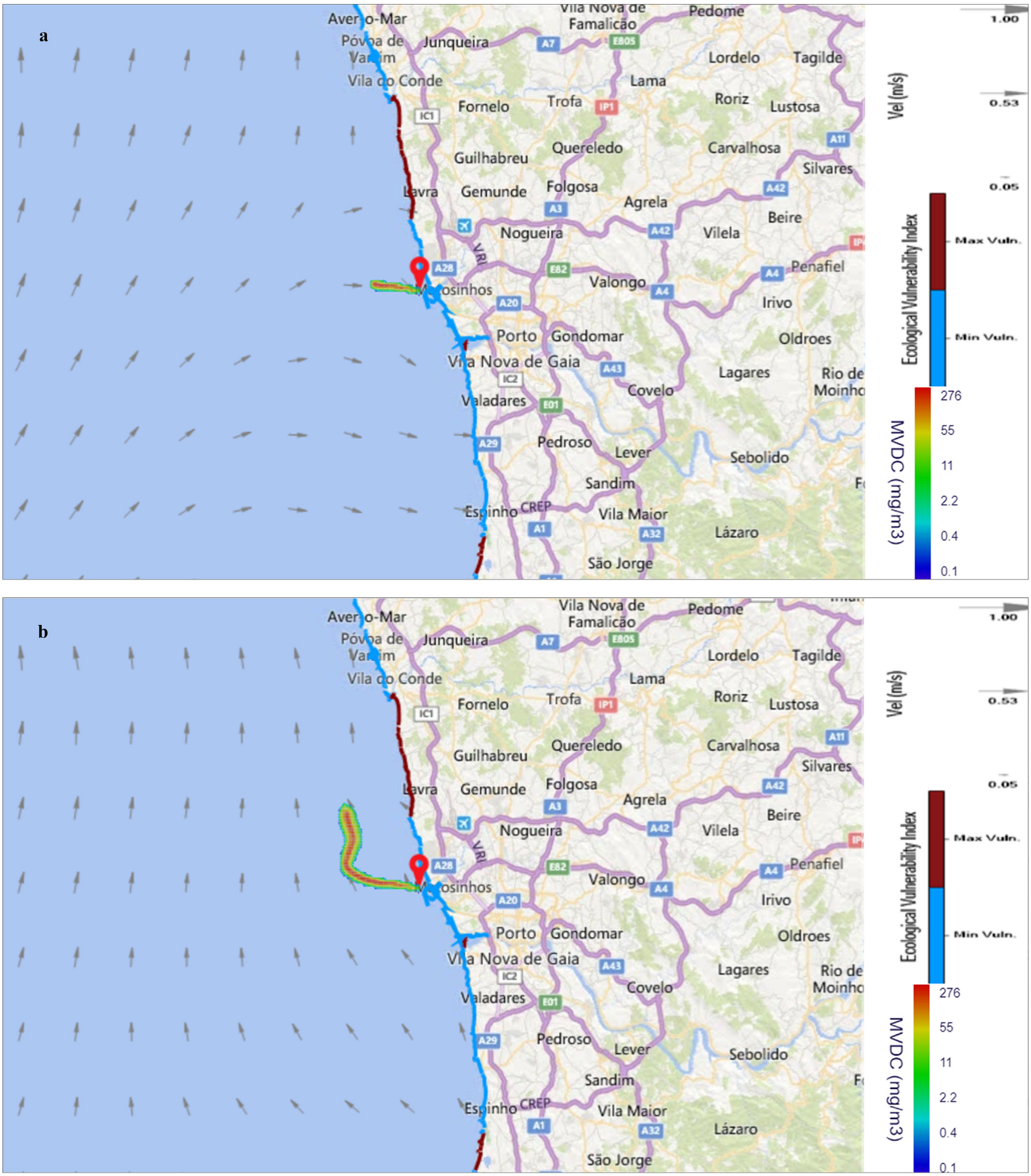

Fig. 2. Maximum time-integrated vertical dissolved concentration (MVDC, mg/m^3) after 6 (a), 24 (b), 48 (c) and 72 h (d) post 4-NP spill simulation. The red circle bullet represents the spill emission point and grey arrows the current velocity (m/s). The ecological vulnerability index is represented in a contour along the shoreline. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

