

Environmental risk assessment of enhanced oil recovery solutions

by

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Thesis submitted in fulfilment of
the requirements for the degree of
PHILOSOPHIAE DOCTOR
(PhD)



University
of Stavanger

Faculty of Science and Technology
Department of Safety, Economics and Planning
2023

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ISBN: 978-82-8439-161-8

ISSN: 1890-1387

PhD: Thesis UiS No. 696

Preface

This thesis is submitted in partial fulfilment of the requirements for the degree of Philosophiae Doctor (PhD) at the University of Stavanger, Faculty of Science and Technology, Norway. The PhD project has been funded by the Research Council of Norway and the industry partners, ConocoPhillips Skandinavia AS, Aker BP ASA, Vår Energi AS, Equinor ASA, Neptune Energy Norge AS, Lundin Norway AS, Halliburton AS, Schlumberger Norge AS, Wintershall DEA and The National IOR Centre of Norway. The financial support has been gratefully acknowledged.

The primary goal of the research work was to generate new knowledge and methods for environmental risk assessment of enhanced oil recovery solutions. The emphasis was also on developing a bridge between the fields of environmental/ecological risk assessment and risk science. This was done by applying concepts and principles from the risk science literature to a commonly used method in environmental risk assessment.

I would like to extend my sincere gratitude to everyone who helped and guided me in various ways throughout my research work. Their contributions are gratefully acknowledged and appreciated.

First and foremost, I would like to express my sincere gratitude to my supervisors, Professor Roger Flage and Associate Professor Steinar Sanni, for their exceptional guidance, support, and patience throughout my research work. It has been a privilege to be your PhD student, and I will forever be grateful for the enriching opportunity and the wealth of knowledge I have gained from both of you. I would also like to express my gratitude to my supervisor, Professor Merete Vadla Madland, for her advice and support at important stages during my PhD.

Next, I would like to express my gratitude to Ms. Emily Lyng, Researcher at the Norwegian Research Centre, for providing training and

guidance on the non-standard use of a simulation model used in several parts of the research and for always patiently clarifying my doubts.

My sincere gratitude to Professor Aksel Hiorth, Associate Professor Roald Kommedal, PhD candidate Eystein Opsahl, and Post-Doc Rockey Abhishek, for their valuable guidance and feedback related to the paper on the fate of polymers. Next, I would like to thank Mr. John-Sigvard Gamlem Njau – Master student at UiS, for his efficient and meticulous collaboration, which was instrumental in the successful publication of a paper on the environmental risk of tracers. Many thanks to all the co-authors with whom I have had the pleasure of collaborating.

My sincere thanks to Professor Daniela Pampanin and PhD candidate Giovanna Monticelli for the training and guidance provided on conducting toxicity experiments. I would also like to thank laboratory engineers, Ms. Julie Nikolaisen, Ms. Eli Drange Vee, Mr. Erling Berge Mosen, and Mr. Hans Kristian Brekken, for their guidance and support in conducting the laboratory experiments.

A special thanks to Professor Eirik BJORHEIM ABRAHAMSEN and Professor Jon Tømmerås Selvik for teaching me the fundamentals of risk assessment through a PhD course. The knowledge gained during this course has been of great help during the research work in this thesis.

Many thanks to Ms. Linda March for the excellent proofreading of all my written work in this thesis. My thanks to all the staff members at the National Improved Oil Recovery Centre of Norway and at the Faculty of Science and Technology, for all their help and assistance throughout the PhD period.

Finally, my deepest gratitude to all my family members for their unwavering encouragement and support throughout my thesis work.

Mehul Vora

Stavanger, February 2023

Summary

The overall objective of the research presented in this thesis is to contribute new knowledge about the environmental risk related to shortlisted products and processes developed at the National Improved Oil Recovery (IOR) Centre of Norway and about how to assess such risk.

According to the World Energy Outlook report presented by the International Energy Agency in 2021, oil and natural gas will continue to be important contributors to the energy mix over the next 20 years. Implementing enhanced oil recovery (EOR) solutions is important to maintain oil production from existing fields, as it is becoming increasingly difficult to discover new oil and gas reserves. An EOR screening study conducted across 53 reservoirs in 27 of the largest fields on the Norwegian Continental Shelf (NCS) found significant potential for additional oil recovery through EOR solutions. The (IOR) Centre of Norway has been developing new products and processes as part of EOR solutions to improve oil recovery on the NCS. Using these products and processes offshore poses an environmental risk to the marine environment and atmosphere, which needs to be assessed and managed.

This thesis explores existing environmental risk assessment (ERA) approaches for offshore oil production and identifies knowledge gaps related to assessing the environmental risk of EOR solutions. The knowledge gaps are filled by using laboratory studies to generate new data, using this data in models to generate key insights, and by developing new methods for ERA of EOR solutions and proposing improvements to existing methods. The research conducted in this thesis has resulted in five scientific papers that are summarized below.

Paper I presents a literature review on ERA guidelines relevant to offshore oil production. A review of the primary sources of environmental impacts and key environmental stressors resulting from offshore oil and gas production is also conducted. The main sources of

environmental impacts from offshore oil production include operational discharges of produced water (PW), drilling waste to the marine environment, and air emissions from energy production using fossil fuels. The literature review indicates that current ERA practices may form a basis for ERA of EOR solutions; however, there are also knowledge gaps related to the ERA of new products and processes planned to be used as a part of EOR solutions. Based on the review, a generalized ERA framework for PW and drilling waste into the sea and for air emissions is proposed in Paper I.

Several products and processes are developed at the IOR Centre to quantify and increase oil recovery as a part of EOR solutions. Using these new products and processes results in their back-production with PW, which is typically discharged into the marine environment. As a result, the main focus of this thesis is on the ERA of PW discharges caused by the implementation of EOR solutions.

Quantifying residual oil saturation is important for the successful implementation of EOR solutions. The IOR Centre has proposed a group of seven chemicals (tracers) for potential use in quantifying residual oil saturation in oil reservoirs. Using these tracers in offshore oil fields results in their operational discharges (e.g., with PW) into the marine environment. Once released into the sea, marine organisms may become exposed to the tracers, thereby posing an environmental risk to the ecosystem. Paper II first reports on laboratory experiments conducted to measure the biodegradability and toxicity of seven tracer compounds. A hypothetical case of using tracer compounds on the NCS is then assumed. Discharge of PW containing tracers, along with other production chemicals from the Brage field (used as a proxy case), is simulated using the dynamic risk and effects assessment model (DREAM), which estimates the contribution to the environmental impact factor (EIF) values from each tracer. In addition, the seven tracer compounds are ranked from low to high in terms of their environmental

impact. This ranking of the tracers can be used to shortlist the tracer(s) with minimum environmental impact for offshore applications.

Polymer flooding is a process in which high molecular weight synthetic polymers are injected into an oil reservoir to increase oil recovery. Injected polymers are usually back-produced with the PW, which is typically discharged into the sea. These synthetic polymers have slow microbial degradation rates under aerobic conditions, unless the molecular weight is reduced to less than 3 kilodaltons. Photocatalytic depolymerization rates for several different synthetic EOR polymers have been measured as a part of another project at the IOR Centre. In Paper III, a novel method is proposed to estimate the residual lifetime of synthetic polymers in the marine environment. Residual lifetime is the amount of time the discharged synthetic polymer takes to reach a molecular weight, below which it becomes biodegradable in the sea. The proposed method uses the DREAM model to estimate the concentration distribution of polymers in the sea. Subsequently, the concentration distribution is linked with the depolymerization rate equations to estimate the residual lifetime of synthetic polymers in the sea. The applicability of this developed procedure is demonstrated by estimating the residual lifetime of synthetic polymers discharged from single and multiple oil fields on the NCS.

