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PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA DE PRODUÇÃO

A METHODOLOGY FOR QUANTITATIVE ECOLOGICAL RISK ASSESSMENT FOR INDUSTRIAL ACCIDENTS

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BY

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"A METHODOLOGY FOR QUANTITATIVE ECOLOGICAL RISK ASSESSMENT FOR INDUSTRIAL ACCIDENTS"

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RESUMO

Recentes acidentes industriais, como vazamentos tóxicos, têm causado danos catastróficos ao meio ecológico (i.e. plantas e animais), de modo que um método efetivo para analisar riscos ecológicos tem sido demandado. Em primeiro lugar, este trabalho tem como objetivo propor uma metodologia capaz de quantificar riscos ecológicos inerentes a eventos raros como acidentes industriais. Utiliza-se a modelagem populacional para simular futuras mudanças na abundância populacional de espécies-chave em risco e, assim, estimar a probabilidade de extinção ou declínio, tempo para extinção e outras medidas, para cada cenário acidental. Assim, foi possível desenvolver uma abordagem que combina os danos ecológicos (previstos através da modelagem populacional) com a frequência de ocorrência do cenário acidental (estimada através de dados históricos e análise de confiabilidade). O resultado é uma curva de risco FN (similar ao resultado de uma análise de risco a humanos), onde N é o declínio populacional médio e F a frequência acumulada de acidentes com declínio maior ou igual a N. Em segundo lugar, o trabalho apresenta uma aplicação da metodologia para quantificar os riscos ecológicos provenientes de acidentes associados ao transporte e manuseio de petróleo que abastece uma refinaria no Complexo Industrial Portuário de Suape-PE, no Nordeste do Brasil. Esta instalação está localizada próxima a um rico ecossistema aquático de alta biodiversidade. A população de uma espécie nativa foi estrategicamente escolhida para representar o ecossistema, alguns cenários de derramamento de petróleo foram simulados e suas frequências de ocorrência estimadas. Para cada cenário acidental, a concentração de óleo que atinge a população foi prevista via modelagem de destino e transporte. Os riscos ecológicos foram quantificados e apresentados em uma curva FN. Uma análise de sensibilidade foi feita para explorar como mudanças em parâmetros específicos causam mudanças nas medidas de risco. Além disso, a incerteza foi medida como um intervalo (limite superior e inferior) para as medidas de riscos com base em cenários pessimistas e otimistas. Finalmente, a metodologia mostrou-se viável, eficiente, conveniente e flexível, apesar de que algumas melhorias ainda podem ser feitas e estas foram propostas para trabalhos futuros.

Palavras-chave: Análise Quantitativa de Risco; Análise de Riscos Ecológicos; Acidentes industriais; Modelagem ecológica.

ABSTRACT

Recent industrial accidents such as toxic spills have caused catastrophic damage to ecological environments (plants and animals), so that an effective method to assess ecological risks has been demanded. Firstly, this work aims at proposing a methodology capable of quantifying ecological risks related to rare events such as industrial accidents. One uses population modeling to simulate future changes in the population abundance of key species at risk and therefore estimate the probability of extinction or decline, time to extinction and other measures, for each accidental scenario. Thus, it was possible to develop an approach that links the ecological damage (predicted via population modeling) with the frequency of occurrence of the accidental scenario (estimated via historical data and reliability analysis). The result is a FN risk curve (similar to the result of a human quantitative risk assessment), where N is the average population decline number and F the cumulative frequency of accidents with N or greater abundance decline. Secondly, the work presents an application of the methodology to quantify ecological risks originating from accidents associated with transport and handling of crude oil to supply an oil refinery in the Suape Port and Industrial Complex, in the Northeast of Brazil. This is located near a very rich aquatic ecosystem with a high biodiversity. A population of a native species was strategically chosen to represent the ecosystem, some scenarios of oil spill were simulated and their frequencies of occurrence estimated. For each accidental scenario, the concentration of oil that reaches the population was predicted via fate and transport modeling. The ecological risks were quantified and presented as a FN curve. A sensitivity analysis was made to explore how changes on specific parameters cause changes in risk measures. Also, uncertainty was measured by estimating a range (lower bound and upper bound) to risk measures based on best case and worst case scenarios. Finally, the methodology proved to be practicable, efficient, convenient and flexible, although some improvements can still be made and were proposed for future works.

Keywords: Quantitative Risk Assessment; Ecological Risk Assessment; Industrial accidents; Ecological modeling.

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CETESB – Environmental Company of the state of São Paulo, Brazil

CPR – Committee for the Prevention of Disasters, Netherlands

EC – Effect Concentration

EEA – European Environmental Agency

ERA – Ecological Risk Assessment

EPA – United States Environmental Protection Agency

IUCN – International Union for Conservation of Nature

LC – Lethal Concentration

LOEL – Lowest Observed Effect Level

NOEL – No Observed Effect Level

PDF – Probability Density Function

PHA – Preliminary Hazard Analysis

QRA – Quantitative Risk Assessment

QERA – Quantitative Ecological Risk Assessment

RNEST – Abreu e Lima oil refinery

SPIC – Suape Port and Industrial Complex

1. INTRODUCTION

This work is within the field of Ecological Risk Assessment (ERA), which has become an important part of the decision-making process for managing environmental problems [1; 2] and can be used to evaluate risks to plants and animals as a result of human impact. It has been considered in programs administered by the U.S. Environmental Protection Agency (EPA) and in similar programs administrated by environmental agencies in Canada, Europe, New Zealand and Australia. For instance, ERAs has been used in pesticide regulatory programs, support in decision-making about waste discharges, and remedial actions to clean up or treat contaminated areas, and installation of new industrial facilities. This work focuses on the last one, which makes ERA an important field of research within Production Engineering, since it is particularly useful in industrial establishments for providing information necessary to the processes of licensing, risk management, and environmental management.

In general, risk assessment in industrial risk management should deal with risks to the totality of the surrounding environment originating from an industrial installation or activity, including the ecological environment (sometimes known as the natural environment), the human health and structures/technology/physical materials. Each one of these entities has little similarity in the variables used to perform a risk assessment, so that they usually need distinct methodologies, especially if it is a quantitative assessment. As consequence, ERA has become a particular field of study within the Risk Assessment. This work centers its attention in ecological risks, which means risks with potential to cause adverse ecological effects, and does not contemplate risks to the human health or to physical materials. In addition, because fire and explosion are events that usually cause minor ecological damage than toxic spills, we focus on threats caused by toxic spills, although the former can be treated as initiator events of the latter.

With regard to current studies in the field of ERA, most of them (e.g., [2; 3; 4]) focus on risks caused by chronic interference (continuous and persistent) such as, for example, waste discharge, so that there is a missing link between ecological risks and industrial accidents. For that reason, this work falls within the context of ERA for industrial accidents, i.e. it deals with (rare) events with low frequency of occurrence but that may cause catastrophic damage. For the purposes of this work, rare events are defined as events that happen less than once per year.

In the recent Brazilian context, ERAs for toxic spills rely on subjective rules-of-thumb or opinions [5]. In other words, it is usually done by the comparison of the estimated concentration of the toxic substance in an ecosystem with reference values given by toxicological information, such as the Toxicological Information Sheet (TIS) provided by CETESB [5]. Therefore, this work focuses on quantitative assessments (i.e. estimate of quantitative values to the ecological risks related to accidents), in an effort to provide numerical basis to decisions in environmental and risk management.

It is worth mentioning that the proposed methodology in this work was already published in the European Safety and Reliability Association Annual Conference, ESREL 2011 [6]. Also, an extended abstract of the application example of this work was accepted to be presented as oral presentation in the Society for Risk Analysis (SRA) 2011 Annual Meeting [7]; and a paper about an improved version of the proposed methodology was accepted to be published in the Probabilistic Safety Assessment (PSAM) 11 & ESREL 2012 Annual Conference [8], the major international event in probabilistic risk assessment in 2012.

1.1 Rationale and Contribution

Recent industrial accidents such as toxic spills have cause catastrophic damage to the environment and consequently great economic losses to the responsible company. That is what British Petroleum (BP) painfully learned after the oil spill on April 20 of 2010, with the explosion of the Deepwater Horizon platform in the Gulf of Mexico, causing one of the most severe ecological disasters in history and a loss for the company estimated at 37 billion dollars to be spent on cleanup, fines and repairs. However, this leak could have been avoided with the purchase of an equipment of U$500,000, able to seal the well in case of accident. This resulted in a loss 74,000 times higher to BP, not counting the corporate image degradation and the loss in the value of its shares [9].

Several others dramatic industrial accidents have also occurred in recent years, resulting in the discharge of chemicals and damaging valuable ecosystems [10; 11; 12; 13]. For instance, the wrecks of the oil tankers Rena (2011), Prestige (2002) and Erika (1999); and the chemical spills at Doñana (Spain) in 1998 and Baia Mare (Romania) in 2000. Table 1 presents a summary of recent accidents in the world, whereas Table 2 presents accidents in Brazil. Besides these, a high number of less harmful incidents happen every year [11].

Table 1 – Recent most severe industrial accidents worldwide.

Industrial Accident	***Event Year***	***Location***	***Impact***
Marine oil spill by a stricken container ship	*2011*	*Coast of New Zealand*	*About 350 tonnes of oil into the sea. Oil has washed up along about 60 kilometers of the coast. Nearly 1,300 birds have died in the spill. It is seen as New Zealand's worst environmental disaster in decades.*
Explosion in the Deep Water Horizon platform	*2010*	*Gulf of Mexico*	*Death of 11 people, more than 600 endangered species.*
Marine oil spill by the tanker Prestige	*2002*	*Coast of Spain*	*More than 35,000 tonnes spilled, with a similar amount left inside the sunken tanker. Almost 20,000 birds found dead, several hundred kilometers of coast polluted in Spain and France.*
Chemical spill caused by rupture of a dam at a mining company Aznalcóllar	*1998*	*Guadiamar river, Donana National Park (Spain)*	*Enormous environmental impact: 3 600 hectares of cropland destroyed, 12 tonnes of dead fish collected.*
Spill of almost 100,000 cubic meters of polluted water caused by the break of a dam at the mining company AURUL SA SC	*2000*	*Region of Baia Mare in northwestern Romania*	*More than 1,000 km of contaminated area; hundreds of tonnes of fish killed; drinking water supply was interrupted in 24 locations, affecting over 2.5 million people.*
Marine oil spill by the tanker Erika	*1999*	*Atlantic coast of France*	*20,000 tonnes of oil spilled, 400 km of coast polluted, 45,000 birds found dead.*
Marine oil spill by the tanker Exxon Valdez	*1989*	*Coast of Alaska*	*About 100 million birds killed and 2,000 kilometers of contaminated coast, about 2% of the oil spilled is still polluting the area.*
Explosion of one of the four reactors at Chernobyl	*1986*	*Ukraine*	*High radiation released and nuclear cloud; immediate death of 32 people, other 10,000 died in the following years; contamination of thousands of forests; diseases in more than 40 000 people.*

Table 2 – Recent most severe industrial accidents in Brazil.

Industrial Accident	***Event Year***	***Location***	***Impact***
Marine oil spill caused by the explosion of the tanker Vicuña	*2000*	*Porto f Paranaguá, PR*	*About 1.5 million liters of oil spilled, affecting much of the bay, including environmental preservation areas.*
Oil spill caused by the rupture of a pipeline expansion joint in the refinery Getulio Vargas	*2000*	*Rivers Birigui and Iguaçu, PR*	*About 4 million liters of oil spilled into the Rivers, causing the greatest environmental disaster with oil in Brazil.*
Oil spill caused by a leaking underwater pipeline in the oil refinery Duque de Caxias	*2000*	*Baía de Guanabara, Rio de Janeiro, Brazil*	*At least 1.3 million liters of oil spilled, 40 km² of bay polluted, damaging large swaths of mangrove ecosystem. Among the 12 spills occurred in the Bay, this was considered the most serious.*
Oil spill caused by a leaking underwater pipeline in the oil refinery Duque de Caxias	*1997*	*Baía de Guanabara, Rio de Janeiro, Brazil*	*Spill of 2.8 million liters of oil, reaching 4,000 m² of mangroves in the Bay.*
Oil spill caused by a breaking pipeline	*1994*	*Coast of São Paulo, São Sebastião, SP*	*Spill of 2.7 million liters of oil, polluting beaches and headlands of four municipalities.*
Marine oil spill by the tanker Marina	*March 1985*	*Coast of São Paulo, São Sebastião, SP*	*About 2.5 million liters of oil spilled, affecting bays, inlets, beaches, rocky shores and research areas.*

It can be seen that most accidents are caused by oil spills originated from transport and handling activities in the ocean. In fact, according to the database of the International Tanker Owners Pollution Federation Limited (ITOPF), it is estimated that from 1970 to 2005, about 5.7 million tons of oil were discharged into the sea [14]. It is also estimated that about 700,000 tonnes/year of crude oil and its derivatives are dumped into aquatic environments [15], and the time to recover coastal environments that have been impacted by crude oil can vary from four to one hundred years [15]. Particularly in Brazil, there were about 30 serious accidents with oil spill between 1990 and 2000 [11]. Also, as the global demand for oil grows [16], so does the quantity of this product and its derivatives being produced, processed, stored and transported, and consequently increases the potential to cause serious ecological damage.

The high frequency of industrial accidents, the increasing potential for damage, and the current need for sustainable development suggest that preventive measures must be improved, and the risk assessment is the groundwork for any plan to implement preventive measures. In this sense, the greatest contribution of a QERA is to provide information to maximize the efficiency of risk management measures. Miscalculating risks leads to inefficiency, i.e. underestimating them may lead to inadequate risk management to control and prevent adverse effects to the ecological environment, whereas overestimating them lead to waste of resources to mitigate apparent problems that are not really important.

There are several other benefits of a QERA for establishments that handle hazardous substances [2; 17]:

- allows to systematically identify the existing ecological risks, leading to an improved level of preparation to emergencies;
- allows to examine the population dynamics of native species in surrounding ecosystems;
- it is an iterative process, so that new information can be incorporated into risk assessments in order to improve the results;
- it can be used to express changes in the ecological risks as a function of changes in preventive measures or changes in the project of the establishment. This capability may be particularly useful to the decision maker who must evaluate tradeoffs, examine different alternatives, or determine the extent to which risk must be reduced to achieve a given outcome;
- it can deal with uncertainty, measuring it and communicating it to risk managers on a quantitative basis;
- it can deal with environmental variability (i.e. natural variation of environmental conditions in time and space);
- allows the quantification of risks, which provides a basis for comparing, ranking and prioritizing risks. It can also be useful in cost-benefit and cost-effectiveness analyses related to the alternative management options to the reduction of risk;
- provides numerical basis of knowledge for communicating the risks to stakeholders;
- provides relevant information to tackle many key gaps in environmental management, such as optimal resource allocation for monitoring affected areas, optimal management of threatened and endangered species, and spatial planning for landscape restoration and management;
- the assessment may aggregate value to the product of the organization, by being promoted as sustainable policy.

To help improve the consistency and quality of QERA, some methodologies have been developed. EPA provides a detailed guide to the process of ERA [2], but they consider risks caused by almost surely events only (e.g., use of pesticides, waste discharge, chronic pollution), i.e. events that happen with probability one and usually cause minor ecological damage. They do not contemplate industrial accidents, i.e. (rare) events with low frequency of occurrence but that may cause catastrophic damage.

Camacho [17] proposes a methodology named Quantitative Environmental Risk Assessment. This integrates a methodology to analyze the risk of industrial accidents with another methodology to analyze the potential of chemical effects on not only the wildlife (i.e. ecological risks), but also on others environmental components: humans and economy. However, he presents no definitive procedures for quantifying ecological risks. Actually, in the case study of his work, he considers only effects to the human health, so that the environment is limited to human-beings and the application of his methodology falls in the case of standard human Quantitative Risk Assessment (QRA) methodology [18].

The previous methodologies have a common limitation: the missing link between ecological risks and industrial accidents. In order to tackle this limitation, Stam *et al.* proposes a model to assess risk for the aquatic ecological environment related to industrial installations [19]. This model, called PROTEUS, considers both a probabilistic approach for industrial accidents (particularly industrial spills) and adverse ecological effects. The former is calculated based on standard QRA methodology [18] and uses correction factors needed in order to assess the risk from an activity under local circumstances. The latter is calculated as a volume of potentially contaminated surface water separately for (1) toxic effects, (2) lack of oxygen and (3) formation of a floating layer, and selecting the maximum of these effects.

However, PROTEUS predicts a volume of potentially contaminated water for representing ecological effects, but the presence of a certain quantity of contaminant does not necessarily mean relevant ecological risk [20]. For this reason, one relevant drawback of PROTEUS cannot be ignored: it fails to directly and explicitly quantify impacts on ecological entities (such as populations). For example, the toxic effects are estimated by the inaccurate approach that simply compares the predicted concentration with a toxicity threshold (effect concentration, EC_{50}) for algae, arthropods or fish, i.e. the hazard quotient approach (section 2.4 provides more information about this limitation). Furthermore, even though a volume of potentially contaminated water is calculated, it is hard to determine if the risk is significant or not, because each specific aquatic ecosystem has its specific response to a certain contaminated water volume, so that QERAs with PROTEUS need a qualitative evaluation of at the end. In summary, the results of PROTEUS are not directly useful for risk managers and stakeholders. They still need a subjective evaluation of ecologists before being presented.

As a way around these shortcomings, the main contribution of this work is to provide a methodology that considers both the accident’s frequency and the magnitude of the adverse ecological effects. The proposed methodology is capable of quantifying ecological risks caused by events with low frequency of occurrence and catastrophic consequences. It focus on ecological impacts. Moreover, it uses mathematical modeling applied to ecology (i.e. population modeling [3; 20]) to extrapolate toxicological effects on individual organisms to population-level effects (e.g. effects on abundance or growth rate). The Figure 1.1 illustrates the main goal of the proposed methodology, which is to integrate data on four different studies that provide relevant information to understand ecological risks related to industrial accidents, i.e.: fate and transport models that describe and predict the dispersion and concentration of chemicals in the water, air, or soil; reliability analysis to estimate accidents' frequencies of occurrence; ecotoxicology that provides individual-level effects as a function of toxic exposure; and ecological modeling that translates individual-level into population-level effects.

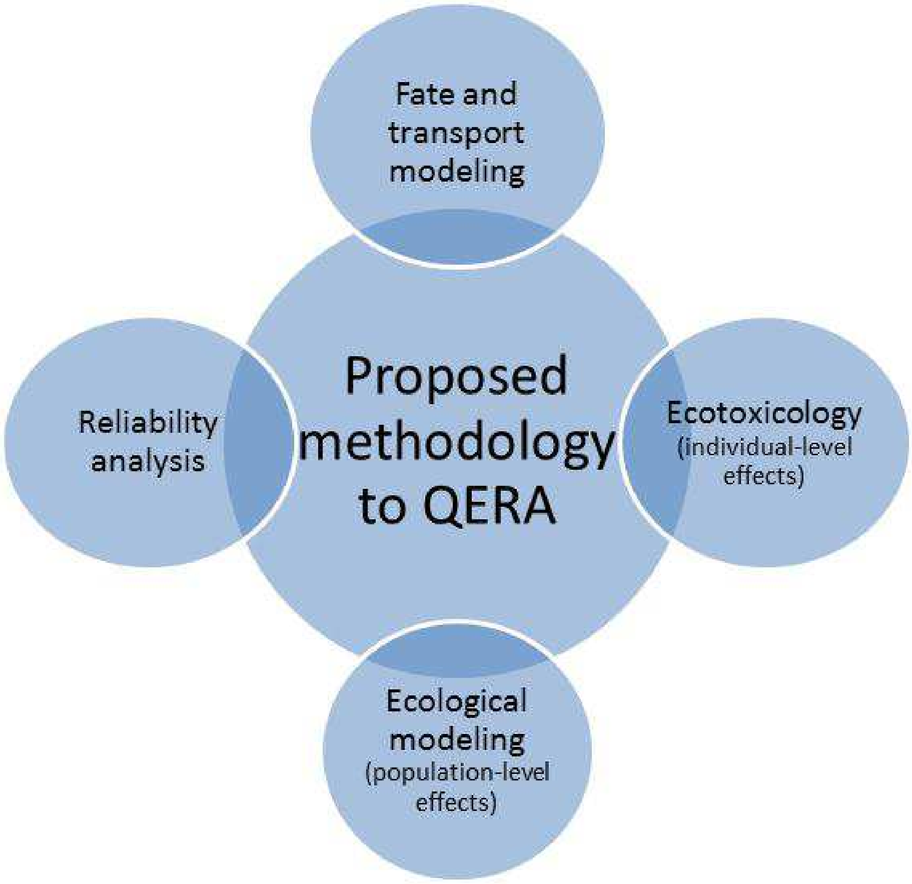

Figure 1.1 - Proposed methodology as a means of integrating data from several fields of study that provide relevant information for ecological risk quantification.

Again and again, the proposed methodology is not limited to assess ecological damage to individuals (individual-level effects), that often leads to inaccurate risk estimates and thus errors in environmental and risk management decisions. The methodology makes use of ecological modeling in risk assessment [3; 20], that explicitly quantify impacts on ecological entities and can provide a more powerful basis for expressing ecological risks. This way, it incorporates population modeling in order to predict the responses of population to toxic exposure (population-level effects) and taking into account the relationships between individuals, the life history and ecology of a native species in the surrounding ecosystem.

1.2 Objectives

1.2.1 General objective

To propose a methodology for quantitative risk assessment for industrial accidents with potential to cause adverse effects on ecological environments, i.e. plants and animals (excluding people, pets and physical materials).

1.2.2 Specific objectives

- To select and integrate ideas, possibilities, methods and guidelines that could improve the process of quantifying ecological risks;
- To propose the quantification of the frequency of occurrence of accidental scenarios via reliability analysis;
- To propose exposure and consequence assessment (e.g. fate and transport modeling, exposure-response assessment, population modeling) as means of describing the ecological damage (i.e. quantifying the magnitude of the consequences) caused by accidental toxic spills;
- To contemplate both the frequency of occurrence and consequences in a single risk measure;
- To divide the methodology into steps and describe them in details;
- To employ worst-case criteria throughout the proposed methodology to screen out accidental scenarios that have insignificant contribution to the final ecological risk, thus avoiding waste of resources and time;
- To build a comprehensive scheme that illustrates the steps and criteria in conducting the methodology;
- To justify all assumptions and criteria of the methodology;
- To test the efficiency and practicability of the methodology by applying it to conduct a QERA in an industrial activity that deals with huge amounts of toxic chemicals, i.e. activities of transport and handling of crude oil to supply the

Abreu e Lima oil refinery (RNEST), to be constructed within the Suape Port and Industrial Complex (SPIC), in Ipojuca, Pernambuco, Brazil.

1.3 Expected results

It is expected that the methodology will be capable of effectively quantifying ecological risks (at population-level) caused by accidental toxic spills. More specifically, it is expected that the methodology should:

- Make predictions that are relevant to environmental and risk management;
- Provide information that allows the comparison among accidental scenarios, as a basis for prioritizing risk management actions under limited resources;
- Provide a single risk measure that summarizes the ecological risks originating from accidents in a hazardous industrial activity, as simple way of communicating to stakeholders the total ecological risks;
- Deal with uncertainty, measuring it and communicating it to risk managers on a quantitative basis;
- Deal with environmental variability in time and space;
- Be convenient and practicable in terms of costs, time and data needs.

1.4 Structure of the work

This work is organized as follows. Chapter 2 presents a review of the theoretical background for understanding this work. Chapter 3 presents the proposed methodology and explains how it can tackle limitations of other methodologies. Chapter 4 aims at validating the proposed methodology. It consists of an application of the methodology to perform a QERA in an industrial activity. Lastly, chapter 5 is concerned with the concluding remarks, i.e. the most important goals and limitations of the methodology, practical implications of the results, conclusions taken from the application example and future developments.

2 THEORETICAL BASIS

2.1 Basic Concepts of Ecology

Ecology is the science that studies the relations of living beings with one another and with the environment in which they live as well as their reciprocal influences, including the human aspects that affect and interact with the natural systems of the planet [21].

For the purposes of this work, it is important to be clear about the definitions of environment and ecological environment. In accordance with EPA, environment is “the sum of all external conditions affecting the life, development and survival of an organism” [22]. So environment encompasses humans, physical materials and the ecological environment itself (i.e. wildlife plants and animals).

As stated previously, ecology studies the relations of living organisms to each other and to the environment. The biological world is very complex, so it was divided into biological hierarchy levels, as shown in Figure 2.1. The ecology studies only from individual organism level to higher levels and EPA provides definitions to these [22]:

- Organism refers to “any form of animal or plant life”.
- Population refers to “a group of interbreeding organisms occupying a particular space”. Each population has its own characteristics such as abundance, birth rate (fecundity), deaths rate (mortality), age distribution, dispersion, growth rate.
- Community refers to “an assemblage of populations of different species within a specified location in space and time. Sometimes, a particular subgrouping may be specified, such as the fish community in a lake or the soil arthropod community in a forest”.
- Ecosystem refers to “the interacting system of a biological community and its non-living environmental surroundings”.
- And landscape refers to “the traits, patterns, and structure of a specific geographic area, including its biological composition, its physical environment, and its anthropogenic or social patterns. An area where interacting ecosystems are grouped and repeated in similar form”.

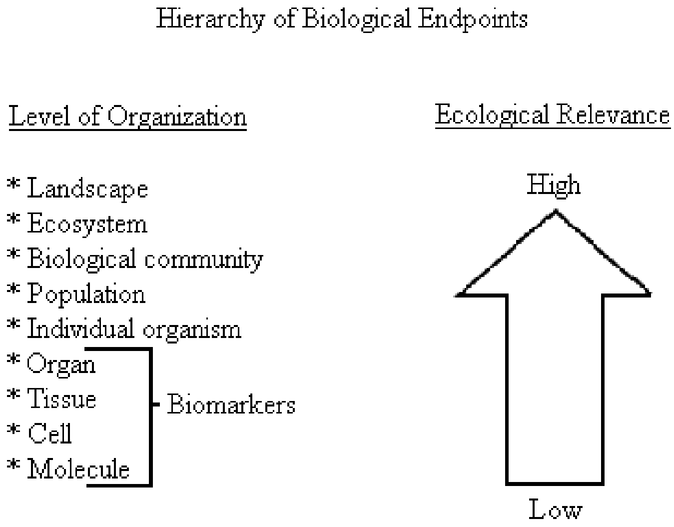

Figure 2.1 - Hierarchy of biological endpoints.
(From the ref. [3])

By the way, habitats used by most species around industrial sites are becoming increasingly fragmented by human activities and, consequently, several distinct populations of same species are living spatially separated, in spite of interacting at some level (e.g. exchange of individuals). In fact, there are relatively few cases where the entire population resides within a same area. Hence, most species are distributed across space as a large population of connected subpopulations, that is, as a metapopulation. According to Pastorok *et al.*, "a metapopulation is a set of populations of the same species in the same general geographic area with a potential for migration among them" [3].

With regard to levels lower than individual organisms, i.e. organ, tissue, cell and molecule, they can be biomarkers. These are measures of body fluids, cells, tissues or measures taken on the whole organism, which indicate (in biochemical, cellular, physiological, compartmental or energetic terms) the presence of contaminants or the magnitude of the response of the target organism [23]. Still, the National Institute of Environmental Health Sciences (NIEHS) states that "biomarkers play an important role in understanding the relationships between exposure to environmental chemicals, the development of chronic human diseases, and the identification of subgroups that are at increased risk for disease" [24].

All these explanations complement each other and help to understand that ERA can be conducted at all levels within the biological hierarchy (including biomarkers). Nevertheless, the methodology proposed in this work focus on population- and metapopulation-level risks, i.e. the potential for adverse effects on (meta)populations. Readers are referred to the reference [3] for models that are potentially useful for risk assessment at higher-levels and to a series of four papers, commissioned by the European Science Foundation [25; 26; 27; 28], for the use of biomarkers in ERA.

2.1.1 Ecotoxicology

The term ecotoxicology was proposed in 1969 by the toxicologist René Truhaut during a meeting of the Committee of the International Council of Scientific Unions, in Stockholm. According to Truhaut, ecotoxicology is defined as "the branch of toxicology concerned with the study of toxic effects, caused by natural or synthetic pollutants, to the constituents of ecosystems, animal (including human), vegetable and microbial, in an integral context" [29].

In the 1960s, based on acute toxicity tests results, the Water Quality Act – USA established the first water quality standards in order to protect the aquatic life. In the same period, researches were developed focusing on the selection of sensitive and representative organisms of the aquatic environment and on the cultivation of organisms in laboratory. In the same decade, the book Silent Spring, written by Rachel Carson, was published. It was widely read and began to diffuse to the public concerns about pesticides and environment pollution. In the book, she calls attention to the harming and killing of not only animals and birds but also humans caused by the uncontrolled and unexamined pesticide use.

Throughout 1970s, some American researchers noticed that limits established for many toxic agents separately could not preserve, effectively, the water quality necessary to maintain the aquatic life. With this in mind, the aquatic toxicology had a rapid development due to the knowledge of complex liquid effluents toxicity and the interactions between toxic agents in effluents and its effects on aquatic biota. Besides that, sophisticated systems were developed in order to conduct acute and chronic toxicity tests, using fish eggs and larvae to evaluate the toxic effects of chemical substances on different life stages of organisms. [30]

During the 1980s and 1990s, validation studies of laboratory toxicity tests and collected aquatic water field data results showed the importance of selecting representative species of to evaluate toxic effects on an ecosystem. Afterwards, the implementation of ecotoxicology tests was intensified for the establishment of water quality standards. [30]

Nowadays, the ecotoxicology plays an important role in ERA because it provides basis of knowledge about toxic effects on individual organisms caused by chemical exposure as well as about the representative species in an ecosystem. Knowledge on individual-level effects is essential to predict higher-level effects such as on population abundance (or density), on community species richness, on productivity, or on distributions of organisms. Likewise, because the assessment of all species of an ecosystem would require huge costs and long time, knowledge on which are representative species is necessary to make the assessment tractable.

2.1.2 Population dynamics

Population dynamics is an ecology discipline which studies changes in the population abundance. These studies are important to analyze and understand what happens to the population in natural conditions (without chemical exposure). Incidentally, population models are used to predict and simulate the dynamics of a population. This section will introduce the main components in population dynamics, whereas section 2.5 will present a comprehensive overview of population modeling.

The populations that constitute an ecosystem are open systems, i.e., they exchange energy and matter with the external environment. Hence, any attempt to describe and predict a population dynamics requires knowledge about the interactions between: (*i*) system components, i.e., organisms which compound the population and (*ii*) the system and the external environment [21]. In view of that, to characterize the dynamics of a population it is necessary to define its survival, mortality and fecundity, as well as migration, foraging behavior and density-dependence when appropriate.

Firstly, survival means the number of individuals in a population that are alive after a given period of time and the survival rate indicates the proportion. Pastorok et. al. [3] defines the age-specific survival rate $[S_i\,(t)]$ as "the proportion of individuals present in a given year (t) within a given age class (i) that survives into the next age class $(i+1)$ in the following year $(t+1)$". Age-specific survival rates can be estimated by the equation below:

$$S_i(t) = N_{i+1}(t+1)/N_i(t) \quad (2.1)$$

Where

$S_i(t)$ = survival rate of individuals in age classe i at time t

$N_{i+1}(t+1)$ = number of individuals in age class $(i+1)$ at time $(t+1)$

$N_i(t)$ = number of individuals in age class (i) at time (t)

In face of that, mortality is the number of individuals of a population that died in a given period of time. The death rate can be expressed as 1-$S_i(t)$.

With regard to fecundity (F), by definition, it means "the number of live offspring per individual in a given age class that will survive to be counted in the first age class" [31]. Incidentally, calculating fecundity depends on the available data and two brief examples might clarify it. On the one hand, e.g., for oviparous animals, fecundity can be estimated by the equation:

$$F = \binom{actual\ eggs}{per\ female} \times \binom{probability}{of\ hatching} \times \binom{probability\ of\ hatching}{surviving\ to\ age\ 0\ year}, \tag{2.2}$$

where the probability of hatching and the probability of hatching surviving to age 0 year are empirically derived species-specific value between 0 and 1. In this case, it is not enough to derive F on the basis of knowledge about only the actual number of eggs laid, i.e. one has to include the probability of hatching and the probability that the newly hatched fry will survive until the next census to recruit into age class 0.

On the other hand, if sufficient data is available, fecundity can be estimated by the equation:

$$F_{age\ i}(t) = \frac{\binom{proportion\ of\ age\ 0\ year\ juveniles\ that\ were}{produced\ by\ individuals\ in\ age\ class\ i\ at\ time\ t} \times \binom{\text{number of juveniles at}}{\text{time } t+1}}{number\ of\ individuals\ in\ age\ class\ i\ at\ time\ t} \tag{2.3}$$

In an effort to estimate survival and fecundity, field data need to be collected. Determining survival rates requires a minimum of two consecutive yearly field censuses; in fact, the results will be more reliable if data from three of more consecutive years are available. In addition to that, Pauwels suggests that the censuses should be consecutive to follow the age classes from one year to the next and to estimate age-specific survival rates, but if data for the target species are insufficient then one could extrapolate the information from the related species to the target species [31].

Let us now examine features concerning the movement of a population, i.e. migration and foraging behavior. The term migration denotes the movement of all or part of a population from one habitat to another [32]. Incidentally, it is the main way of interaction between populations within a metapopulation.

Foraging behavior consists in all methods used by an organism to acquire and utilize sources of energy and nutrients. This encompasses location, storage, consumption and retrieval of resources. Moreover, the foraging theory tries to predict how an animal would choose to forage within its habitat, considering the knowledge of competition, predation risk, and resource availability [33]. The larger the foraging area, more food will be available. In contrast, the organism will spend more energy and take more risk, since the exposure to predators in areas beyond its natural habitat will be greater. It is important to emphasize that the population foraging area should be considered in a QERA when the spatial structure of the environment has important effects on the population dynamics.

Another very important mechanistic process within the population dynamics is its regulation via density dependence on survival, mortality, fecundity and movement of populations. It is the phenomenon of population growth rate depending on the current population density (or abundance). In other words, according to Akçakaya, density dependence "is any non-constant relationship between population growth rate and the current population size" [34].