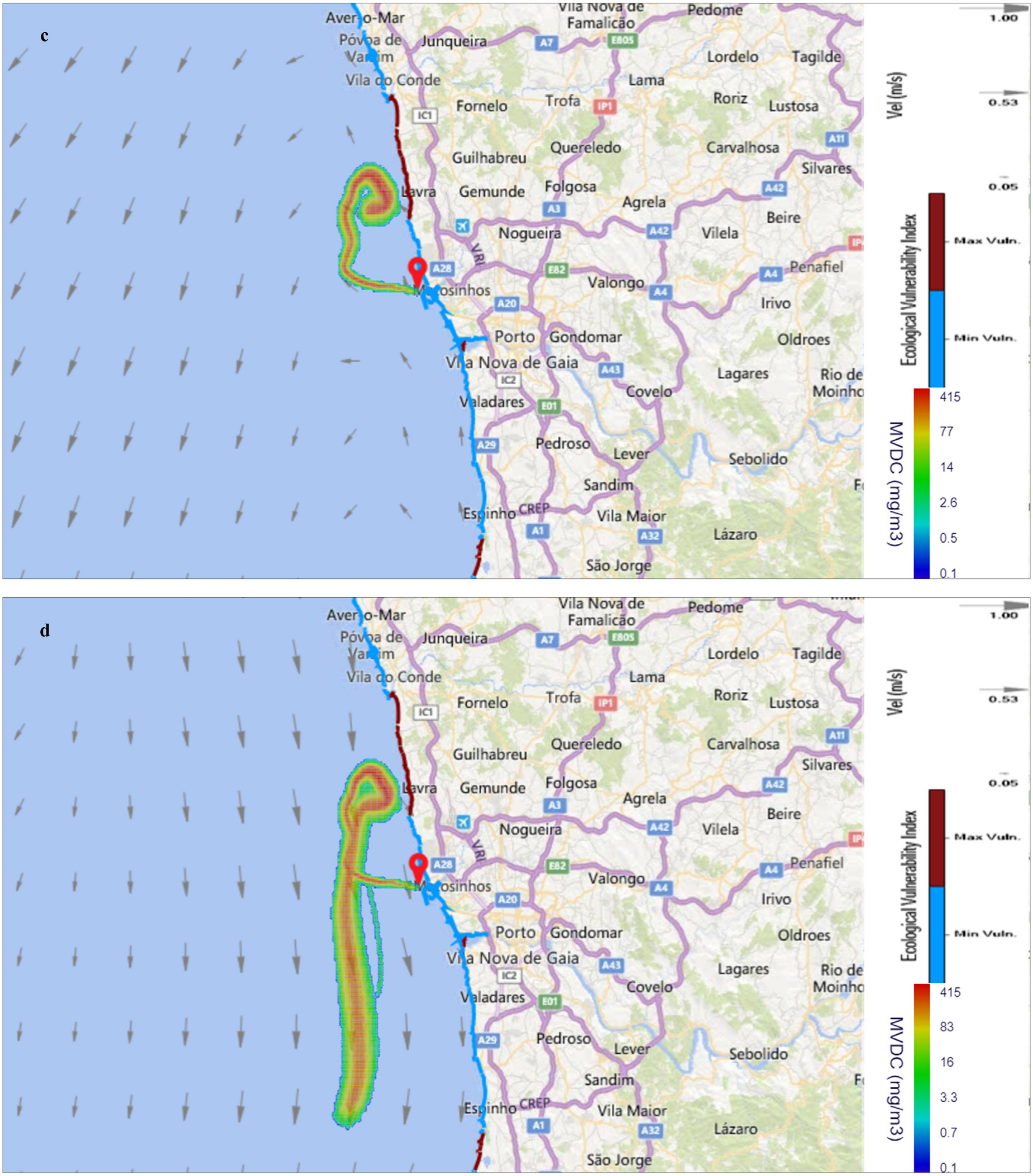

Fig. 2 (*continued*).

application to a single species from the coastal food web, or the need of further calibration. Nonetheless, the linkage of the amphipod population model with the chemical dispersion model, demonstrates the potential of such an integrative approach and the need to further develop this type of hydrodynamic-ecological tools to predict the consequences of HNS spills at the ecosystem level.