Paper IV assesses the exposure and effects of discharging synthetic EOR polymers into the sea. Two main approaches are used: The first is based on estimating the EIF values of discharging PW-containing polymers using near-field simulations (where the discharge point is placed within a 50*50-kilometer grid). The estimated contribution to EIF values from synthetic polymers suggests negligible environmental impact when no assessment factor (AF) is used and low/moderate impact when an AF of 50 is used. The AF is a simple way to account for uncertainty in the assessment. The second approach, based on far-field simulations (where the discharge point is placed within a 1200*1800-kilometer grid), is primarily studied to assess polymer build-up in the sea, as synthetic EOR

polymers show resistance to microbial degradability. In one of the far-field simulations, polymers are repeatedly released annually over a 10-year period from seven arbitrarily chosen oil fields on the NCS. The highest concentration values (based on the 75 percentiles) during the first and tenth years of discharge are used in a regression analysis against the amount of polymer discharged each year. The regression analysis indicates that polymers will not build up within the simulation area at the expected amounts of polymers discharged each year. Moreover, there is a considerable margin of safety between the highest concentration values calculated by the model and the concentration at which harmful effects in aquatic species are predicted.

Paper V focuses on the use of species sensitivity distributions (SSDs) in ERA. An SSD is used to determine the threshold effect levels of stressors, below which unacceptable effects on a group of species are not expected. A literature review is performed to understand how risk is currently defined and how uncertainties are addressed when using SSDs in ERA. It is found that current ways of handling uncertainties while using SSDs are not based on unified guidance provided by the field of risk science. In Paper V, a risk-oriented framework is proposed that addresses uncertainties in a systematic manner while using SSDs. The proposed framework addresses uncertainties due to both lack of knowledge and variability. Furthermore, a scheme for assessing bias in theoretical and practical assumptions underlying SSDs is included in the framework. Lastly, a qualitative method is proposed to characterize the strength of knowledge underlying the SSDs.

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List of papers

- I. Vora, M., Sanni, S. & Flage, R. (2021). An environmental risk assessment framework for enhanced oil recovery solutions from offshore oil and gas industry. *Environmental Impact Assessment Review*, 88, 106512. <https://doi.org/10.1016/j.eiar.2020.106512>
- II. Vora, M., Gamlem Njau, J.-S., Sanni, S. & Flage, R. (2022). Environmental risk assessment of inter-well partitioning tracer compounds shortlisted for the offshore oil and gas industry. *Energy Exploration & Exploitation*, 40(6), 1743–1759. <https://doi.org/10.1177/01445987221097999>
- III. Vora, M., Opsahl, E., Abhishek, R., Sanni, S., Hiorth, A., Kommedal, R., Lyng, E. & Flage, R. (2023a). Modeling the fate and transport of synthetic enhanced oil recovery polymers in the marine environment. Draft ready for submission.
- IV. Vora, M., Sanni, S., Lyng, E. & Flage, R. (2023b). Exposure and effects of synthetic enhanced oil recovery polymers on the Norwegian Continental Shelf. Submitted for possible publication in *Regional Studies in Marine Science*.
- V. Vora, M., Flage, R. & Sanni, S. (2023c). Implementing a risk-oriented framework for addressing uncertainties in species sensitivity distributions. Submitted for possible publication in *Integrated Environmental Assessment and Management*.

Part I

1 Introduction

1.1 Background

According to the World Energy Outlook (WEO) report presented by the International Energy Agency (IEA) in 2021, oil and natural gas will continue to be important contributors to the energy mix over the next 20 years (IEA, 2021). Most oil companies are now focusing on improving the recovery factor (RF) from existing oil fields, as it becomes more difficult to find new oil and gas reserves (Muggeridge et al., 2014). The average RF from oil fields is currently between 20% and 40% (Muggeridge et al., 2014). Enhanced oil recovery (EOR) solutions such as polymer flooding, water alternating gas (WAG) injection, and low salinity/smart water injection are known for increasing oil recovery and, thus, the RF of existing fields (Torrijos et al., 2018; Muggeridge et al., 2014). Improved oil recovery (IOR), a term used at times as equivalent to EOR, implies the use of EOR solutions or other advanced reservoir management and monitoring techniques during an ongoing oil recovery process. Using EOR solutions in combination with IOR techniques could help increase the RF to between 50% and 70% (Muggeridge et al., 2014). Improving the RF is not only economically beneficial as it helps to improve the oil recovery, but it may also be environmentally favorable compared to setting up an oil field in a newly discovered petroleum province. In this thesis, the term EOR is used to represent both IOR and EOR solutions for oil recovery.

An EOR screening study was conducted by the Norwegian Petroleum Directorate (NPD) across 53 reservoirs in 27 of the largest fields on the Norwegian Continental Shelf (NCS). The study identified the potential for additional oil recovery of up to 3.7 billion barrels by implementing different EOR solutions (Smalley et al., 2020). The National Improved Oil Recovery (IOR) Centre of Norway has been developing new products and processes to improve oil recovery on the NCS (The

National Improved Oil Recovery (IOR) Centre of Norway, 2022). Using new products and processes on the NCS raises the question of how this affects the environmental risk to the marine environment and atmosphere. This question can be answered by conducting environmental risk assessments (ERAs) of the new products and processes before implementing these in the offshore oil and gas fields.

Oil and gas production from offshore reservoirs poses an environmental risk to the marine environment and the atmosphere (Bakke et al., 2013; Norwegian Oil and Gas Association, 2018). Operational discharges of produced water (PW), drilling waste to the marine environment, and air emissions from energy production using fossil fuels are common sources of environmental impacts from offshore oil and gas activities (Norwegian Oil and Gas Association, 2018). Most of the products and processes developed at the IOR Centre of Norway involve injecting new chemicals into the reservoir to quantify or increase the oil recovery. Injected chemicals are back-produced with the PW, which is typically discharged into the marine environment or re-injected into the reservoir. The back-produced chemicals pose an environmental risk to aquatic species (Bakke et al., 2013). Furthermore, there could also be a need to drill new injection wells into the reservoir to inject water/other chemicals for the EOR process. Drilling injection wells will produce drilling waste, which, if discharged into the marine environment, poses an environmental risk to the ecosystem (Bakke et al., 2013). Lastly, air emissions on the offshore platform may increase due to increased energy requirements for producing smart water or injecting water/polymers into the reservoir. Methods to assess environmental risk from the above-mentioned sources are well established and routinely used by the oil and gas industry on the NCS (Bakke et al., 2013; Norwegian Oil and Gas Association, 2013 and 2018). However, using new products and processes developed as a part of novel EOR solutions creates a need for new knowledge about both the risks related to these and how to assess them.

1.2 Research objective

The overall objective of the research presented in this thesis is to contribute new knowledge about the environmental risk related to shortlisted products and processes developed at the National IOR Centre of Norway and about how to assess such risk. The latter includes investigating the understanding of risk and uncertainties for a method used in traditional ERA and making suggestions for systematically addressing uncertainties as prescribed by concepts on handling uncertainties in the risk science literature. The research objective is elaborated using three main research questions introduced in the next section.

1.3 Research questions, approach, and scope

The first research question explores relevant guidelines and current practices used for ERA of offshore oil and gas production.

- Research question 1: How can the environmental impact and risk of implementing EOR solutions in offshore oil and gas reservoirs be assessed?

To answer the first research question, existing ERA guidelines relevant to the ERA of offshore oil and gas production are reviewed. Furthermore, existing literature on different sources of environmental impacts from offshore oil production and approaches used for ERA of these is investigated. The literature review reveals that current approaches used for ERA of the main sources of environmental impacts from offshore oil production, i.e., PW, drilling discharges to the marine environment, and air emissions, are well established. These approaches form a basis for the ERA of new products and processes developed at the IOR Centre.

Several products and processes have been developed at the IOR Centre to improve the oil recovery from oil and gas reservoirs. Hence, it is necessary to shortlist products and processes for conducting ERA in this

thesis. To this end, seven tracer compounds developed for quantifying residual oil saturation and a process of polymer flooding to increase oil recovery are shortlisted in this thesis. These tracers and polymers are typically injected into an oil reservoir. These injected chemicals are back-produced with the PW, which is typically discharged into the sea, posing an environmental risk to aquatic species of organisms. The research scope is thus narrowed down to assessing the environmental risk of PW discharges into the sea. However, the suitability of existing approaches for assessing the environmental risk of drilling discharges and a new approach for the ERA of air emissions are included in the discussion when answering the first research question.