As is observed in wildlife populations, they are often changing in size, but fluctuating around an equilibrium abundance for long time periods, unless a disturbance occurs (e.g. pollution, harvest, culling, poaching, catastrophe, etc.). Consequently, it is important to incorporate density dependence to describe a population dynamics because it causes the population to reach a stationary state (which may fluctuate due to stochasticity only). The equilibrium abundance is also known as the carrying capacity. In other words, as stated by Akçakaya, "the carrying capacity is the level of abundance above which the population tends to decline" [35].

There are many possible mechanisms that yield density dependence: fecundity may decrease, mortality may increase with competition for limited resources, the crowded conditions may lead to social strife or cannibalisms. Population growth may also be affected negatively as population size reach very low levels. This phenomenon, arising from Allee effects [36; 37], draws a small population away from the carrying capacity and toward extinction.

Usually, to enhance population growth, density dependence factors decrease mortality, increase fecundity, decrease emigration, or increase immigration (i.e. positive density dependence). By contrast, to retard population growth, they increase mortality, decrease fecundity, increase emigration, or decrease immigration (i.e. negative density dependence). A brief example can clarify the concept of density-dependence: on the one hand, when there are too many organisms living in the same space and being part of the same population, food may become less available and competition among the individuals starts. Consequently, negative density dependence manifests itself (e.g., more individuals dying and emigrating) so that the abundance will decrease to a quantity in which food is sufficient for all individuals again.

To conclude, another fundamental component of a population dynamics is the natural variability in all its components. In other words, changes in survival, fecundity, migration and carrying capacity may occur in an unpredictable fashion. For this reason, any attempt to describe a population dynamics should account for stochasticity in those parameters to better represent reality. Section 2.5.2 and section 2.5.3 provide guidance on how to model density dependence and on how to account for stochasticity, respectively.

2.2 Risk, Hazard, Threat, Control Measure, Recovery Measure, Consequences and Accidental Scenario

There are many definitions of risk in the literature, some are complementary, some are supplementary and others are even antagonistic. Each area of knowledge seeks to give its specific meaning; therefore there is no uniformity neither in the interpretations of risk nor in the methodologies to risk assessment.

Camacho [17] transcribes the several definitions of risk which were the theme of discussion and decision of the SRA Committee on Definitions held in San Diego in 1987, entitled “Defining Risk”. It is presented a definition that is considered necessary and sufficient for the interpretation of risk in this work: the American Institute of Chemical Engineers (AIChE) defines risk as a measure of human injury, ecological damage or economic loss in terms of both the accident likelihood and the magnitude of the consequences [38].

As this work focuses on ecological risks, the magnitude of the consequences regards ecological damage and is quantified as a measure of time and population probability of extinction (or decline). This measure is widely accepted and used by the scientific community in ERA as well as is the quantitative measure used by the International Union for Conservation of Nature (IUCN) to classify plants and animals at risk [39].

However, from an economical point of view, this measure does not completely value the magnitude of the consequences in terms of undesirability. Utility theory is used to value an unwanted event and so provide the most objective and relevant measure that a decision maker could have to rationally take decisions while exposed to uncertainty. Describing an unwanted event in terms of time and population probability of extinction (or decline) consists of about 80% of the efforts needed to value such an event in terms of undesirability. To whom it may concern, Campello [40] presents the new methods for assigning value to undesirable events, including a measure of risk aversion.

To the purposes of this work, on the one hand, is the likelihood of occurrence of an accidental scenario and, on the other, is the measured consequence of this scenario in terms of time and population extinction (or decline). The former is estimated using historical records and reliability analysis techniques (e.g. event tree, Event Sequence Diagrams, Bayesian Belief Networks) and it may involve both equipment failures and human errors. The latter is predicted via exposure and consequence assessment (e.g. fata and transport modeling, exposure-response assessment, population modeling).

It is beyond the scope of this work to provide guidance on reliability analysis; for a general view on reliability theory, models, methods and applications, see the references [41; 42; 43]; and for specific information about techniques such as Event Sequence Diagrams (ESD), Bayesian Belief Networks (BBN) and Human Reliability Analysis, see the references [44; 45; 46; 47; 48; 49]. Likewise, human damage are not within the context of this work; for methods to calculate the vulnerability and consequence on human health see the references [18; 50].

It is also important to differentiate between the terms hazard and risk. The former is a potential source of damage whereas the latter is the combination of the likelihood of occurrence of damage and the severity of that damage (in defined circumstances). For example, on the one hand, a great volume of oil under pressure has potential to cause damage, so it is a hazard. On the other hand, overpressure may cause an oil spill with defined circumstances (such as total mass released, time of spill, hydraulic flow) and cause a particular damage that can be measured. The combination of the oil spill's likelihood of occurrence with the magnitude of the damage characterizes the risk.

Concerning threats, control and recovery measures, and consequences, Figure 2.2 is a very interesting way of illustrating it. As already mentioned, hazard is a potential source of damage (usually in the form of energy). Threats are the initiator events which could cause the hazard to be released, although hazard and threats are sometimes taken to mean the same. Control measures (e.g., safety management systems, alarms, automatic stops) are barriers and preventive actions which can control the threats and avoid the occurrence of the top event, so that they reduce the top event's frequency of occurrence and so reduce the risk. The top event is actually the accident. Recovery measures (e.g. re-routing of spills, burning the oil before it reaches an ecosystem, pollution remediation, habitat protection, translocation or reintroduction of individuals in the population) are mitigation actions which could reduce the magnitude of the consequences and so reduce the risk. Consequences are the damage, impacts, or effects. Importantly, preventive measures include both control and recovery measures. And finally, an accidental scenario is consolidated by defined circumstances to all this factors.

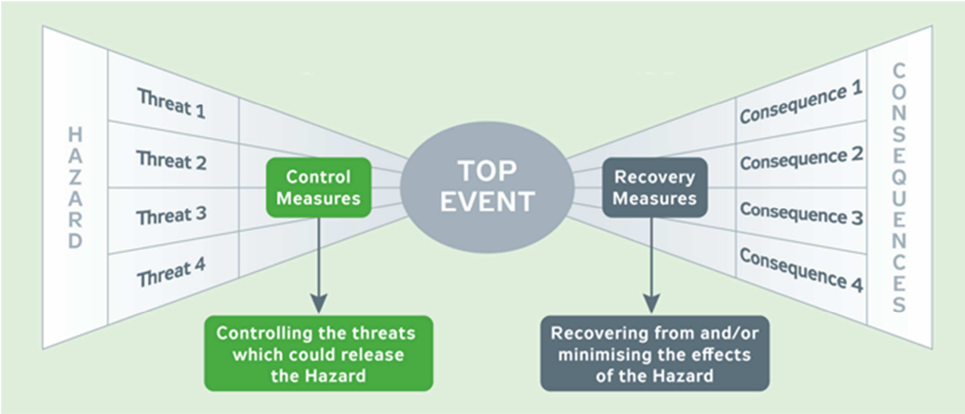

Figure 2.2 - The bow tie that represents the relationships between hazards, threats, controls, top event, recovery measures and consequences.
(From the ref. [51])

Lastly, there are two types of toxic risks: risk to human health and ecological risk. The former refers to the potential that adverse effects to the human health may occur or are occurring due to exposure to a toxic substance. The latter refers to the potential that adverse ecological effects may occur or are occurring as a result of exposure to a toxic substance.

2.3 Quantitative Risk Assessment

A Quantitative Risk Assessment (QRA) allows the quantification of risks, concerning since the frequent incidents with small impacts to even the rare events with major consequences. Thus, the QRA is necessary for objective decision making related to the security of the establishment, surrounding communities and ecological environment. The major motivation of carrying out a QRA is that in order to optimize risk management measures, they should be taken based on the results of a QRA.

In other words, the QRA is used to demonstrate the risks caused by the establishment and thus help to prioritize which risks require some sort of action and in the decision to choose between different actions to reduce those risks. The actions for risk reduction may be quantitatively evaluated and compared according to their implementation costs through a cost-benefit analysis.

In Brazil, particularly in the state of São Paulo, since the publication of the declaration Nº 1, 01/23/1986 [52], by the Environment National Council (*Conselho Nacional do Meio Ambiente* – CONAMA), which created the requirement of an Environmental Impact Statement (*Estudo de Impactos Ambientais* – EIA/ *Relatório de Impacto Ambiental* - RIMA) for licensing activities significantly affecting the environment, studies of risk assessment started to be incorporated into this process, for certain types of enterprises, so that, besides the problems related to chronic pollution, the prevention of major accidents should be also included in the process of licensing [50]. Thus, one more contribution of QRA is that it also provides the competent authority with relevant information for enabling decisions on the acceptability of risk originating from accidents.

Currently, there are several manuals for implementation of a QRA. The Committee for the Prevention of Disasters (CPR), from the Netherlands, is a worldwide reference in the area. They published four books identified by colors (the purple, yellow, red and green books) [18; 53; 54; 55], which are often used in environmental permits, based on the Environmental Protection Law, and in the fields of labor safety, transport safety and fire safety. Those books provide methods for the determination of probabilities, possible damage and physical effects, as well as guidelines for human quantitative risk assessment.

In Brazil, the Environmental Company of the State of São Paulo (*Companhia Ambiental do Estado de Sao Paulo* – CETESB) published in 2000 a guidelines manual for preparation of studies in risk assessment (version only in Portuguese). This is the main reference on QRA in the country [50].

Although CETESB [50] cites the risk to the environment as a totality (humans, animals, plants, etc.) and highlights several times the importance of considering impacts to the ecological environment, they describe a methodology for QRA capable of quantifying risks to the human health only (surrounding communities), and not to the ecological environment. Likewise, CPR [18] describes in detail a methodology for human QRA and presents separately (in its chapter seven of only one page), a few basic guidelines and references for Quantitative Ecological Risk Assessment (QERA), which are hardly enough for the purposes of this work. Hence, the next section presents the author`s view about QERA and the main references he used to form it. In advance, to our purposes, a QERA is nothing more than a QRA focused on ecological risks.

2.4 Quantitative Ecological Risk Assessment

Ecological Risk Assessments (ERAs) are conducted in an effort to translate scientific data into meaningful information about risks to the ecological environment. This meaningful information may be provided by assigning values to the risks (i.e. by quantifying the risks), so that an ERA can be addressed as a QERA.

The references [1; 2; 56; 57; 58] provide detailed guidelines for the process of ERA. Among them, the main theoretical reference used in this work is the one published by the U.S. Environmental Protection Agency (EPA) [2], for being the most current and on the same plot as the others.

EPA defined ERA as "a process that **evaluates the likelihood (author`s bold)** that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors". However, for the purposes of this work, it was added the term "quantitative" to emphasize that the assessment attaches a value or a price to the risk, because that is the objective of our proposed methodology. As a result, we adjust EPA's definition and consider QERA as "a process that **evaluates and quantifies the likelihood** that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors".

Adverse ecological effects are "changes that are considered undesirable because they alter valued structural or functional characteristics of ecosystems or their components. An evaluation of adversity may consider the type, intensity, and scale of the effect as well as the potential for recovery" [2]. They are evaluated through endpoints, i.e. assessment endpoints and measurement endpoints. According to Pastorok *et al.* [3], "*assessment endpoints* are defined as environmental characteristics or values that are to be protected (e.g. wildlife population abundance, species diversity, or ecosystem productivity) and "*measurement endpoints* are quantitative expressions of an observed or measured biological response, such as the effects of a toxic chemical on survivorship or fecundity, related to the valued environmental characteristic chosen as the assessment endpoint".

Endpoints could be expressed as effects on individual organisms, populations, communities, ecosystems and landscapes. Thus, the definition of QERA allows for risk assessment to be conducted at the various levels within the biological hierarchy (Figure 2.1). However, many QERAs consider only individual endpoints and fail to consider population, ecosystem, or landscape endpoints.

Indeed, the typical QERAs suggests that ecological risk is characterized as a hazard ratio of predicted or measured exposure to predicted no-adverse-effect level expressed as a concentration or dose. This approach is also known as the hazard quotient, which is simply the estimated exposure divided by a toxicity threshold. Thus, one has a value to the risk, which tells whether effects on individuals are expected (in case it is greater than 1) or not (in case it is less than 1). Typically, a measured No-observed-effect-level (NOEL) or Lowest-observed-effect-level (LOEL) – see glossary for details - for the individual-level endpoint of interest are used as toxicity threshold.

Nevertheless, the hazard quotient approach can only evaluate individual-level effects and is not able to provide useful information for determining risks to populations in a QERA. Furthermore, Pastorok *et al.* [3] presents several limitations of the hazard quotient approach, such as:

- it can only indicate whether effects on individuals are expected, not the magnitude of effects;
- the results are difficult to interpret when the hazard quotient for one endpoint (e.g. mortality) conflicts with that for another endpoint (e.g. fecundity);
- results are sometimes ambiguous depending on the toxicity threshold chosen (e.g. LOEL, NOEL);
- usually does not provide enough information to make a management decision;
- population-level processes may compensate for adverse effects on individuals;
- the life history and ecology of a species can strongly influence the effects of toxic chemicals at the population level;
- at best, the hazard quotient can only be used to screen out risks that are clearly not a problem (when the hazard quotient is considerably less than 1).

Hence, a QERA that ignores population-level effects and focuses only on individual-level endpoints may lead to inaccurate risk estimates. This will cause errors in environmental and risk management decisions and lead to inefficiency. Overestimation of risk can lead to waste of resources to mitigate apparent problems that are not really important, whereas the underestimation of risk can lead to inadequate risk management to control and prevent adverse effects to the ecological environment.

As a matter of fact, most toxicity data are expressed as adverse effects on individual organism, i.e. individual-level endpoints. So how to assess higher-level effects, if there are no toxicity data expressed as higher-level endpoints?

Population-level effects or higher-level effects can be obtained with the use of ecological models in the QERA. Such ecological models are essentially used to translate responses in individual-level endpoints into effects on population, ecosystem, or landscapes endpoints. Particularly, when they focus on population-level effects, they are called population models.

In a very simple case, a population model can predict the expected numbers of individuals in a population in the future from estimates of survivorship and fecundity for individual organisms. Thus, chemical effects can be modeled by perturbing the survivorship and fecundity values on the basis of knowledge about changes in these parameters obtained from toxicity test results. [3]

By the way, at the end of August 2009, a group of approximately 30 stakeholders from industry, government regulatory bodies, and academia met for a 2-day workshop in Roskilde, Denmark (RUC09). The purposes of the workshop were to discuss future uses of population modeling in risk assessment by industry as well as its understanding and acceptance by regulators. Forbes *et al.* found that "A major motivation behind this initiative is that, for the sake of more transparency and better risk communication, ecological risks need to be expressed in more relevant (value-relevant) units than hazard ratios, and these units will often be at a population level" [20].

Moreover, the predictive accuracy of population models has already been validated. For instance, Brook et al. [59] validated the prediction of abundance and risks of decline by comparing the historic trajectories of 21 populations (collected from long-term monitoring studies) with the results of population models for these populations. They found that predictions were surprisingly accurate: "the risks of population decline closely matched observed outcomes, there was no significant bias, and population size projections did not differ significantly from reality".

All things considered, one advocates the QERA approach based on the use of ecological models (particularly population models) to obtain population-level measures, so that risk analysis can assess the probability of a population extinction (or decline) in the future under several environmental conditions, accidental scenarios and management actions. The next section introduces theoretical basis on the use of ecological modeling in risk assessment.

2.5 Ecological Modeling in Risk Assessment

Pastorok *et al.* states that "an ecological model is a mathematical expression that can be used to describe or predict ecological processes or endpoints such as population abundance (or density), community species richness, productivity, or distributions of organisms" [3]. Thus, population and metapopulation (i.e. set of populations of same species living spatially separated but with potential for migration among them) models are a classification of ecological models, in which the mathematical expression is essentially used to translate individual-level effects (e.g., increased mortality, reduced fecundity) into population-level effects (e.g., reduced abundance, increased risk of extinction), so that one can estimate the risk of adverse effects on a population via toxicity data expressed as adverse effects on the individual organism.

The best way to choose the assessment endpoints is to check if they are directly relevant to environmental and risk managers of the enterprise. That is, the risk assessor should keep in contact with these managers to build the ecological model.

With regard to the use of ecological models in the context of QERA, they should also include toxicity extrapolation models, which are used to extrapolate toxicity data in order to describe effects on individuals depending on the species, measurement endpoint and exposure duration. Thus, with the use of ecological models, individual-level effects can be translated into higher-level effects (i.e. effects on population, ecosystem or landscape), and that is the basic rationale for ecological modeling in risk assessment.

As a result, one can estimate the risk of adverse effects on populations, ecosystem or landscape via toxicity data expressed as adverse effects on individual organisms (i.e. individual-level endpoints). Moreover, once formulated the ecological model, it may aid in assessing natural recovery, in developing monitoring programs, in planning restoration of strategies, or in deriving remedial action goals [3].

To sum up, ecological models are used to extrapolate a measurement endpoint to an assessment endpoint. They can predict responses in the population, ecosystem or landscape (using assessment endpoints) via measured individual-level responses (using measurement endpoints). In the specific case of a population model, it is a mathematical expression where the dependent variable (usually the future population abundance) is predicted through measure endpoints (such as survival and fecundity rates) and the population abundance at the present time.

It is important to note that there are several other components in population dynamics rather than survival and fecundity, as described in section 2.1.2, and they can also be incorporated into a population model. Some extensions to a population model are showed below (for more details see the references [3; 34; 35]):

- age or stage structure;
- sex structure;
- parameters vary with time due to stochasticity;
- parameters vary with time due to deterministic trend;

- parameters vary in space: population-specific models for metapopulations (e.g., ref [12]);
- parameters vary with abundance: density dependence;
- additive effects: introduction, harvest, migration between subpopulations in a metapopulation, and **catastrophes (e.g., industrial accidents)**.

Figure 2.3 and Figure 2.4 illustrate the idea of a very simple ecological model at population-level (i.e. population model); the former illustrates the natural dynamics of the population in the future (i.e. without chemical exposure) whereas the latter includes chemical exposure. In this very simple illustration, the future population abundance (assessment endpoint) is predicted through the survival and fecundity rates (measurement endpoints) and the initial population abundance. Once again, there are several other variables which can influence the future population abundance. Sometimes they may not matter much, but sometimes they may matter a lot. It depends mostly on the knowledge of the modeler about the population, on the available data and resources, and on the objectives of the modeling. On the one hand, including other variables makes the model more realistic, on the other, it becomes more complicated and more data is required.

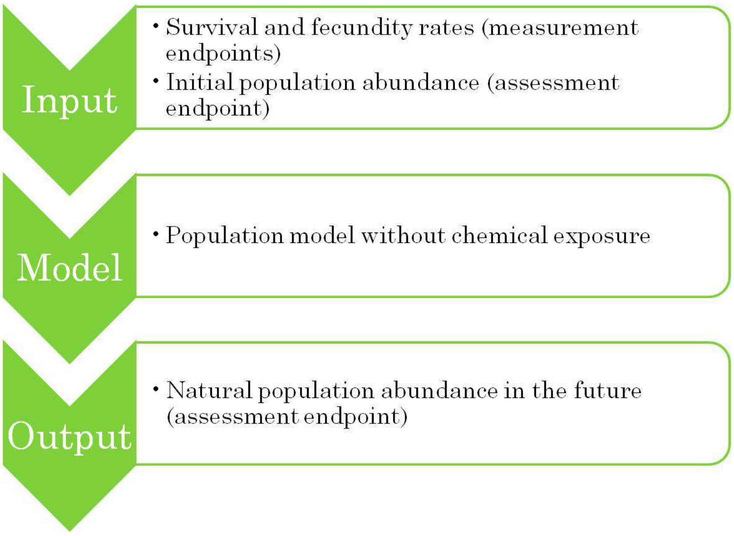

Figure 2.3 - Basic idea of a population model without chemical exposure

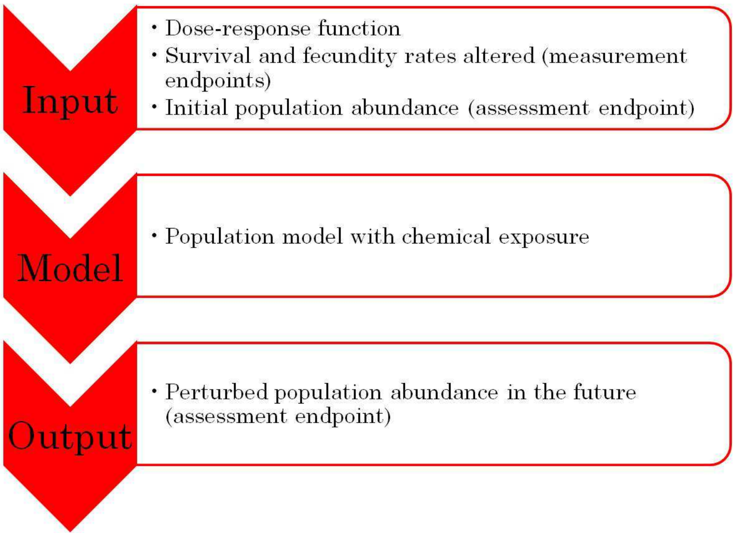

Figure 2.4 - Basic idea of a population model with chemical exposure

Generally, field sampling is used for the estimation of values to the measurement endpoints and the initial conditions of the assessment endpoints, whereas an exposure-response assessment is conducted in order to describe the relationship between the concentration of the chemical and the magnitude of the individual-level responses of native species (represented by changes in measurement endpoints). This relationship is usually specified by a dose-response function, so that it is necessary data on long-term effects of the chemical on the species being analyzed.

Several ecological models and software are already available for use in risk assessment of toxic substances. Pastorok *et al.* [3] conducted a critical evaluation of ecological models that are potentially useful for QERA and ranked the various candidate models based on evaluation criteria that include: realism and complexity of the model (i.e. whether key processes are included and how they are presented); prediction of relevant assessment endpoints and utility relative to regulatory compliance; flexibility; treatment of uncertainty; degree of development, consistency and validation; ease of parameter estimation; regulatory acceptance; credibility (e.g. prevalence of users, availability or published reviews); and resource efficiency. Furthermore, the best models were selected for a more detailed evaluation and testing.

Nonetheless, selecting the best model depends on the specific problem, so that the modeler must decide it taking into account the management objectives, the ecosystem, chemicals of concern, receptors and endpoints of interest, quality and quantity of available data, and available resources. Thus, model selection is usually site- or issue-specific. Besides that, the level of realism and precision wanted as well as the quality and quantity of data will influence the complexity of the model selected [60].

Habitats used by most species around industrial sites are becoming increasingly fragmented by human activities and, consequently, several distinct populations of same species are living spatially separated, in spite of interacting at some level (e.g. exchange of individuals). In fact, there are relatively few cases where the entire population resides within a same area. Hence, most species are distributed across space as a population of connected populations, i.e. metapopulation. According to Pastorock *et al.*, "a metapopulation is a set of populations of the same species in the same general geographic area with a potential for migration among them" [3]. This way, some ecological models are designed to link Geographic Information System (GIS) with a metapopulation model, combining geographic and demographic data for risk assessment.

By the way, the purpose of the proposed methodology is to conduct a QERA at population-level. Hence, this work does not delve into concepts related to QERA at higher levels and it might be referring to "Population Modeling" instead of "Ecological Modeling". The reason for choosing (meta)population modeling instead of higher levels modeling is that apart from providing ecologically relevant endpoints, (meta)population models are much more tractable than higher level models. Figure 2.5 illustrates this point of view.

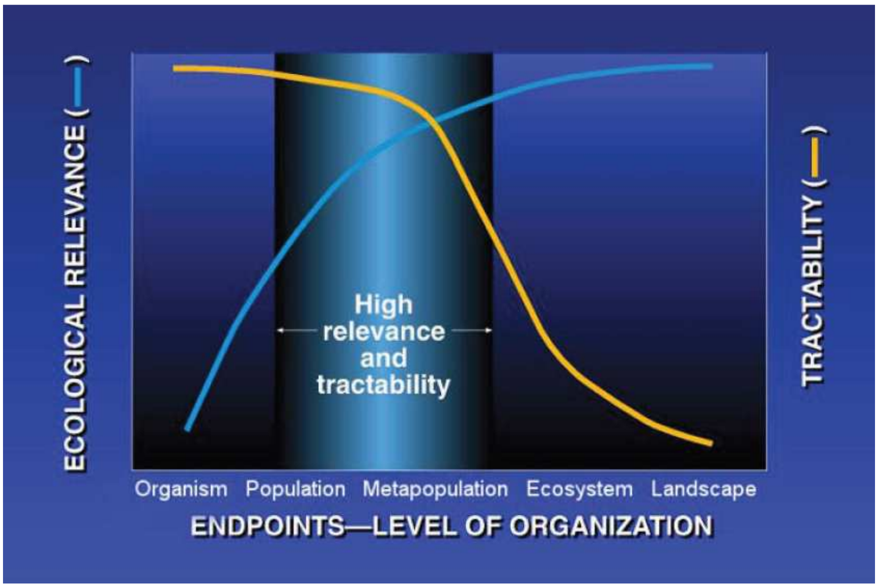

Figure 2.5 - Evaluation of modeling endpoints based on ecological relevance and tractability. (From the ref. [61])

Other several advantages of using population models in risk assessments are related in the reference [61]. Among them, Pastorok *et al.* states that

> “Risk estimation based on population modeling yields value-relevant output (e.g. reduced wildlife population abundance, increased extinction risk) that can be used in cost-benefit analyses to support management decisions concerning siting of facilities and mitigation actions” [61].

It is important to stress here that population modeling will be incorporated into the methodology for QERA proposed in this work, which will then be capable of assessing population-level and metapopulation-level risks only, but not higher-level (ecosystem or landscape) risks. Despite that, it is possible to strategically choose (meta)populations of native species that can effectively represent the ecosystem integrity.

Implementing a population model for a QERA is actually an iterative process that involves data gathering, modeling, model validation, uncertainty and sensitivity analysis. The steps in implementing a population model for a QERA will be described in section 3.5. For a detailed guidance on population modeling see the reference [35] as well as the reference [3] for population modeling applied to risk assessment.

Once a population model is formulated (i.e. a mathematical expression), one has a deterministic model (i.e. no probabilistic components) to predict adverse effects on populations given the exposure to a chemical (in concentration or dose). However, as already mentioned, any realistic attempt to model population dynamics should account for stochasticity, especially because fluctuation is an obvious and often predominant feature of ecological environments. More on this regard will be discussed in section 2.5.3.

2.5.1 Age and stage structure

The age or stage structure of a population refers to age/stage classes within the population. They attempt to consider the fact that individuals of different ages have different characteristics, which are reflected in their vital rates (e.g. survival and fecundities rates), whereas individuals of same age have similar characteristics. For instance, juveniles may have lower survival rates than adults or juveniles may not be able to reproduce until they become adults. Conversely, in an unstructured (scalar) population model, the population is represented by a single age/stage, which denotes the totality of the population. Thus, unstructured models are considered to be a special case of structured models, with only one class of organisms [35].

Structured models are useful if the vital rates of individuals in different classes are different enough to justify the discretization of their life span. Individual classes mean their ages or stages. For example, population model of a fish with a life span of nearly 4 years could be structured by their ages, e.g.: zero year old, one year, two years and three year; or by their stages: juveniles (zero year old) and adults (one year old or more). The criteria to structure a model by stages instead of ages are: individual's ages are unknown; vital rates depend on stage or size rather than age; growth is plastic, some individuals are retarded or have accelerated development of vital rates.

Those individuals that are the same age/stage are assumed to have the same survival and fecundity rates. However, those rates may differ between classes. This way, an structured population model has a survival rate, S_x, a fecundity rate, F_x, and an abundance at time t, $N_x(t)$ for each age/stage class x. The abundances for each class form a vector of numbers (one for each class), whereas the vital rates are combined to form a transition matrix that is used in most population models to account for age/stage structure. In fact, it is a transition matrix which has a special structure, called a Leslie matrix for age-structured models [11; 62] and a Lefkovitch matrix for stage-structured models [63]. Above is an example of a Leslie matrix.

$$L = \begin{bmatrix} F_0 & F_1 & F_2 \\ S_0 & 0 & 0 \\ 0 & S_1 & 0 \end{bmatrix} \tag{2.1}$$

Where

$$S_i = survival\ rate\ of\ individuals\ in\ age\ class\ i$$
$$F_i = fecundity\ rate\ of\ individuals\ in\ age\ classe\ i$$

The reason for arranging the survival rates and fecundities in the form of a matrix is to provide a convenient way to make projections of population's structure from one generation to the next [35]. For example, for an age-structured model the distribution of abundances in the next step is given by the matrix multiplication:

$$\begin{bmatrix} N_0(t+1) \\ N_1(t+1) \\ N_2(t+1) \end{bmatrix} = \begin{bmatrix} F_0 & F_1 & F_2 \\ S_0 & 0 & 0 \\ 0 & S_1 & 0 \end{bmatrix} \times \begin{bmatrix} N_0(t) \\ N_1(t) \\ N_2(t) \end{bmatrix} \tag{2.2}$$

Where

$$N_i(T) = number\ of\ individuals\ at\ age\ classe\ i\ at\ time\ T$$

Assessors may then choose which age/stage classes they are interested in assess. In most case, they will be interest in the total population abundance, which will be the sum of the age abundances. In some cases, however, the may be interested in the abundance of a specific class only.

2.5.2 Density-dependence

Section 2.1.2 introduced the natural mechanism of populations to regulate themselves (i.e. density dependence). This section is particularly concerned about the mathematical modeling of density dependence. For more details on density dependence see the reference [35], chapter 3.

To model density dependence, one must

- Decide which stages will count towards the abundance. At times a great amount of individuals in a certain life stage will not cause impact on the population's vital rates. For example, when adult birds compete for territory, only the adult stage would count towards density dependence. The abundance taken into account may depend on all stages, selected stages or even on an average of all stages weighted by their respective fecundities.
- Determine the vital rates to be altered. Depending on the behavior of the population, density dependence may affect fecundity, survival, migration rates, or a combination of these. This selection needs to be coherent with the transition matrix. For example, in a model with a single stage, density dependence cannot affect survival rates because there are none.
- Choose the form of the density dependence function. Modelers can define a density dependence function themselves, but there are functional forms of density dependence used in the literature, they are [35]:
    - Exponential: no density dependence. All parameters related to density dependence are ignored, only the stage matrix is used in calculations.
    - Scramble: as population size increases, the amount of resources per individual decreases. If the available resources are shared more-or-less equally among the individuals, there will not be enough resources for anybody at very high densities. This process of worsening returns leads to scramble competition, and can be modeled by logistic or Ricker equations [64].
    - Contest: if the available resources are shared unequally so that some individuals always receive enough resources for survival and

reproduction at the expense of other individuals, there will always be reproducing individuals in the population. This will be the case, for example, in populations of strongly territorial species, in which the number of territories does not change much even though the number of individuals seeking territories may change a lot. This process of diminishing returns leads to contest competition, and can be modeled by the Beverton-Holt equation [65].

  - Ceiling: exponential growth to a ceiling. At each time step, the population grows exponentially, but if N is greater than the ceiling, then N is set equal to the ceiling.

- Select function parameters. In case of scramble or contest competition, the carrying capacity (K) maximal growth rate (R_{max}) need to be estimated. The carrying capacity is the level of abundance above which the population tends to decline. Therefore one should observe the equilibrium population size for which the number of individuals at the next time step tends to remain the same. R_{max} is the maximal rate of increase when the population that is regulated by density dependence is not yet influenced by it because of low density. The greatest growth rate observed might be skewed because of stochasticity, causing wrong estimation of the parameter. Therefore a more convenient form of finding the value one wishes for is by making a graph of R(t) as a function of N(t) (number of individuals at time t) and using the y-intercept as R_{max}. Since considering R(t) equal to N(t+1)/ N(t) would cause both the independent and dependent variables to be affected by N(t) measurement errors, a less biased option would be to consider R(t) equal to the geometric average of N around the time step *t*, i.e. $\sqrt{N(t+1)/N(t-1)}$. In case of Allee effects [36; 37], the A parameter is the population size at which the vital rates are reduced to half of the original value.

It is important to note that including density-dependence in a population model to evaluate the impacts of pollution (i.e. chemical risk assessment) makes the assessment less conservative, because density-dependence effects cause population to recover faster after a pollution episode (except in the case of Allee effects). There is an intuitive way to understand this: after chemical exposure, population suffers from decreasing abundance as long as significant amounts of chemical remain present; on the one hand, if density dependence is ignored, the population growth rate remains the same and population takes longer to recover; on the other hand, if density dependence is considered, then after a decrease in population abundance, the growth rate suffers an increase (positive density dependence), so that population recovers faster.

2.5.3 Stochasticity

The variability and uncertainty in populations and in the environment they live is a fundamental component of population dynamics, so that population models that assume all parameters to be constant (i.e. deterministic models) fail to account for unpredictable fluctuations of real population dynamics. Conversely, stochastic models allow us to consider these fluctuations. They involve replacing constant parameters, such as survival and fecundity rates, and carrying capacity, with random variables responding to a probability distribution function (PDF), usually a normal or lognormal with a certain mean and variance.

There are many different kinds of stochasticity to be incorporated into a stochastic population model, such as:

- environmental temporal fluctuations (i.e. temporal variation in parameters);
- spatial variation (e.g., population-specific parameters for metapopulations);
- measurement and sampling errors that introduce additional uncertainty in parameter estimates of a population;
- demographic stochasticity (because individuals only occur in whole numbers and most parameters may be fractional numbers, there will be additional uncertainty in the number of survivors and births in the next time-step);
- model uncertainty (i.e. uncertainty concerning the structure of the equations used to describe the population)
- catastrophes (i.e. extremely environmental events that adversely affect large proportions of a population, e.g., fire, drought, flood).

Each one of them needs a different approach to modeling the effects of their fluctuations. This work will not delve into each one of them; readers are referred to the reference [35] for details on this issue.

Nevertheless, catastrophes will be an especial type of stochasticity in the proposed methodology, because it allows accidental scenarios to be considered as extremely and rare environmental events included in a population model with a certain probability of occurrence per time step that may either be constant or vary with time. In other words, at each time step a catastrophe (or an accidental scenario) may happen with a certain probability. If it happens, its effects of pollution can be modeled by changes in parameters since the present time step; if not, all parameters remain the same. Section 2.5.5 presents this approach in more details.