4. Conclusions

HNS have a wide range of potential fate and behaviour characteristics once released into the marine environment. Selection of the appropriate response to an incident requires fast, easy and comprehensive knowledge on the physicochemical and ecotoxicological properties of the substance involved. CIIMAR HNS database, which provides this information, was further updated and dynamically linked with an HNS numerical dispersion model coupled with an ecological vulnerability index - all this integration was accomplished through a cross-platform and responsive web interface. The dispersion model (MOHID) estimates the fate and the distribution of HNS in the water, accounting for spreading, evaporation, transport, dispersion, emulsification, entrainment, dissolution, volatilization, partitioning, sedimentation and degradation. Model outputs from MOHID, specifically estimated MVDC in the water column, were utilized to demonstrate the use of RQ in characterizing

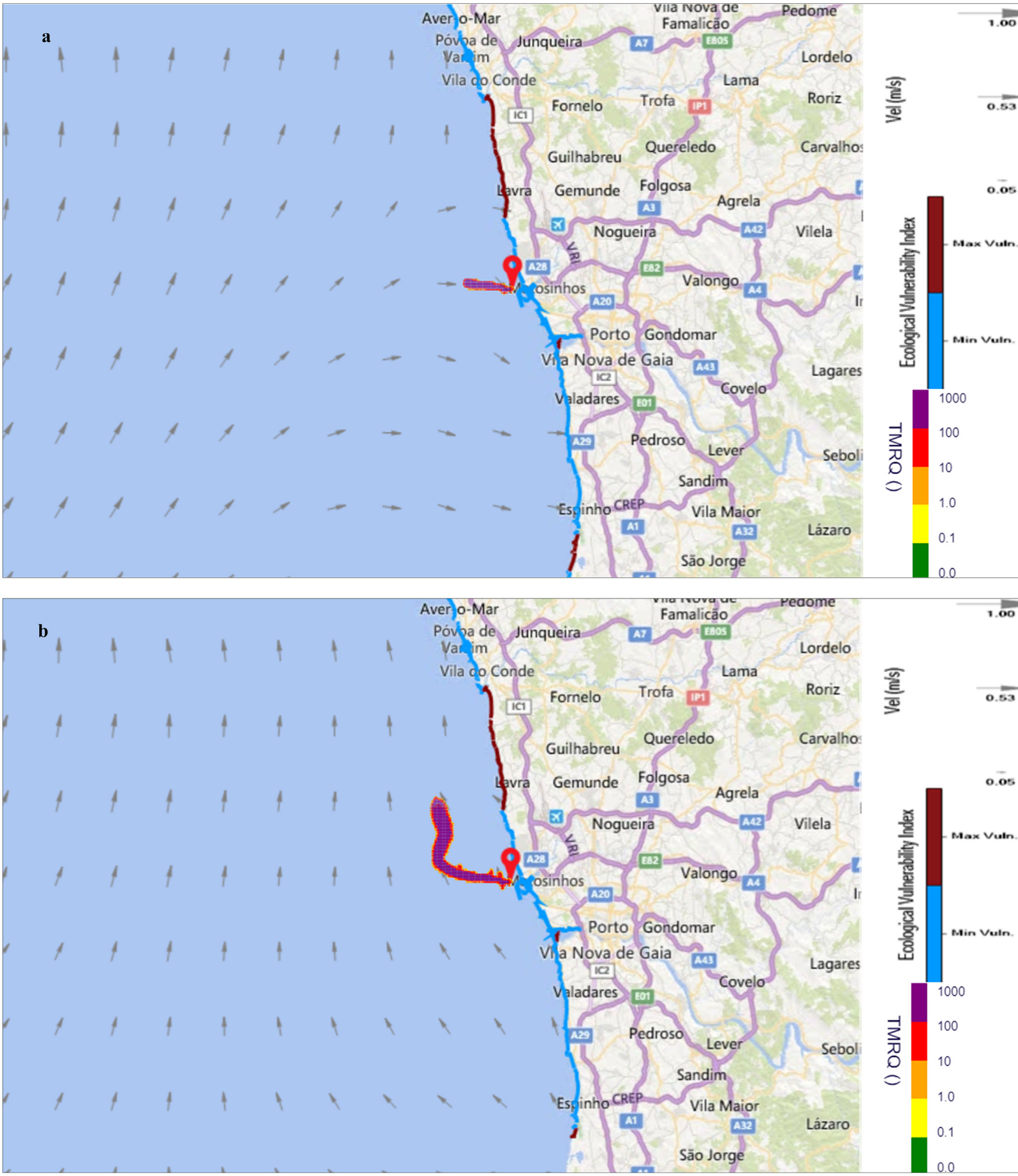

Fig. 3. Toxicity|maximum time-integrated Risk Quotient (TMRQ) after 6 (a), 24 (b), 48 (c) and 72 h (d) post 4-NP spill simulation. The red circle bullet represents the spill emission point and grey arrows the current velocity (m/s). The ecological vulnerability index is represented in a contour along the shoreline. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

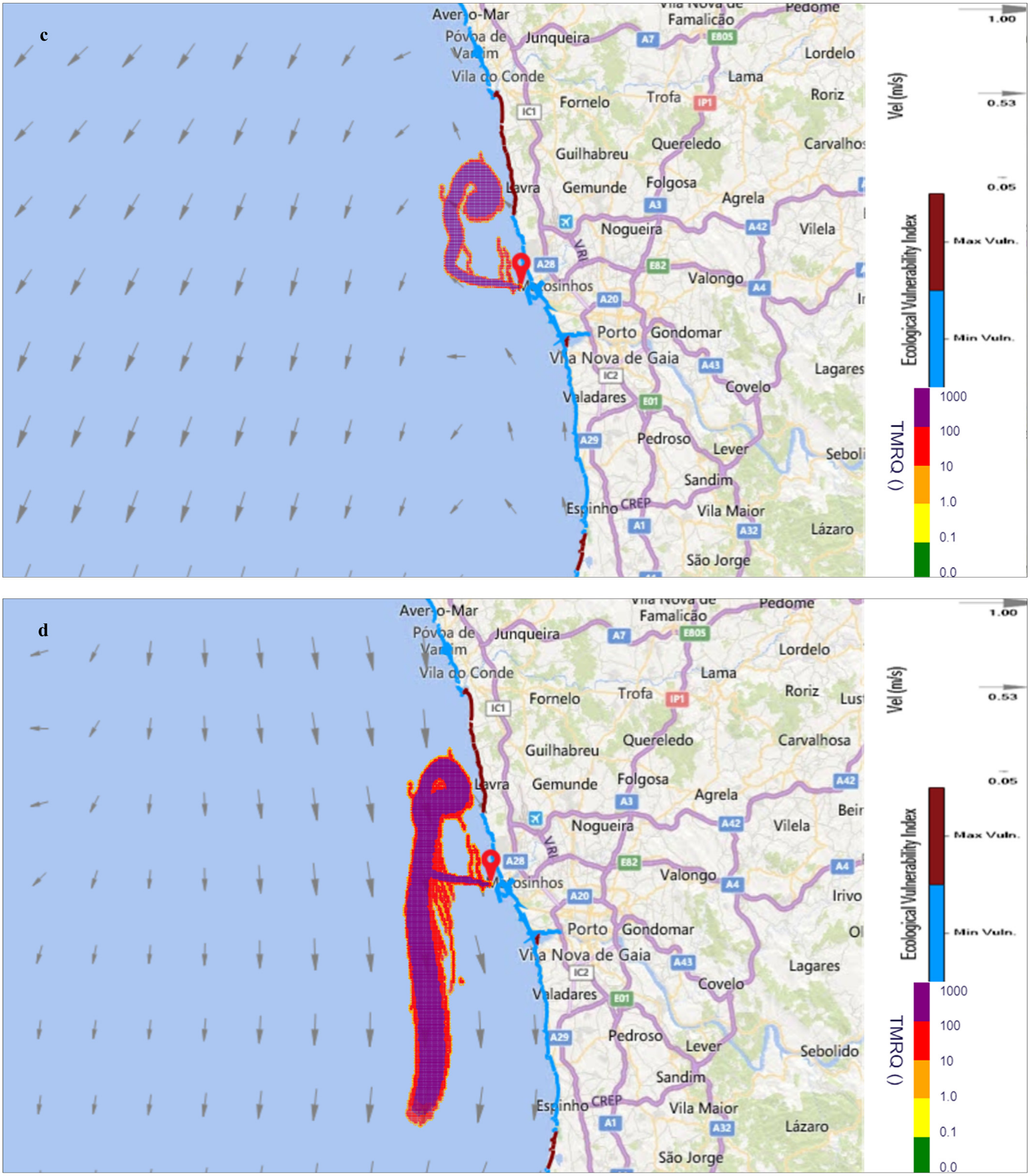

Fig. 3 (*continued*).