While addressing the first research question, it became clear that several knowledge gaps exist concerning the ERA of tracers and the polymer flooding process. The second research question is formulated to fill the identified knowledge gaps.

- Research question 2: How can the environmental impact and risk of tracer compounds and a polymer flooding process be assessed?

The research approach used for ERA of the tracers and polymer flooding process can be explained for each of the following three sub-topics:

- ERA of tracers: Tracers are used for quantifying the residual oil saturation in an oil reservoir. The approach used to assess the environmental risk of tracer compounds in the thesis is based on laboratory studies that generate key ecotoxicological data needed for ERA. These ecotoxicological data are then used in a simulation tool to assess the exposure and effects of discharging tracer compounds into the sea.
- Fate of synthetic polymers in the marine environment: Synthetic polymers are injected into an oil reservoir in a process called polymer flooding to increase the oil recovery

from the reservoir. These polymers show large resistance to microbial degradation, until the molecular weight is reduced to around 3 kilodaltons (El-Mamouni et al., 2002). Hence, there are environmental concerns about discharging these polymers into the sea. At the IOR Centre, photocatalytic depolymerization rates for several different synthetic polymers are measured as a part of another project. Using these depolymerization rates, a novel method is proposed to estimate the residual lifetime of synthetic polymers in the marine environment.

- Exposure and effects of synthetic polymers: Aquatic species may be exposed to synthetic polymers if these polymers are discharged into the sea. Under this topic, existing ecotoxicological data (Hansen et al., 2019; Farkas et al., 2020) are used in a simulation tool to characterize the environmental risk of discharging these polymers on the NCS. Furthermore, polymer build-up is possible, as synthetic polymers show resistance to microbial degradation. Hence, the possibility of an increase in concentrations due to polymer build-up on the NCS is evaluated simulating repeated discharges from multiple fields over time.

The first and second research questions mainly focus on applied risk analysis, partly by establishing and testing a methodology for conducting environmental risk analyses and partly by conducting such risk analyses as far as the currently available data allow. The topic of the third research question is chosen to address some foundational issues related to certain key concepts used in ERA. Species sensitivity distributions (SSDs) are widely used to estimate threshold concentrations, below which the risk of adverse effects is considered acceptable for the group of species in the ecosystem (Posthuma et al., 2002). This threshold concentration is

normally used in ERAs of different chemicals/stressors. The final research question reviews whether the existing literature on SSDs is consistent in defining risk and addressing uncertainties according to recently developed approaches in the risk analysis literature. Based on the review, a way of systematically dealing with uncertainties when using SSDs is proposed.

- Research question 3: How can uncertainties be addressed in a transparent manner when using SSDs in ERAs?

The answers to the three main research questions result in five research papers that are included in Part II of this thesis. Figure 1 illustrates how the five papers contribute to answering the three research questions and how the output from Paper I serves as a foundation and link to all the other papers. Although the research in each paper is presented independently, all the papers are closely related. Paper I proposes an ERA framework for EOR solutions. Papers II, III and IV use the framework from Paper I and contribute to the ERA of tracers and polymer flooding. Paper V proposes a framework to handle uncertainties in a method commonly used in ERA, inspired by the framework in Paper I.

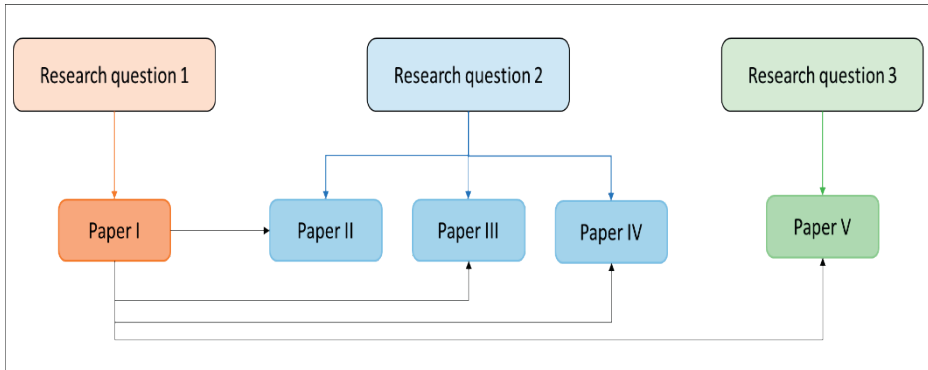


Figure 1: Outline of the research process, questions, and papers

1.4 Research classification and general aims

The research process/approach is described in Section 1.3. The present section focuses on a broad classification of the research carried out in this thesis based on different types of research described in the literature (e.g., Kothari, 2004). These types include applied vs. fundamental, descriptive vs. analytical, qualitative vs. quantitative, and conceptual vs. empirical research. The research performed in this thesis combines the research types mentioned above. Most of the research (e.g., Papers I, II, III and IV) is of an applied nature, as it is related to specific activities and contributes to solving practical issues faced by industry. Part of the research (e.g., Paper V) is fundamental, as it focuses on SSDs as a theoretical concept of relevance to a broader set of ERA applications. Moreover, the work combines quantitative (Papers II, III and IV) and qualitative (e.g., Papers I and V) research. Some of the work is descriptive (e.g., part of Paper I), as it reports on existing approaches available for ERA of EOR solutions, while most of the work (e.g., Papers II, III and IV) is analytical, as it uses existing and proposes new methods to contribute to an ERA of EOR solutions. The work is partly empirical (e.g., Paper II), as it follows the experimental approach to generate new data; and it is partly conceptual (e.g., Paper V), as it focuses on handling

uncertainties in a transparent manner, in line with recent developments in the field of risk science.

The research conducted in the thesis aims to fulfill the criteria of originality, solidity, and relevance, as highlighted by the Norwegian Research Council (NRC) (NRC, 2000). Originality refers to contributing new concepts, data and methods to the existing academic literature. The research in this thesis maintains originality by, for example, applying existing ERA methods to the new application area of tracers, by proposing a new method for fate assessment of polymers, and by improving existing concepts involved in addressing uncertainties in SSDs. The work is solid in the way that it provides a clear and concise explanation of the scientific methodology used, and the results are critically evaluated. And the research is relevant, as the results fill existing knowledge gaps in assessing the environmental risk of EOR solutions.

1.5 Thesis structure

The thesis is structured in two parts, the first of which consists of a framing, summary and discussion of the scientific work performed in the thesis, while the second part contains a set of scientific papers. The first part of the thesis begins with an introduction of the research objective and the research questions, process, and scope, in Section 1. Section 2 then serves as a theoretical foundation for the thesis, by presenting the concept of risk and the risk description, ERA methodology, and EOR solutions. The ERA methodology is explained using an example of PW discharges from EOR solutions. Section 3 summarizes, links, and discusses the findings related to the main research areas of the thesis. In Section 4, potential directions for future research are presented. Part II of this thesis contains five scientific papers resulting from research conducted in collaboration with other researchers at the IOR Centre.

2 Theoretical background

This section aims to establish a clear understanding of the key concepts and methodology used for the ERA of EOR solutions. It begins by explaining and distinguishing the concept of risk and its description, thus outlining the risk perspective adopted in the thesis. This is followed by a description of the main steps of the ERA process used in the thesis. An example of PW discharges to the marine environment is used to explain the ERA process. Finally, a brief overview is given of the EOR solutions for which the environmental risk is assessed in this thesis.

2.1 Risk

2.1.1 Risk analysis science (risk science)

Risk analysis is a knowledge field or discipline that covers relevant educational programs, journals, papers, research groups, etc. (Aven, 2016). From the risk analysis field or discipline, a risk analysis science (risk science) can be defined with reference to “the most warranted statements that this field or discipline is producing” (Aven, 2018, p. 878). In recent years, many advances have been made in the field of risk analysis, mainly focusing on the following two types of knowledge generation (Aven, 2018).

1. Type A: This type of knowledge generation focuses on solving real-world risk problems, for example, the risk associated with climate change, the design of a process plant, the use of a medical drug, the operation of an offshore installation, etc. The knowledge generation provides answers to questions like: What do the data indicate that can be worth worrying about? What might go wrong? What could be the cause and consequences if something goes wrong? What are the uncertainties? What

precautions can be taken to prevent the consequences? (Aven, 2018).