Pastorok *et al.* states that there are two kinds of model endpoints: state variables and risk estimates:

> *State variables* are expressed as population, ecosystem, or landscape indicators, such as population abundance, species richness, or landscape fragmentation index, respectively. [...] *Risk estimates* can be derived from the model output for state variables in several ways, but the most common is to run the simulation multiple times in a Monte Carlo analysis to account for variability and uncertainty in input variables as well as initial conditions". [3]

In other words, what Pastorok *et al.* meant is that risk can be estimated through multiple simulations of the ecological model via Monte Carlo. Since a stochastic model has probabilistic components characterized by random variables responding to a PDF, there will be a different result for each single run. Thus, the results will also form a PDF which will characterize the risk estimates (e.g., risk of extinction, risk of population decline). Following such a procedure will allow variability to be evaluated as a degree of confidence, as well as to estimate upper and lower bounds on risk measures to evaluate uncertainty.

A simpler way to deal with uncertainties is to use them to derive worst and best case estimates of extinction risks, based on manual changes on parameters. Such procedure allows estimating a range (upper and lower bounds) to risk measures, such as time to extinction, or risk of decline. The greater are the uncertainties in parameter values, the wider will these bounds be. If they are too wide, uncertainty may be unacceptable and do not meet the needs of risk managers. At best, the bounds should be narrow enough to make decisions taken by risk managers based on the lower bound the same as those based on the upper bound (i.e. the difference between the lower and upper bound should be regardless for risk managers).

All in all, a population model with random variables (and it should be present to better represent reality) is a stochastic model, since the input variables and/or initial conditions respond to a PDF. Hence, the model does not provide a single result, but a distribution of consequences associated to probabilities. The next section presents the ways of expressing the results of a stochastic population model.

2.5.4 Ways of expressing the risk estimates

The most traditional measure to summarize the results of a population model is the expected population trajectory (i.e. the expected number of individuals in a population in the future), which is usually expressed by a mean, a ±1 standard deviation, a minimum and maximum values. However, several ecological-related problems and questions that population models address are phrased in terms of probabilities. For instance, a certain population of a certain species may have a 50% chance of extinction in the next 10 years (i.e. a "critically endangered" population according to IUCN, the International Union for Conservation of Nature [39]).

The probability is usually derived from multiple runs (Monte Carlo) of a population model and may be expressed in many ways as bellow [3]. The selection of a specific expression for the probability depends partly on the objectives of the assessment and partly on available information for the species being modeled [3].

- **Interval decline probability:** the probability of a population declining by as much as a given percentage of its initial value at any time during the period of prediction.
- **Interval extinction probability:** the probability of a population falling as low as a given abundance at any time during the period of prediction.
- **Terminal decline probability:** the probability of a population being as much as a given percentage lower than its initial value at the end of a simulation.
- **Terminal extinction probability:** the probability of a population being as low as a given abundance at the end of a simulation.
- **Interval explosion probability:** the probability of a population equaling or exceeding a given abundance at any time during the period of prediction.
- **Terminal explosion probability:** the probability of a population being as great as or greater than a given abundance at the end of a simulation.
- **Time to extinction:** the time required by a population to decrease to less than a given threshold abundance. This work basically uses two threshold: total extinction (i.e. zero individuals) and "half loss" (i.e. 50% population decline).
- **Time to explosion:** the time required by a population to exceed a given threshold abundance.

Thus, for instance, to estimate the terminal extinction probability, one runs the simulation multiple times and counts the occurrences in which the population ends the simulation lower than a given abundance. The probability (of a population being as low as the given abundance at the end of the period) will be the number of such occurrences divided by the total number of rounds. Clearly, the greater is the number of rounds, the more precise is the probability.

By the way, explosion probabilities and time are especially useful when a population increase may be unwanted. For example, one may want to estimate the probability that a certain seaweed species outbreak will reach an ecological damaging level, because it consumes most oxygen available for fishes in the sea.

Also, explosion probabilities and time are useful to evaluate recovery chances, when the objective is to estimate the recovery of a population under risk management actions. In such cases, it may be useful to estimate the time it will take the population to increase to a certain abundance (i.e. time to recovery, analogous to the time to explosion), or the probability of recovery within a specified time period (analogous to the explosion probability).

To conclude, there are other useful single measures to summarize the predictions of the risk curves [34], i.e.:

- **Expected minimum abundance:** the average (over all replications) of the minimum population abundance of the trajectory. It is an estimate of the smallest population size that is expected to occur within the simulated time period.
- **Median time to extinction:** represents the most likely time required by a population to decrease to less than a given threshold abundance. It is the median value in the PDF of the time to extinction.

2.5.5 Assessing impacts and risks of each accidental scenario

Through evolution, most species go naturally extinct, typically within ten million years or so of their first appearance [66]. Furthermore, human impact may accelerate this time. By human impact one means not only industrial accidents, but several other kinds of human perturbations to the ecosystem that may be continuously affecting a wildlife population, especially if the ecosystem surrounds an industrial activity. Thus, even under the condition that no accidental scenarios might happen, a population has already an implicit risk of extinction.

Therefore, assessing impacts and risks of an accidental scenario alone is not enough. It must be compared against the present environmental condition (i.e. a non-impact scenario) to evaluate the changes in risks. In a non-impact scenario, no future impacts may occur (e.g., accidental scenarios), but only impacts that are already affecting the population.

An accidental scenario can be compared with a non-impact scenario in two ways. Both of them can provide relevant information, so that a QERA should, at best, present results using both approaches. The first one considers only the impacts (i.e. the consequences) of the accidental scenario of concern, whereas the second considers both the frequency of occurrence and the consequences (i.e. the risks).

2.5.5.1 Assessing impact

It considers that the accident is sure to occur at a specified time during the simulation. This approach ignores that the accident is a rare event and considers it as an almost surely event at specified time. This is particularly useful to evaluate the impacts (i.e. consequences) of the accident, because it presents the population dynamics before and after the accident. Hence, one could compare an impact scenario to a non-impact scenario as a means of evaluating the accidental scenario in terms of increase in consequences. Then the results may be used to determine whether the predicted consequences are substantial enough to require pro-active response or action. For instance, this approach provides information to answer questions such as:

- Does the population go extinct before the accident? And what about after the accident?
- What will the population abundance of a species (e.g. sardine) be 1 year after exposure to the concentration of toxic substances (e.g. hydrocarbons) released by the accident?
- How long after the accident would it take for the exposed population to decline by a certain value (say 20 or 30%)?
- What is the probability of extinction in the population after the accident?
- What is the probability of the population dipping below a given threshold (say 20 or 30% from the original population) at some point in the next year after the accident?
- If we invest a certain quantity of money (say U$100,000) in mitigation actions that reduce the magnitude of impacts, what will be the extinction probability decrease?

2.5.5.2 Assessing risks

It considers that the accident might happen with a certain probability (equal to the accident's frequency of occurrence) at any time during the simulation. This is similar to the catastrophe stochasticity type (section 2.5.3). Thus, the results represents not only the consequences of the accident, but the risks (i.e. a measure that encompasses both consequences and frequency of occurrence). This approach allows the comparison of a non-impact scenario with a potential accidental scenario, in terms of changes in risk measures (e.g., risk of extinction, risk of half loss). Also, it allows the comparison of the accidental scenarios among themselves, which is useful for prioritizing management actions. For instance, this approach provides information to answer questions such as bellow, considering that there is a certain chance of a catastrophic toxic spill:

- How will the population abundance fluctuate during a period of 50 years?
- What is the change in the risk of extinction in the population?
- What is the risk of the population dipping below a given threshold (say 20 or 30% from the original population) at some point in a 50-year simulation?
- How serious are the changes in risk measures in a simulation with a potential accidental scenario when compared to a simulation with a non-impact scenario? Changes may be serious if species jumps categories of risk (risk categorization will be discussed in section 2.5.7).
- If we invest a certain quantity of money (say U$100,000) in mitigation actions, what will be the extinction risk decrease?
- And if we invest the same amount of money in control measures that reduce the accident's frequency of occurrence, what will be the extinction risk decrease?
- If we have only U$100,000 available for risk management, how to allocate this money in an effort to reduce risks the most? Which accidents prioritize?

2.5.6 Cumulating risks of all accidental scenarios

Quantifying risks of each accidental scenario provides a basis for categorizing them, comparing them against a non-impact scenario, and prioritizing management actions. However, it may also be useful to cumulate risks of all accidental scenarios as a basis for communicating the total ecological risk. Therefore, this work also proposes an approach for cumulating risks of all accidental scenarios in only one measure, i.e. the FN risk curve (similar to the FN curve for the social risk in human QRA).

Once again, N is the average population decline number (of native species strategically chosen to represent ecological effects) and F the cumulative frequency of accidents with N or greater abundance decline. This way, the greater the number of accidental scenarios in the assessment, the more points will have the FN curve, and so will it be more continuous. More details on how to build a FN curve will be given in section 3.6.

2.5.7 Risk categorization

Establishing risk criteria for acceptability in the FN curve is a slow and complicated process that requires the participation of society and other interested parties in its judgment. It was not an aim of this work to establish risk criteria for acceptability, which is a proposal for future works though.

Nevertheless, the risk status originated from the approach in section 2.5.5.2 can be categorized according to the International Union for Conservation Nature (IUCN) threat categories [39]. One of the IUCN criteria (the only quantitative one) are expressed in terms of time and risk of extinction, so either risk curves or cumulative time to extinction can be used to categorize risk based on these definitions. This way, a threatened population may be classified into one of the 3 risk categories:

- CRITICALLY ENDANGERED: at least 50% probability of extinction within 10 years or 3 generations: whichever is longer (up to a maximum of 100 years);
- ENDANGERED: at least 20% probability of extinction within 20 years or 5 generations, whichever is longer (up to a maximum of 100 years);
- VULNERABLE: at least 10% probability of extinction within 100 years;

The IUCN risk criteria are expressed in terms of total extinction (zero individuals). However, these criteria are intended to classify species at high risk of global extinction in an effort to convey the urgency of conservation issues to the international community. It is used to classify species affected by a whole range of environmental changes and human impact at global-level, not to classify the interaction of a single establishment with a local population or metapopulation.

In this context, establishing risk criteria for the purposes of a QERA was one of the main themes of discussion and decision in a workshop on ecological modeling at Applied Biomathematics, Setauket, New York, on August 24-26 of 2011. The author of this work was present at this workshop, together with some of the most cited authors in the field of ecological modeling. They concluded that it may be more appropriate to express risk criteria in terms of “half loss” (i.e. 50% population abundance decline) instead of total extinction. As a result, they proposed the following risk categories for the purposes of a QERA:

Table 3 - Categories for assessing risks of each accidental scenario in a QERA.

Category	**Risk of half loss**	**Years**
Critically Endangered	> 50%	10
Endangered	> 20%	20
Vulnerable	> 10%	100
Low risk	> 0.1%	100
Negligible	> 0.001%	100
Background risk	< 0.001%	100

2.5.8 Case studies

This section is especially concerned with a bibliographic review of published applications of ecological modeling in risk assessment. For instance, Naito *et al.* applies an ecosystem model for ERA of chemicals in a Japanese lake [67]; Pauwels presents a case study to show how risks to a brook trout (*Salvelinus frontinalis*) population exposed continually to a contaminant (in this case the pesticide toxaphene) can be assessed and quantified using ecological modeling, as well as describes the data needed to parameterize a fish population model [31]; Bartell *et al.* presents an aquatic ecosystem model for estimating ecological risks posed by toxic chemicals in rivers, lakes, and reservoirs in Québec, Canada [68]; finally, Chen uses an aquatic ecological risk assessment model to analyze exposure and ecological effects and to estimate community-level risks to fish, aquatic insects and benthic macroinvertebrates in Keelung River in northern Taiwan, associated with chemicals of potential concern such as ammonia, copper and zinc [69].

All those works were very useful as a basis of knowledge on ecological and toxicity extrapolation models. It is worth noting, however, that none of them are within the context of industrial accidents, as we aim to do in this work.

In addition, there are several other works on using ecological models not specifically in risk assessment related to chemical exposure, but manly in species conservation and management (see reference [70]). They are also very useful though, since they contain demonstrations of how an ecological model is implemented. Such reference was essential as guidance on the application example of this work, because it contains a collection of case studies of models applied to a variety of species (including fishes) and implemented in the population modeling and viability analysis software RAMAS GIS 4.0, which is an older but similar version to the same software that will be used in the application example of this work [34].

3 PROPOSED METHODOLOGY

The proposed QRA methodology is directed to industrial accidents with potential to cause ecological adverse effects. The methodology considers both the accident's frequency of occurrence and the magnitude of the adverse ecological effects, so that it is capable of quantifying ecological risks caused by events with low frequency of occurrence and catastrophic consequences. It is not restricted to assess ecological risks via individual-level endpoints that often leads to inaccurate risk estimates. It is also able to predict the responses of populations to toxic exposure (via population-level endpoints), taking into account the relationships between individuals, the life history and ecology of a species. This way, the methodology can assess the risk of a population extinction (or decline) in the future under the conditions that catastrophic accidents might happen. The proposed methodology is applicable only for ecological risks caused by toxic substances. It is not able to assess ecological risks of fire or explosion caused by accidents with substances that are solely flammable.

There are similarities between the methodology and the basic guidelines for preparation of studies in risk assessment provided by CETESB in the reference [50], which is applicable to the assessment of industrial accidents with potential to cause damage to humans outside the establishment (i.e. harm to people in surrounding areas, located beyond the establishment boundaries). The main similarities are in the qualitative risk assessment step that involves the consolidation of accidental scenarios via techniques such as Preliminary Risk Analysis (PRA); and in the risk quantification expressed as a FN curve, which is similar to the FN curve to quantify social risks used by CETESB. By contrast, the main difference is that the methodology seeks to assess ecological risks only, whereas CETESB focus on human risk assessment.

The steps of the proposed methodology are as follows (shown in Figure 3.1).

1. Problem characterization;
2. Identification of hazards and consolidation of accidental scenarios;
3. Exposure assessment
4. Frequency estimates;
5. Population modeling;
6. Risk quantification and evaluation.

The methodology is interactive, so that revaluation may occur during any part of the assessment, although deficiencies that must be revaluated may jeopardize resources available to complete the QERA (e.g. time and money). The methodology uses objective criteria throughout the second, third and fourth steps in order to rule out accidental scenarios that will not significantly contribute to the final ecological risk, avoiding waste of resources.

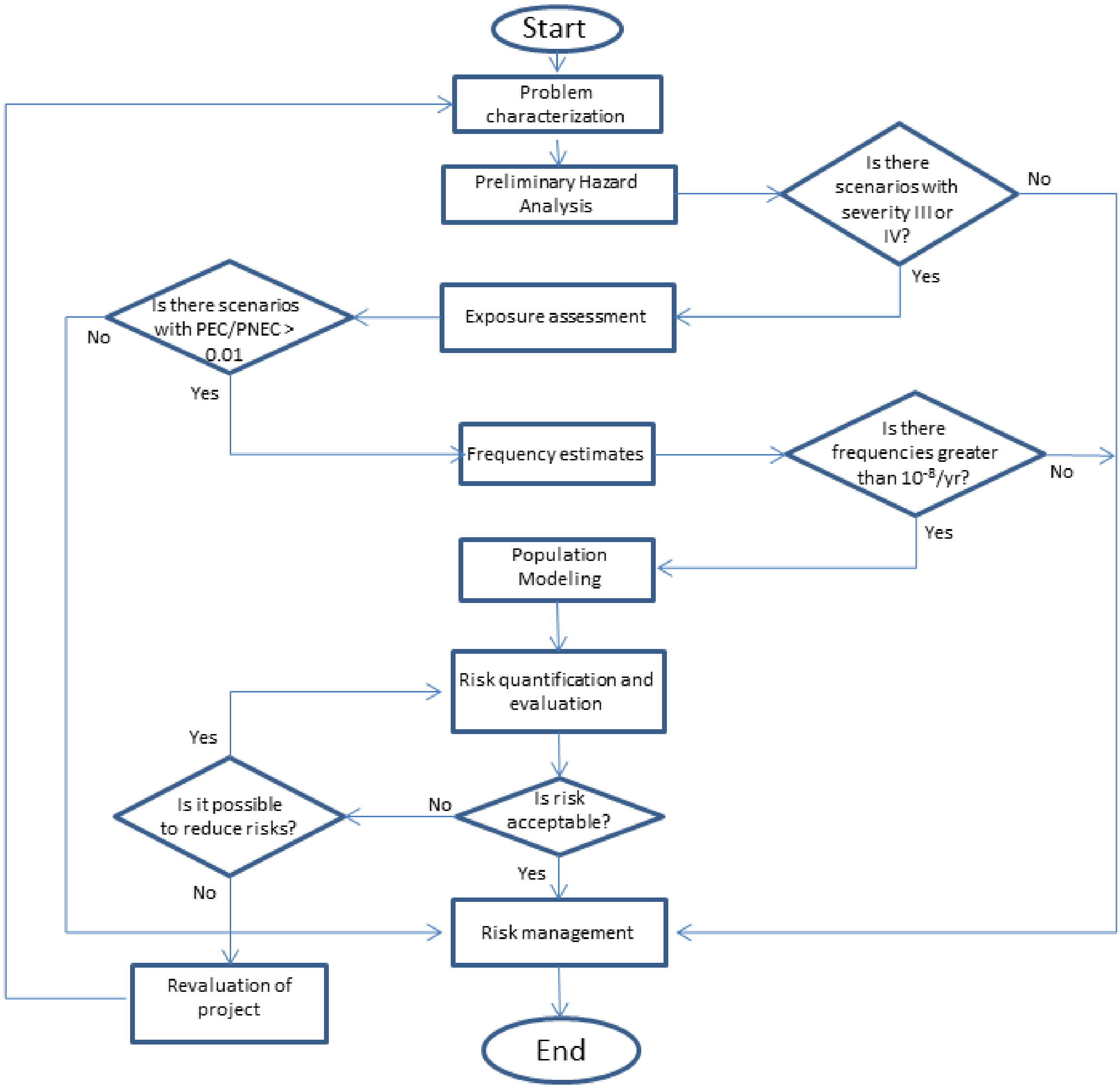

Figure 3.1 – Steps in conducting the methodology to Quantitative Ecological Risk Assessment for industrial accidents.

In the next sections, the aforementioned steps are discussed.

3.1 Problem characterization

The first step is a planning phase on which the entire risk assessment depends. It requires engagement between the risk assessor and others experts such as: risk managers, environmental managers, ecologists, technical managers, operators and others interested parties when appropriate (e.g. industrial leaders, government, environmental groups, any segment of society concerned about ecological risks).

They should be able to (1) define risk assessment issues and objectives, (2) characterize the establishment and installations (e.g. storage tanks, transport units, pipelines, loading equipment) to be included in the QERA and (3) characterize ecological components (habitats, species, life stages) in the region. Information to answer many of these issues may already be available from other studies such as an Environmental Impact Assessment (EIA) or even from a human QRA.

3.1.1 Risk assessment issues and objectives

The risk assessor should ensure that the results of the risk assessment will meet the needs of risk managers, i.e. how will risk assessment help the process of risk management. This way, they should reach a general agreement on characteristics such as:

- Nature of the problem (e.g. licensing process, company's own initiative, providing guidance, legal mandates).
- Objectives for the QERA, including criteria for success.
- Scale of the assessment (e.g. small area evaluated in depth or large area in less detail).
- General spatial (e.g. local, regional, or national) and temporal (i.e. the time frame over which effects will be evaluated) boundaries of the problem.
- Expected outputs of the QERA and the resources available to complete it (e.g. personnel, time, money).
- Policy considerations (corporate policy, societal concerns, environmental laws).
- Data and information already available. When data are few, further field work is needed to collected more data and that requires more resources for the assessment. When more resources are not available and new data cannot be collected, it may be possible to extrapolate from existing data. In this case, the risk assessor and risk managers must reach an agreement about what is known and what will be extrapolated from what is known.
- Acceptable level of uncertainty. If after the end of the QERA, the output does not meet the acceptable level of uncertainty, investment of new resources may be requested in order to develop ways of reducing uncertainty. The obvious way to reduce uncertainty is further field work to collect more data, so that additional

resources will be necessary. This way, the acceptable level of uncertainty should comply with the resources available to complete the assessment.

- Ecological impacts caused by past accidents.

3.1.2 Characteristics of the establishment

Here the risk assessor should collect technical information that characterize the establishment with regard to its physical structure, process conditions, chemicals of potential concern and installations (e.g. storage tanks, transport units, pipelines, loading equipment) in the establishment that deals with those chemicals.

Some installations may not significantly contribute to the risk because they do not deal with a considerable amount of hazardous chemical; therefore it is not worth considering all installations in the QERA. It is the responsibility of the risk assessor to select installations to be included in the QERA, under consultation of competent professionals and experts. The Committee for the Prevention of Disasters provides a selection method to determine which installations should be considered in a human QRA, provided in the second chapter of the reference [18]. This recommends a selection method of installations with potential to cause ecological damage, because this method is not dependent on consequences to humans, but on the amount of substance present in the installations and on the process conditions.

More specifically, the risk assessor should, if possible, gather relevant information about:

- Location of the establishment.
- Layout of the establishment, pointing the hazardous installations to be included in the QERA. If transport units are included as dangerous installations, the transport route should be specified.
- Updated plants or aerial photographs showing ecological environments near dangerous installations.
- Chemicals of potential concern identified by the official nomenclature, including: amount; ways of processing, handling, transport and storage; physicochemical properties. Raw materials, intermediate and finished products, byproducts, residues and wastes should also be considered.
- Description of processes in each hazardous installation and operational routines. If possible, besides a written description, it should include drawings, diagrams and flowcharts.

- Operational data (e.g. flow, pressure, temperature) on the processes with chemicals of potential concern.
- Protection and safety systems.

3.1.3 Characteristics of the ecological components

The purpose here is to gather information about ecological features in the environment possibly affected by accidents in the establishment. Hence, consultants such as environmental managers and ecologists may help the risk assessor out here, who should determine characteristics such as:

- Location of ecosystems possibly affected by accidents in the establishment.
- Area (spatial boundaries) of ecosystems to be evaluated, highlighting zones of permanent preservation.
- Ecological receptors (plants and animals) in the area, highlighting key species, e.g.: indicator species that are thought to be more sensitive and therefore serve as an early warning indicator of ecological effects; species of scientific and economic importance; rare and endangered species; or any species to be protected. For aquatic environments, indicator species are usually fishes, invertebrates or green algae. For sediment and soils, they are terrestrial plants, sediment dwelling organisms or earthworms. For air[1], representative species are typically birds.
- Geographic location and boundaries of populations or metapopulations of key species to be evaluated.
    - Geographic distribution of local populations within the metapopulation (when appropriate).
- Gather relevant information about the biology of key species.
- Define assessment endpoints that can effectively provide information about the population of key species of concern. Population-level endpoints are usually abundance, population growth rate, age/size structure, and spatial distribution [3]. For the purposes of this methodology, at least the population abundance must be considered.

[1]For these types of ecosystems, the toxic concentration in air is usually so low that sophisticated risk assessments are not worthwhile.

- Define the life stages of the species of concern and the points at which chemicals may affect an individual [3].
- Physical stressors (e.g. hunting, fishing, boat traffic, thermal effluents, extreme weather changes) already affecting the key species.
- Chemical stressors already affecting the key species.

It is important to stress that risk will be quantified via population models that describe the population dynamic of key species chosen here. Consequently, the process of choosing key species should be carefully conducted by the risk assessor and consultants, because it will have a great influence on the results of the QERA. Populations or metapopulations of key species should be strategically chosen in a way that at least: they are representative in the ecosystem possibly affected; there is enough geographic and demographic data on the population to build a population model; and there is enough ecotoxicological data on the key species of concern (or on related species).

When possible, one should build a visual representation of the relationships among representative biotic groups of ecological receptors in order to illustrate the flows of energy, carbon, or contaminants. For example, a food web relationships among representative biotic groups within a ecosystem is useful to illustrate the key species' position in the food web, which helps to qualitatively understand the ecological adverse effects at higher levels than population-level (i.e. community- and ecosystem-level).

Most information gathered in this phase will be necessary to guide the mathematical representation of the population dynamics, in the sixth step of the methodology.

3.2 Identification of hazards and consolidation of accidental scenarios

This step is similar to the second step of the basic guidelines for human QRA provided by CETESB in the reference [50]. The difference is that here the focus is only on the identification of accidents that may cause damage to the ecological environment.

This is a qualitative step of a risk assessment which aims at identifying all the initiator events of accidents and its possible consequences, i.e. to consolidate accidental scenarios. Structured techniques are applied in order to (1) systematically consolidate all accidental scenarios, to (2) qualitatively rank the risks related to each accidental scenario according to their frequency and severity, and to (3) select those accidental scenarios that should be subjected to a more detailed risk assessment (i.e. quantitative assessment) in the next steps.

The methodology makes use of the technique named Preliminary Hazard Analysis (PHA) to perform this step, although other techniques such as Hazard and Operability Analysis (HazOp), "What If?", Failure Mode and Effect Analysis (FMEA), among others, may be used when the risk assessor finds it is suitable for the installation being studied. More information about PHA and other hazard analysis techniques is provided in the reference [71].

A worksheet is generally used to report the qualitative information that consolidate each accidental scenario, such as: hazard, initiator event (what, where, when), causes, control measures, possible consequences to the ecological environment, as well as frequency and severity classes. A typical PHA worksheet is presented in Table 4.

Table 4 – Typical Preliminary Hazard Analysis worksheet.

Preliminary Hazard Analysis (PHA)								
Identified hazards	Probable causes	Possible effects	*Control Measures*	*Freq.*	*Sev.*	*Risk*	*Recommendations and Observations*	*Accidental Scenario*

Below is the description of information to be filled according to the PHA worksheet above:

- Identified hazards: hazards with potential to cause damage to the ecological environment. At best, it should contain the identification of the substance (CAS number), its temperature, pressure and flow rate.
- Probable causes: description of the causes that may lead to the identified hazard (i.e. initiator events), such as cracking or breaking certain pipeline or equipment.
- Possible effects: possible physical effects from the event (e.g. contamination of the beach nearby, death of fishes, decrease fecundity of fishes, restrict photosynthesis of marine plants, reduce the abundance of affected populations).
- Control measures: barriers and preventive actions which could avoid the occurrence of the initiator event.
- Frequency class: classification of the event on its frequency, according to Table 5.
- Severity class: classification of the event on its severity, according to Table 6.

- Risk rank: qualitative value to the risk level of each accidental scenario, which is a result of crossing the classes of frequency and severity, as illustrated in the Table 7. The risk is classified as Acceptable (A), Moderate (M) or Not Acceptable (NA). For acceptable risks, there is no need for additional measures, i.e., monitoring is necessary and sufficient to ensure that the control and recovery measures are maintained. To risks qualified as moderate, additional control and recovery measures should be evaluated, aiming at risks reduction. The classification as not acceptable risks is an indication that existing control and recovery measures are insufficient. Alternative methods should be considered for reducing the likelihood of occurrence and magnitude of consequences.
- Recommendations and observations: recommendations for control and recovery measures that should be taken to decrease the frequency and/or severity of the accidental scenario.
- Accidental scenario: Identification number to the accidental scenario.

Table 5 - Frequency classes.
(Adapted from the ref. [72])

Class	***Description***
A Very unlikely	*Conceptually possible, but extremely unlikely in the lifetime of the installation. Without historical references.*
B Remote	*Not expected to occur during the lifetime of the installation, although there are historical references.*
C Ocasional	*Likely to occur even once during the lifetime of the installation.*
D Probable	*Expected to occur more than once during the lifetime of the installation.*
E Frequent	*Expected to occur several times during the lifetime of the installation.*

Table 6 - Severity classes.
(Adapted from the ref. [72])

Class	***Description***
I Minor	*No damage or minor system damage, but does not cause ecological damage.*
II Major	*Irrelevant ecological damage.*
III Critical	*Considerable ecological damage caused by release of chemicals, reaching areas beyond the boundaries of the establishment. Accidental scenario results in ecological damage with short recovery time.*
IV Catastrophic	*Catastrophic ecological damage caused by release of chemicals, reaching areas beyond the boundaries of the establishment. Accidental scenario results in ecological damage with long recovery time.*

Table 7 - Risk ranking: Acceptable (A), Moderate (M) or Not Acceptable (NA).

		Frequency Categories				
		A	***B***	***C***	***D***	***E***
Severity Categories	***IV***	*M*	*M*	*NA*	*NA*	*NA*
	III	*A*	*M*	*M*	*NA*	*NA*
	II	*A*	*A*	*M*	*M*	*M*
	I	*A*	*A*	*A*	*A*	*M*

After all accidental scenarios have been identified, one should select the most relevant to a more detailed assessment. Therefore, one should clearly establish the criterion considered in the selection of the relevant accidental scenarios. For a conservative approach, one can use a criterion based only on the severity class. Therefore, in this work, it is adopted the criterion of severity III or IV to trigger accidental scenarios for further analysis in the next step [50].

Because PHA is often used as an initial risk study in an early stage of a project, the results of this step may be already available. In fact, in a human QRA, accidents with potential to cause damage to humans are identified and they usually have potential to cause ecological damage as well. In this case, most accidents have been already identified and the risk assessor should just review the ecological effects (i.e. possible consequences) caused by these accidents. Conversely, if a previous PHA was not conducted yet, this is a great opportunity to do it. Likewise, this PHA might be used in a human QRA.

At the end of this step one should have a set of accidental scenarios characterized by qualitative information as in Table 4. As already mentioned, all accidental scenarios classified with severity III or IV should be selected for further analysis in the next step. In addition, this step allows to systematically identify the existing accidents and their possible ecological damage, leading to an improved level of preparation to emergencies.

3.3 Exposure assessment

This step should be conducted for all accidental scenarios selected in the previous step to a further and more detailed assessment. Firstly, it consists of applying mathematical models that simulate the occurrence and movement of toxic releases in the water, atmosphere and soil.

More specifically, one must estimate exposure of key species to the chemical released, for each accidental scenario. This includes describing the chemical dispersion and predicting the concentration that reaches key species of concern in each instant of time, i.e. concentrations $C_i(x,y,z,t)$ within a defined area (spatial boundaries), for each accidental scenario, i. Chemical fate and transport models have been often used to describe and predict distribution and concentration of chemicals in the environment. Guidance on fate and transport models is beyond the scope of this work; one suggests the references [73; 74] for additional information.

For most accidental scenarios, meteorological conditions may influence the chemical dispersion and, consequently, the estimated exposure concentration. In such cases, it is necessary to generate a set of meteorological scenarios for each accidental scenario, *i*. Thus, if one has *x* accidental scenarios selected from the second step and *y* meteorological scenarios defined here, one has now $x \times y$ new accidental scenarios, each one with a specific function of exposure concentrations $C_i(x,y,z,t)$. In other words, each meteorological scenario defined in this step within each accidental scenario from the previous step will have a specific function of predicted chemical concentration that vary in time and space.

A meteorological scenario is defined by meteorological parameters that depend on the kind of environmental media (e.g. air, soil, water) the chemical moves through. Such meteorological parameters could be, e.g., weather stability class; wind direction and speed; air, soil/bund, water temperature; ambient pressure; humidity; tides of the sea; currents of the ocean; season of the year; etc. To do not yield an exaggerated number of new accidental scenarios for the QERA, it is useful to group the data in a limited number of representative meteorological parameters.

Subsequently, because the next steps of the methodology do require additional costs and special expertise, one should decide whether the chemical concentration estimated is expected to cause ecological adverse effects, for all accidental scenarios. In other words, one should select the accidental scenarios in which population-level effects are likely to occur, so that population-level ecological risks should be quantified. This way, the methodology needs a criterion to trigger accidental scenarios for further QERA. The hazard quotient (i.e. an exposure concentration divided by an effects concentration) is a commonly applied criterion for that [2; 75]. They are quick and simple to use and do not require special expertise from risk assessors.

In this sense, Pastorok *et al.* [3] states that “at best, deterministic hazard quotients […] can only be used to screen out chemicals, receptors, or site areas that are clearly not a problem (when the hazard quotient is considerably less than 1)”. In addition to that, EurEco found in recent study that most of the chemicals, pesticides and marine schemes developed for ERA, use the hazard quotient, calculated as the Predicted Environmental Concentration (PEC) divided by the Predicted No Effect Concentration (PNEC), to indicate low risk when it is less than 0.01 [75]. For a conservative approach in the proposed methodology, the PEC will be the local maximum[2] of $C_i(x,y,z,t)$, whereas PNEC is the concentration below which exposure to a substance is not expected to cause adverse effects on an individual organism. The former is provided by the results of chemical fate and trasnport models and the latter by ecotoxicologial data on the species being assessed, usually as a concentration based endpoint known as No Observed Effect Level (NOEL - see glossary for details). The ECOTOX database can be used as a source for locating single chemical toxicity data for plants and animals [76]. It is important to note that the PNEC is an individual-level endpoint and so is the hazard quotient.

As a result, the proposed methodology uses the criterion PEC/PNEC > 0.01 to pick accidentals scenarios to the next step. Because it is a very conservative approach, it is likely that no accidental scenarios that considerably contribute to the ecological risk will be ruled out. Nonetheless, if it concerns the risk assessor, he might evaluate other chemical aspects such as: persistence and biodegradability; bioaccumulative potential (via bioaccumulation factor); and solubility in water (in case of an aquatic ecosystem). For example, if the chemical is readily degradable, population-level effects are not likely to occur, even if PEC/PNEC is greater than 0.01.

Finally, at the end of this step one should have a set of accidental scenarios that are likely to contribute to cause population-level effects. Several parameters consolidate each accidental scenario, they are mainly: hazard, initiator event, causes, control measures, meteorological parameters, chemical concentration $C_i(x,y,z,t)$, and hazard quotient.

3.4 Frequency estimates

For the selected accidental scenarios in the previous step, the frequency of occurrence should be estimated. The output of the QERA is very dependent on this estimate, so that an under- or sub-estimate of this value can lead to rough errors in calculating the ecological risk.

In some risk assessments, the frequency of occurrence of an accident can be estimated from historical records contained in databases or references, since they are actually representative to the case. Generic frequencies and times are presented in the reference [18]. In the third chapter of this reference, Loss of Containment Events (LOCs) (caused by e.g., corrosion, construction errors, welding failures, blocking of tanking vents, mechanical impact, natural causes, domino effects, etc.) are described and their generic frequencies of occurrence are estimated, for various systems in an establishment, including stationary installations and

[2] By local we mean that it is within the spatial boundaries of populations being evaluated as well as within the simulated time period.

transport units such as: pressurized stationary tanks and vessels, atmospheric stationary tanks and vessels, gas cylinders, pipes, pumps, heat exchangers, pressure relief devices, warehouses, storage of explosives, road tankers, tank wagons, and ships.