HNS ecotoxicological risk. Maximum chemical concentrations from MOHID were used as a precautionary approach biased towards overprotection of aquatic species. Furthermore, as a case study, a simple population model was developed to better project HNS effects at higher ecological levels. While a very high RQ was observed and MVDC reached concentrations associated with 4-NP ecotoxic effects to amphipods, *G. locusta* population was able to recover as 4-NP weathered. It must be highlighted that the developed population model is a simple approach describing a population without resource limitation that attains asymptotic growth after approximately 300 d. Any future implementation of the present framework will require further improvements on incorporated population models. Nonetheless, this innovative framework allows not only to predict the behaviour of priority HNS during accidental spills, but also to assess the environmental risks associated

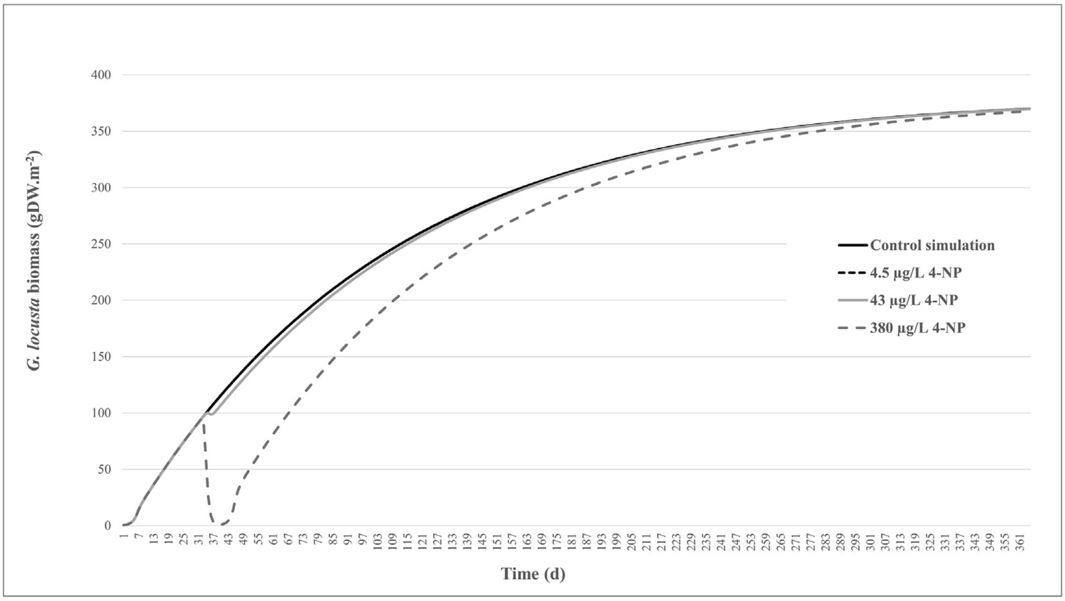

Fig. 4. *Gammarus locusta* population model simulations (360 d) upon a 3 d exposure to 4-NP: Solid black line- control simulation (without 4-NP); Dash tight black line- simulation with 4.5 μg/L of 4-NP; Solid grey line- simulation with 43 μg/L of 4-NP; Dash spaced grey line- simulation with 380 μg/L of 4-NP.

with the chemical dispersion. Moreover, potential hazards to the marine environment and associated ecosystem services, such as fisheries and recreational activities, can be anticipated. Thus, this approach fosters improved preparedness, effective decision-making and spill management in the different stages of crisis (before, during and after spill incidents), by the competent authorities. The concept presented here can be easily transferable to other geographic areas, as well as several types of spills, such as oil spills. Furthermore, this approach can be further extended to other species and trophic levels if species-specific ecotoxicological and physiological parameters are known and incorporated into the population model. We expect in the future to expand this model to the ecosystem-level by including a representative trophic web of the targeted marine ecosystems, thereby improving ecological predictions.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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