2. Type B: This type of knowledge deals with developing fundamental concepts, principles, theories, frameworks, approaches, methods, and models to understand, characterize, communicate, and manage risk (Aven, 2018).

The core of risk science is largely defined by the knowledge generation of Type B. Applying risk analysis methods to a real-world activity (Type A) contributes new insights and a better understanding of how to conduct risk assessment methods in practice (Aven, 2016). The first two research questions in this thesis focus on the knowledge generation of Type A, while the third question focuses on Type B knowledge generation, albeit in the context of environmental risk and not in a fully generic manner.

2.1.2 The risk concept and its description

Many definitions of risk are available in the literature (e.g., Aven and Renn, 2009; Aven et al., 2011; Haimes, 2009). A traditional way of defining risk is by a duplet of consequences (C) and associated probabilities (P), which schematically can be written as $\text{risk} = (C, P)$. However, this definition has been challenged (e.g., Aven and Renn, 2009; Aven, 2016). For example, it does not distinguish between the consequences specified by the risk analyst(s) and the actually occurring consequences, where surprises may occur if the former does not cover the latter; and it does not reflect the background knowledge and the strength of this knowledge, e.g., the knowledge that the probabilities are based on.

The concept of risk and its description as presented and defined here is in line with the Society of Risk Analysis (SRA) glossary (SRA, 2018) and contemporary risk science literature on the concept of risk (e.g., Aven, 2012; Aven, 2016). If a future activity is considered, e.g., the

implementation of EOR solutions offshore, risk is defined in relation to the future – and thus uncertain – consequences of this activity, with respect to something that humans value. The emphasis is usually on undesirable consequences, e.g., harmful effects on aquatic species due to the release of chemicals or drilling waste into the sea. Risk as a concept, then, has two dimensions: the consequences (C) and the uncertainty (U) associated with these consequences, i.e., risk is conceptualized and defined as the duplet (C, U). Schematically, this can be written as $\text{risk} = (C, U)$. Although the role of uncertainty in defining risk has been acknowledged earlier in the risk analysis literature (e.g., Kaplan and Garrick, 1981; Kaplan, 1997), it is only more recently that uncertainty has been explicitly included and developed as a core component of risk (e.g., Aven, 2012; Aven, 2014; SRA, 2018).

A more detailed structure is sometimes introduced for the consequence component (C) of risk as conceptualized above. This component is then conceptualized as comprising risk sources (RS) that can lead to events (A) and the effects/consequences (C) of these risk sources/events. Risk can then alternatively be defined as (RS, A, C, U), which is equivalent to the (C, U) conceptualization. The concept of vulnerability can be viewed as "conditional risk," defined as $(C, U|RS/A)$, which means the consequences and associated uncertainties are conditional on the occurrence of a risk source RS or an event A. The concept of impact, as commonly used in ERA, can be understood as the effects/consequences C on a specific value, such as human health or the environment, of a given risk source RS or event A. That is, impact can be understood as the C component when conceptualizing risk as (RS, A, C, U) and vulnerability as $(C, U|RS/A)$.

The above definitions of risk and vulnerability imply a distinction between the concept of risk (vulnerability) and the description of risk (vulnerability). A risk description is obtained by specifying a set of events (A') (e.g., the release of a chemical into the ocean), a set of risk sources (RS') that could lead to these events (e.g., rupture of a storage

tank where the chemical is stored), and a set of effects/consequences (C') that may result from these events and risk sources (e.g., harmful effects on the species in the ecosystem). Uncertainties related to RS', A' and C' are then assessed and characterized by using some measure of uncertainty (Q). Probability (P) is a commonly used measure of uncertainty, but other measures also exist, such as interval probability, possibilistic measures, or qualitative measures (e.g., Flage et al., 2014).

Suppose that the same value is assigned for the probabilities in two different situations. In one case, the probability is supported by a substantial amount of relevant data, but, in another case, by effectively no relevant data. The probability values alone do not reflect this discrepancy. Hence, a probability or other measure of uncertainty without any account of the background knowledge supporting it may not give sufficient understanding of the risk picture.

The strength of the background knowledge is thus crucial. An example of a qualitative characterization scheme for the strength of knowledge (SoK) is suggested by Flage and Aven (2009). The background knowledge (K) and a judgment of its strength (SoK) become an integral part of the risk description. Specifically, background knowledge (K) is considered a main component of the risk description, along with the specified consequences (C' or (RS', A'C')) and the uncertainty measure (Q). The strength of knowledge judgment is considered part of the uncertainty measure, which may then comprise, for example, probability combined with strength of knowledge judgments related to these, which can be expressed as $Q = (P, \text{SoK})$. The risk description can then be conceptualized as (RS', A', C', Q, K) or, equivalently and more compactly, as (C', Q, K). A risk metric is here interpreted as a quantitative or qualitative measure used to express the magnitude of risk. For example, an expected value is a risk metric used to summarize the combination of consequences and associated probabilities.

Both (C',P) and (C',Q,K) can be viewed as risk descriptions. The latter is more general, as it is defined in terms of a general uncertainty measure, rather than the specific probability measure, and includes the knowledge component, which the former does not. A risk description and a risk metric are different from the concept of risk itself, and the appropriateness and the suitability of a risk description/metric can always be questioned and depend on the situation (SRA, 2018). For example, in environmental risk assessments, a common risk metric is the risk characterization ratio, which is described and discussed in Section 2.2.

The concept of risk and its description, as presented in this section, is a general formulation, depicted with examples relating the general concepts to the environmental risk context. The next section presents a typical procedure for carrying out an environmental risk assessment.

2.2 Environmental/ecological risk assessment (ERA)

Several approaches are available for how to assess and manage environmental impact and risk due to anthropogenic activities. These approaches are usually implemented in response to environmental authorities' regulatory requirements or independently by an organization. Some of these approaches include environmental impact assessment (EIA), environmental/ecological risk assessment (ERA), sustainability assessment (SA), and strategic environmental assessment (SEA) (Zhang et al., 2010). Although these approaches correlate to some extent, there is a clear distinction regarding the scope and objective of the different approaches. Of all the approaches mentioned above, the objectives of environmental risk assessment and ecological risk assessment overlap the most. Environmental risk assessment typically aims to assess the likelihood and magnitude of adverse impacts on some organisms (humans, animals, plants, or microbes) due to exposure to a stressor. A stressor can be of chemical origin (such as pesticides, pharmaceutical

products, and oil) or non-chemical origin (such as suspended particles and burial in the sediments) (Singsaas et al., 2008). Although broadly similar, ecological risk assessment typically aims to assess the likelihood and magnitude of adverse effects on organisms other than humans, due to exposure to a stressor. An ecological risk assessment additionally considers the indirect effects on the ecosystem's functioning, populations, and species groups, due to mass and energy fluxes (US-EPA, 1998). Other approaches, such as EIA and SA, mainly focus on environmental and socio-economic impacts, respectively (Sadler, 1996). This thesis uses the abbreviation ERA to represent both environmental and ecological risk assessment.

The basic methodology for conducting an ERA is prescribed by various ERA guidelines and adopted in several regulatory frameworks around the world, as well as being used in scientific applications (ECHA, 2008, 2016a, 2016b; Government of Canada, 2012; OSPAR, 2021; US-EPA, 1998). Broadly, all guidelines agree on four key phases of a basic ERA methodology, as explained below and illustrated in Figure 2.