However, those generic frequencies describe average situations and may need corrections concerning specific circumstances of the installation under assessment. Due to the complexity of some installations, it might be necessary to use expert opinion and Reliability Engineering techniques (e.g., event tree, Event Sequence Diagrams, Bayesian Belief Networks) in order to correct the generic frequencies taking into account the influence of control measures (e.g., safety management systems, alarms, automatic stops), as well as human errors that might contribute to the occurrence of the accidental scenario. In other words, the risk assessment team might need to conduct a reliability analysis involving generic equipment failures, control measures and human error. It is beyond the scope of this work to provide guidance on reliability analysis; for a general view on reliability theory, models, methods and applications, see the references [41; 42; 43; 77]; and for specific information about techniques such as Event Sequence Diagrams (ESD), Bayesian Belief Networks (BBN) and Human Reliability Analysis see the references [44; 45; 46; 47; 48; 49].

In addition to that, for each accidental scenario the frequencies concerning meteorological parameters that consolidate each accidental scenario (defined in the previous step) should be also taken into account. Consequently, meteorological statistics (deduced, for example, from a nearby and representative meteorological station) should be used to define fractional frequencies or number of observations to each meteorological scenario.

Finally, only accidental scenarios that contribute significantly to the ecological risk should be included in the QERA under the conditions that (1) the frequency of occurrence is equal to or greater than 10^{-8} per year and (2) PEC/PNEC is greater than 0.01. The criteria therefore are used to trigger accidental scenarios for risk quantification and evaluation via population modeling in the next step. The first criterion is taken from reference [18], where it is stated that “a threshold of 10^{-8} per year as criterion for including LOCs is considered reasonable since generic LOCs leading to the release of the complete inventory have failure frequencies in the range 10^{-5} and 10^{-7} per year”. The second criterion is taken from the previous step of the proposed methodology and was already explained.

The output of this step is then a set of accidental scenarios that are likely to contribute to the ecological risk, with their respective frequency estimates of occurrence. Several parameters consolidate each accidental scenario, they are mainly: hazard, initiator event, causes, control measures, meteorological parameters, chemical concentration $C_i(x,y,z,t)$, hazard quotient, and frequency estimate of occurrence (that is equal or greater than 10^{-8} per year).

3.5 Population modeling

This step is an iterative process (see Figure 3.2). Firstly, a population model is formulated (see section 2.5) in an effort to describe the natural population dynamics of key species in the area (without exposure to the chemical of concern). It is necessary to formulate a population model to each key species, if more than one is being analyzed. The population dynamics must be described via assessment endpoints defined in the first step. The predicted chemical concentration, $C_i(x,y,z,t)$ - for each accidental scenario, i, that may affect a population of concern - will be used as input variable to describe the population dynamics with chemical exposure.

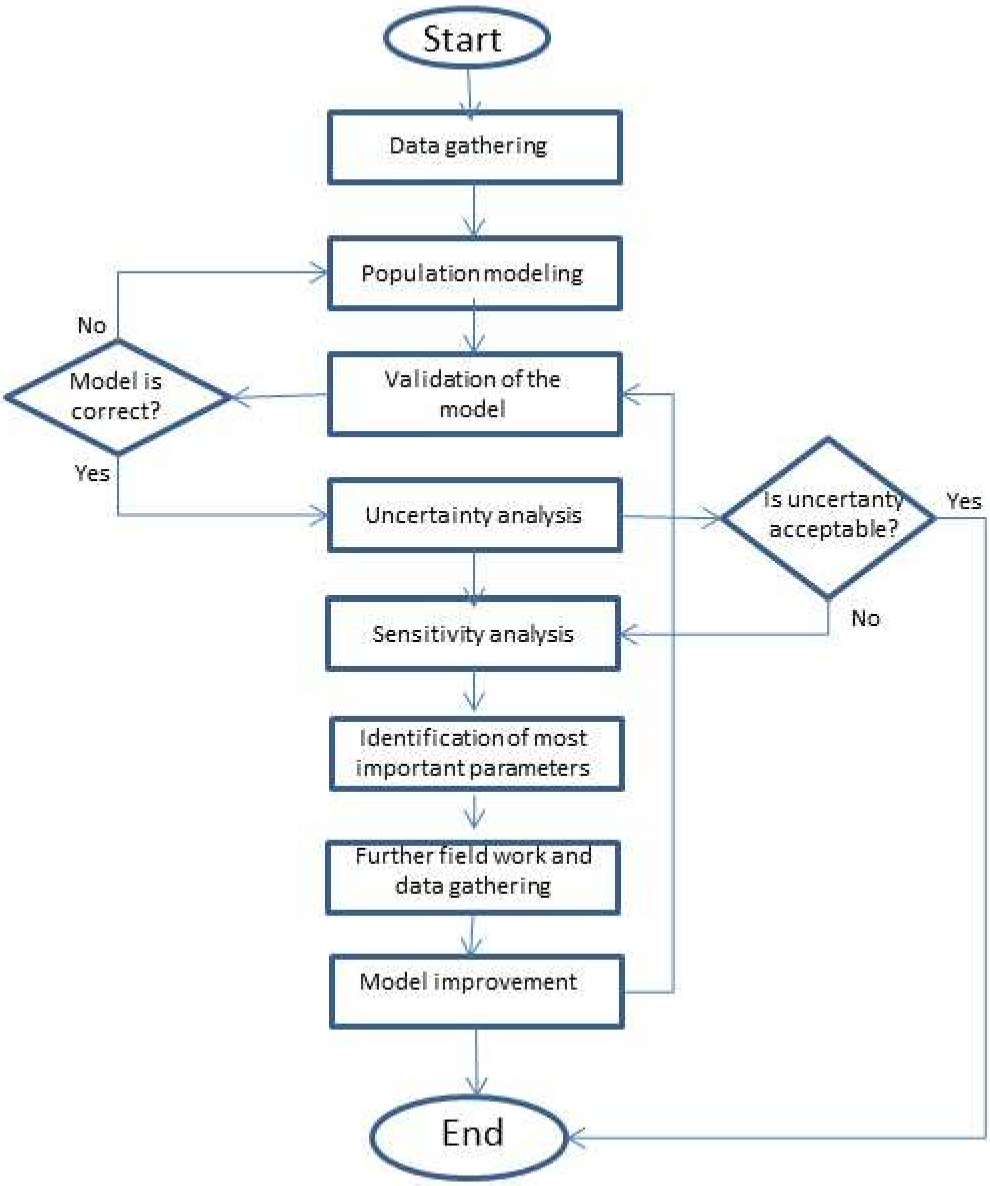

Figure 3.2 - Iterative process of population modeling.

Pastorok *et al.* [3] provides a detailed guidance on ecological modeling in risk assessment. He also makes a critical evaluation of software designed for a QERA, pointing their possible uses and limitations.

Input data will be necessary to parameterize the population model. The quality and predictiveness of the model depends mostly on the quality and quantity of these data. If data for the key species are insufficient, then one could extrapolate the information from related species.

Typically, a population model requires information on the following input variables [3; 31]: age/size structure; specific survival and fecundity rates for each age/size; rates of immigration or emigration; initial abundance for each age/size; estimates of variability for the vital rates and initial abundances; density dependence effects; geographic and habitat distribution of key species; and foraging behavior. The required level of detail for a particular variable depends on the assessment objectives.

Once the population model is formulated, it should be validated in order to make sure that the model is a good approximation of reality and provides reliable predictions. The validation of a model is typically done by measuring the conformance of predictions with empirical data. This measure may be used to characterize the reliability of other predictions.

It is still a limitation of this methodology to provide an effective method for validation. However, there is some ways to validate a model. For example, if there is hardly no chemical/physical stressors currently affecting the population, there is a very simple way to validate the model: to run the population model multiple times for a non-impact scenario and assess its predictions. For non-impact scenarios, it is expected that the population abundance will remain steady (for short and middle-term predictions) or will decrease very slightly (for long-term predictions, because it is expected that every species goes naturally extinct, although it takes thousands of years). This way, if the population model considers no physical and chemical stressors, and the predictions show either high risk of extinction or high risk of explosion, the model may be not correct and should be reviewed.

After validation of the model, an uncertainty analysis of risk estimates should be conducted in order to determine if the level of uncertainty is acceptable. A simple way to deal with uncertainties is to use them to derive worst and best case estimates of extinction risks, based on changes on parameters. Such procedure will let the risk assessor to estimate a range (upper and lower bounds) to risk measures, such as time to extinction, or risk of decline. The greater are the uncertainties in parameter values, the wider will these bounds be. If these bounds are too wide, uncertainty may be unacceptable and do not meet the needs of risk managers. At best, these bounds should be narrow enough to make decisions taken by risk managers based on the lower bound the same as those based on the upper bound (i.e. the difference between the lower and upper bound should be regardless for risk managers).

It is important to stress that there are several other ways to measure and communicate uncertainty. To study them and provide an effective method to evaluate uncertainty is proposal for future developments in this methodology.

If the model is appropriate to describe the population dynamics of concern, uncertainties about risk estimates are mostly because of uncertainties about parameters (e.g., survival rate, fecundity rate, carrying capacity, initial population abundance), what is originated from incomplete knowledge, limited sample size, measurement error and use of surrogate data. More precise estimates for parameters can improve the model by narrowing the ranges of risk measures. This requires further field work and data gathering, what costs resources such as equipment, technology, staff, time, etc.

Obviously, resources are limited, so its allocation should be optimized in a way that uncertainty is reduced the most. With this in mind, a systematic sensitivity analysis can point out to the most important parameters to allocate resources for further data gathering. This can be done by observing the effects of changes in any model parameter on population extinction risk.

In summary, if uncertainty is acceptable, then it is the end of this step. Otherwise, if the present model provides risk estimates with an unacceptable level of uncertainty, then a sensitivity analysis can point out to the most important parameters which need better estimates. Then, further field work and data gathering on these parameters can improve the model. Finally, one has an improved model (with a validated structure and more precise parameters) which must be further analyzed until it is validated and uncertainties are acceptable.

3.6 Risk quantification and evaluation

The output elements from the previous steps are necessary as input for this step, essentially:

- a population model for each key species;
- a predicted concentration $C_i(x,y,z,t)$ within the area of concern for each accidental scenario, i; t in the same unit as the time-step of the model;
- the frequency estimate of each accidental scenario per time-step of the model;

General temporal boundaries were determined in the first step. The risk assessor should now define specific temporal boundaries for each accidental scenarios, i.e. the expected time frame over which the accidental scenario causes ecological effects, which depends basically on the concentration $C_i(t)$ within the area and on remedial actions to remove chemical from the area. This will also become an input variable (i.e. the time of the simulation).

Subsequently, an exposure-response assessment should be conducted in order to describe the relationship between the concentration, *C(x,y,z,t)*, of the chemical and the magnitude of the individual-level responses of key species (represented by changes in measurement endpoints, e.g., survival rate, fecundity rate, carrying capacity). It will be usually necessary to specify a dose-response function, which can be built from data on long-term effects of the chemical on key species. These are ecotoxicological data at individual-level that basically look at the effects of life-cycle chemical exposure on input variables such as age-specific fecundity, survival and mortality. Because this is a major step in the ecological risk assessment, this topic is not addressed in the reference [3]. Instead, they suggest the references [1; 56; 58] as considerable guidance on how to analyze for toxicity and exposure-response relationships.

By linking exposure-response relationships to the population model, one can now predict how different concentrations of the chemical (note that for each accidental scenario there is a predicted chemical concentration) would cause adverse effects on populations of key species.

The probability of adverse effects may be represented by probability-consequence curves. For example, Figure 3.3 shows the consequences over time on population abundance for three different scenarios of chemical exposure. The several ways of expressing those curves were presented in section 2.5.4 and the two ways of assessing impacts and risks of each accidental scenario were described in section 2.5.5. The risks should also be categorized according to section 2.5.7. Lastly, a sensitivity analysis may add insight to the QERA by exploring the sensitivity to assumptions.

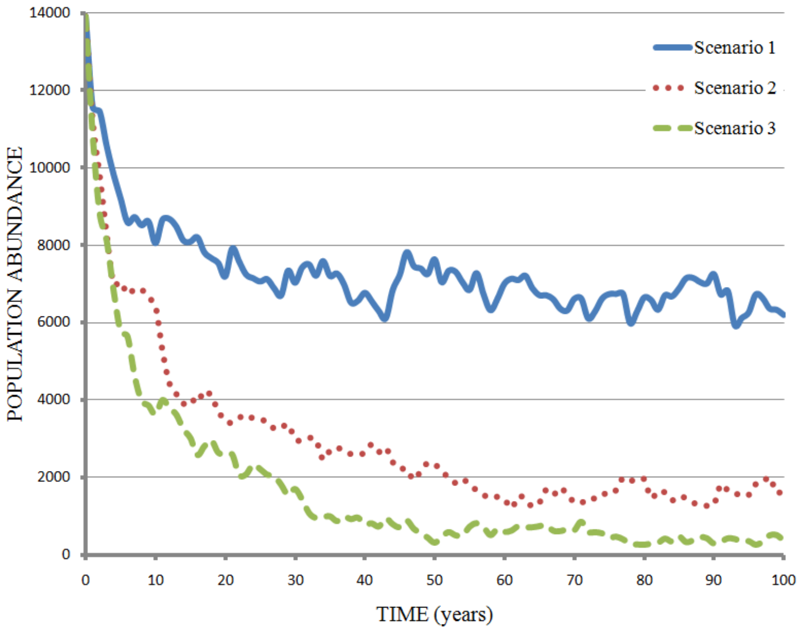

Figure 3.3 – Illustrative example of effects on a fish population for a 100 years simulation, for three different concentrations of oil exposure. Scenarios 1, 2 and 3, respectively: C(x,y,z,t) < 1 ml/L; C(x,y,z,t) = 16 ml/L; C(x,y,z,t) = 30 ml/L.

To quantify the ecological risks of all accidental scenarios in only one measure, the values of the consequence estimates should be combined with cumulative frequency estimate of occurrence. This regard was introduced in section 2.5.6. As a result, one builds a FN curve, where N is the average population decline number and F the cumulative frequency of accidents with N or greater abundance decline. For that, the following steps should be conducted:

a. Select a key species, *s*.
b. Set the average population abundance decline at the end of the simulation, N_{si}, for each accidental scenario, *i*, for each key species, *s*.
c. Build a list of average abundance decline, N_{si}, and its respective frequency estimate of occurrence, $F_{si}(y^{-1})$. It is necessary a list for each key species.
d. The FN curve is now constructed by cumulating all frequencies in each list (i.e. for each key species) for which N_{si} is greater than or equal to N:

$$F_s(N) = \sum_{\forall i: N_{si} \geq N} F_i \tag{3.1}$$

The Figure 3.4 shows an example of an FN curve that characterizes the ecological risks originating from accidents in an establishment.

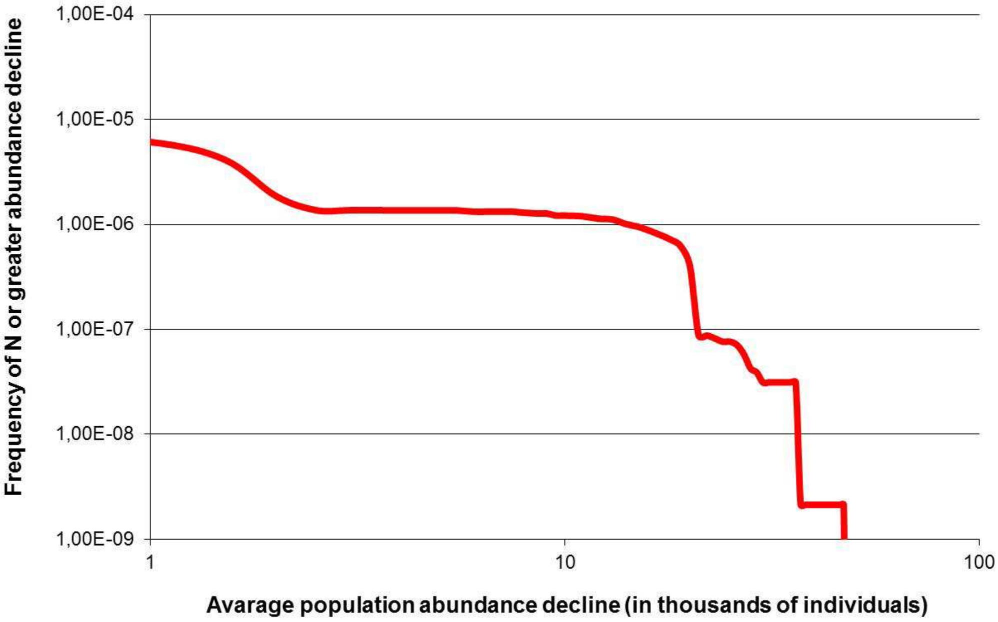

Figure 3.4 - FN curve for representation of the ecological risks related to accidents in an establishment (figure for demonstration purposes only).

Together, the risk curves (for each particular accidental scenario) and the FN curve can be used in making conservation decisions that involve planning future fieldwork, assessing impacts and evaluating management actions. For all these cases, the objective of the decision must be specified. It is assumed that the objective is minimizing the risk. Then a cost-benefit analysis can be made with the results of a series of assessments. The cost is actually the implementation cost of alternatives to reduce risk, and the benefit is the quantified risk reduction itself. Consequently, the selection criterion for the best alternative can be based on minimizing the cost:benefit ratio while satisfying either a cost or a risk constraint.

To sum up, the results of the methodology can support decisions such as for example:

- if we invest a certain quantity of money (say U$100,000) in control measures, what will be the frequency reduction in the FN curve?
- How best to allocate this U$100,000 in order to maximize risk reduction? Which accidental scenarios prioritize?
- If we change the layout of the establishment, setting hazardous installations more distant from ecological environments, what will be the new FN curve?
- What are the best conservation options (e.g., re-routing of spills, pollution remediation, habitat protection, translocation or reintroduction of individuals in the population)?

- To which value an accident’s frequency of occurrence must be reduced in order to achieve a risk level of acceptability?

The last question is particularly dependent on risk criteria for acceptability. In fact, after quantification of the risks to populations, they can be evaluated by stakeholders (enterprise leaders, government, environmental agencies, etc.) to determine whether the risks are acceptable or not. However, establishing risk criteria for acceptability is a slow and complicated process that requires the participation of society in its judgment. Once completed the process, there is now a standard, i.e. a value or interval where the risk is considered acceptable. It makes law clearer, so that less money is spent with lawyers and so more money can be spent with environmental and conservation management.

Some scientists believe that the interpretation of the results of a QERA is a political process that requires criteria imposed by the society rather than by the scientific community alone. Others believe that scientists nevertheless have a responsibility to provide guidance [35]. It is not an aim of this work to provide guidance on risk criteria for acceptability. Although it was proposed risk categories for assessing a particular accidental scenario in terms of probability and time to half loss (see section 2.5.7), this work does not devise risk categories in the FN curve that cumulates risks of all accidental scenarios.

Determining risk categories in the FN curve is still a shortcoming of the proposed methodology. With this in mind, the FN curve makes the process of devising risk categories for acceptability less difficult, because it is expressed in the same way as the societal risk in human QRA. For example, one should determine what is the acceptable frequency of a population declining by a given percentage (say 20%), or the acceptable frequency of a population extinction. And that is much more general than, for example, determining risk categories for the volume of contaminated water, as in PROTEUS model [19], because each specific ecosystem has its specific responses caused by exposure to a given volume of contaminated surface water, so that risk categorization relies on a subjective evaluation of ecologists.

4 APPLICATION EXAMPLE

In the Brazilian industrial current scenario, the Suape Port and Industrial Complex (SPIC), located in the state of Pernambuco, detaches itself by being the most complete shipping hub in the Northeast Region of Brazil for the location of port and industrial business. With a complete infrastructure to fulfill the needs of the most diverse enterprises, Suape has attracted an increasing number of companies that are interested in either placing their products in the regional market or exporting to other countries [78].

The SPIC can be considered as the largest center of investments in Brazil. Today, the sum of investments is about U$ 21.3 billion, spent by more than 100 active enterprises and other 35 in their implementation phase. An oil refinery, three petrochemical plants and two shipyards are in construction there. The attraction of such an amount of investment is mainly due to the privileged geographical location of the state of Pernambuco, allowing the transport of products from/to more than 160 ports worldwide. Furthermore, it has been seen a great investment on research by universities in the region, with the purpose of developing and improving the production and operation in SPIC. [78]

With an investment of about U$ 4 billion, the Abreu e Lima oil refinery (RNEST) is the biggest establishment in the industrial complex, still in implementation phase. In fact, the company Petrobras (Brazilian multinational energy company and the largest company in Latin America) has decided to build 3 refineries in the Northeast region of Brazil, for its closer distance to consumer markets such as Europe and the USA.

The refinery RNEST has a project that predicts a processing of 200 thousand barrels of heavy oil per day, according to API (American Petroleum Institute) classification, and aims the maximal production of diesel. The processed oil will come from the Campos Basin in Rio de Janeiro, Brazil, and from Orinoco, Venezuela [79]; which will supply RNEST through an external harbor in SPIC that is expected to receive oil tankers up to 170,000 DWT (Deadweight Tons). Considering the great amount of oil transported to RNEST, accidents with potential to cause serious damage to the ecological environment might happen. For example, a marine spill of a great volume of oil, forming a plume of hydrocarbons that spreads out into a very thin layer across the surface of the water and may come ashore, damaging the ecological environment in the coast of Pernambuco.

The coastline of the state of Pernambuco has a very rich ecological environment, composed by ecosystems such as beaches, estuaries, mangroves, coral reefs, coastal islands, resting and atlantic forests, each of them interacting with one or more. Moreover, several species are important to the economy of the state as well as for feeding of local population. Hence, any exposure to toxic substances may cause significant consequences.

This section aims at testing the capability of the proposed methodology to quantify ecological risks, as well as its feasibility in terms of data and resource needs. This is achieved by performing a QERA via the proposed methodology in the activities of oil handling and transport to RNEST at the external harbor.

Several sources of information were used to perform this QERA:

- Environmental Impact Statement of the establishment and associated documents [79; 80; 81];
- Ecotoxicological database [76];
- Comprehensive database of information about fish species [82];
- Case studies on population modeling [70];
- Published articles about the key species chosen and related species [83; 84].
- Demographic data about fish populations on the coastline of Pernambuco, provided by the Tropical Fish Ecology Lab of the University of Pernambuco (UPE);
- Results of a fate and transport model designed to predict the oil dispersion in the ocean after several accidentals scenarios of spill, provided by the Center for Studies and Essays in Risk and Environmental Modeling (CEERMA) of the Federal University of Pernambuco (UFPE);
- Personal communication
    - with ecologists of the Tropical Fish Ecology Lab of the University of Pernambuco (UPE);
    - with chemical engineers from CEERMA (*Centro de Estudos em Risco e Modelagem Ambiental)* of the Federal University of Pernambuco (UFPE).

4.1 Problem Characterization

Figure 4.1 illustrates the steps in conducting this methodology and detaches the current step.

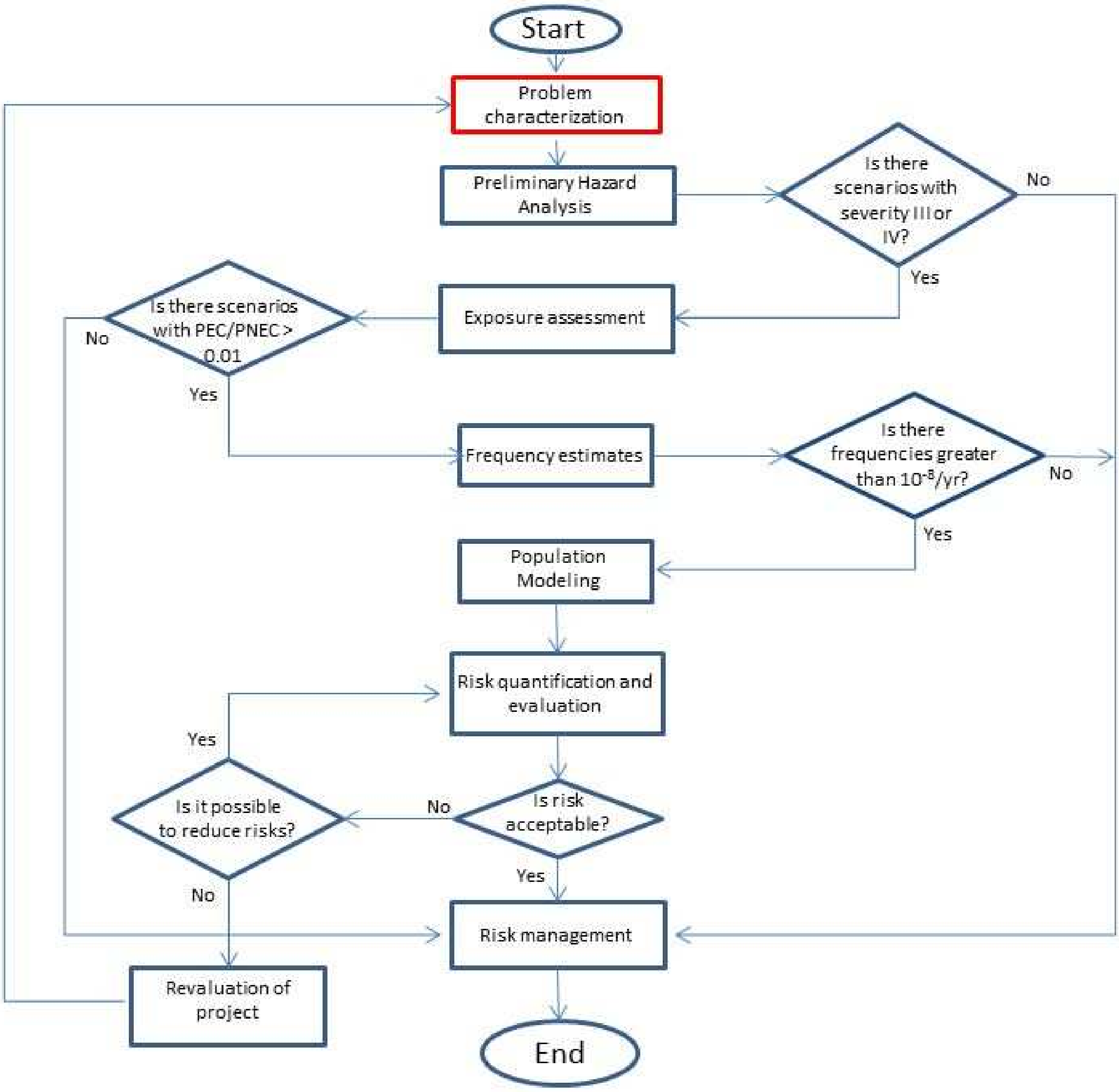

Figure 4.1 - Step 1 within the flowchart of the methodology.

The problem consists of quantifying ecological risks originating from accidents associated with transport and handling of crude oil that supplies RNEST, which is to be constructed within the SPIC, in Ipojuca, Pernambuco, Brazil.

4.1.1 Risk assessment issues and objectives

- Objectives of the QERA: this assessment aims at providing risk managers objective answers about the ecological risks associated with transport and handling of crude oil to supply the oil refinery RNEST. To ensure that the results of this assessment would meet the needs of risk managers, the following specific objectives were determined:
    - to identify the significant ecological risks;

    - to examine the dynamics of an representative species population in the surrounding ecosystem;
    - to quantify potential risks of accidental events – originating from ship transportation of crude oil that supplies RNEST – to the aquatic ecosystem on the coastal region of Suape, PE, Brazil;
    - to be as conservative as possible in parameterization, predicting worst-case scenarios;
    - to provide numerical basis of knowledge for communicating risks;
    - to provide a basis for comparing, ranking and prioritizing accidental scenarios;
    - to conduct a sensitivity analysis that expresses changes in risks measures as a function of changes in the accidents' frequencies of occurrence;
    - to conduct a sensitivity analysis that express changes in risks measures as a function of changes in the magnitude of the consequences;
    - to deal with uncertainty in the results of significant accidental scenarios, measuring it by estimating a range (best case and worst case) to risk measures;
    - to deal with natural (environmental) variability in time;
- Scale of the assessment: small area evaluated in depth;
- General spatial boundaries: local;
- General temporal boundaries: 100 years;
- Expected outputs of the QERA:
    - for a non-impact scenario: abundance trajectory summary, risk curves of extinction and time to population half loss (i.e. 50% decline);
    - for each accidental scenario: abundance trajectory summary, risk curves of extinction, time to population half loss (i.e. 50% decline), and risk category;
    - comparison of results between accidental scenarios and a non-impact scenario;
    - FN curve for cumulating risks of all accidental scenarios;
    - to point out further work that can effectively improve results.
- Resources available:

- personnel: a risk assessor (i.e. the author of this work). Additionally, support was given by an ecologist, an oceanographer (for fate and transport modeling), and a reliability engineer;
- time: 5 months;

- Data and information already available: Environmental Impact Statement of the establishment and associated documents [79; 80; 81].
- Acceptable level of variability in results: variability is considered acceptable as long as the width of the 95% confidence interval in the results of the time to “half loss” (i.e. 50% population decline) is smaller than 1%.
- Ecological impacts caused by past accidents: none, the refinary is still in implementation phase.

4.1.2 Characteristics of the establishment

The refinery RNEST has a project that predicts a processing of 230 thousand barrels of heavy oil per day. The crude oil might be 50% Marlin, originating from the Campos Basin in Rio de Janeiro, Brazil, and 50% Mejorado Carabobo, originating from Orinoco, Venezuela [79]; or, alternatively, 100% Marlim.

The refinery will be built in the peripheral industrial zone 3B (3B-ZI) of the CPIS in the northeast region of Brazil, 50 kilometers south from the town of Recife, next to latitude 8º17’S and longitude 35º15’W [80]. It was provided to RNEST an area of 6.3 square kilometers within the industrial complex. The following Figure 4.2 presents an aerial photograph of the CIPS.

Figure 4.2 - Aerial photograph of the Suape Port and Industrial Complex. From ref [78].

The refinery is located about 6 kilometers from the external harbor. This is expected to receive oil tankers up to 170,000 DWT (Deadweight Tons) and is surrounded by: to the north, the Cocaia island, Tatuoca islands, Tatuoca river, Massangana river, Suape beach and Cape of Santo Agostinho; to the south, Gamboa point and Muro Alto beach (Figure 4.3). The refinery is then supplied by 8 pipelines connected to the external harbour.

Figure 4.3 - General view of the CIPS and the area selected to the construction of RNEST. From the ref [79]

As this QERA is concerned only with accidents associated with transport and handling of crude oil for supplying RNEST, no accidental scenarios within RNEST are considered, but only transport units (i.e. oil tankers) and their routes to the external harbor. This way, the coastal area was divided into 24 quadrants (1A, 1B, 1C, 1D, 2A, …, 6D), as in Figure 4.4. The central point of each quadrant (1a, 1b, 1c, 1d, 2a, …, 6d) represents a specific possible location for an accidental oil spill. It is worth stressing that an accidental oil spill in the specific point 3a covers not only failures caused by external impact (e.g., collision, stranding) but also failures in unloading activities (e.g., full bore rupture of the unloading arm, leak of the unloading arm). Conversely, accidental spills in other points cover only external impact, since the oil tanker is not docked at the harbor.

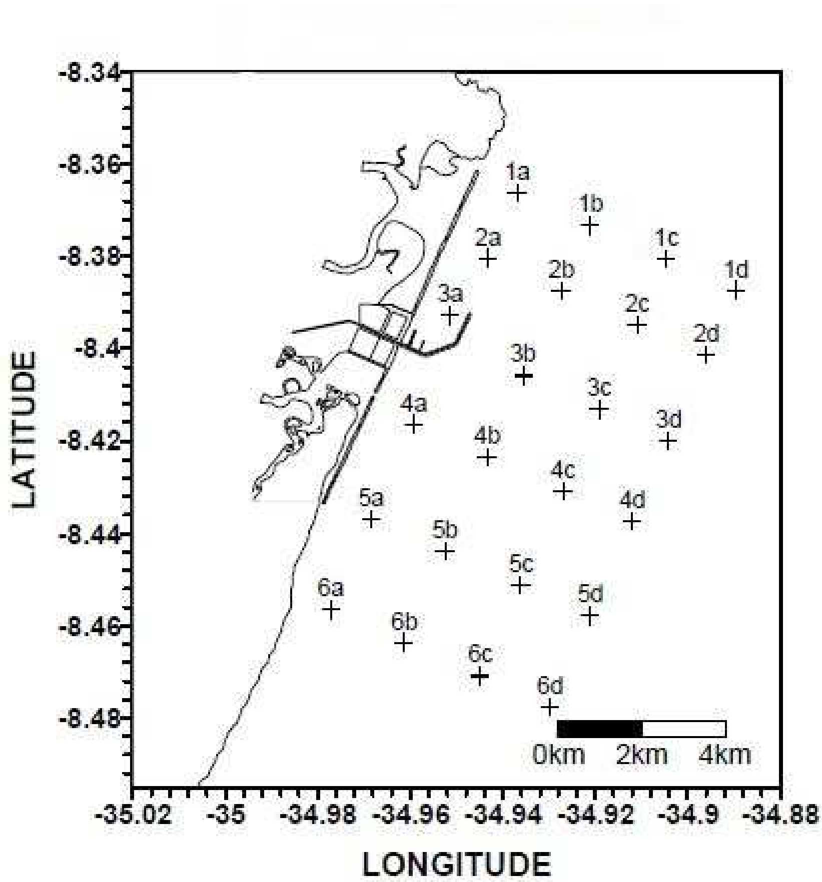

Figure 4.4 - Possible points of oil spill to be included in the QERA.

The Figure 4.5 presents a side view of an oil tanker. Also, there are some other technical information related to the transport of crude oil to the external harbor [78]:

- transportation ships are double-walled oil tankers, which is compulsory;
- about 1138 ships come in and out the harbor every year;
- 24 hours is the average duration of unloading per ship;
- 144 is the average number of transhipments per year for supplying RNEST;

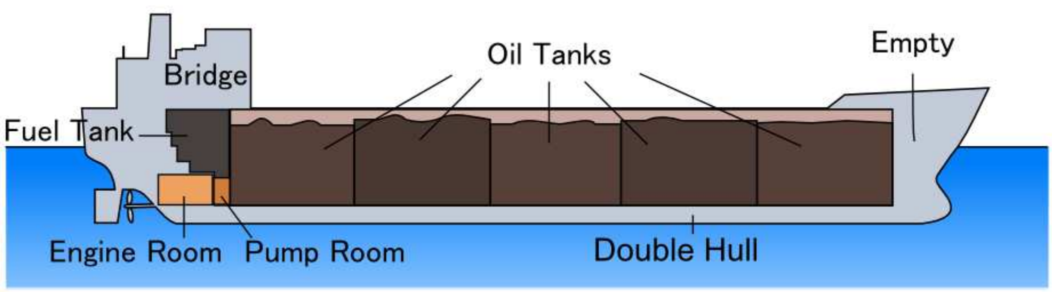

Figure 4.5 - Side view of an oil tanker.
From the ref [85].

Finally, crude oil is the only chemical of potential concern in this assessment, also named as crude petroleum, petroleum, crankcase oil or petroleum oil, CAS number: 8002059.

4.1.3 Characteristics of the ecological components

Among the species in the wild fauna and flora of the coastal region of Suape, it was chosen to analyze fishes because [86; 87]:

1. They have a relatively large size. Although oil causes immediate effects throughout the entire spill site, it is the external effects of oil on larger wildlife species tha are often immediately apparent.
2. Life-history information is extensive for most fish species.
3. Their position at the top of the aquatic food web in relation to invertebrates and green algae helps to provide an integrative view of the watershed environment.
4. Fishes are relatively easy to identify. This tends to decrease data collection errors.
5. Fishes are typically present, even in the most polluted waters.

After personal communication with professor Simone Ferreira Teixeira from the Tropical Fish Ecology Lab of the University of Pernambuco (UPE), it was chosen as indicator a local fish population of a native species, i.e. *Diapterus rhombeus*, order Perciformes, family Gerreidae, common name Caitipa mojarra (or *Carapeba* in Portuguese). *Diapterus rhombeus* (Figure 4.6) is one of the most common Gerreidae species in the estuarine region of Suape, Northeastern Brazil. They feed most on small benthic invertebrates and plant materials. These fishes are thought to be more sensitive and therefore serve as an early warning indicator of ecological impacts. Also, they have significant economic and social importance to the state of Pernambuco, since local human communities feed on them as well as sell them as a means of livelihood.

Figure 4.6 - Photograph of a a Caitipa mojarra.

The Tropical Fish Ecology Lab of the University of Pernambuco (UPE) provided demographic data about those fishes, collected at the mangrove channel of the Tatuoca river during 24 consecutive months (from March 2008 until February 2010). Two net catches were made each month, i.e. catch 1 (C1) and catch 2 (C2), and the sampler area was 20 m^2. Both C1 and C2 were made in the same area consecutively without releasing the fishes after the first catch, since they aimed at obtaining the abundance on the site and only one catch would be less valuable (i.e. those fishes may be schooling and a catch could be sampled over a school, overestimating the population abundance). For each catch it was counted the number of individuals as well as measured the total length, fork length and standard length (for concepts see Fish Measurement in Glossary) of each individual.

However, there were no available data about the specific geographic location of the fish population. Consequently, the geographic location and boundaries of populations were estimated via expert opinion only. They say that juveniles use shallow waters of the Suape beach and mangrove channels for breeding and for a growth phase, and migrate to areas of greater depth as soon as they become adults. Indeed, such opinion was validated by analyzing the demographic data discussed in the previous paragraph, i.e. these data were collected in shallow waters and only 0,2% of all collect fishes presented a total length greater than 13.4 centimeters, which is, according to the reference [82], the average length at which a *Diapterus* *rhombeus* juvenile mature for the first time and thus becomes an adult. In summary, only 0,2% of all collected individuals in shallow waters were adults.

All this considered, it was determined that the population is located at the Suape beach (at the latitude 8º 22’ 18.668’’ S and longitude 34º 57’ 7.160’’ W) within a region of about 7850 square meters, as illustrated in Figure 4.7.

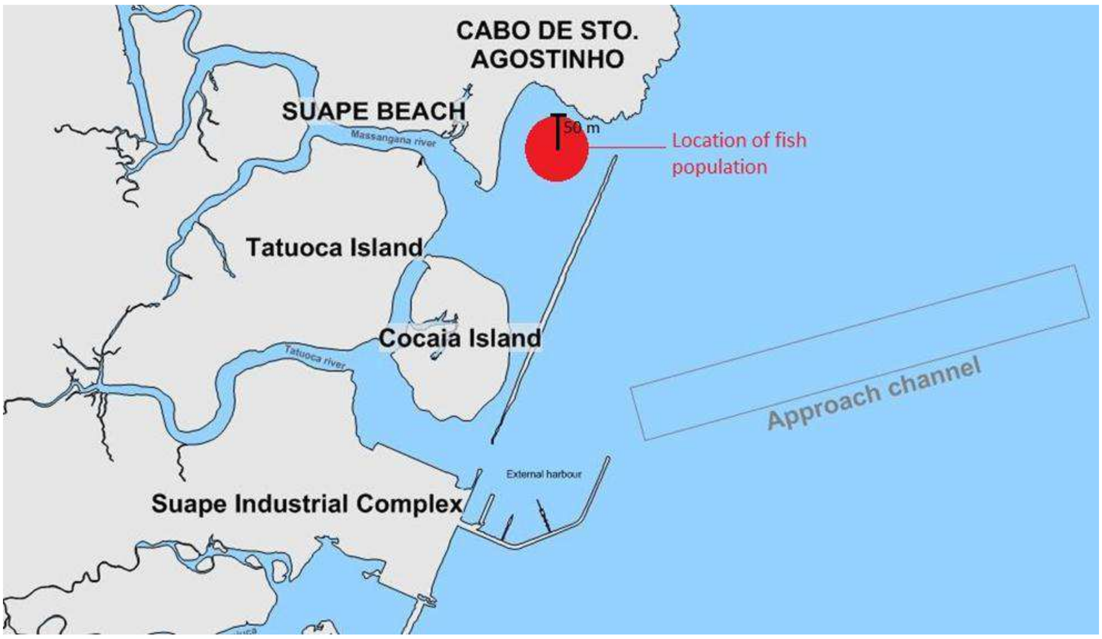

Figure 4.7 - Location of the fish population representing the ecosystem integrity.

Finally, the chosen assessment endpoint to provide information about the population of concern was its abundance. Then, the initial population abundance was estimated at 22,111 based on population demographic data.

4.2 Identification of hazards and consolidation of accidental scenarios

Figure 4.8 illustrates this step within the flowchart of the methodology.

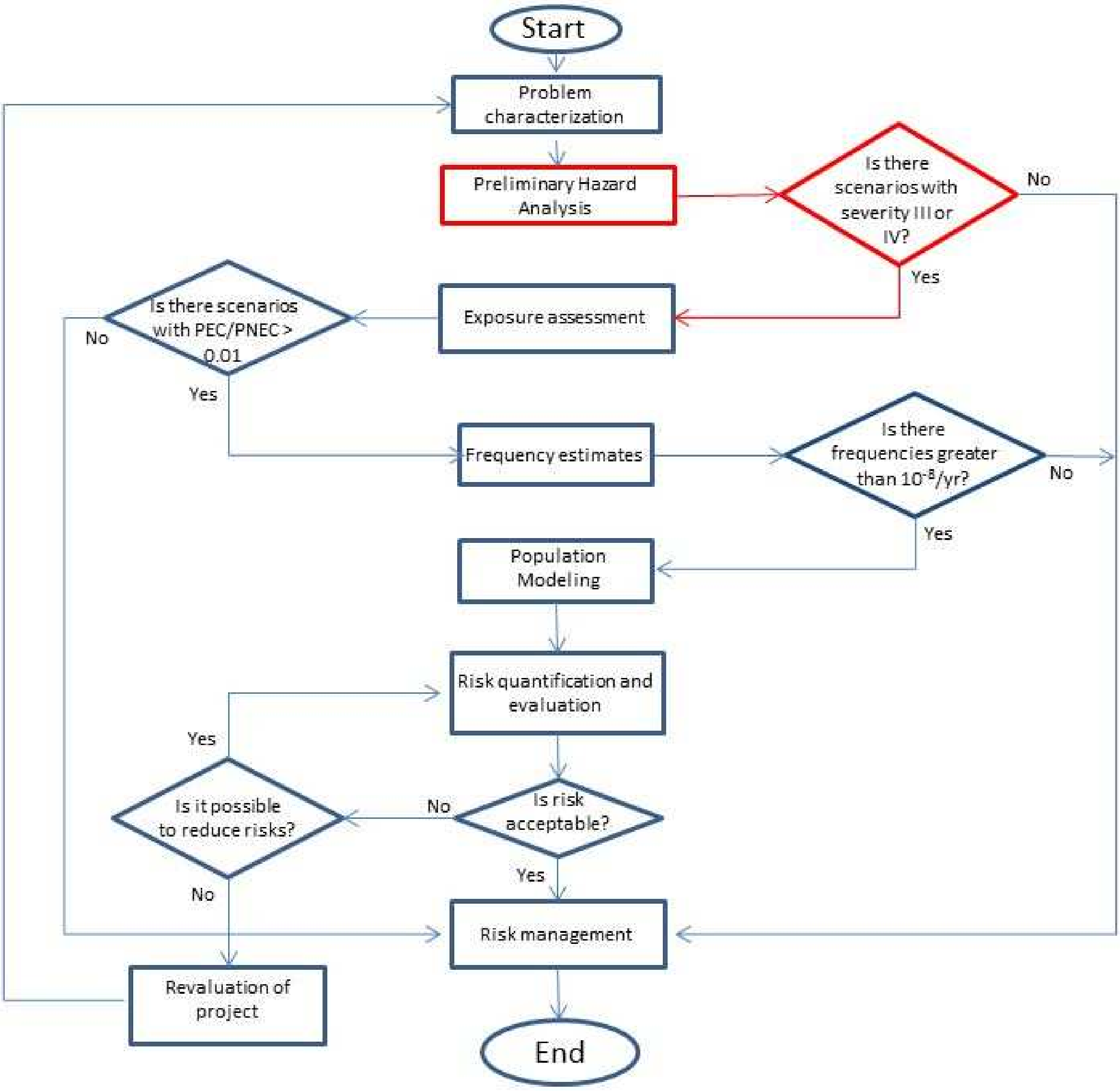

Figure 4.8 - Step 2 within the flowchart of the methodology.

Each point in Figure 4.4 represented a possible location for an oil spill and so consolidated an accidental scenario. It was conducted a PHA for each one of the 24 locations and only three of them had a severity class III or IV. These were selected for a detailed analysis in the next step. More specifically, two scenarios had catastrophic severity class IV (i.e. 1a and 2a) and one had critical severity class IV (i.e. 3a), as illustrated in Figure 4.9.

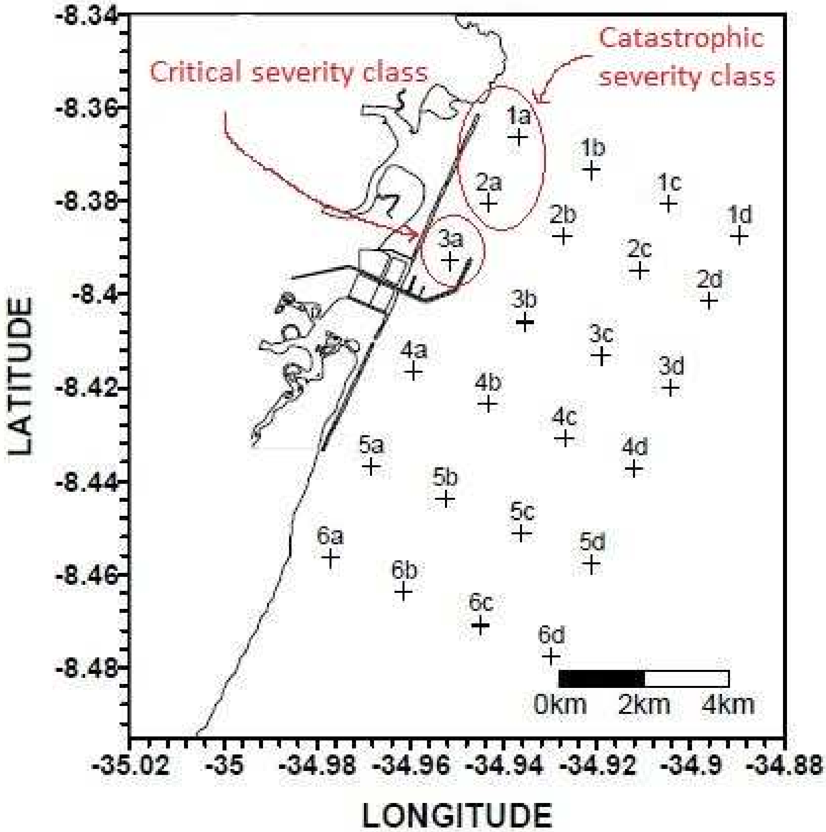

Figure 4.9 - Accidental scenarios selected to the next step.

Once again, accidental events in location 3a cover external impact as well as unloading activity. However, it is further from the fish population of concern in comparison with locations 2a and 1a. Hence, until this phase of the assessment, it can be qualitatively stated that the accidental scenario 3a has a greater frequency of occurrence but smaller severity in the consequences; whereas accidental scenarios 2a and 1a have greater severities, because they are closer to the fish population, and smaller frequencies, because they cover spills due to external impact only. Which of them has higher risks is still unknown.

4.3 Exposure assessment

Some meteorological conditions (i.e. topography, tide conditions, and the distribution of temperature and salinity of the water) influence the dispersion of oil in the ocean and thus the chemical concentration to which the fish population is exposed after an accident. An analysis of previous works conducted on the coast of Suape [88; 89; 90] has shown that information on the rainy season (from March to August) could be grouped in one meteorological scenario named “Winter”. Similarly, data on the spring and summer (from September to February) were grouped for the numerical representation of the dry scenario named “Summer”. Then, for each period of the year two tidal conditions were considered, based on information collected by tide gauges installed in the coastal Suape [88; 89; 90].

Hence, each of the three accidental scenarios from the previous step was divided into 4 new scenarios dependent on: the season of the year (summer or winter); the tide of the sea (spring tide or neap tide). This way, this step actually evaluates $3 \times 4 = 12$ accidental scenarios.

4.3.1 Fate and transport modeling

The Princeton Ocean Model (POM) [91] was used to describe the costal ocean circulation in the region of concern. The POM is a three-dimensional, primitive equation, time-dependent, σ coordinate, free surface, estuarine and coastal ocean circulation model, incorporating a turbulence closure model to provide a realistic parameterization of the vertical mixing processes. The computational code of the POM, now in public domain, was developed in the 80’s by Blumberg & Mellor [92]. Nowadays, it is one of the most tested and used models by the scientific community to this kind of application (e.g., [88; 89; 90; 93; 94; 95]).

Nonetheless, the original code of the POM model does not contemplate a routine that simulates the dispersion of chemical plumes. For this reason, it was added to the hydrodynamic POM model a subroutine that calculates the chemical dispersion based on the equation of advective-diffusive fate and transport of pollutants developed by the Ocean Modeling Laboratory (LABMON) of the University of São Paulo [96]. Therefore, once the ocean circulation is established by the POM, a new simulation is ran by injecting a certain flow rate of oil at the release point (x_r,y_r) on the surface of the water.

The POM is based on the primitive equations of momentum for a Newtonian fluid. It basically integrates the Reynolds theorem discretized by finite difference method. The prognostic variables are the three components of velocity field, temperature, salinity, and two quantities which characterize the turbulence (i.e. the turbulence kinetic energy and the turbulence macroscale). A key feature of the POM is the use of the sigma vertical coordinate (fraction of the local depth), which allows to consider both the surface and bottom layers of the ocean as curved surfaces in the horizontal (Figure 4.10). The sigma coordinate system makes the POM appropriate for dealing with significant topographical variability such as that encountered in estuaries or over continental shelf breaks and slopes (as is the case of this application).

The sigma coordinate system is based on the transformation:

$$x^* = x;\ y^* = y;\ \sigma = \frac{z-\eta}{H+\eta};\ t^* = t \quad (4.1)$$

where x, y, z are the conventional cartesian coordinates; $D \equiv H + \eta$ where $H(x, y)$ is the bottom topography and $\eta(x, y, t)$ is the surface elevation. Thus, σ ranges from $\sigma = 0$ at $z = \eta$ to $\sigma = -1$ at $z = H$.

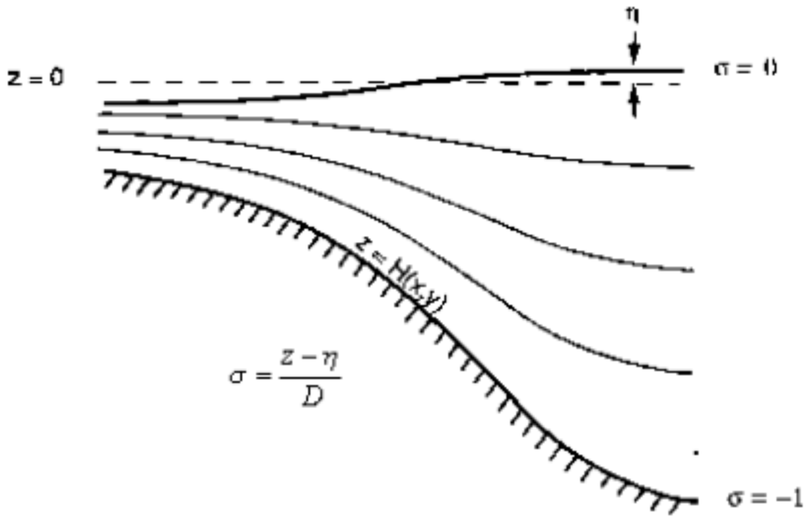

Figure 4.10 – The sigma coordinate system in the Princeton Ocean Model.

In this study, the x-axis is considered perpendicular to the coastline in the northeast direction, the y-axis is parallel to the coastline in the northwest direction, and the z-axis is perpendicular do the average surface of the ocean. The simulation grid has its origin at the point of the coastline situated 2800 meters south of the external harbor (Figure 4.11).

The equations which form the basis of the circulation model are described as follows:

- The continuity equation

$$\frac{\partial U}{\partial \mathrm{x}} + \frac{\partial U}{\partial \mathrm{y}} + \frac{\partial U}{\partial \mathrm{z}} = 0 \quad (4.2)$$

- The Reynolds momentum equations

$$\frac{\partial U}{\partial \mathrm{t}} + U\frac{\partial U}{\partial \mathrm{x}} + V\frac{\partial U}{\partial \mathrm{y}} + W\frac{\partial U}{\partial z} - fV = -\frac{1}{\rho_0}\frac{\partial P}{\partial x^*} + \frac{\partial}{\partial z}\left(K_M\frac{\partial U}{\partial z}\right) + F_{\mathrm{x}} \quad (4.3)$$

$$\frac{\partial V}{\partial \mathrm{t}} + U\frac{\partial V}{\partial \mathrm{x}} + V\frac{\partial V}{\partial \mathrm{y}} + W\frac{\partial V}{\partial z} + fU = -\frac{1}{\rho_0}\frac{\partial P}{\partial \mathrm{y}} + \frac{\partial}{\partial z}\left(K_M\frac{\partial V}{\partial z}\right) + F_{\mathrm{y}} \quad (4.4)$$

$$\rho \mathrm{g} = -\frac{\partial P}{\partial z} \quad (4.5)$$

- Equation of state

$$\rho = \rho(S, \theta, P) \tag{4.6}$$

- Conservation equation for temperature

$$\frac{\partial \theta}{\partial t} + U\frac{\partial \theta}{\partial x} + V\frac{\partial \theta}{\partial y} + W\frac{\partial \theta}{\partial z} = \frac{\partial}{\partial z}\left(K_M \frac{\partial \theta}{\partial z}\right) + F_\theta \tag{4.7}$$

- Conservation equation for salinity

$$\frac{\partial S}{\partial t} + U\frac{\partial S}{\partial x} + V\frac{\partial S}{\partial y} + W\frac{\partial S}{\partial z} = \frac{\partial}{\partial z}\left(K_M \frac{\partial S}{\partial z}\right) + F_S \tag{4.8}$$

where,

$U, V - horizontal\ velocities$;

$W - vertical\ velocity$;

$f - Coriolis\ parameter$;

$\rho_0 - reference\ density$;

$\rho - in\ situ\ density$;

$P - pressure$;

$K_M - coefficient\ of\ vertical\ turbulent\ viscosity$;

$K_H - coefficient\ of\ vertical\ turbulent\ diffusity\ for\ heat\ and\ salt$;

$g - gravitational\ acceleration$;

$\theta - potential\ temeprature$;

$S - salinity$.

The terms F_x, F_y, F_θ and F_S represent all of the motion induced by small-scale processes not directly resolved by the model grid (subgrid scale). They are parameterized in terms of horizontal mixing processes. For more details on how the POM model was used to conduct this application, readers are referred to [88].

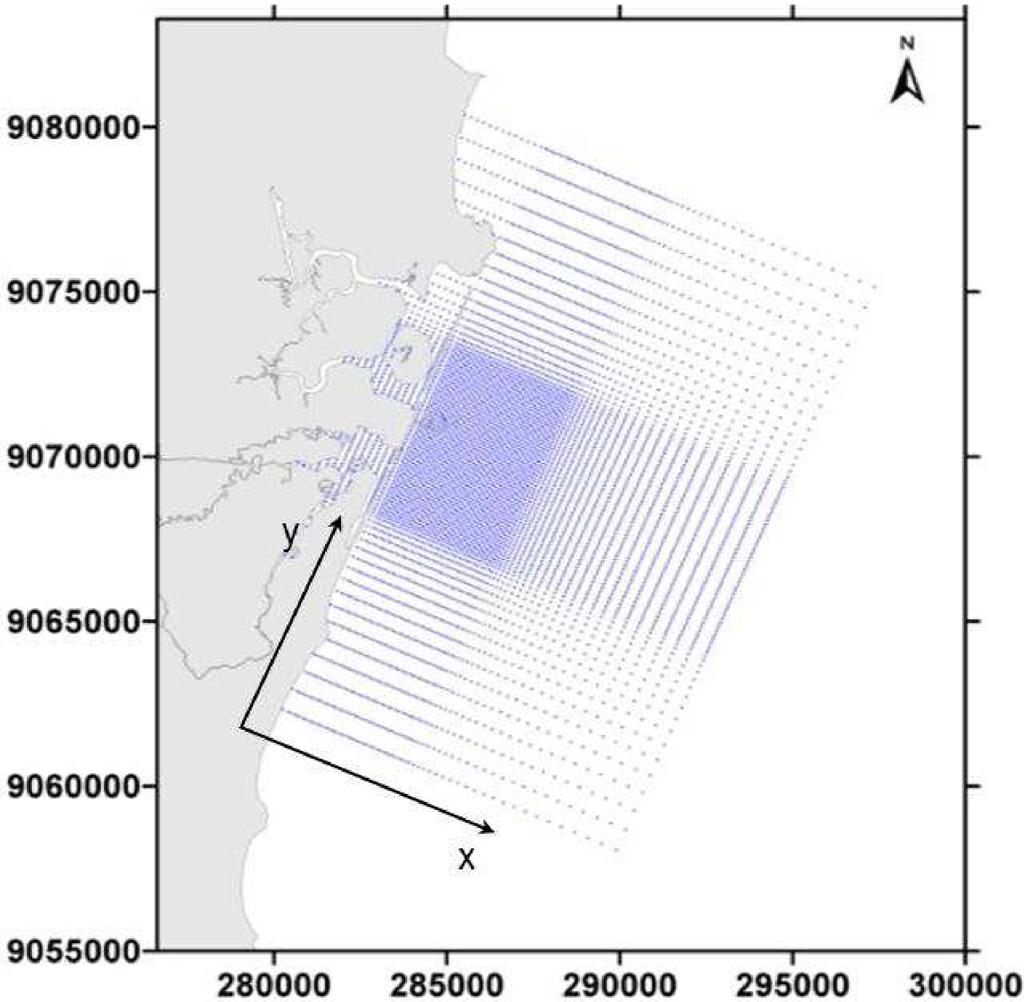

Figure 4.11 - Discretization grid of the coastal region of the external harbor of Suape (integration domain).

The figures (Figure 4.12 to Figure 4.15) present an example of the fate and transport simulation for accidental scenario 3a, i.e. as the oil plume disperses through the ocean after an oil spill in location 3a, considering meteorological conditions winter/spring tide.

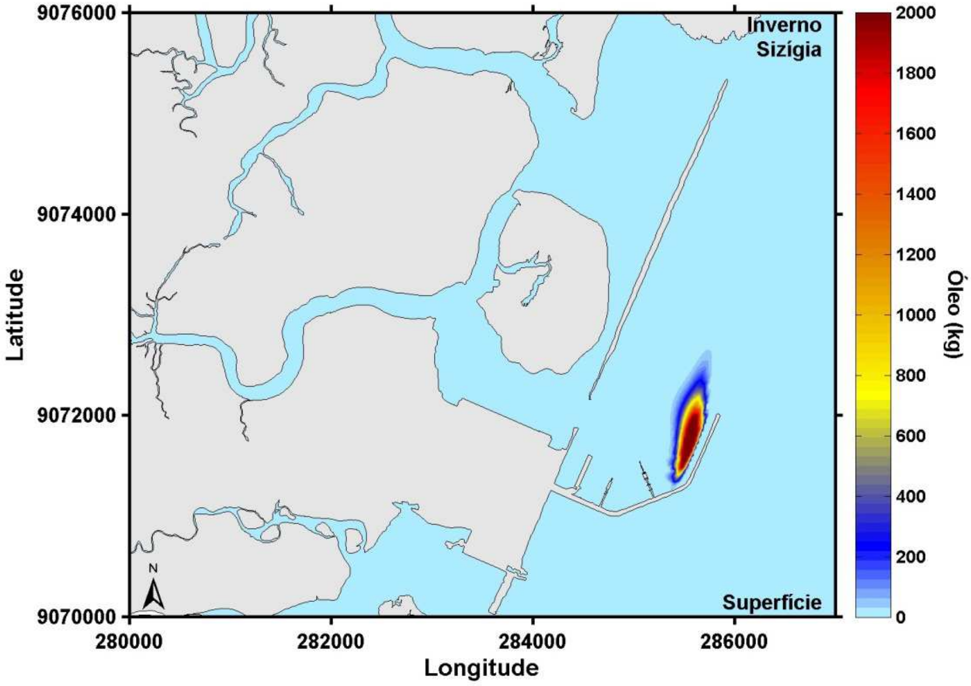

Figure 4.12 - Dispersion of the oil plume in winter/spring tide 3 hours after oil spill in location 3a.

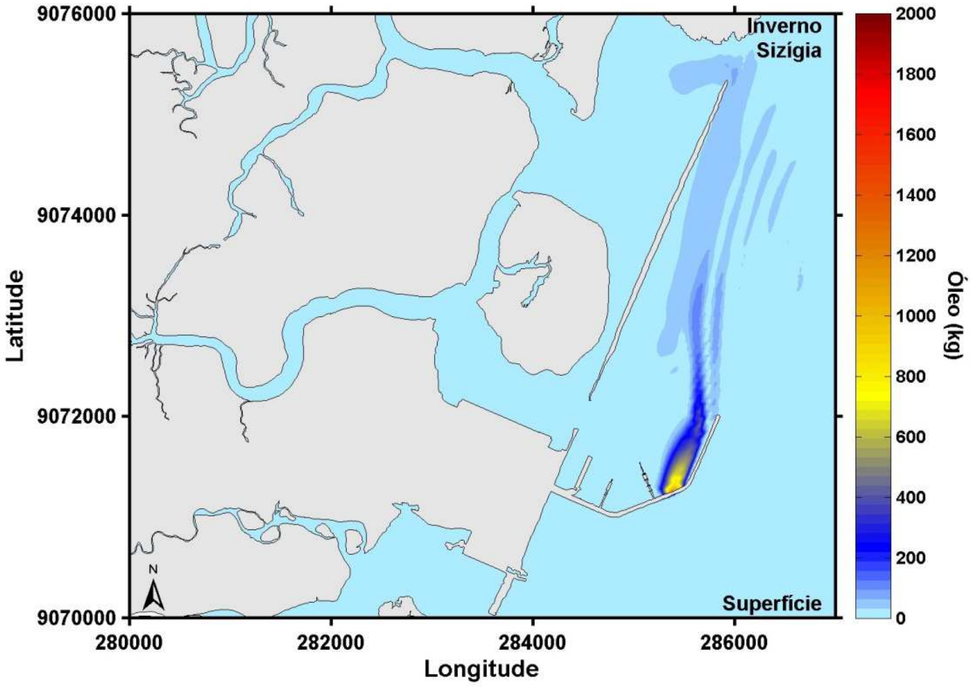

Figure 4.13- Dispersion of the oil plume in winter/spring tide 17.5 hours after oil spill in location 3a.

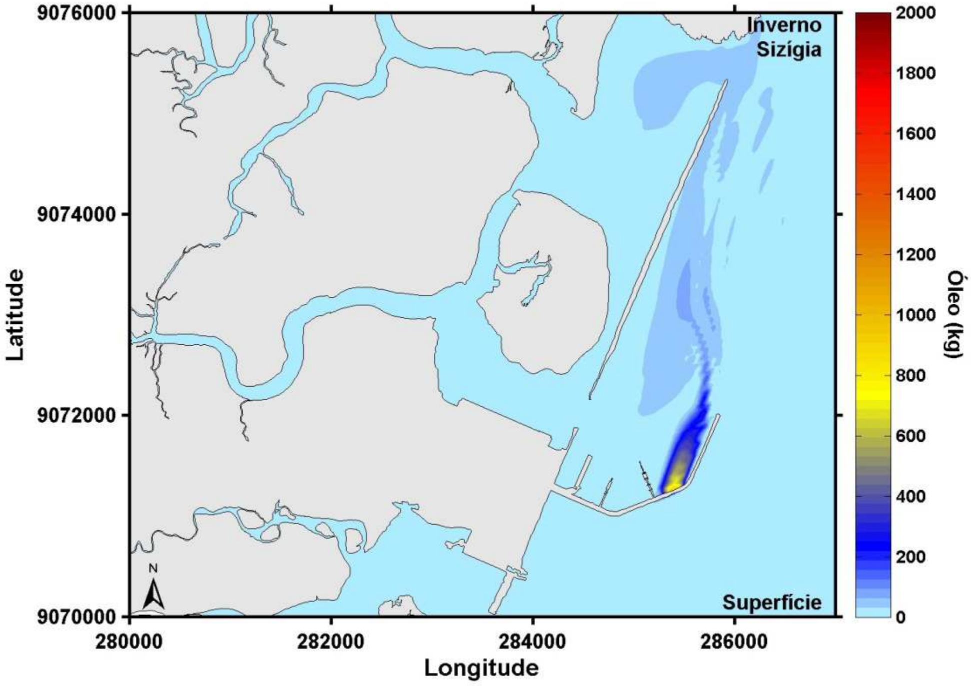

Figure 4.14 - Dispersion of the oil plume in winter/spring tides 19 hours after oil spill in location 3a.

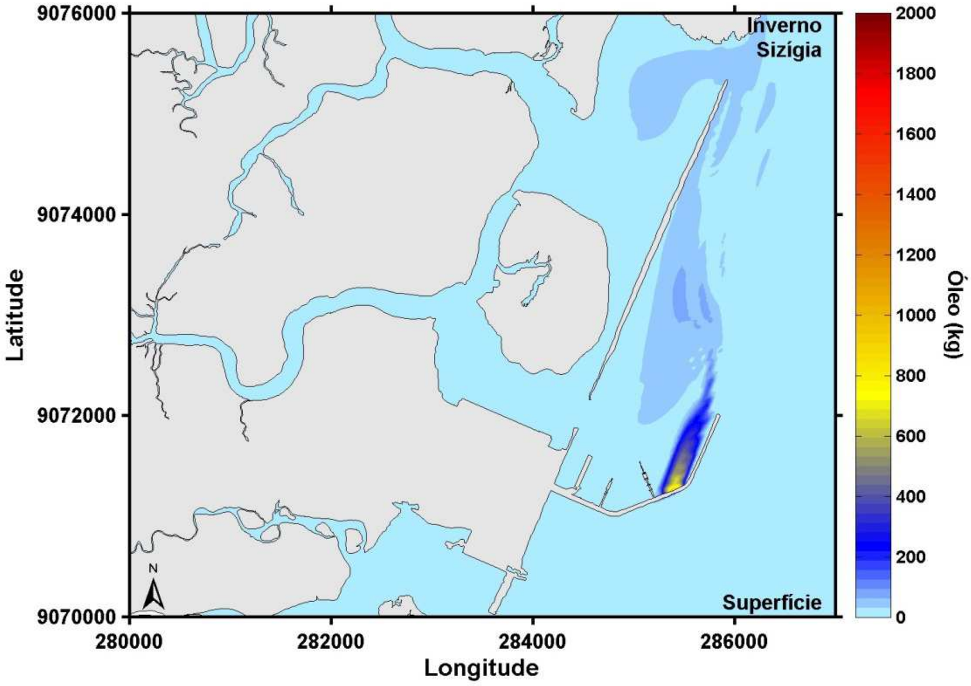

Figure 4.15 - Dispersion of the oil plume in winter/spring tide 19.5 hours after oil spill in location 3a.

For each one of the 12 accidental scenarios, the fate and transport model predicted the weight of oil (in kilograms), $W_{dxdy}(t)$, on the surface of the water within each cell $dx \times dy$ of Figure 4.11. The fish population under assessment covers three of these cells. It was calculated the average oil concentration in time, $C_i(x,y,z,t)$, for each accidental scenario, i, within the boundaries of these three cells (i.e. $C_i(x_0, y_0, z_0, t)$). To do so, it was made the following calculation:

- From a data map with the depth in each point of the ocean one gets dz (in meters) at the center of each cell $dx \times dy$ (in meters);
- One calculates the volume of water in $dx \times dy \times dz$ (in liters), $V_{water}(t) = 1000 \times dx \times dy \times dz$;
- From the results of the fate and transport model, one gets the predicted weight of oil (in kilograms) per $dx \times dy$, $W_{dxdy}(t)$, and considers the same amount of oil per $dx \times dy \times dz$, i.e. $W_{dxdy}(t) = W_{dxdydz}(t)$;
- The total weight of oil within the three population cells is $W_{exposure}(t) = W_{dxdydz,cell\ 1}(t) + W_{dxdydz,cell\ 2}(t) + W_{dxdydz,cell\ 3}(t)$;
- Considering the density of oil equal to 910 kg/m^3, one calculates the volume of oil (in milliliters) within the population cells, $V_{oil}(t) = 1000000 \times {W_{exposure}(t)}/{910}$;
- The predicted concentration within the population cells is then calculated as $C_i(x_0, y_0, z_0, t) = {V_{oil}(t)}/{V_{water}(t)}$, where (x_0,y_0,z_0) is the central point of the population's location (Figure 4.7).