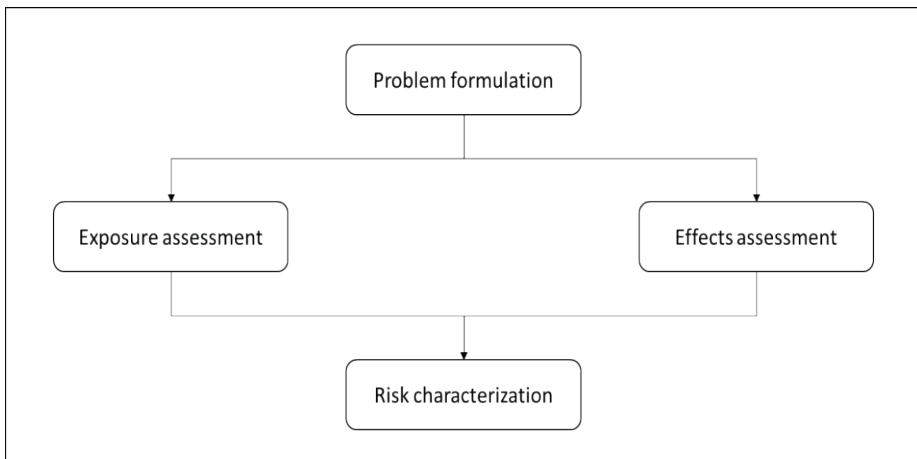


Figure 2: Key phases of the ERA process (Figure adopted from Vora et al., 2021)

2.2.1 Problem formulation

Problem formulation is an important phase of any ERA process. The scope of the problem formulation is usually based on overall site management goals and relevant environmental regulations applicable for maintaining the desired condition of the site in the context of future site use. The problem formulation phase aims to specify the risk assessment goals, collect information about hazard sources, contaminants, and stressors of concern, and lay down the methodology to characterize exposure and effects for an explicitly stated problem (Government of Canada, 2012; US-EPA, 1998). Environmental impacts from EOR solutions are expected to occur in the marine environment due to operational discharges of PW and drilling waste and could potentially occur due to accidental releases of chemicals during storage, handling, or injection into the reservoir. The chemicals (tracers, polymers, etc.) used when implementing EOR solutions will be back-produced with PW, which is typically discharged into the marine environment or re-injected into the reservoir. This thesis focuses mainly on the assessment of the environmental risk due to operational discharges of PW containing chemicals that are used during the implementation of EOR solutions.

2.2.2 Exposure assessment

Exposure assessment is the process of estimating stressor exposure in terms of magnitude, space, and time in units that can be combined with an effects assessment to characterize risk. The degree to which an organism can become exposed to environmental stressors from different hazard sources is determined in an exposure assessment (US-EPA, 1998). In the context of EOR solutions, an example of a stressor is a chemical that is back-produced and discharged into the sea along with the PW. In light of Section 2.1, the discharge of PW into the sea can be conceptualized as a specified event (A') that may have specified potential effects/consequences (C') for aquatic species. An exposure assessment is typically focused on providing a prediction or estimate A*

of a quantity or set of quantities characterizing the specified exposure event A'. The so-called predicted environmental concentration (PEC) is defined and estimated in the exposure assessment (ECHA, 2016a). The PEC is the estimated concentration of a chemical in a given environmental compartment (e.g., water, soil, air, etc.). The PEC of a chemical is calculated based on its environmental fate properties such as its octanol-water coefficient (distribution of the chemical between oil and water) and degradation (both microbial and photocatalytic) (ECHA, 2016a; Oslo and Paris Commission (OSPAR) guidelines, 2020). Some other key factors affecting the PEC include the transport and dilution of chemicals in the marine environment due to ocean currents/winds, the PW discharge volume, and the chemical concentration in the PW (Johnsen et al., 2000).

2.2.3 *Effects assessment*

The effects assessment aims to characterize the adverse effects of a stressor (e.g., a chemical) on a receptor (e.g., marine organisms) under a certain exposure condition (e.g., a certain concentration of the chemical). In light of Section 2.1, the specified effects/consequences (C'), i.e., harmful effects on the aquatic species, are assessed and characterized as conditional on a specified exposure (A') to chemicals resulting from PW discharges. An effects assessment usually focuses on providing a prediction or estimate C* of a quantity or set of quantities characterizing the effects/consequences of the predicted or estimated exposure A*, i.e., focused on providing a prediction or estimate C*|A*. The predicted no-effect concentration (PNEC) is an estimated threshold concentration, below which adverse effects are likely not to occur or to occur at a level considered acceptable in a receptor during short- or long-term exposure to a stressor. Several methods are available to estimate the PNEC of chemical compounds. The adverse effects of stressors on a receptor are typically measured in the laboratory by conducting acute and chronic toxicity tests. The European Chemical Agency (ECHA) and the OSPAR

guidelines prescribes the need for toxicity data for species from three trophic levels (standard species: algae, crustaceans, and fish) for estimating the PNEC (ECHA, 2008; OSPAR guidelines, 2020). The PNEC is then calculated by dividing the lowest measured toxicity data by an appropriate assessment factor (AF) (ECHA, 2008). An AF is used to account for uncertainties due to extrapolation from toxicity data measured in the laboratory and to be used in the field, from short-term toxicity data in the laboratory to assess actual chronic effects in the field, etc. (Johnsen et al., 2000; ECHA, 2008).

Another method, based on SSDs, is also widely applied for calculating the PNEC of a stressor (Posthuma et al., 2002; Sorgog and Kamo, 2019). An SSD is derived by fitting a suitable statistical distribution to the toxicity data for a chemical compound (Posthuma et al., 2002). The PNEC is then calculated using the estimated hazardous concentration (HC_p) for the percentage p of species that is considered acceptable as unprotected – most often 5% (HC_5), which means that the threshold is protective of 95% of the species. This is derived from the estimated SSD and by dividing the obtained concentration by a suitable AF (see above) (Chen et al., 2018; Posthuma et al., 2002; Sorgog and Kamo, 2019). Lastly, an ecosystem modeling approach that considers interactions among the species can also be used to calculate the PNEC values (De Laender et al., 2008a, 2008b). This thesis uses a method based on toxicity data and a suitable AF (see above) to derive PNEC values of chemicals used in EOR processes (ECHA, 2008; OSPAR guidelines, 2020). In addition, the thesis discusses the SSD-based method, more specifically, the concept of an SSD in relation to risk, uncertainty, assumptions, and their bias.

2.2.4 Risk characterization

The risk characterization step combines information from the exposure and effects assessments to assess the likelihood and magnitude of adverse environmental impacts of a stressor on a receptor. Such a

characterization of risk is in agreement with a risk (description) definition as the combination of consequences and probabilities, i.e., as (C, P); cf. Section 2.1.2. Although uncertainties related to data and models are mentioned in the ERA guidelines, the definition of risk presented in Section 2.1.2 has not been explicitly used in existing ERA guidelines; however, an attempt has been made in this thesis to apply the concepts described in Section 2.1.2 to a method commonly used in ERA.

Risk characterization of chemicals used during the implementation of EOR solutions is usually done based on the PEC/PNEC ratio, which is also known as the risk characterization ratio (RCR) (ECHA, 2016b; Johnsen et al., 2000). The stressor is conventionally considered to pose an unacceptable environmental risk to the aquatic species if the RCR is found to be greater than 1. When using SSDs, an RCR ratio of 1 generally corresponds to expected harmful effects on a certain percentage (p%) of the species in the ecosystem. The choice of percentage is a policy decision intended to protect (100-p)% of the community species in question. As mentioned in Section 2.2.3, a commonly used p value is 5%, thus intending to protect 95% of the species (Karman, 1994; Karman and Reerink, 1997).

Currently, several modeling tools are available to characterize the risk related to PW discharges. Some of these modeling tools are the dynamic risk and effects assessment model (DREAM), the pollution risk offshore technical evaluation system (PROTEUS), MIKE, and Delft3D (De Vries and Karman, 2009). The basic methodology adopted in these modeling tools is to calculate the fate of chemical compounds (or other stressors), based on dilution, dispersion, biodegradation, etc., and compute the PEC of the chemicals in aquatic space at each time step. The environmental risk is then characterized by comparing the PEC to the PNEC of each chemical compound present in the PW. In this thesis, the DREAM model is used to characterize the risk of chemical compounds used in EOR processes. A PEC/PNEC ratio of 1 here corresponds to environmental impact on 5% of the aquatic species in the ecosystem (Karman, 1994;

Karman and Reerink, 1997). The DREAM model calculates the PEC/PNEC ratio of individual chemicals present in the PW and corresponding fractions of species that might be affected. The combined effect of all the chemicals in the PW is calculated by adding the fractions of species affected by individual chemicals and subtracting the fraction(s) of species that are commonly affected by all chemicals together. An environmental impact factor (EIF) is then calculated by the DREAM model to characterize the combined risk of the chemicals discharged into the sea (Johnsen et al., 2000; Reed and Hetland, 2002; Reed and Rye, 2011). An EIF value of z is defined as a volume of $z \times 100,000 \text{ m}^3$ (based on 100 meters by 100 meters by 10 meters concentration grid) of water, where the combined effect from all chemicals is expected to be on 5% or more species. In addition to EIF values, the DREAM model computes the average contribution of individual chemicals to these EIF values. The average contribution from individual chemicals is calculated based on the fractions of species individually affected by a chemical at respective exposure concentration over time.