This is a very conservative approach because when one makes $W_{dxdy}(t) = W_{dxdydz}(t)$, it is considered that 100% of the toxic components of oil on the surface of the water will actually dissolve in water. The uncertainty of such assumption will be further evaluated in section 4.6.6.

4.3.2 Hazard quotient

To select only accidental scenarios that may significantly contribute to the final ecological risks, it was performed a conservative screening assessment of the toxicological effects at individual-level for each accidental scenario. It was used the hazard quotient for that, i.e. the ratio of Predicted Environmental Concentration (PEC) to a Predicted No Effect Concentration (PNEC).

The PEC was the maximal value through time of $C_i(x_0, y_0, z_0, t)$; whereas PNEC was taken from ecotoxicological data in the reference [76]. The value for the PNEC was the LC_0 (i.e. lethal concentration to 0% of test organisms) of a related species (i.e. *Parupeneus barberinus*, that is a fish of the same order as *Diapterus rhombeus*, i.e. Perciformes) associated with crude oil. This extrapolation was needed because there were no such data on *Diapterus rhombeus*.

Table 8 shows the PECs, PNECs and hazard quotient for each accidental scenario. The toxicological test parameters and results are detailed in Appendix A. It can be seen that PEC/PNEC is much greater than 0.01 for all accidental scenarios in the winter, justifying their selection for the next step (Figure 4.16). Conversely, all accidental scenarios in the summer had PEC/PNEC equal to zero, because in this season the oil plume moves to the south and does not reach the population of concern. Although it may reach other ecosystems to the south, those are out of the spatial boundaries of this assessment. Hence, accidental scenarios in summer could be ruled out of this assessment.

Table 8 - PEC and PNEC for each accidental scenario in milliliter of oil per liter of water, and the corresponding hazard quotient (PEC/PNEC).

Accidental scenario	**PEC (ml/L)**	**PNEC (ml/L)**	**Hazard quotient (PEC/PNEC)**
3a-winter-neap tide	17.49	1	17.49
3a-winter-spring tide	10.12	1	10.12
2a-winter-neap tide	21.47	1	21.47
2a-winter- spring tide	14.91	1	14.91
1a-winter-neap tide	23.79	1	23.79
1a-winter- spring tide	18.10	1	18.10

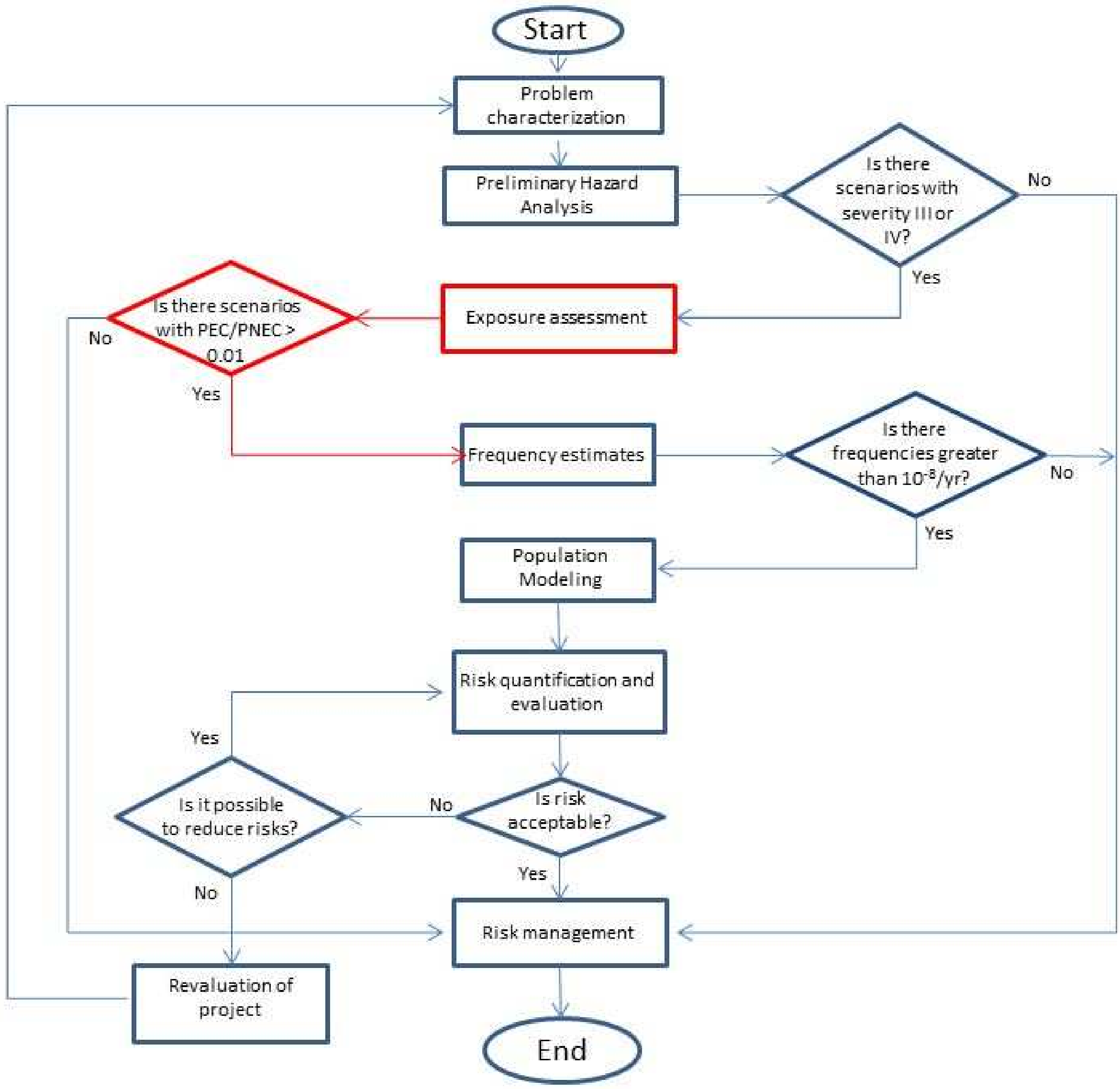

Figure 4.16 – Flowchart of the proposed methodology, detaching step 3 and the criterion for selecting accidental scenarios for step 4.

4.4 Frequency estimates

It was conducted a screening reliability analysis based on generic frequencies of Loss of Containment Events (LOCs) for ships in an establishment covering loading and unloading activities, and external impact. The reference [18] provides values for such frequencies per year, as well as simple procedure to calculate them, which is dependent on some specific circumstances about the activity of concern (those were defined in section 4.1.2). It is worth noting that such frequencies may overestimate risks because they do not take into account other specific circumstances that could reduce their values (e.g., safety management systems, alarms, automatic stops).

Table 9 presents the generic frequencies for each specific LOC. Note that all ships transporting oil to RNEST are double-walled tankers.

Table 9 - Frequencies of LOCs for ships in a establishment. The base accident failure rate, f_0, is equal to $6.7 \times 10^{-11} \times T \times t \times N$, *where T is the total number of ships per year on the transport route or in the harbor, t the average duration of loading/unloading per ship (in hours) and N, the number of transhipments per year.*
(From the ref [18])

Ship/LOC	**Full bore rupture of the unloading arm (L.1)**	**Leak of the unloading arm (L.2)**	**External impact, large spill (E.1)**	**External impact, small spill (E.2)**
single-walled liquid tanker	6×10^{-5} per transhipment	6×10^{-4} per transhipment	$0.1 \times f_0$	$0.2 \times f_0$
double-walled liquid tanker	6×10^{-5} per transhipment	6×10^{-4} per transhipment	$0.006 \times f_0$	$0.0015 \times f_0$
gas tanker, semi-gas tanker	6×10^{-5} per transhipment	6×10^{-4} per transhipment	$0.025 \times f_0$	$0.00012 \times f_0$

Accordingly, Table 10 shows the possible LOCs for the accidental scenarios 1a, 2a and 3a. Note that ships perform unloading activities in location 3a only. The variables for estimating the base accident failure rate, f_0, were determined in section 4.1.2 and are presented again in Table 11. Then, the frequency estimates for each accidental scenario, that is the sum of the frequencies for each possible LOC, were calculated as follows:

$$F_{1a}(year^{-1}) = F_{2a}(y^{-1}) = (0.006 + 0.0015) \times f_0 = 1.98 \times 10^{-6}$$

$$F_{3a}(y^{-1}) = F_{2a}(y^{-1}) + (6 \times 10^{-5} + 6 \times 10^{-4}) \times N = 0.09504198$$

Table 10 - Possible LOCs for accidental scenarios 1a, 2a and 3a.

Accidental scenario	**Full bore rupture of the unloading arm (L.1)**	**Leak of the unloading arm (L.2)**	**External impact, large spill (E.1)**	**External impact, small spill (E.2)**
1a			X	X
2a			X	X
3a	X	X	X	X

Table 11 – The base accident failure rate, f_0, and their variables. The base accident failure rate, f_0, is equal to 6.7× $10^{-11} \times T \times t \times N$.

Total number of ships per year in the harbor (T)	1138
Average duration of unloading per ship (t)	24 hours
Number of transhipments per year (N)	144
Base accident failure rate (f_0)	2.635×10^{-4}

Also, it was defined fractional frequencies to the meteorological conditions. As already mentioned (section 4.3), the summer meteorological scenario varies from March to August (6 months) and the winter from September to February (6 months). Therefore, it was considered that half of the year is winter and the other half is summer. Likewise, one sees spring tides during half of the year and neap tides during the other half, since tides alternate on a weekly basis. This way, each pair of meteorological condition has a frequency of 0.25 per year. As a result, Table 12 presents the final frequency estimates for each accidental scenario with their meteorological conditions. It can be seen that the values justify all accidental scenarios to be selected for the next steps of the methodology, since they are greater than 10^{-8} per year (Figure 4.17).

Table 12 - Frequency estimates for each accidental scenario with their meteorological conditions.

Accidental scenario	Frequency estimate (per year)
3a-winter-neap tide	$0.09504198 \times 0.25 = 0.02376049$
3a-winter-spring tide	$0.09504198 \times 0.25 = 0.02376049$
2a-winter-neap tide	$1.98 \times 10^{-6} \times 0.25 = 4.9 \times 10^{-7}$
2a-winter- spring tide	$1.98 \times 10^{-6} \times 0.25 = 4.9 \times 10^{-7}$
1a-winter-neap tide	$1.98 \times 10^{-6} \times 0.25 = 4.9 \times 10^{-7}$
1a-winter- spring tide	$1.98 \times 10^{-6} \times 0.25 = 4.9 \times 10^{-7}$

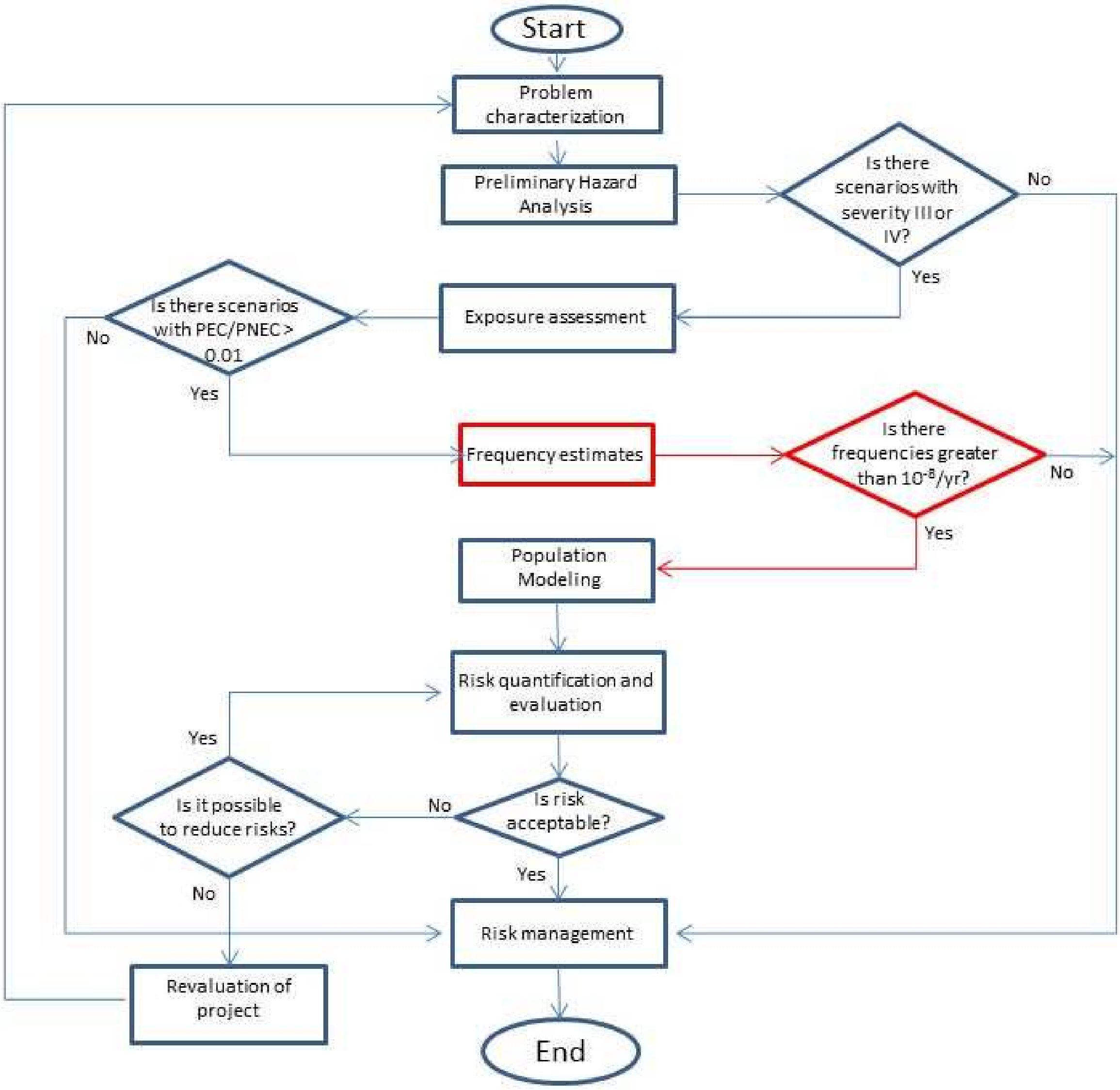

Figure 4.17 - Flowchart of the proposed methodology, detaching step 4 and the criterion for selecting accidental scenarios for step 5.

4.5 Population modeling

4.5.1 Data gathering

As already mentioned, it was used demographic data on juveniles of the species of concern, collected at the mangrove channel of the Tatuoca river during 24 consecutive months (from March 2008 until February 2010).

4.5.2 Population modeling

The population used in modeling was that described in section 3.1.3 and illustrated in Figure 4.7. Data was on one stage class only (i.e. juveniles), because they were collected in shallow waters of the Suape beach and mangrove channels, and fishes migrate to deeper waters as soon as they become adults. Hence, this population is made up of juveniles only. In addition, data provided the total length of each collected fish, so one could estimate their age based on the von Bertalanffy growth function [97]:

$$L_t = L_{inf}\left(1 - e^{-K(t-t_0)}\right);\ where$$

L_{inf} *is the total lenght that the fish of a population would reach if they were to grow indefinitely (also known as asymptotic lenght);*

L_t *is the total lenght at age* t;

K *is a parameter that expresses the rate* $(1/year)$ *at which the asymptotic lenght is approached;*

t *is the age (in years) of the fish;*

t_0 *is the hypothetical age (in years) the fish would have had at zero lenght, had their early life stages grown in the manner described by the equation;*

There are many methods for estimating the parameters of the von Bertalanffy growth function (i.e. life history parameters) for a certain species. If one or more growth studies about the species in question are available in FishBase [82], they provide a list of the different estimates for different population (i.e. from different localities). There were two studies about *Diapterus rhombeus*: in a population located in the southwest coast of Puerto Rico, in northeastern Caribbean Sea; and in a population located in the south coast of Margarita Island, Venezuela. Both studies presented very similar life history parameter estimates, so that any choice between them would be irrelevant for our purposes. Therefore, it was randomly chosen to use life history parameter estimates from the study in Puerto Rico, i.e.: $L_{inf} = 22\ cm;\ K = 2.21/year;\ and\ t_0 = -0.08\ years.$

Afterwards, it was estimated the age, *t*, for each collected fish and it could be observed that 99,8% of individuals in the data were younger than 4 months[3]. As a result, the time-step of the model was defined at 4 months. In addition, this value is approximate to this species' generation time (i.e. 4.8 months) provided by life history data on *Diapterus rhombeus* in the reference [82].

A population model was then implemented in the population modeling and viability analysis software RAMAS GIS v. 5 [34]. As the generation time of the species is approximately 1 time-step, the model should be scalar (i.e. unstructured): there should be just one stage, and the stage matrix should have a single element that is the growth rate of the population (*R*). Also, for a conservative approach, it was not include density-dependence effects in the model. Once again, including density-dependence in a population model to assess impacts of pollution would make the assessment unrealistically optimistic, because population would recover very fast after chemical exposure.

Therefore, the model projected the population abundance (*N*) forward 100 years (or 300 time-steps) from the initial population abundance estimate (22,111 individuals) using the mathematical expression: $N(t+1) = R(t) \times N(t)$. Temporal variability was incorporated into *R* by establishing a lognormal distribution with a mean equal to 1.001 and a standard deviation (SD) equal to 0.01. It was made a simulation with 10,000 replications. For each time-step during each replication, a value to *R* was randomly selected.

All parameters of the model in question are summarized in Table 13. Note that the model with such parameters describes the natural population dynamics (without chemical exposure). In other words, it describes a non-impact scenario.

Table 13 – Input parameters for population model without chemical exposure (non-impact scenario).

Parameter	**Value**
Replications	10,000
Duration	300 time steps = 100 years
Stages	1 (scalar model)
Sex structure	All individuals (males and females)
Stage matrix (mean)	[1.001]
Stage matrix (SD)	[0.01]

[3] 0,2% of the individuals were older than 4 months. These outliers were probably adults that do not live in shallow waters but were there to make reserves to the spawning period.

Environmental stochasticity distribution	Lognormal
Initial abundance	22,111

4.5.3 Validation of the model

It was used the subprogram RAMAS Metapop included in the software RAMAS GIS v.5 [34] to run the population model and check the future natural population dynamics (i.e. without chemical exposure). RAMAS GIS and RAMAS Metapop have already been validated at the program level, by checking all subunits and algorithms of the subprograms, by making sure that the program does what is described in the manual, by checking the lower-level algorithms for consistency (e.g., environmental stochasticity distribution) [98].

It is worth mentioning that RAMAS GIS and RAMAS Metapop do not allow users to change their algorithms. If the modeler finds that such algorithm is not capable of simulating the case-specific model, one should think about either programming its own algorithm or using other software. Several software are already available for use in risk assessment of toxic substances. Pastorok *et al.* [3] conducted a critical evaluation of ecological models that are potentially useful for QERA.

Not only the validation at the software level, but also the validation at the model level is responsibility of the modeler. To validate the model, it was verified the following issues:

- Do the results of the model address the risk assessment objectives? Yes, the results provide risk measures (e.g. risk of extinction, population abundance decline) that are within the expected results of the QERA.
- Do the assumptions and limitations of the model fit the species being modeled? Yes. The assumptions make a close approximation to reality that is sufficient for the objectives of the assessment. Most of the limitations are not originated from the model, but from poor data.
- Are the parameters of the model reasonable? Yes. In fact, since there is no chemical exposure, it is expected that the population abundance will remain stable. This means that the population growth rate should be something around 1. The population growth rate is given by the eigenvalue of the stage matrix, which is equal to 1.001 and approximate to 1.

The Figure 4.18 shows one of the results of the model. It can be seen that the population abundance increases slightly and this is, in fact, expected since the population growth rate is slightly greater than 1. Actually, it would be more realistic if the population abundance fluctuated around the same level, what could be modeled by including density-dependence effects. On the one hand, it would make the assessment of a non-impact scenario more realistic; on the other, it would make the assessment of an accidental scenario extremely optimistic and even unrealistic, because density-dependence effects would cause the population to recover very fast after an accident. In other words, massive population mortality would happen after an accident, and so would density-dependence effects cause the population growth rate to increase. This is quite unrealistic because after an oil spill it is expected that fishes find difficulties to feed and reproduce.

All things verified and justified, the model was considered to be correct.

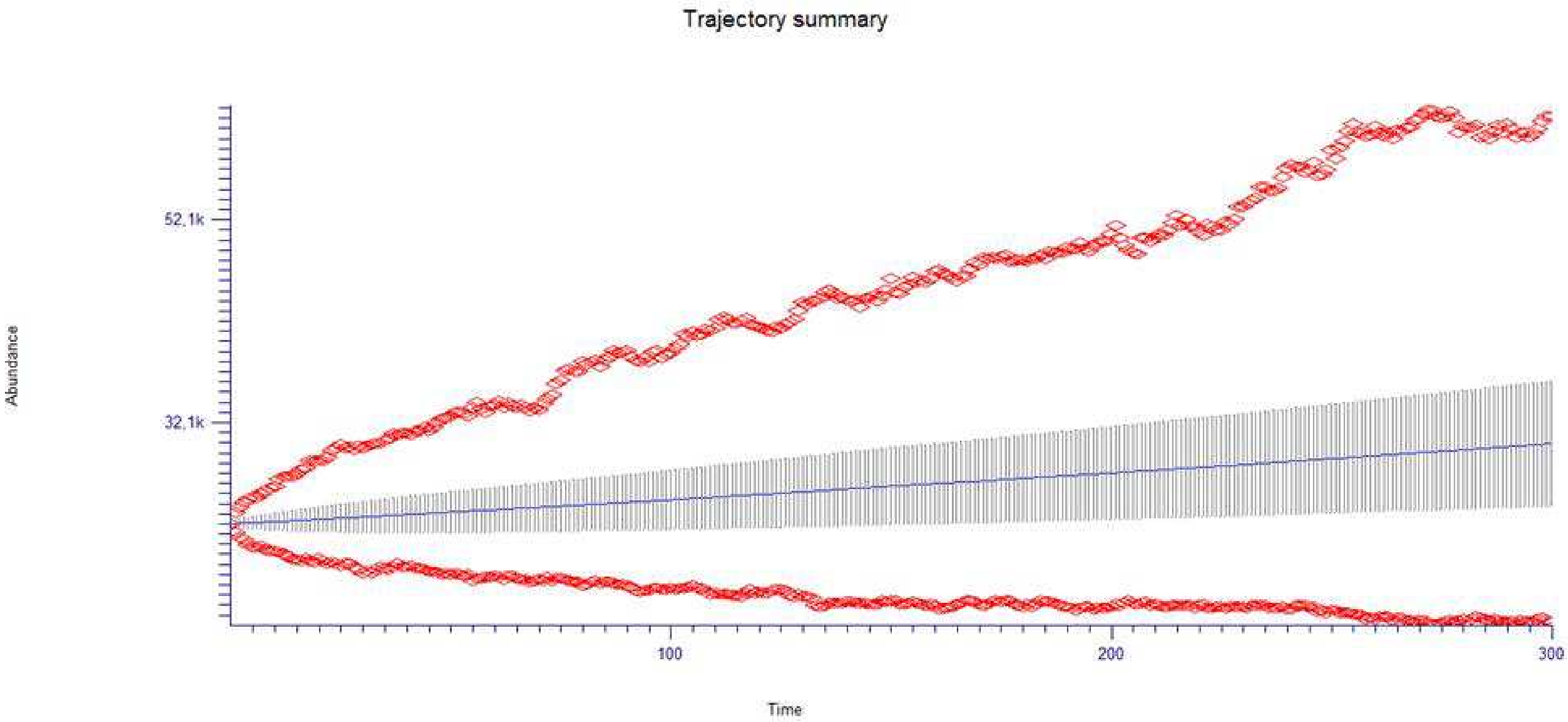

Figure 4.18 – Population abundance as it changes through time (without chemical exposure). The solid blue line represents the average value over 10,000 replications at time t; the vertical blue bars represent ±1 standard deviations; and the red points represent the minimum and maximum values.

4.5.4 Uncertainty analysis

This section deals with variability in the results originated from environmental stochasticity in population modeling. Uncertainty in the results of the whole QERA will be further evaluated.

As defined in the risk assessment objectives, variability is considered acceptable as long as the width of the 95% confidence interval in the results of the time to “half loss” (i.e. 50% population decline) is smaller than 1%. The results of this measure for this population model showed that the widest 95% confidence interval varies from 0 (i.e. 0% risk of half loss for all *t*) to 0.0089 (i.e. 0.89% risk of half loss for all *t*). As a result, uncertainty was accepted and that is the end of this step.

4.6 Risk quantification and evaluation

Here, there is essential need for the following input elements, which are output elements of the previous steps:

- A population model for the population of *Diapterus rhombeus*, located at the Suape beach (next to latitude 8º39’S and longitude 34º87’W) within a region of about 7850 square meters, as illustrated in Figure 4.7. This was formulated in the fifth step of the methodology.
- The time-step of the population model is 4 months.
- A predicted concentration $C_i(x_0, y_0, z_0, t)$ at the center of the population boundaries, for each accidental scenario, *i*; *t* in the same unit as the time-step of the model. These are presented in Table 14.
- The frequency estimate of each accidental scenario, *i*, per time-step of the model, $F_i(t^{-1})$. As the time step is 4 months and there are 12 months in a year, $F(t^{-1}) = F(year^{-1})/3$. These values are also presented in the Table 14.

Table 14 – Input elements for risk quantification and evaluation. The time-step, t, is 4 months. *$C_i(x,y,z,T)$ is the predicted average concentration of oil within the area of concern T units of time-step after the occurrence of the accidental scenario, i. $F_i(t^{-1})$ is the frequency of occurrence of the accidental scenario per time-step.*

Accidental scenario	$C_i(x_0, y_0, z_0, T)$	$F_i(t^{-1})$
3a-winter-neap tide	$\begin{cases} 17.49, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	0.00792016

3a-winter-spring tide	$\begin{cases} 10.12, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	0.00792016
2a-winter-neap tide	$\begin{cases} 21.47, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	1.63×10^{-7}
2a-winter- spring tide	$\begin{cases} 14.91, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	1.63×10^{-7}
1a-winter-neap tide	$\begin{cases} 23.79, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	1.63×10^{-7}
1a-winter- spring tide	$\begin{cases} 18.10, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	1.63×10^{-7}

4.6.1 Exposure-response assessment

To build a dose-response function, ecotoxicological data were extrapolated from a related species (i.e. *Parupeneus barberinus*, that is a fish of the same order as *Diapterus rhombeus*) associated with crude oil. The toxicological data, test parameters and results are detailed in Appendix A. These data provide three points for an exposure-response assessment, as related in Table 15.

Table 15 – Lethal concentrations LC_0, LC_{50} and LC100 of oil to the organisms of the species Parupeneus barberinus.

Response (in fraction of mortality)	Concentration (ml/L)
0	1
0.5	6.7
1	30

Based on these three points, it was added a logarithmic trendline, since it was expected that the rate of change in the function quickly increases and then levels out. Also, it was the best-fit curved line among several attempts of other five different trend or regression types (e.g., linear trendline, polynomial, power, exponential, or moving average trendline). The R-squared value was 0.9953, which is a relatively good fit of the line to the data.

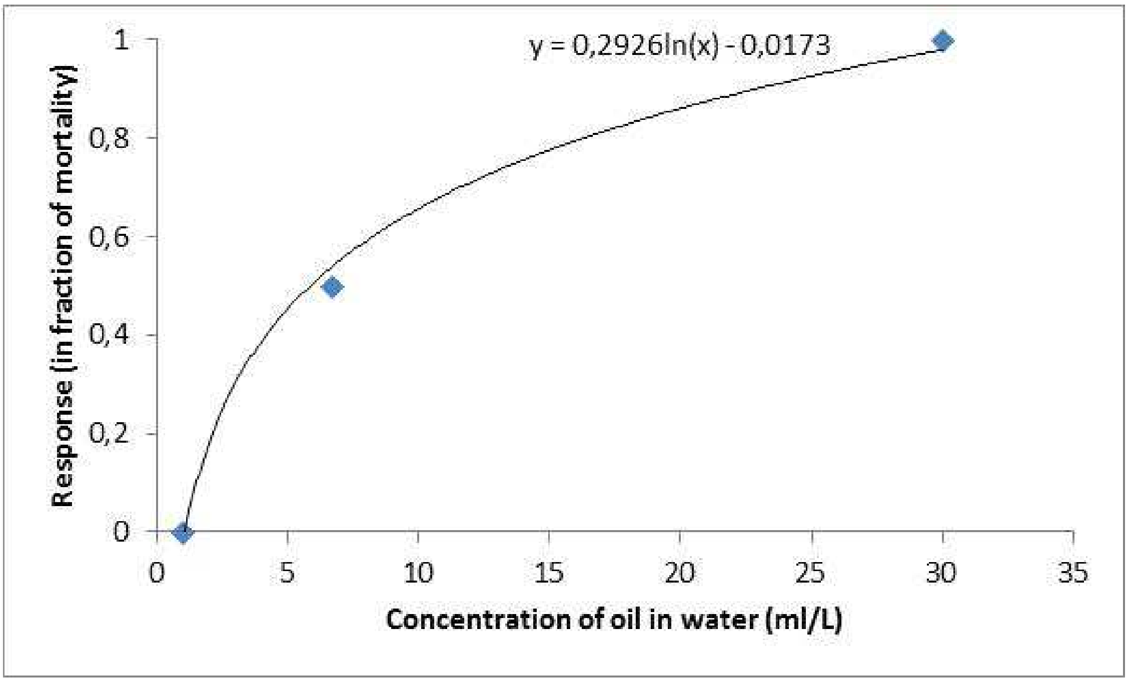

Figure 4.19 - dose-response function.

The fitted curve was then defined as the dose-response function. As a result, Table 14 can be updated by defining the response in function of $C_{AS}(x_0, y_0, z_0, T)$, as presented in the Table 16.

Table 16 - Input elements for risk quantification and evaluation. The time-step, t, is 4 months. Response is the predicted fraction of mortality in the population T units of time-step after the occurrence of the accidental scenario. $F_i(t^{-1})$ is the frequency of occurrence of the accidental scenario per time-step.

Accidental scenario	**Response**	$F_i(t^{-1})$
3a-winter-neap tide	$\begin{cases} 0.82, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	0.00792016
3a-winter-spring tide	$\begin{cases} 0.66, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	0.00792016
2a-winter-neap tide	$\begin{cases} 0.88, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	1.63×10^{-7}
2a-winter- spring tide	$\begin{cases} 0.77, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	1.63×10^{-7}
1a-winter-neap tide	$\begin{cases} 0.91, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	1.63×10^{-7}
1a-winter- spring tide	$\begin{cases} 0.83, for\ T = 0 \\ 0, for\ T > 0 \end{cases}$	1.63×10^{-7}

4.6.2 Assessing impacts and risks of each accidental scenario

Firstly, a simulation of a non-impact scenario was made, so that it could be compared with the accidental scenarios. The input parameters for a non-impact scenario were already presented in Table 13. Subsequently, one assesses impacts and risks of each accidental scenario through the two approaches described in section 2.5.5.

4.6.2.1 Assessing impacts of each accidental scenario

This approach compared only the impacts of each accidental scenario. By ignoring its frequency of occurrence, one considers that the accidental scenario is sure to occur.

Note that for all accidental scenarios, massive population mortality happens only at the time step that the oil spill occurs (T = 0), i.e. the first four months after an oil spill. That is because it takes at most 3 days until the oil plume reaches the population and one time-step is much longer than that. In the next time steps (T > 0), no mortality happens because of the accidental scenario[4]. Consequently, there was no need to assess impacts through time, but only at the time step T = 0. In other words, a simulation was not necessary to estimate the average population mortality associated with each accidental scenario, that would be simply the initial population abundance (i.e. 22,111 individuals) times the fraction of mortality. Table 17 presents the number of deaths associated with each accidental scenario.

Table 17 – Number of deaths associated with each accidental scenario, based on the initial population abundance (i.e. 22,111 individuals) and on the fraction of mortality.

Accidental scenario	Fraction of mortality	Number of deaths
3a-winter-neap tide	0.82	18,131
3a-winter-spring tide	0.66	14,593
2a-winter-neap tide	0.88	19,458
2a-winter- spring tide	0.77	17,025
1a-winter-neap tide	0.91	20,121
1a-winter- spring tide	0.83	18,352

[4] Mortality would keep happening through time if, for example, accidental scenario consisted of a continuous oil spill from an oil well during more than one time-step.

4.6.2.2 Assessing risks of each accidental scenario

Three new models were implemented to represent accidental scenarios 1a, 2a and 3a. To do so, one incorporated into the non-impact scenario model a source of environmental stochasticity that is independent of the year-to-year temporal variation of the growth rate. This is known as *catastrophe*.

It was included two catastrophes for each of the three new models, representing their possible meteorological conditions in the winter (i.e. neap tide or spring tide). All catastrophes had a certain frequency of occurrence per time-step (4 months), i.e. $F(t^{-1}) = F(year^{-1})/3$. Thus, for each time-step of each replication, a catastrophe was randomly selected to strike. If it does, it causes a certain fraction of mortality (originated from the dose-response function) to the population at that time-step.

Table 18 shows the parameter values for each of the three new models.

Table 18 - Input parameters for population model with potential accidental scenarios.