2.3 EOR solutions

The production of oil from an oil reservoir takes place in different phases described as primary, secondary, and tertiary oil recovery (Ahmed, 2010). In the primary recovery phase, the oil is produced mainly due to high reservoir pressure that naturally drives the oil up to the surface. Once the reservoir pressure drops, there is a need to implement secondary and tertiary oil recovery techniques to ensure continued oil production. For the successful implementation of secondary and tertiary oil recovery methods, it is necessary to identify pockets of oil and quantify the residual oil saturation. Chemical compounds called tracers are generally used for this purpose in the form of a single well / inter-well tracer test (Cooke, 1971; Viig et al., 2013). At the IOR Centre, a group of potential tracer compounds has been shortlisted for inter-well

tracer tests (Silva et al., 2018, 2019, 2021). The chemicals used as tracers in the field will be back-produced with PW, which is typically discharged into the marine environment.

Secondary oil recovery techniques mainly include water injection or water-alternating-gas (WAG) injection into the reservoir for maintaining the reservoir pressure. An RF of between 20% and 50% could be achieved by primary and secondary oil recovery methods (Ahmed, 2010; Hemmati-Sarapardeh et al., 2022). The remaining 50% to 80% of the oil is trapped in the reservoir, mainly due to changes in wettability and reduction in mobility. If the reservoir changes from water-wet to oil-wet, it means that oil is somehow attached to the surface of the reservoir rock and unable to leave. This may be a result of primary and secondary oil recovery methods (Ahmed, 2010). Tertiary recovery methods, also known as enhanced oil recovery methods, are used to recover the trapped oil from the reservoir. Over the years, several enhanced oil recovery solutions have been developed that can be broadly categorized into thermal, chemical, miscible gas injection, and other emerging methods such as microbial, low salinity, and smart water EOR (Balasubramanian et al., 2018; Nwider et al., 2016). A specific EOR method or a combination of methods is selected for implementation based on reservoir characteristics, the type of oil in the reservoir, and economic considerations. This thesis focuses on the assessment of the environmental risk related to using tracers and a polymer-based chemical EOR method.

2.3.1 Chemical EOR - Polymer flooding

The main influencing mechanisms for recovering oil by chemical EOR are wettability alteration, reduction in interfacial tension, viscosity improvement, and improved sweep efficiency (Ahmadi et al., 2022). Different chemicals used for EOR purposes include polymers, alkalis, surfactants, and foam. These chemicals are injected independently in the form of polymer flooding or surfactant flooding, or they are combined

with one another in the form of alkali-surfactant-polymer (ASP) flooding or alkali-surfactant flooding. First implemented in the 1950s, polymer flooding is a mature EOR process that is being successfully used to enhance oil recovery in several different oil fields worldwide (Standnes and Skjevrak, 2014). In polymer flooding, high molecular weight synthetic polymers are used to increase the viscosity of injected water. The high viscosity of injected water helps to improve the oil sweep efficiency in the reservoir (Ahmadi et al., 2022; Nwidee et al., 2016; Thomas et al., 2012). Several types of polymers and copolymers are used for polymer flooding, the most common being hydrolyzed polyacrylamide (HPAM) (Standnes and Skjevrak, 2014; Thomas et al., 2012). Most polymer flooding projects are currently being implemented in onshore reservoirs, but there is growing interest in their application in offshore oil and gas reservoirs.

3 Research areas

The research described in this thesis was initiated as a result of a recommendation from the IOR Centre's scientific committee. The committee proposed assessing the environmental risk of new EOR solutions prior to their field implementation. Following this recommendation, as described in Section 1.2, the overall objective of the thesis is to contribute new knowledge and methods related to ERA of EOR solutions. This objective is achieved by formulating and answering the three main research questions described in Section 1.3 and repeated below.

- Research question 1: How can the environmental impact and risk of implementing EOR solutions in offshore oil and gas reservoirs be assessed?
- Research question 2: How can the environmental impact and risks of tracer compounds and a polymer flooding process be assessed?
- Research question 3: How can uncertainties be addressed in a transparent manner when using SSDs in ERAs?

The answers to these three research questions resulted in five scientific papers. A summary of these papers and the answers to the above research questions is provided in this section. Figure 3 shows how the scientific papers in the thesis relate to the research questions. The research described in Paper I through Paper IV involves knowledge generation of type A (cf. Section 2.1.1), i.e., the knowledge generated helps solve specific real-world risk problems. In contrast, the research described in Paper V is of type B knowledge generation, i.e., the knowledge generated relates to fundamental concepts and helps to better understand and assess risk.

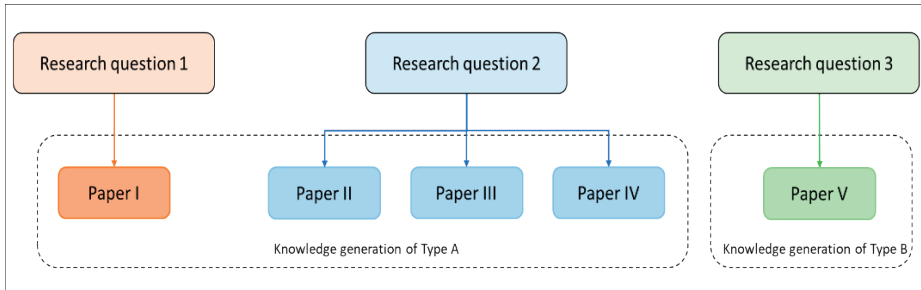


Figure 3: Overview of the research questions addressed and the resulting scientific papers

The literature review conducted to answer the first research question identifies four key phases in any ERA process. Figure 4 illustrates these phases, how they relate, and how each thesis paper contributes to them. Each of the five papers contributes to at least one phase of the ERA process, with some papers contributing to more than one phase.

Paper I proposes an ERA framework for EOR solutions. The framework outlines an approach to define the risk assessment goals in the planning phase, to assess the exposure and effects of different stressors, and to characterize environmental risk related to these stressors resulting from the implementation of EOR solutions. The paper thus contributes to all four phases of the ERA process. It presents an ERA framework for each of the three main types of operational discharges relevant to the implementation of EOR solutions, i.e., PW and drilling waste discharges into the sea and greenhouse gas (GHG) emissions to the air (Bakke et al., 2013; Norwegian Oil and Gas Association, 2018). The remaining papers of the thesis mainly focus on ERA of PW discharges, as new products and processes used during EOR processes will be discharged along with PW discharges into the sea.

Papers II, III, and IV apply the ERA framework for PW discharges presented in Paper I and contribute new data and methods for ERA of tracers and polymer flooding.

- Paper II measures the biodegradability and eco-toxicity of tracers, thereby contributing to both exposure and effects assessment. Furthermore, it estimates EIF values of tracers, which contribute to characterizing the risk of these chemicals.
- Paper III contributes to exposure assessment by proposing a novel method to estimate the residual lifetime of synthetic polymers in the marine environment.
- Paper IV uses existing eco-toxicity data to characterize the risk of synthetic polymers in the marine environment.

Finally, Paper V proposes a framework to address uncertainties related to the SSD, a commonly used tool to determine threshold concentrations (PNEC) in effect assessments. The framework in Paper V also frames the SSD in the context of an uncertainty-based risk conceptualization, i.e., when conceptualizing risk as a duplet of consequences and the uncertainty associated with these consequences, as outlined in Section 2.1.2. Furthermore, the framework proposes criteria for assessing the strength of knowledge related to SSDs used for ERA.