Parameter	**Accidental scenario 1a**	**Accidental scenario 2a**	**Accidental scenario 3a**
Replications	10,000	10,000	10,000
Duration	300 time steps = 100 years	300 time steps = 100 years	300 time steps = 100 years
Stages	1 (scalar model)	1 (scalar model)	1 (scalar model)
Sex structure	All individuals (males and females)	All individuals (males and females)	All individuals (males and females)
Stage matrix (mean)	[1.001]	[1.001]	[1.001]
Stage matrix (standard deviation)	[0.01]	[0.01]	[0.01]
Environmental stochasticity distribution	Lognormal	Lognormal	Lognormal
Initial abundance	22,111	22,111	22,111
Catastrophe 1	Name: 1a-winter-neap Probability = 0.0000002 $Abundance\ multiplier = \begin{cases} 0.09, for\ T = 0 \\ 1, for\ T > 0 \end{cases}$	Name: 2a-winter-neap Probability = 0.0000002 $Abundance\ multiplier = \begin{cases} 0.12, for\ T = 0 \\ 1, for\ T > 0 \end{cases}$	Name: 3a-winter-neap Probability = 0.00792016 $Abundance\ multiplier = \begin{cases} 0.18, for\ T = 0 \\ 1, for\ T > 0 \end{cases}$
Catastrophe 2	Name: 1a-winter-spring Probability = 0.0000002 $Abundance\ multiplier = \begin{cases} 0.17, for\ T = 0 \\ 1, for\ T > 0 \end{cases}$	Name: 2a-winter-spring Probability = 0.0000002 $Abundance\ multiplier = \begin{cases} 0.23, for\ T = 0 \\ 1, for\ T > 0 \end{cases}$	Name: 3a-winter-spring Probability = 0.00792016 $Abundance\ multiplier = \begin{cases} 0.34, for\ T = 0 \\ 1, for\ T > 0 \end{cases}$

Then, the results of each model were compared to the results of the model for a non-impact scenario. Figures (Figure 4.20 and Figure 4.21) compare a non-impact scenario with each of the accidental scenarios. In the former, each point in the curve can be interpreted as “there is a Y% risk that, 100 years from now, the population abundance will be less than X”. In the latter, each point can be interpreted as “there is a Y% risk that the population abundance will fall by 50% (half loss) in or before time-step X”.

Over 100 years, there is a chance that the population will naturally become extinct. This chance is defined as the background risk. As the potential consequences of different accidental scenarios are measured in terms of probabilities, it is possible to compare them against the background risks that a population faces in the absence of any potential accidental scenario (i.e. a no-impact scenario). Added risk means the increase in risk of extinction (or decline) that results from some impact on a natural population [35].

It can be seen that accidental scenario 3a is the only one that causes significant increase in risk of extinction when compared with a no-impact scenario. Extinction risk curves for no-impact scenario and accidental scenarios 1a and 2a are statistically superimposed. Also, the accidental scenario 3a is the only one with significant chances to cause population “half loss” in the next 100 years. This certainly happens because accidental scenarios 1a and 2a are extremely rare (i.e. frequency of occurrence is too small).

All things considered, the accidental scenario 3a is the only one that may need management actions in order to reduce its risks. However, some further assessment is needed to make such a conclusion.

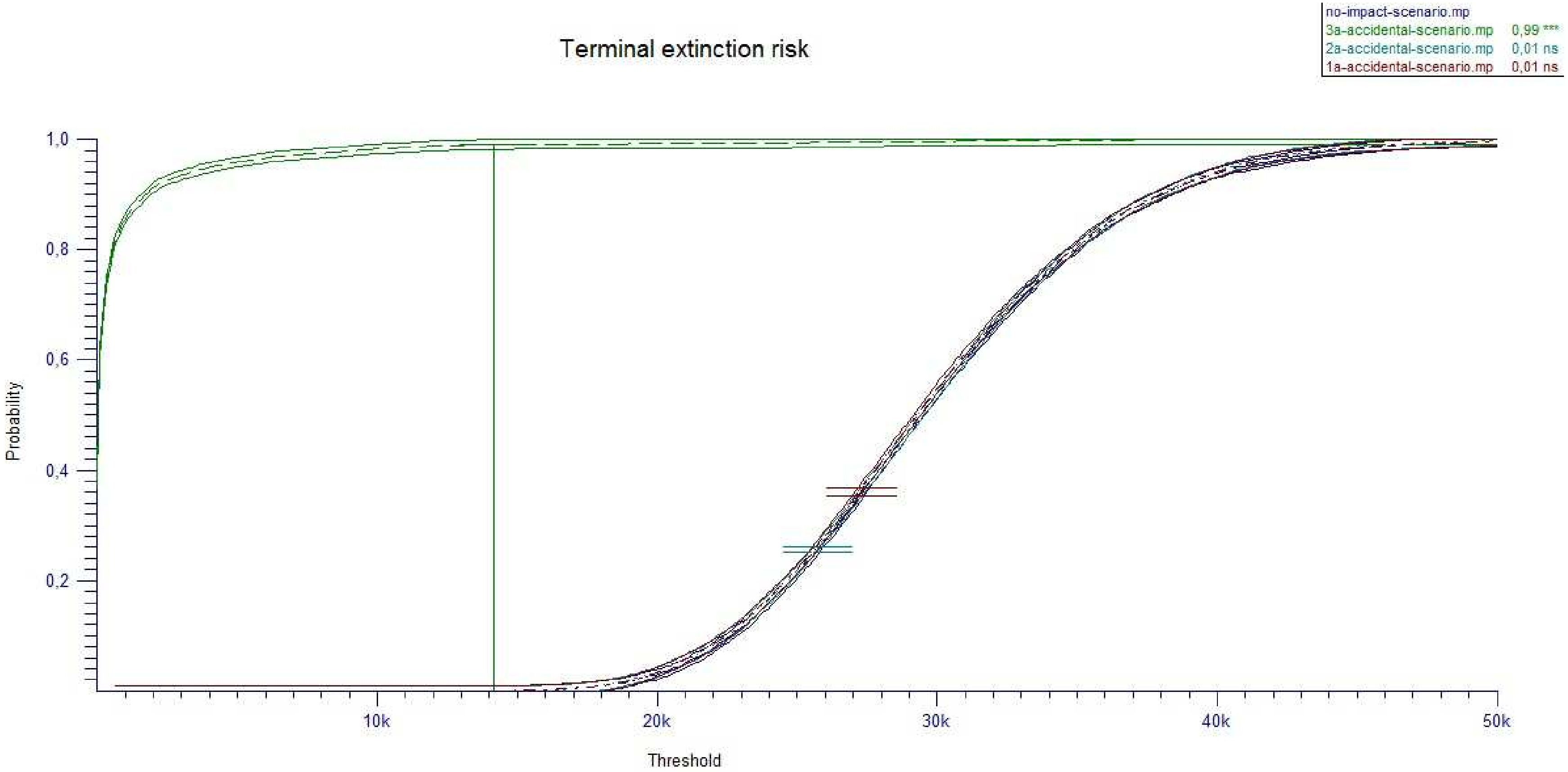

Figure 4.20 – Comparison of a non-impact scenario with each of the accidental scenarios, in terms of terminal extinction risk. Each point in a curve can be interpreted as "there is a Y% risk that, 100 years from now, the population abundance will be less than X". The dotted line indicates the average value, whereas the solid lines the 95% confidence intervals. The 3 vertical bars with two horizontal tabs represent the maximum difference between a non-impact scenario and an accidental scenario. The difference is measured as the maximum vertical distance between the curve. The location of the maximum difference (the threshold value at which the difference is maximum) may be different for different curves. The box to the upper right reports the values of the differences. The color of the text is the same as the color of the risk curve with which the first (dark blue) curve is compared. The reported number is the Kolmogorov-Smirnov test statistic D (which is the maximum vertical difference). The asterisks give the significance level (: 0.05, **: 0.01, ***: 0.001, ns: not significant), based on two-sample Kolmogorov-Smirnov test [34; 99].*

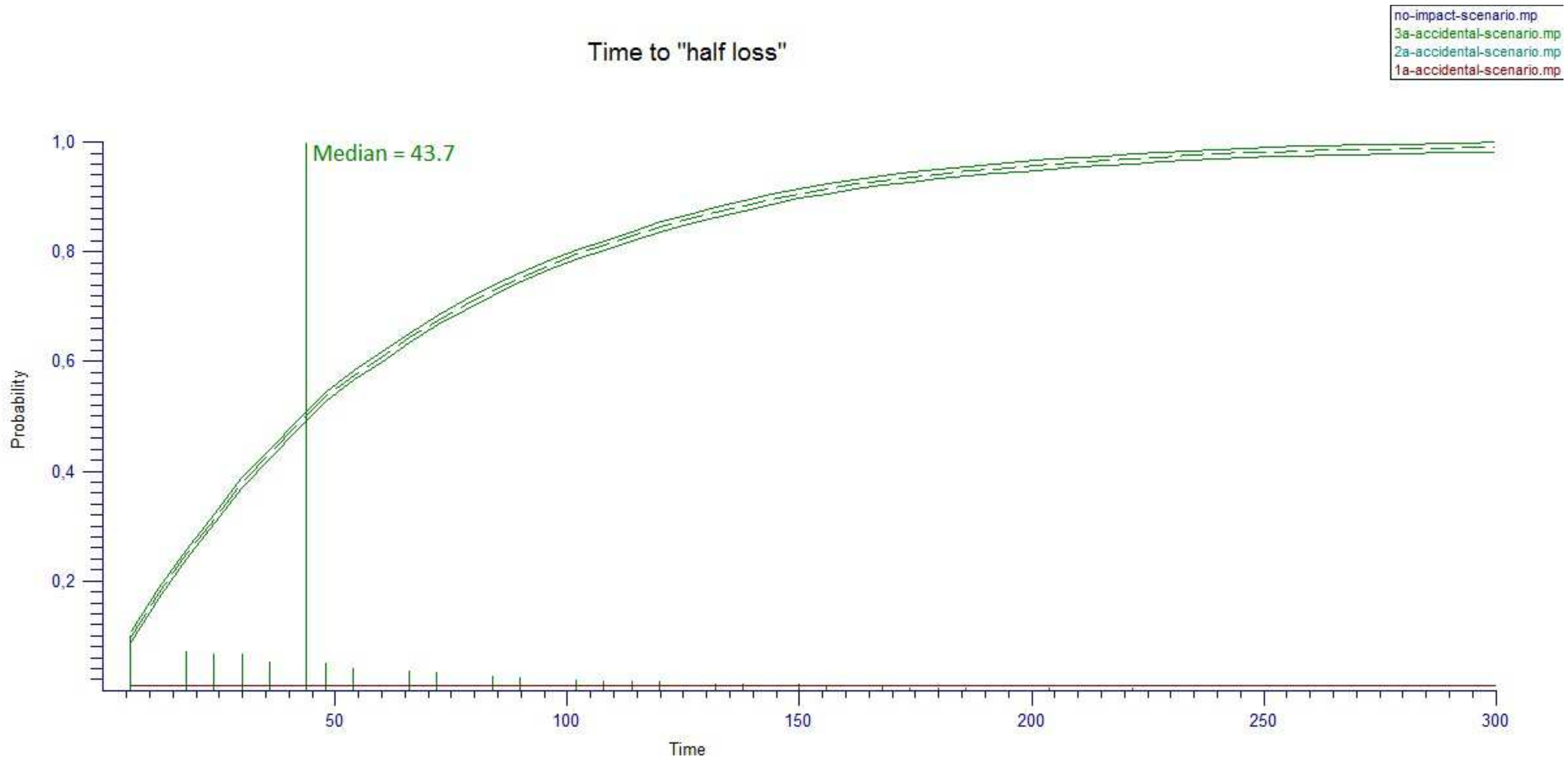

Figure 4.21 - Comparison of a non-impact scenario with each of the accidental scenarios, in terms of time to "half loss" (i.e. 50% population abundance decline). Each point in a curve can be interpreted as "there is a Y% risk that the population abundance will fall by 50% (half loss) in or before time-step X". In this graph, there are two plots for each scenario. The histogram (vertical bar graph) shows the probability that the population size will fall below the specified threshold exactly at a specific time step. The continuous curve is the cumulative probability distribution, and it shows the probability of falling below at or before a specific time step. The 95% confidence intervals are also plotted together with the continuous curve. The graph is scaled according to the cumulative distribution and that is why the histogram is nearly imperceptible. If the median of a distribution is within the simulated time period (as happens with accidental scenario 3a), it is indicated by the solid vertical line. Both the line and the number for the median are in the same color as the distribution, so one can identify which simulation the median refers to.

4.6.3 Risk categorization

It was used the risk criteria proposed in section 2.5.7, Table 3. For better reading, they are copied here:

Table 19 - Categories for assessing risks of each accidental scenario in a QERA.

Category	Risk of half loss	Years
Critically Endangered	> 50%	10
Endangered	> 20%	20
Vulnerable	> 10%	100
Low Risk	> 0.1%	100
Negligible	> 0.001%	100
Background risk	< 0.001%	100

Both accidental scenarios 1a and 2a are statistically equal (in terms of 95% confidence interval) to a non-impact scenario, so that they belong to the same risk category. Looking at the data that originates the Figure 4.21, the cumulative probability of the time to half loss, there is a 0% risk (95% confidence interval from 0% to 0.0089%) that the population abundance will fall below 11,055 (half loss) individuals in or before time-step 300 (i.e. 100 years). This way, they vary from a “Background risk” to a “Negligible” category.

Concerning accidental scenario 3a, Figure 4.22 illustrates its risk categorization. The necessary points for such categorization are related in the Table 20. One could then conclude that accidental scenario 3a causes the population of concern to be categorized as “Endangered”.

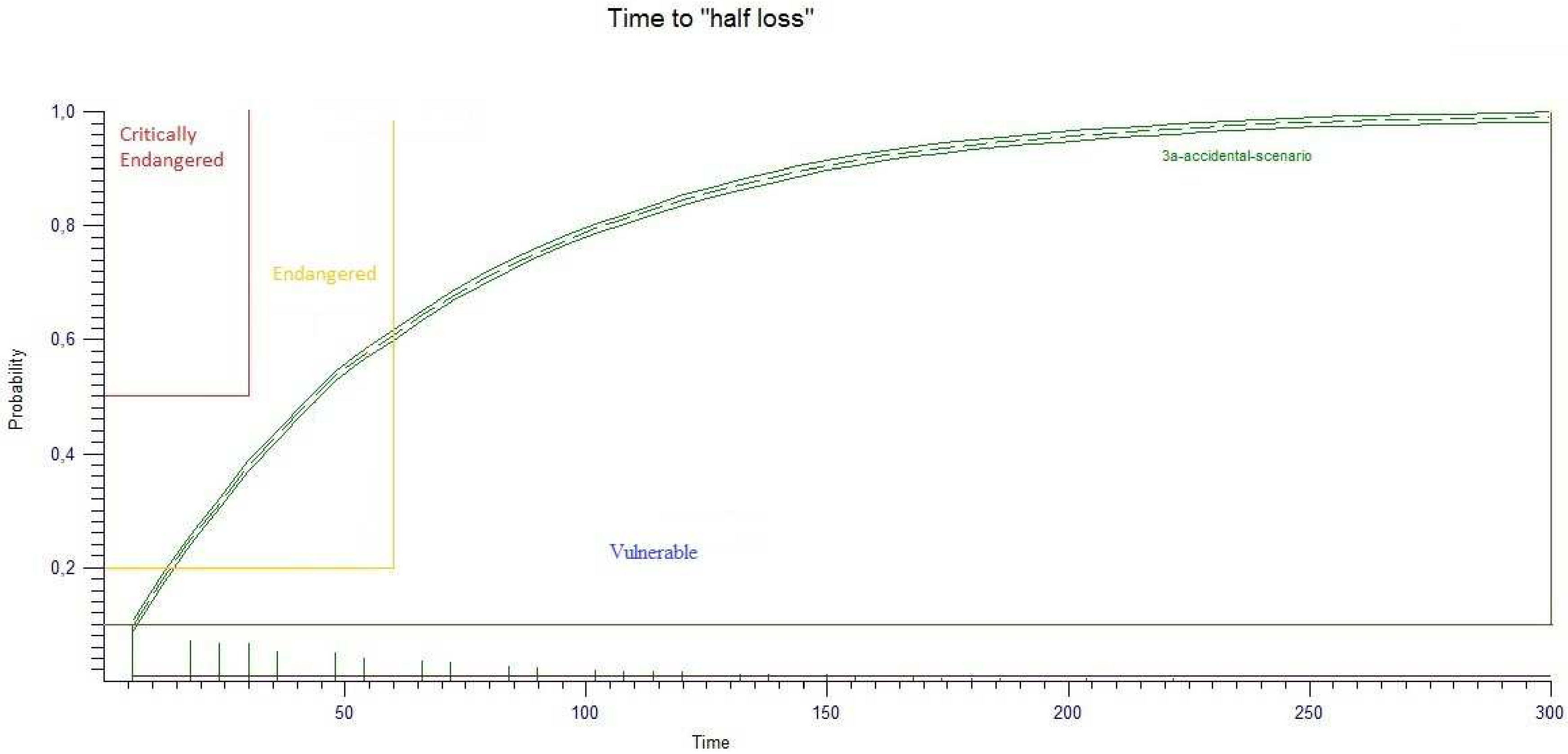

Figure 4.22 - Risk categorization for accidental scenario 3a.

Table 20 – Cumulative probabilities of the time to half loss associated with accidental scenario 3a.

Time (years)	Time-step (4 months)	Cumulative probability of the time to "half loss"	Lower bound (95% confidence interval)	Upper bound (95% confidence interval)
10	30	38.04%	37.15%	38.93%
20	60	60.81%	59.92%	61.70%
100	300	99.09%	98.20%	99.98%

4.6.4 Cumulating risks of all accidental scenarios

It is considered here all accidental scenarios selected to the current step of methodology (risk quantification and evaluation), i.e. accidental scenarios 1a, 2a and 3a in the winter. By cumulating the frequencies (Table 21) for which the number of deaths of a particular accidental scenario, N_{si} , is greater than or equal to N, it was built the FN curve presented in the Figure 4.23.

The y-axis is in logarithmic scale and that is because the frequency of occurrence of 20121 or more deaths was defined at $10^{-8}/year$ instead of zero. The value of $10^{-8}/year$ is the frequency criterion (in the fourth step of the methodology, i.e. frequency estimates) to screen out accidental scenarios that are irrelevant in terms of risk. Therefore, ecological risks from any event that occurs with a frequency less than that are considered to be none (zero).

Table 21 - Sorted list of frequencies.

Frequency (per year)	Number of deaths (N)	Frequency of N or more deaths (per year)
0.00000049	20121	1E-8
0.00000049	19458	0.00000049
0.00000049	18352	0.00000098
0.02376049	18131	0.00000147
0.00000049	17025	0.02376196
0.02376049	14593	0.02376245

---------------	0	0.04752294

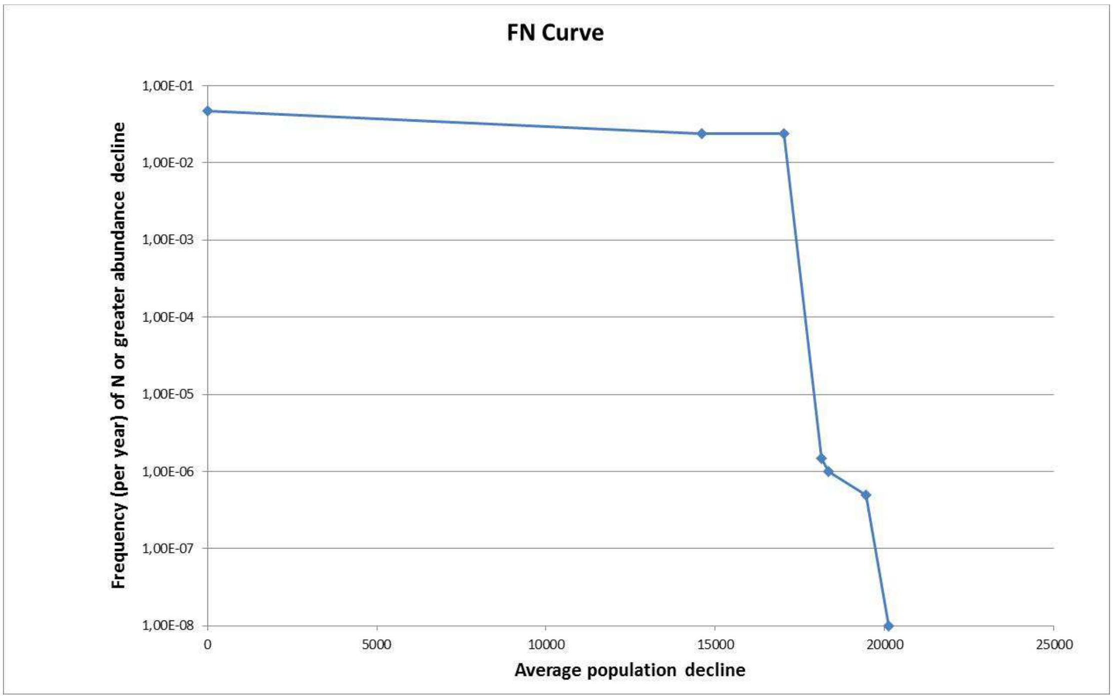

Figure 4.23 – FN curve for cumulating risks of all accidental scenarios.

4.6.5 Sensitivity analysis

It is worth exploring the sensitivity to parameters of the model for accidental scenario 3a, so that one can understand how changes on specific parameters cause changes in risk measures. Firstly, one analyzed how reductions in the frequency of occurrence can reduce ecological risks. This is mostly useful to understand how important is the fourth step (i.e. frequency estimates) of this methodology to the results of this specific QERA. As already mentioned, the methodology is interactive. In this sense, if the risk assessor finds it appropriate, more work on reliability analysis can be done in order to calculate more accurate frequency estimates, and so more accurate risks. Moreover, analyzing the sensitivity to the frequency estimates provides information to the risk manager who wishes to evaluate control measures and preventive actions (e.g., safety management systems, alarms, automatic stops) which can reduce the accidental scenario's frequency of occurrence and so reduce the risks.

Several simulations were made with the primary model for accidental scenario 3a, gradually reducing the frequency of occurrence. The Figure 4.24 presents the results of 4 simulations in which frequencies were reduced by 20%, 50%, 90% and 98%. It can be observed that even after a 98% reduction in its frequency of occurrence, risks remain still high, i.e. 0.0843 risk of half loss in the next 100 years (95% confidence interval from 0.0754 to 0.0932).

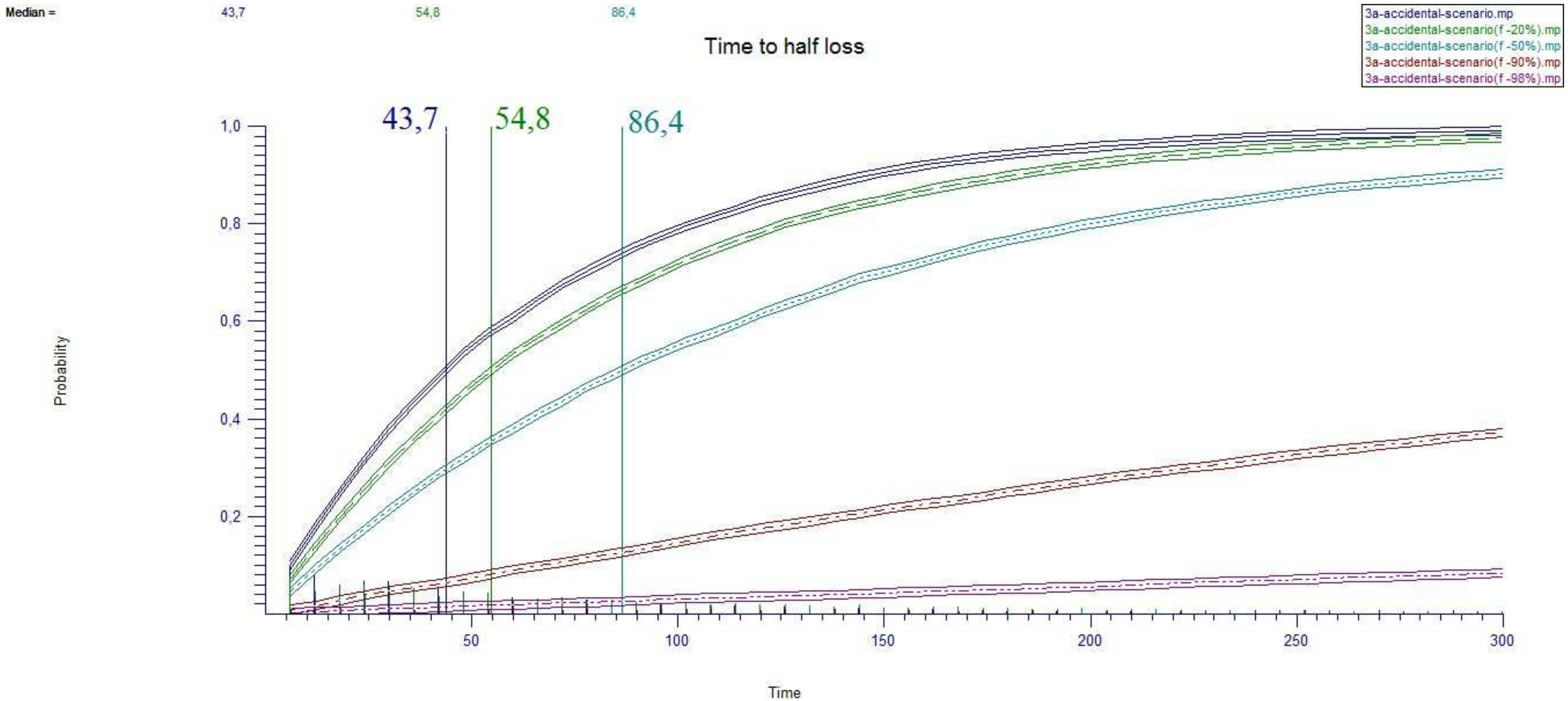

Figure 4.24 - Sensitivity analysis that express changes in risks measures(i.e. cumulative probability of the time to half loss) as a function of changes in the frequency of occurrence of accidental scenario 3a. Each point in a curve can be interpreted as "there is a Y% risk that the population abundance will fall by 50% (half loss) in or before time-step X". If the median of a distribution is within the simulated time period, it is indicated by the solid vertical line. Both the line and the number for the median are in the same color as the distribution, so one can identify which simulation the median refers to.

Secondly, it was analyzed how reductions in the consequences can reduce ecological risks. This is useful to the risk manager who wants to evaluate recovery measures and mitigation actions (e.g. re-routing of spills, burning the oil before it reaches an ecosystem, pollution remediation, habitat protection, translocation of individuals) which can reduce the magnitude of the consequences and so reduce the risks.

Several simulations were made with the primary model for accidental scenario 3a, gradually reducing the adverse effects on population (in fraction of mortality). Figure 4.25 presents the results for 3 of them, in which the fraction of mortality was reduced by 30%, 50% and 80%.

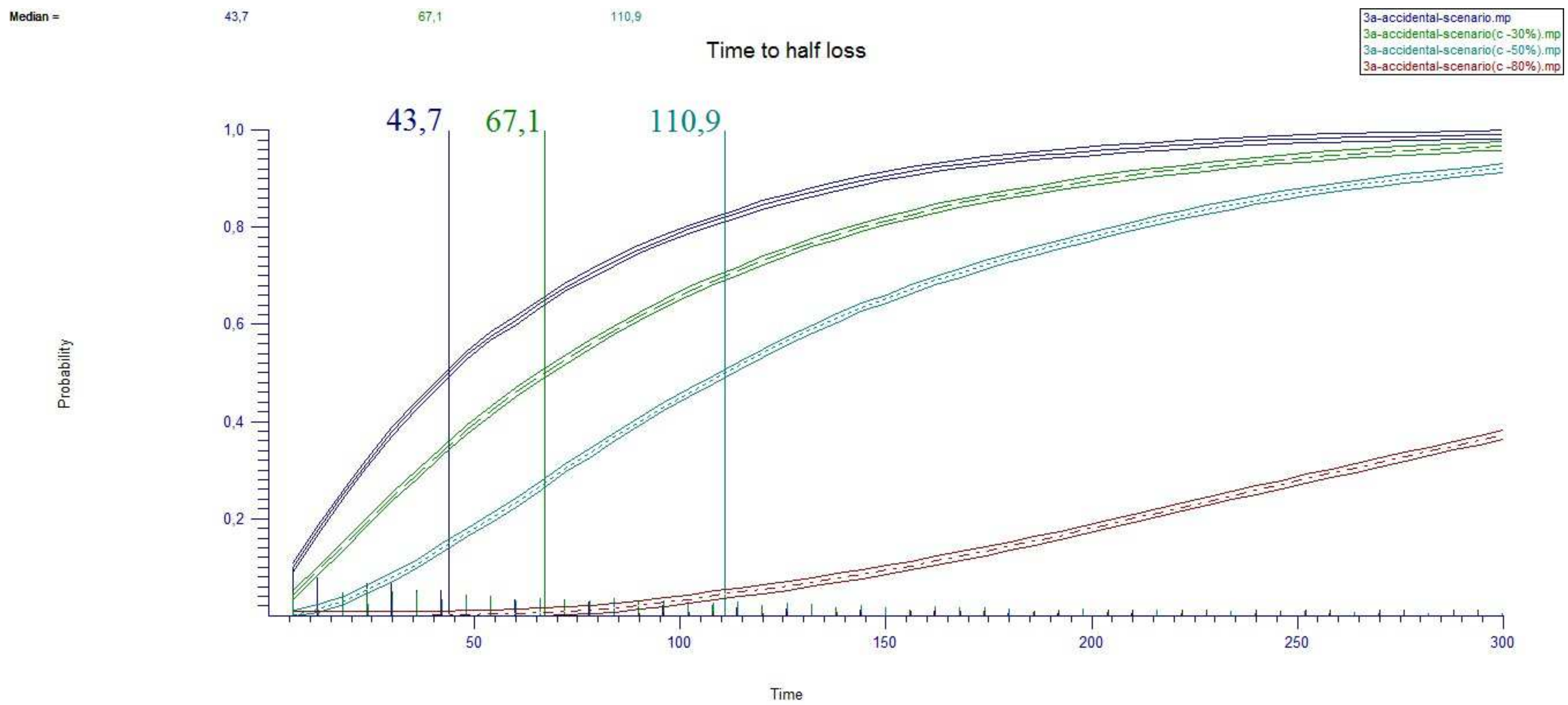

Figure 4.25 - Sensitivity analysis that express changes in risks measures(i.e. cumulative probability of the time to half loss) as a function of changes in the magnitude of the consequences. Each point in a curve can be interpreted as "there is a Y% risk that the population abundance will fall by 50% (half loss) in or before time-step X". If the median of a distribution is within the simulated time period, it is indicated by the solid vertical line. Both the line and the number for the median are in the same color as the distribution, so one can identify which simulation the median refers to.

Lastly, it was included density dependence in both primary models for a non-impact scenario and accidental scenario 3a. Density dependence included affects the single element in the stage matrix (i.e. the growth rate, *R*); density dependence type is Scramble because it is thought that resources are shared more-or-less equally among the juveniles; maximal growth rate (R_{max}) is 1.222; carrying capacity (*K*) is equal to the initial population abundance (i.e. 11,222 individuals); standard deviation of K is zero.

The rationale for analyzing the sensitivity to density dependence was to reinforce what had already been stated in this work: including density dependence in a population model to assess impacts of pollution makes the assessment less conservative, because population recovers faster after exposure. In other words, modeling density dependence may underestimate ecological risks originated from industrial accidents.

It is worth stressing that an accidental scenario's model that includes density dependence has to be compared with a non-impact scenario's model that also includes density dependence. The Figure 4.26 shows such comparison. As expected, the maximum difference between risks including density dependence (i.e. 0.27) was smaller than the maximum difference between risks not including density dependence (i.e. 0.99, see Figure 4.20). Therefore, changes in risks from a non-impact scenario to accidental scenario 3a are smaller if density dependence is included in both models.

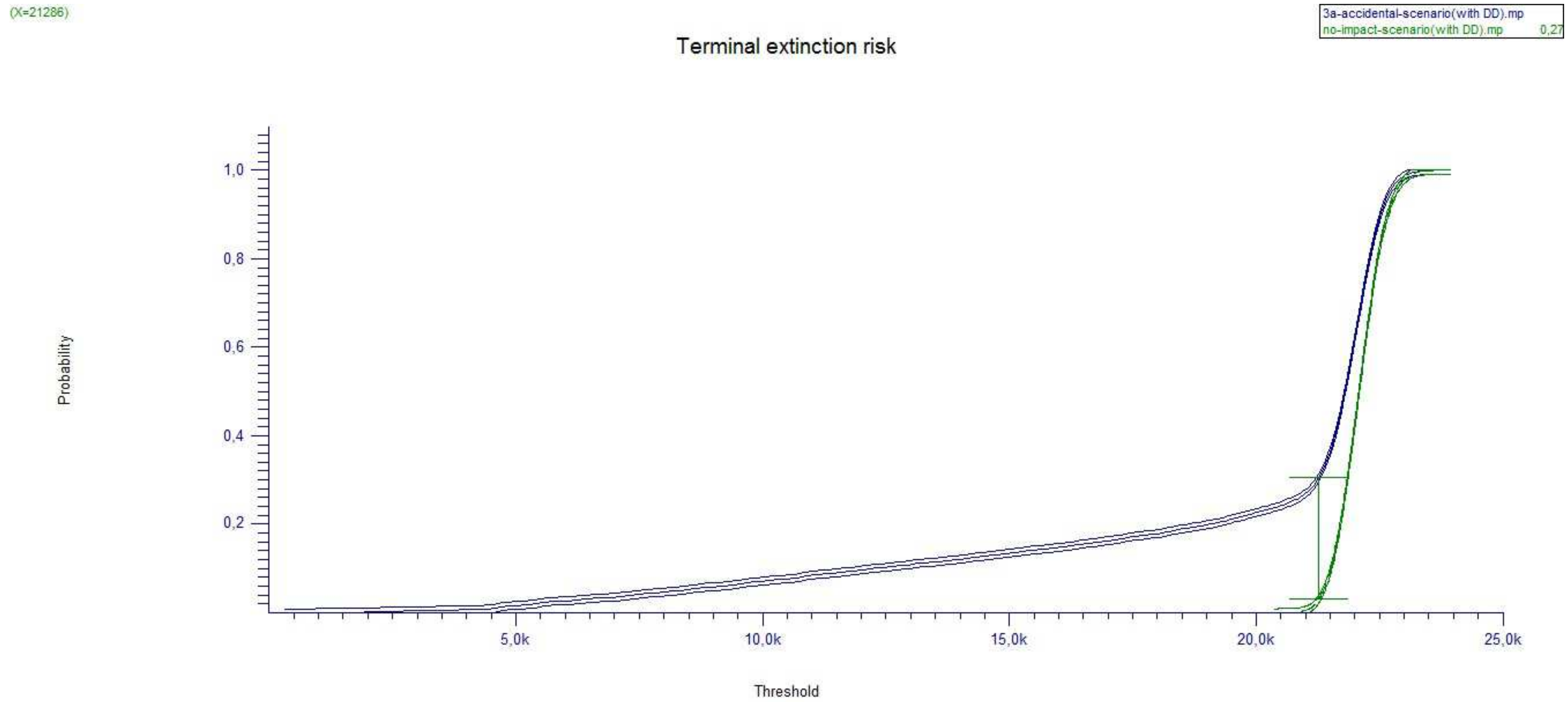

Figure 4.26 – Risk sensitivity to density dependence in both models for a non-impact scenario and accidental scenario 3a. This figure must be compared with Figure 4.20 to understand the changes. Each point in a curve can be interpreted as "there is a Y% risk that, 100 years from now, the population abundance will be less than X". The dotted line indicates the average value, whereas the solid lines the 95% confidence intervals. The vertical bar with two horizontal tabs represent the maximum difference between a non-impact scenario and accidental scenario 3a. The box to the upper right reports the value of the difference. The color of the text is the same as the color of the risk curve with which the first (dark blue) curve is compared. The reported number is the Kolmogorov-Smirnov test statistic D (which is the maximum vertical difference). The value X to the upper left is the x-value at which the difference is maximum.