The key findings from each paper are summarized in the following sections. The first three sections (Sections 3.1-3.3) address each of the three research questions before the fourth section (Section 3.4) provides an overall discussion.

methods for ERA exist. Based on this review, an ERA framework for implementing EOR solutions offshore is presented in Paper I. This framework paper presents and combines existing methods and models, as well as identifying the knowledge gaps and challenges in applying existing methods for ERA of EOR solutions. The knowledge gaps are filled by generating new data and proposing novel methods to contribute to ERA of shortlisted EOR solutions (Papers II, III, and IV) in this thesis.

Paper I: An environmental risk assessment framework for enhanced oil recovery solutions from the offshore oil and gas industry

In response to the first research question, five ERA guidelines from different geographical areas worldwide are reviewed, to understand the basic approach and key elements used in an ERA process. The ERA approach described in these guidelines is broadly similar and serves as a foundation for an ERA framework for EOR solutions. In addition, the main sources of operational discharges from offshore oil production and the methods used for their ERA are reviewed. Based on the review, three ERA frameworks are proposed in Paper I, i.e., one for PW, one for drilling discharges into the sea, and one for GHG emissions to air.

PW discharges are routine operational discharges from offshore oil and gas activities. Using new chemicals as a part of EOR solutions will lead to their back-production along with PW, which is typically discharged into the marine environment. The chemicals discharged along with the PW into the sea are environmental stressors that pose an environmental risk to the ecosystem. Figure 5 shows the framework presented in Paper I to assess the environmental risk of PW discharges into the sea. The environmental stressor in the PW discharges is the chemical (e.g., tracers, polymers, etc.) that is injected during the implementation of the EOR processes. The framework contains important elements needed for the ERA, including methods to assess the exposure and effects of discharging chemicals into the sea. In the exposure assessment, the concentration of the chemical(s) is estimated (PEC) based on different

fate and transport processes, such as biodegradation, octanol-water coefficient, ocean currents, and winds. The effects assessment focuses on estimating the threshold concentration (PNEC) of chemicals, below which unacceptable effects on the group of aquatic species will most likely not occur. The risk characterization phase involves combining information from exposure and effects assessment in the form of the PEC/PNEC ratio, also known as the RCR, to assess the environmental risk of discharging a particular chemical into the sea (ECHA, 2016b). Similar ERA frameworks for drilling discharges and air emissions are also presented in Paper I and briefly summarized below; however, the application of these frameworks is not prioritized in this thesis.

Implementing EOR solutions offshore may require the drilling of new wells to inject water to maintain reservoir pressure and/or polymer/other chemicals to improve oil recovery. Drilling new wells generates drilling waste, which is typically discharged into the sea. The drilling waste discharges pose environmental risk in two compartments: the water column and the sediments. A total of six types of stressors can be considered in an ERA of drilling discharges: two in the water column (toxicity of chemicals and suspended particles) and four in the sediments (toxicity of chemicals, oxygen depletion, change in grain size of sediments, and burial) (Smit et al, 2006; Singsaas et al., 2008). Among these, oxygen depletion, change in grain size and burial are non-chemical stressors. A detailed framework to assess the environmental risk of discharging drilling waste into the sea is presented in Paper I.

The production of low-salinity water/injection of polymers on the offshore platform may increase energy requirements. GHG emissions into the air may increase if fossil fuels are used to meet this increase in energy requirements. Paper I suggests using a methodology based on a greenhouse gas protocol to quantify GHG emissions due to increased energy requirements (Gillenwater, 2005). The main challenge in an ERA of GHG emissions is to assess the indirect effects of GHG emissions into the air. For instance, an increase in GHG emissions is expected to cause

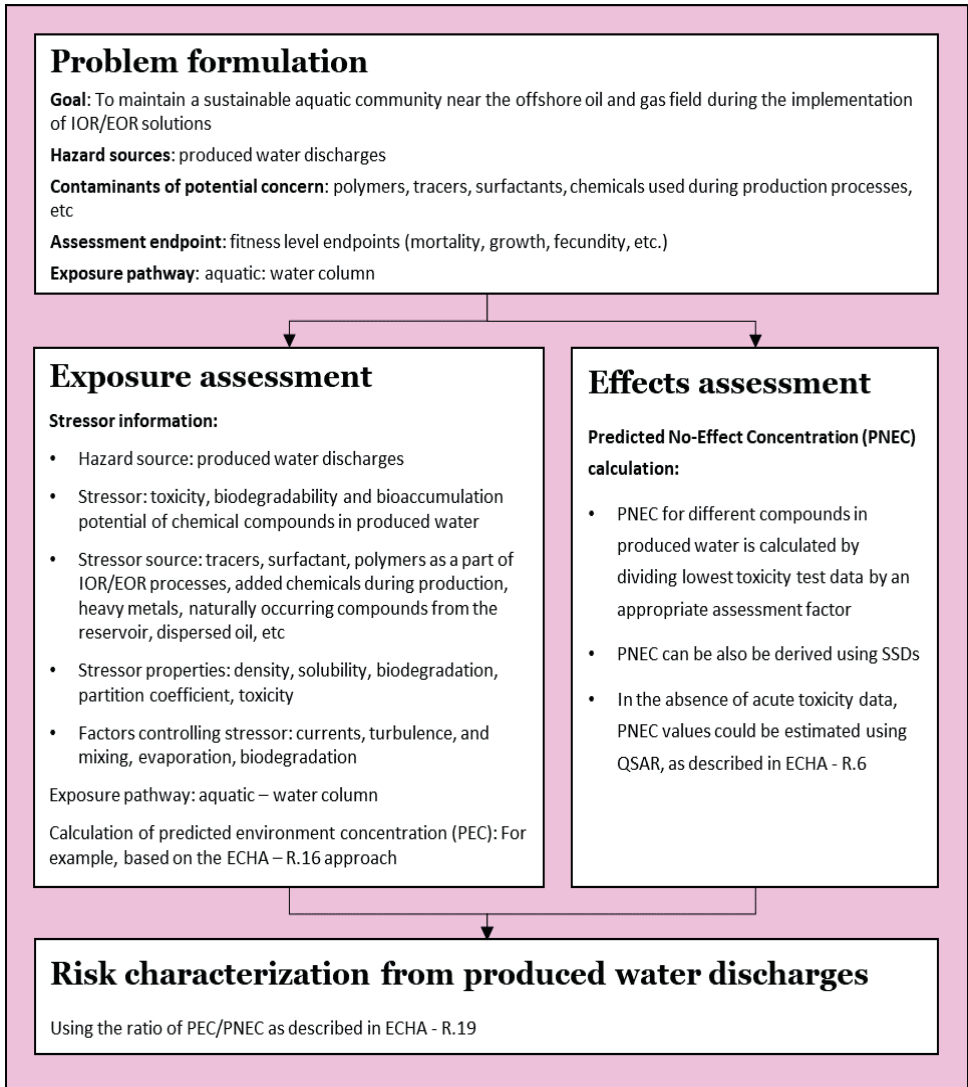


Figure 5: Framework for an ERA of produced water discharges from EOR solutions (Figure adopted from Vora et al., 2021)

several indirect impacts, such as acidification in the ocean, storms and floods, and loss of agricultural productivity (Interagency Working Group, 2010). A metric called the social cost of carbon (SCC) estimates economic damage associated with indirect adverse effects of increased GHG emissions (Interagency Working Group, 2010). Some of the effects

included in estimating the SCC are net change in agricultural productivity, ocean acidification, and coastal destruction. The total GHG emissions to air may be combined with the SCC to assess the risk of increased GHG emissions in terms of SCC. A detailed framework explaining the method for ERA of GHG emissions is presented in Paper I.