4.6.6 Uncertainty analysis

This section is concerned with one of the objectives of the QERA (defined in the first step), i.e. to deal with uncertainty of significant accidental scenarios. In this context, uncertainty was measured by estimating a range (lower bound and upper bound) to risk measures based on the best case and worst case of accidental scenario 3a.

Up until here, all parameters for the assessment had been defined from a conservative point of view. Consequently, the presented risk measures associated with accidental scenario 3a represent the worst case. It was then conducted a simulation from an optimistic point of view in an effort to represent the best case of accidental scenario 3a. As a result, the following changes were made in the primary model for accidental scenario 3a (i.e. that of its worst case):

- Frequencies were reduced by 20%.
- Density-dependence was included in the model. Density dependence included affects the single element in the stage matrix (i.e. the growth rate, *R*); density dependence type is Scramble; maximal growth rate (R_{max}) is 1.2497; carrying capacity (*K*) is 10,990; standard deviation of *K* is zero.
- It was considered that only 50% of the components of oil on the surface of the water will actually dissolve in water, i.e. $W_{dxdydz}(t) = 0.5 \times W_{dxdy}(t)$. This way, PNECs were further calculated using the procedure in section 4.3. Afterwards, the responses (in fraction of mortality) were calculated through the dose-response function in section 4.6.1.

The new frequencies and fractions of mortality for a best case scenario are presented in Table 22. The results for measuring uncertainty (lower and upper bounds) are presented in the Figure 4.27. Looking at time step 60 (i.e. 20 years), one can conclude that even from an optimistic point of view, risks originated from accidental scenario 3a cause the population of concern to be categorized as “Endangered” (i.e. at least 20% risk of half loss in the next 20 years, according to section 2.5.7.

Table 22 - Input parameters for a best case accidental scenario 3a.

Accidental scenario	**Fraction of mortality**	**Frequency of occurrence**
3a-winter-neap tide	0.62	0.006336
3a-winter-spring tide	0.46	0.006336

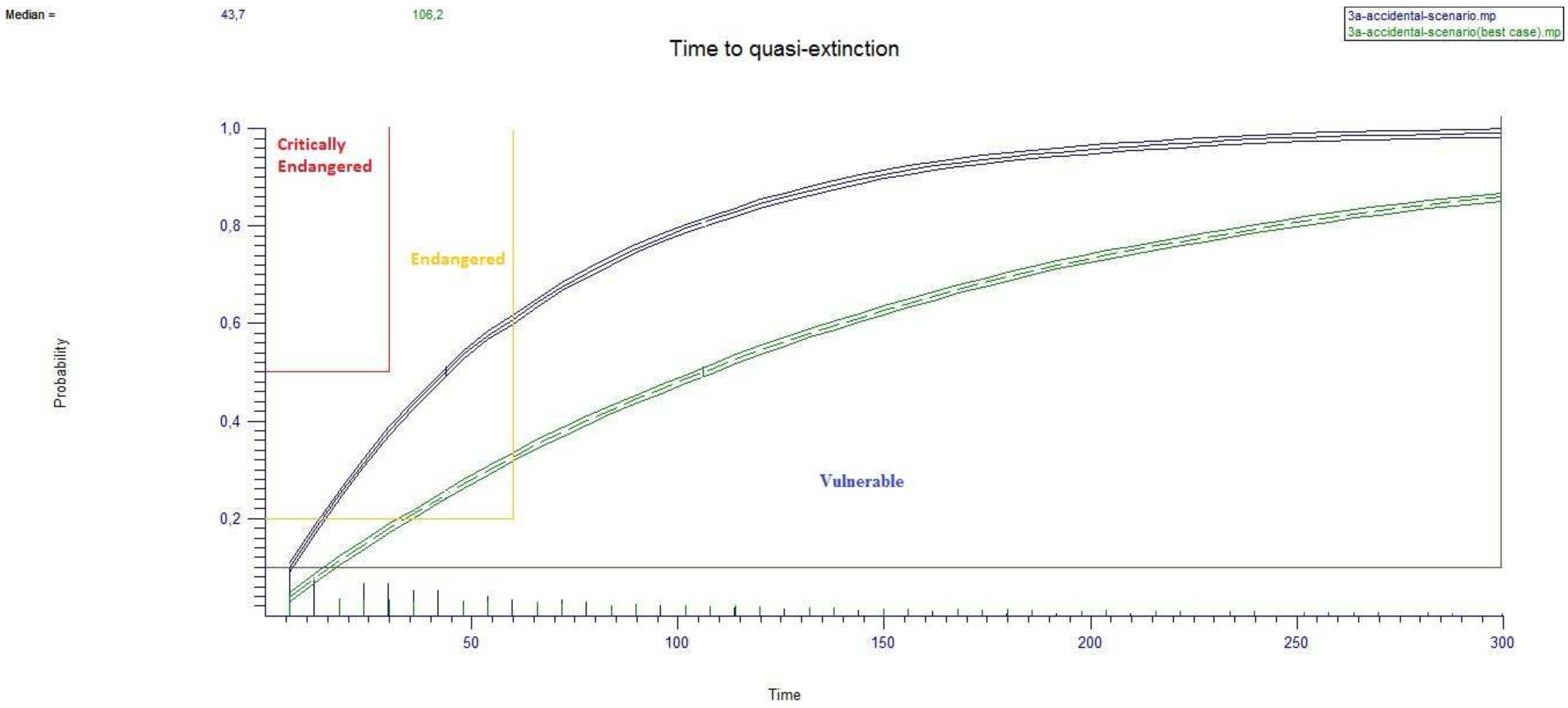

Figure 4.27 – Measuring uncertainty as the range between risks for the worst case of accidental scenario 3a (upper bound) versus risks for the best case of accidental scenario 3a (lower bound).

5 CONCLUSIONS

The primary objective of this work was to develop and propose a methodology for QERA for industrial accidents. Indeed, it was presented a methodology capable of quantifying ecological risks caused by events with low frequency of occurrence but that may cause catastrophic ecological damage. The main goal of the proposed methodology was to integrate information from four different studies that can contribute to quantify ecological risks originating from rare events. Besides that, the specific objectives of this work were achieved since the methodology:

- uses reliability analysis for estimating frequencies of occurrence of accidental scenarios caused by equipment failure or human error;
- uses fate and transport modeling to predict individual-level exposure in case of a particular accidental scenario;
- uses dose-response modeling and hazard quotient to estimate individual-level adverse effects;
- uses population modeling to translate individual-level into population-level adverse effects;
- provides results that allows for the comparison among accidental scenarios, as a basis for prioritizing risk management measures under limited resources;
- presents the total ecological risks of an establishment in a single risk measure (i.e. FN risk curve), as a simple way to communicate risks to stakeholders;
- deals with environmental variability in time and space;
- can point out further work that can effectively improve results via a sensitivity analysis;
- can deal with uncertainty, measuring it and communicating it to risk managers on a quantitative basis;
- is flexible in terms of data needs, i.e. can use several types of data;
- uses objective criteria throughout the second, third and fourth steps in order to rule out accidental scenarios that will not contribute to the final ecological risk, avoiding waste of cost and time;
- was tested in an application example and proved to be practicable, efficient and convenient. Because most data for applying the methodology was already available from other studies and public databases, the methodology could be

applied in a relatively short period of time, i.e. about 5 months. If no data were available, it is estimated that collecting data for such an assessment and applying the methodology would take about 2 years.

More benefits of the methodology are described step by step as follows. The first step of the methodology allows for an improved knowledge about dangerous installations within an establishment, chemicals of concern and characteristics of the ecological environments possibly affected by accidents. It also encourages interaction of the risk assessor with other professionals such as risk managers, environmental managers, ecologists, technical managers and operators of the establishment. The second step allows to systematically identify the existing accidents and their possible ecological damage, causing an improved level of preparation to emergencies.

The third step provides a screening assessment of the ecological damage possibly caused by the identified accidents. Individual-level exposure is predicted via fate and transport models. Most of these models are deterministic and some uncertainty in the results of the QERA is originated from their predictions. Uncertainty can be reduced by identifying the most influent meteorological conditions and creating meteorological scenarios.

The frequencies of the accidental scenarios are estimated in the fourth step. Also, some uncertainty in the results of the QERA is originated from frequency estimates. This can be minimized by conducting a detailed case-specific reliability analysis.

The fifth step of the methodology uses mathematical modeling applied to ecology (i.e. population modeling) to translate individual-level exposure (predicted in the third step) into population-level effects. Population modeling proved to be an efficient approach to quantify ecological impacts caused by industrial accidents, providing results in more relevant units than individual-level effects. The iterative process in implementing a population model was presented in a comprehensive scheme built by the author.

Some uncertainty in the final results of the QERA is originated from uncertainty in the population model, which is originated from: difficulties in data gathering; difficulties in parameter estimation; weak ability to validate population models; effects of alternative model structures. Nonetheless, uncertainty is an indelible characteristic of any future prediction. It does not make population modeling unfeasible as long as it is evaluated and communicated to decision makers. To make this claim, one needs to correctly represent uncertainty in the results. In this sense, the methodology measures uncertainty by estimating a range (lower bound and upper bound) to risk measures based on the best and worst case of accidental scenarios.

Besides being useful to a QERA for industrial accidents, the population model built in the fifth step provides relevant information to tackle many key gaps in environmental management, such as optimal resource allocation for monitoring affected areas, optimal management of threatened and endangered species, and spatial planning for landscape restoration and management.

The ecological risks originating from accidents in an establishment is quantified in the sixth step. Risks can be assessed in two ways: (1) by a comparative approach, in which ecological risks related to each accidental scenario are compared with ecological risks in the absence of any potential accidental scenario (i.e. a no-impact scenario); and (2) by a cumulative approach, in which ecological risks of all accidental scenarios are cumulated and presented as a FN curve. Both ways provide quantitative and relevant information to support the decision-making process for managing possible ecological catastrophes. Thus, the decision maker could evaluate different alternatives of risk reduction via a cost-benefit analysis. It is important to note again that the proposed methodology is interactive, so that revaluation may occur during any part of the assessment or new information can be incorporated to improve results.

It is worth mentioning that the methodology usually requires more than one person to perform it. In other words, the methodology demands team work because specific knowledge on several different fields of studies is necessary. In most cases, team should be composed by an ecological risk assessor, an ecologist, a fate and transport modeler (e.g., an oceanographer, if toxic disperses through the ocean), a reliability analyst and a system engineer.

5.1 Limitations

- There are better ways of measuring and communicating uncertainty than the approach used in the methodology (i.e. based on the difference between the best and worst case of accidental scenarios).
- No risk criteria were proposed in the FN risk curve. Although risk criteria was proposed for categorizing each accidental scenario alone (in terms of probability of the time to half loss), no risk criteria were proposed for the cumulative risks of all accidental scenarios in the FN curve.

- The parameters for the population model are estimated through historical data only, ignoring expert opinion.

5.2 Future studies

In order to tackle the limitations of the methodology, it is proposed the following future studies:

- to study the several concepts and techniques of uncertainty analysis in population models, compare their performances, determine the best way to estimate and communicate uncertainty in a QERA for industrial accidents, and incorporate it into the methodology;
- to propose ecological risk criteria for acceptability in terms of the results provided by the FN risk curve.
- to investigate the role of expert opinion (i.e. ecologists) in order to improve the parameterization of a population model, focusing on the study of Bayesian methods to do so.
- to incorporate expert opinion in the fifth step (i.e. population modeling) of the methodology using Bayesian methods.

5.3 Conclusions to the application example

The results of the QERA showed that ecological risks from accidental scenario 3a cause the fish population of concern to be categorized as “Endangered” (according to section 4.6.3) even in a best case scenario. Conversely, ecological risks from other accidental scenarios are negligible. From this point of view, management actions should be taken to reduce the frequency of occurrence and/or the magnitude of the consequences of accidental scenario 3a, until risks reach an acceptable level (i.e. “Low risk” category).

5.3.1 Limitations

- The fate and transport model predicted the kilograms of crude oil on the surface of the ocean within each cell $dx \times dy$. However, the key species of concern do not live only on the surface of the water, but in a depth range up to 70 meters [100]. In this context, it was made a crude approximation to convert kilograms of petroleum per area of water into milliliter of oil per volume of water.

- The frequencies were estimated based on average situations (i.e. generic frequencies) and did not take into account many specific circumstances of the accidental scenario under assessment (e.g., human error, control measures).
- Input data to parameterize the population model was poor, i.e.:
  - The sampler area was too small (20 m^2), leading to high standard deviations in parameter estimates (e.g., population growth rate).
  - Data did not allow the population model to be age/stage structured, because they were about juvenile individuals only.
  - Data were collected in a specific location where no amount of oil was predicted in case of accident, so there was a need to extrapolate the location of the fish population in order to take into account chemical effects caused by oil exposure.
  - ecotoxicological data to build a dose-response curve was extrapolated from a related species;
- Ecological risks related to accidental scenarios in the summer (when the oil plume moves to the south) were not calculated because the oil plume does not reach the fish population of concern, although it may reach others populations to the south.

5.3.2 Future application

As the methodology is interactive, any new information and revaluation can be incorporated into the assessment at any time, starting a new round of the methodology, until results are reliable enough to be presented to risk managers.

This section concerns about proposing a second round of the methodology in the application example in order to improve results of the first round. In the second round, there is no need to redo every single step of the methodology. Instead, it should tackle the limitations in the results of the first round (section 5.3.1). In this context, the first round was useful to point out what new efforts can effectively improve results, they are:

- To model the fate and transport of oil in the water (i.e. per water columm $dx \times dy \times dz$) instead of on the surface of the water (i.e. per water cell $dx \times dy$). As the POM is a three-dimensional model, it is also indicated for such modeling.

- To conduct a more detailed reliability analysis in order to estimate more accurate frequencies concerning specific circumstances of the accidental scenario under assessment. In fact, reliability engineering is a well-developed field of study, so that a more detailed reliability analysis (including generic equipment failures, control measures and human error) is possible.
- To gather richer input data for the population model. Perhaps, one may need to choose as indicator a population of another representative species in the coastal region of Suape, i.e.:
    - A species that is easier to monitor (i.e. bigger size, smaller abundance, and longer life spam).
    - Ecologists should have been collecting data about this population dynamics since more than 2 years up until the present.
    - Data should include all age/stage classes of the population.
    - Sampler size should be more representative.
    - At best, ecotoxicological data about the species should be available.
    - The location where data is collected should be over a region where significant amounts of oil are predicted (in case of accident). In this context, the first round of the methodology helps to decide this location.
    - If no richer data is already available, it will be necessary to collect these data. This would take at least 2 years. Nonetheless, the first round of the methodology provides basis of knowledge for an effective data collection directed to a QERA.
- To include another population to the south of the release points and to build a metapopulation model with potential for migration between the two populations. This way, ecological risks related to accidental scenarios in the summer could be also quantified.

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APPENDIX A

Ecotoxicological data for Exposure Assessment and Dose-Response curve

(from the ref [82])

***** AQUATIC TEST #: 730181 *****

CHEMICAL

	GRADE	PURITY	FORM.	RADIOLABEL	CAS #
TEST		**100**			**8002059**

NAME: **Petroleum**
COMMENT: **CRUDE OIL, AGHA JARI CRUDE OIL**

TEST CONDITIONS

STUDY TYPE:	**NC**
MEDIA:	**SW**
LOCATION:	**LAB**
CONTROL:	**C**
EXPOSURE TYPE:	**S**
APPLICATION FREQ.:	**1 X**
EXPOSURE DUR.:	**48 hour(s)**
STAND DUR. (D):	**2 day(s)**

SPECIES

SPECIES # (NAME):	**16544 Parupeneus barberinus (Goatfish)**
AGE:	**NR NR**
LIFE STAGE:	**not reported, unknown**
COMMENT:	**0.43 G,<=39.5 MM LENGTH**

PUBLICATION

REFERENCE #:	**5746 Eisler, R., 1975**

TEST CONCENTRATION

CHEM ANAL. METHOD: **unmeasured**
UNIT OF MEASURE: **ml/L** milliliters per liter

TYPE	VALUE	RANGE			STANDARD CONC (ug/L)	ION
F	**1.0**	**NR**	TO	**NR**	1 ml/L	NR

EFFECT RESULTS

EFFECT:	**Mortality**
TREND:	
RESPONSE SITE:	**NR**
% EFFECT:	**NR**
EFFECT MEASUREMENT:	

Mortality

ENDPOINT

ENDPOINT:	**Lethal concentration to 0% of test organisms**
ENDPOINT ASSIGN.:	
SIGNIFICANCE:	**NA**
LEVEL:	**NR**
BCF Value **(F)**:	**NR (NR to NR)**
BCF Value **()**:	**NC (NC to NC)**

EE Comment:

WATER QUALITY	**VALUE**	**RANGE**			**(UNIT)**
TEMPERATURE:	**23**	**NR**	TO	**NR**	**C**
pH:	**NR**	**NR**	TO	**NR**	
HARDNESS:	**NR**	**NR**	TO	**NR**	**NR**
SALINITY:	**NR**	**NR**	TO	**NR**	**NR**

ALKALINITY:	**NR**	**NR**	TO	**NR**	**NR**
CONDUCTIVITY:	**NR**	**NR**	TO	**NR**	**NR**
DISSOLVED OXYGEN:	**NR**	**NR**	TO	**NR**	**NR**
ORGANIC CARBON (**NR**):	**NR**	**NR**	TO	**NR**	**NR**

COMMENTS

OTHER EFFECTS:	
GENERAL COMMENTS:	DNUM/6//

FIELD DATA

HABITAT CODE:			
HABITAT DESC.:			
SUBSTRATE CODE:			
SUBSTRATE DESC.:			
GEOG. LOCATION:			
GEOG. CODE:		DEPTH:	
LATITUDE:		APPLIC TYPE:	
LONGITUDE:		APPLIC RATE:	
HALF LIFE:	**(to)**	APPLIC DATE(SEASON):	**()**

NA = Not Applicable
NC = Not Coded
NR = Not Reported

*** AQUATIC TEST #: 730182 ***

CHEMICAL

	GRADE	PURITY	FORM.	RADIOLABEL	CAS #
TEST		**100**			**8002059**

NAME: **Petroleum**
COMMENT: **CRUDE OIL, AGHA JARI CRUDE OIL**

TEST CONDITIONS

STUDY TYPE:	**NC**
MEDIA:	**SW**
LOCATION:	**LAB**
CONTROL:	**C**
EXPOSURE TYPE:	**S**
APPLICATION FREQ.:	**1 X**
EXPOSURE DUR.:	**48 hour(s)**
STAND DUR. (D):	**2 day(s)**

SPECIES

SPECIES # (NAME):	**16544 Parupeneus barberinus (Goatfish)**
AGE:	**NR NR**
LIFE STAGE:	**not reported, unknown**
COMMENT:	**0.43 G,<=39.5 MM LENGTH**

PUBLICATION

REFERENCE #:	**5746 Eisler, R., 1975**

TEST CONCENTRATION

CHEM ANAL. METHOD: **unmeasured**
UNIT OF MEASURE: **ml/L** milliliters per liter

TYPE	VALUE	RANGE			STANDARD CONC (ug/L)	ION
F	**6.7**	**NR**	TO	**NR**	6.7 ml/L	NR

EFFECT RESULTS

EFFECT:	**Mortality**
TREND:	
RESPONSE SITE:	**NR**
% EFFECT:	**NR**
EFFECT MEASUREMENT:	

Mortality

ENDPOINT

ENDPOINT:	**Lethal concentration to 50% of test organisms**
ENDPOINT ASSIGN.:	
SIGNIFICANCE:	**NA**
LEVEL:	**NR**
BCF Value **(F)**:	**NR (NR to NR)**
BCF Value **()**:	**NC (NC to NC)**

EE Comment:

WATER QUALITY	**VALUE**	**RANGE**			**(UNIT)**
TEMPERATURE:	**23**	**NR**	TO	**NR**	**C**
pH:	**NR**	**NR**	TO	**NR**	
HARDNESS:	**NR**	**NR**	TO	**NR**	**NR**
SALINITY:	**NR**	**NR**	TO	**NR**	**NR**
ALKALINITY:	**NR**	**NR**	TO	**NR**	**NR**
CONDUCTIVITY:	**NR**	**NR**	TO	**NR**	**NR**
DISSOLVED OXYGEN:	**NR**	**NR**	TO	**NR**	**NR**
ORGANIC CARBON (**NR**):	**NR**	**NR**	TO	**NR**	**NR**

COMMENTS

OTHER EFFECTS:	
GENERAL COMMENTS:	DNUM/6//

FIELD DATA

HABITAT CODE:			
HABITAT DESC.:			
SUBSTRATE CODE:			
SUBSTRATE DESC.:			
GEOG. LOCATION:			
GEOG. CODE:		DEPTH:	
LATITUDE:		APPLIC TYPE:	
LONGITUDE:		APPLIC RATE:	
HALF LIFE:	**(to)**	APPLIC DATE(SEASON):	**()**

NA = Not Applicable
NC = Not Coded
NR = Not Reported

*** AQUATIC TEST #: 730183 ***

CHEMICAL

	GRADE	PURITY	FORM.	RADIOLABEL	CAS #
TEST		**100**			**8002059**

NAME: **Petroleum**
COMMENT: **CRUDE OIL, AGHA JARI CRUDE OIL**

TEST CONDITIONS

STUDY TYPE:	**NC**
MEDIA:	**SW**
LOCATION:	**LAB**
CONTROL:	**C**
EXPOSURE TYPE:	**S**
APPLICATION FREQ.:	**1 X**
EXPOSURE DUR.:	**48 hour(s)**
STAND DUR. (D):	**2 day(s)**

SPECIES

SPECIES # (NAME):	**16544 Parupeneus barberinus (Goatfish)**
AGE:	**NR NR**
LIFE STAGE:	**not reported, unknown**
COMMENT:	**0.43 G,<=39.5 MM LENGTH**

PUBLICATION

REFERENCE #:	**5746 Eisler, R., 1975**

TEST CONCENTRATION

CHEM ANAL. METHOD: **unmeasured**
UNIT OF MEASURE: **ml/L** milliliters per liter

TYPE	VALUE	RANGE			STANDARD CONC (ug/L)	ION
F	**30.0**	**NR**	TO	**NR**	30 ml/L	NR

EFFECT RESULTS

EFFECT:	**Mortality**
TREND:	
RESPONSE SITE:	**NR**
% EFFECT:	**NR**
EFFECT MEASUREMENT:	

Mortality

ENDPOINT

ENDPOINT:	**Lethal concentration to 100% of test organisms**
ENDPOINT ASSIGN.:	
SIGNIFICANCE:	**NA**
LEVEL:	**NR**
BCF Value **(F)**:	**NR (NR to NR)**
BCF Value **()**:	**NC (NC to NC)**

EE Comment:

WATER QUALITY	**VALUE**	**RANGE**			**(UNIT)**
TEMPERATURE:	**23**	**NR**	TO	**NR**	**C**
pH:	**NR**	**NR**	TO	**NR**	
HARDNESS:	**NR**	**NR**	TO	**NR**	**NR**
SALINITY:	**NR**	**NR**	TO	**NR**	**NR**
ALKALINITY:	**NR**	**NR**	TO	**NR**	**NR**
CONDUCTIVITY:	**NR**	**NR**	TO	**NR**	**NR**
DISSOLVED OXYGEN:	**NR**	**NR**	TO	**NR**	**NR**
ORGANIC CARBON (**NR**):	**NR**	**NR**	TO	**NR**	**NR**

COMMENTS

OTHER EFFECTS:	
GENERAL COMMENTS:	DNUM/6//

FIELD DATA			
HABITAT CODE:			
HABITAT DESC.:			
SUBSTRATE CODE:			
SUBSTRATE DESC.:			
GEOG. LOCATION:			
GEOG. CODE:		DEPTH:	
LATITUDE:		APPLIC TYPE:	
LONGITUDE:		APPLIC RATE:	
HALF LIFE:	**(to)**	APPLIC DATE(SEASON):	**()**

NA = Not Applicable
NC = Not Coded
NR = Not Reported

APPENDIX B

Loss of Containment Events (LOCs) for ships in an establishment

(from the ref [18])

	LOC for ships in an establishment	
L.1	Full bore rupture of the loading/unloading arm - outflow from both sides of the full bore rupture	
L.2	Leak of the loading/unloading arm - outflow from a leak with an effective diameter equal to 10% of the nominal diameter, with a maximum of 50 mm	
E.1	External impact, large spill	
	- gas tanker	continuous release of 180 m^3 in 1800 s
	- semi-gas tanker (refrigerated)	continuous release of 126 m^3 in 1800 s
	- single-walled liquid tanker	continuous release of 75 m^3 in 1800 s
	- double-walled liquid tanker	continuous release of 75 m^3 in 1800 s
E.2	External impact, small spill	
	- gas tanker	continuous release of 90 m^3 in 1800 s
	- semi-gas tanker (refrigerated)	continuous release of 32 m^3 in 1800 s
	- single-walled liquid tanker	continuous release of 30 m^3 in 1800 s
	- double-walled liquid tanker	continuous release of 20 m^3 in 1800 s

GLOSSARY

Abundance: the total number or density (number per unit area or unit volume) of organisms in a given location.

Acute toxicity: the ability of a chemical to cause a toxic response in organisms immediately or shortly after exposure.

Adverse ecological effects: Changes that are considered undesirable because they alter valued structural or functional characteristics of ecosystems or their components. An evaluation of adversity may consider the type, intensity, and scale of the effect as well as the potential for recovery.

Age Class: a category comprising individuals of a given age within a population.

Agent: Any physical, chemical, or biological entity that can induce an adverse response (synonymous with stressor).

Age-specific fecundity: the number of eggs or offspring produced per unit time by an individual of a specified age.

Age-specific survival: the proportion of individuals of age x alive at time t who will be alive at time t+1.

Assessment endpoint: environmental characteristic or value that is to be protected (e.g. population abundance, species diversity, or ecosystem productivity).

Biodegradation: a process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment.

Biomarkers: measures of body fluids, cells, tissues or measures taken on the whole organism, indicating, in terms biochemical, cellular, physiological, compartmental or energetic, the presence of contaminants substances or the magnitude of the response of the target organism.

Biota: living groups of organisms or species.

Biotic: living organisms, usually referring to the biological components of an ecosystem.

Chronic toxicity: the ability of a chemical to produce a toxic response when an organism is exposed over a long period of time.

Community: an assemblage of populations of different species within a specified location in space and time. Sometimes, a particular subgrouping may be specified, such as the fish community in a lake or the soil arthropod community in a forest.

Conceptual model: A conceptual model in problem formulation is a written description and visual representation of predicted relationships between ecological entities and the stressors to which they may be exposed.

Density dependence: a change in the influence of any factor (a density-dependent factor) that affects population growth as population density changes. Density-dependent factors tend to retard population growth by increasing mortality or emigration or decreasing fecundity as population density increases. They enhance population growth by decreasing mortality or increasing fecundity as population density decreases.

Dose: the amount of chemical taken into an organism per unit of time.

Deadweight tonnage: a measure of how much weight a ship is carrying or can safely carry. It is the sum of the weights of cargo, fuel, fresh water, ballast water, provisions, passengers, and crew.

EC_{50}: the toxicant concentration at which 50% of the test organisms show effects (e.g. mortality).

Ecological entity: A general term that may refer to a species, a group of species, an ecosystem function or characteristic, or a specific habitat. An ecological entity is one component of an assessment endpoint.

Ecological model: a mathematical expression that can be used to describe or predict ecological processes or endpoints such as population abundance (or density), community species richness, productivity, or distributions of organisms.

Ecological relevance: One of the three criteria for assessment endpoint selection. Ecologically relevant endpoints reflect important characteristics of the system and are functionally related to other endpoints.

Ecological risk assessment: The process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors.

Ecosystem: the interacting system of a biological community and its non-living environmental surroundings.

Ecotoxicology: the branch of toxicology concerned with the study of toxic effects, caused by natural or synthetic pollutants, to the constituents of ecosystems, animal (including human), vegetable and microbial, in an integral context.

Emigration: the movement of an individual or group out of an area or population.

Endpoint: the biological or ecological unit or variable being measured or assessed.

Environmental impact statement (EIS): Environmental impact statements are prepared under the national environmental policy act by federal agencies as they evaluate the environmental consequences of proposed actions. EISs describe baseline environmental conditions; the purpose of, need for, and consequences of a proposed action; the no-action alternative; and the consequences of a reasonable range of alternative actions. A separate risk assessment could be prepared for each alternative, or a comparative risk assessment might be developed. However, risk assessment is not the only approach used in EISs.

Exposure: The contact or co-occurrence of a stressor with a receptor.

Exposure-response assessment: a description of the relationship between the concentration (or dose) of the chemical that causes adverse effects and the magnitude of the response of the receptor.

Fate and transport model: a description of how a chemical is carried through the environment. This may include transport through biological as well as physical parts of the environment.

Fecundity: the number of live offspring per individual in a given age class that will survive to be counted in the first age class.

Fish measurement: Standard Length (SL) refers to the length of a fish measured from the tip of the snout to the posterior end of the last vertebra or to the posterior end of the midlateral portion of the hypural plate. Simply put, this measurement excludes the length of the caudal fin;

Total length (TL) refers to the length from the tip of the snout to the tip of the longer lobe of the caudal fin, usually measured with the lobes compressed along the midline. It is a straight-line measure, not measured over the curve of the body; **Fork length (FL)** refers to the length from the tip of the snout to the end of the middle caudal fin rays.

Geographic information system (GIS): software that combines a database and mapping capability; often used in spatially explicit modeling.

Grow rate: the rate of change of population abundance. Depending on the context, growth rate could also refer to the rate of change in mass or size of an organism.

Habitat: the place where animals and plants normally live, often characterized by a dominant plant form or physical characteristic.

Hazard quotient: the ratio of an estimated exposure concentration (or dose) to a toxicity threshold expressed in the same units.

Immigration: the movement of an individual or group into a new population or geographical region.

Indicator species: species thought to be more sensitive and therefore serve as an early warning indicator of ecological effects.

Key species: species strategically chosen to represent ecological effects in the risk assessment. Key species can be, for example, indicator species that are thought to be more sensitive and therefore serve as an early warning indicator of ecological effects, species of scientific and economic importance, rare and endangered species, or any species to be protected.

Landscape: the traits, patterns, and structure of a specific geographic area, including its biological composition, its physical environment, and its anthropogenic or social patterns. An area where interacting ecosystems are grouped and repeated in similar form.

Life stage: a developmental stage of an organism (for example, juvenile, adult, egg, pupa, larva).

Life story: the temporal pattern and habitat association of life stages (e.g. egg, larva, pupa and adult in an insect or egg, fry, smolt, juvenile, and adult in a salmon) and the schedule of births and deaths for a species.

Lowest-observed-effect-level (LOEL): the lowest concentration or amount of a substance, found by experiment or observation under the same defined conditions of exposure, that causes any alteration in morphology, functional capacity, growth, development, or life span of target organisms.

Measurement endpoints: quantitative expressions of an observed or measured biological response, such as the effects of a toxic chemical on survivorship or fecundity, related to the valued environmental characteristic chosen as the assessment endpoint.

Migration: the movement of an individual or group into or out of an area or population.

Mortality: the number of individuals of a population that died in a given period of time.

Neap tide: when the tide’s range is at its minimum.

No-observed-effect-level (NOEL): the greatest concentration or amount of a substance, found by experiment or observation under the same defined conditions of exposure, that causes no alterations of morphology, functional capacity, growth, development, or life span of target organisms.

Organism: any form of animal or plant life.

Population growth rate: the rate at which numbers of individuals are added to the population over time.

Population: a group of interbreeding organisms occupying a particular space.

Predicted Environmental Concentration (**PEC):** the local maximum of a predicted concentration function *C(x,y,z,t)* related to an accidental scenario.

Predicted No Effect Concentration (PNEC): the concentration below which exposure to a substance is not expected to cause adverse effects.

Productivity: the rate of production of living biomass in a population or community.

Receptor: The ecological entity that might be exposed to a stressor.

Recovery: The rate and extent of return of a population or community to some aspect(s) of its previous condition. Because of the dynamic nature of ecological systems, the attributes of a "recovered" system should be carefully defined.

Recovery measures: mitigation actions which could reduce the magnitude of the consequences of an accidental scenario, and so reduce the risk.

Remedial action goals: a subset of remedial action objectives consisting of medium-specific chemical concentrations that are protective of human health and the ecological environment.

Spatially explicit model: a model that tracks spatial information (e.g. the locations of organisms or the pattern of a landscape).

Species: An organism belonging to such a category, represented in binomial nomenclature by an uncapitalized Latin adjective or noun following a capitalized genus name, as in *Ananas comosus*, the pineapple, and *Equus caballus*, the horse.

Species richness: the total number of species in a location or the number per unit area or volume.

Spring tide: when the tide's range is at its maximum. It is not named after the season (i.e. spring) but, like that word, derives from an earlier meaning of jump, burst forth, rise as in a natural spring.

Stressor: any physical, chemical, or biological entity that can induce an adverse response in an organism.

Survival: the number of individuals of a population that are alive after a given period of time.

Threshold: the chemical concentration (or dose) at which physical or biological effects begin to be produced.

Toxicity extrapolation model: any mathematical expression for extrapolating toxicity data between species, endpoints, exposure durations, and so forth. Also includes uncertainty factors.

Toxicity test: a test in which organisms are exposed to chemicals in a test medium (for example, waste, sediment, soil) to determine the effects of exposure.