The ERA frameworks proposed in Paper I serve as a foundation for the research done in Papers II, III, and IV and to some extent in Paper V. The suggested framework can also be adapted to assess environmental risk from other anthropogenic activities such as shipping, aquaculture, dredging and dumping activities, shipwrecks, and seabed mining. To use the ERA framework in this thesis, information about all relevant stressors resulting from a selected anthropogenic activity and the techniques to determine their PEC and PNEC must be available. This availability is discussed more specifically in relation to research questions 2 and 3 in the subsequent papers (Papers II-V).

3.2 ERA of tracers and polymer flooding

Research question 2: How can the environmental impact and risk of tracer compounds and a polymer flooding process be assessed?

The answer to the second research question involves using existing data and methods, generating new data from laboratory studies, and developing new methods for ERA of tracers and polymer flooding. Paper I forms a basis for answering the second research question, by specifying methods and models for ERA of EOR solutions. The research conducted in response to the second research question resulted in three scientific papers:

1. Paper II: Environmental risk assessment of inter-well partitioning tracer compounds shortlisted for the offshore oil and gas industry

2. Paper III: Modeling the fate and transport of synthetic enhanced oil recovery polymers in the marine environment
3. Paper IV: Exposure and effects of synthetic enhanced oil recovery polymers on the Norwegian Continental Shelf

Paper II: Environmental risk assessment of inter-well partitioning tracer compounds shortlisted for the offshore oil and gas industry

Cooke (1971) introduced the use of oil-water partitioning tracers in single-well chemical tracer tests (SWCTTs) or partitioning inter-well tracer tests (PITTs) to quantify residual oil saturation (Cooke, 1971; Viig et al., 2013). Quantifying residual oil saturation is important for successfully implementing IOR/EOR solutions (Sanni et al., 2018). At the IOR Centre, in PITTs, seven chemicals have been proposed for potential use as oil-water partitioning tracers (Silva et al., 2018, 2019, 2020, 2021). Using these tracer compounds in offshore oil fields results in their operational discharges (e.g., with PW) into the marine environment. Once released into the sea, marine organisms may become exposed to the tracers. Accordingly, these pose an environmental risk to the ecosystem (Beyer et al., 2020; Sanni et al., 2017).

Important parameters for assessing the environmental risk of any chemical compound are the biodegradability, octanol-water coefficient, and toxicity of the compound (OSPAR, 2020). Currently, data on the biodegradability and eco-toxicity of the tracers developed at the IOR Centre are lacking. In the research reported in Paper II, laboratory experiments were conducted to measure the biodegradability and eco-toxicity of seven tracer compounds. Table 1 summarizes the resulting biodegradability and eco-toxicity data of seven tracer compounds obtained from the laboratory studies. These eco-toxicological data are then used in the DREAM model to estimate and compare the EIF values of the seven tracer compounds. The EIF value estimates the magnitude

of consequences for a given exposure and thus indicates the environmental risk associated with discharging chemicals into the sea.

Table 1: Summary of biodegradability and toxicity results for the tracers tested. Numbers in brackets indicate 95% confidence intervals (min-max) (Table adopted from Vora et al., 2022)

Tracer tested	% Biodegradation in 28 days	Eco-toxicity studies	
		RTgill-W1 (48-hour EC50 (mg/L))	<i>Skeletonema costatum</i> (48-hour EC50 (mg/L))
2, 3-Dimethyl pyrazine	22	1743 (1506-1979)	1106 (1015-1196)
2, 6-Dimethyl pyrazine	49	756 (678-832)	754 (655-853)
4-Chlorobenzyl alcohol	25	43 (38-48)	71 (64-79)
2, 6-Dichlorobenzyl alcohol	32	50 (42-58)	77 (65-90)
4-Methoxybenzyl alcohol	100	734 (624-844)	317 (292-341)
3, 4-Dimethoxybenzyl alcohol	45	1940 (1724-2156)	540 (480-600)
Pyridine	91	1883 (1647-2119)	347 (314-380)

In Paper II, a hypothetical case of using tracer compounds in the Brage field on the NCS is assumed. Discharge of PW containing tracer/other production chemicals back-produced from the Brage field is simulated using the DREAM model, and the contribution to the EIF values from each tracer is estimated at different discharge concentrations. Table 2 and Figure 6 show the variation in contribution to EIF values from the seven tracer compounds at different discharge concentrations. As tracers are generally used in low quantities for offshore applications, the simulations in this study, which are based on the expected back-produced concentrations (a few micrograms/liter), do not show a contribution to the EIF values above the (low) cut-off values calculated and reported by the DREAM model. To quantify residual oil saturation, two tracers

varying in their octanol-water coefficient values are usually selected in a single application (Silva et al., 2018, 2019; Viig et al., 2013). Simulations at higher concentrations were used to rank seven tracer compounds, based on their contribution to EIF values (Table 2). The ranking of the seven tracers in terms of their EIF values may support the identification of which will have the lowest environmental impact.

Table 2: Summary of contributions to Environmental Impact Factor (EIF) from all tracers at different concentrations (Table adopted from Vora et al., 2022)

Tracer	Contribution to EIF at different concentrations in mg/L					Ranking tracers from low to high contribution to EIF
	0.003	0.03	0.3	3	30	
2, 3-Dimethyl pyrazine	0	0	0	0.021	0.24	1
2, 6-Dimethyl pyrazine	0	0	0.003	0.033	0.46	2
3, 4-Dimethoxybenzyl alcohol	0	0	0.003	0.049	0.69	3
4-Methoxybenzyl alcohol	0	0	0.003	0.054	0.74	4
Pyridine	0	0	0.003	0.072	0.98	5
2, 6-Dichlorobenzyl alcohol	0	0.003	0.055	0.766	9.1	6
4-Chlorobenzyl alcohol	0	0.003	0.068	0.915	11	7

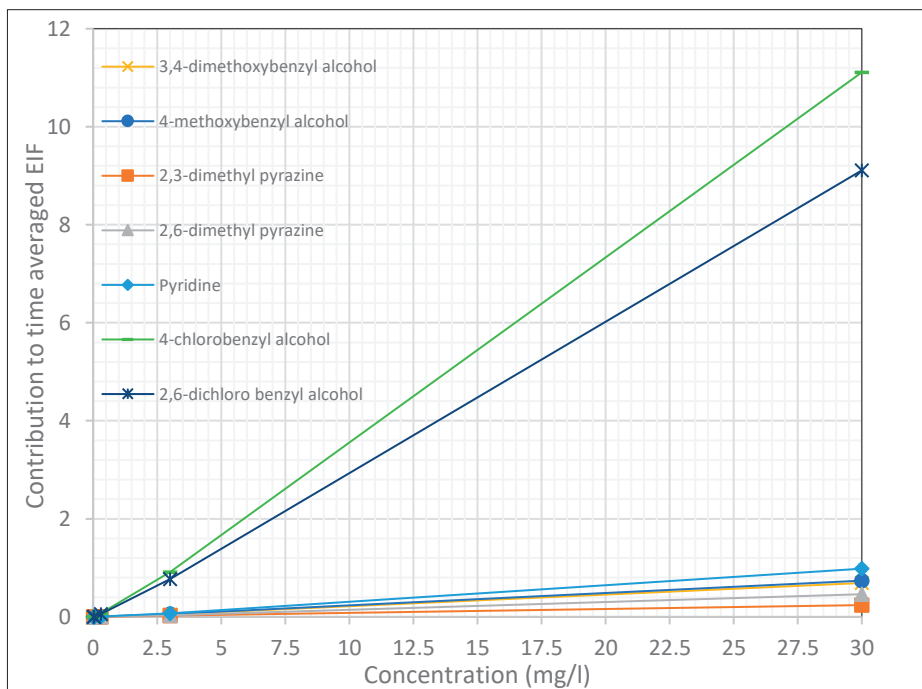


Figure 6: Contribution to time-averaged EIF from all tracers at different concentrations (Figure adopted from Vora et al., 2022)

Uncertainty about the applicability of standard testing methods of biodegradability to the new group of tracers had been expressed (Bjørnstad, IFE, pers. comm.). In Paper II, standard methods were used to measure the biodegradability and eco-toxicity of seven tracer compounds. Paper II's main contribution is the knowledge that standard testing methods are applicable and could be used in the future for measuring eco-toxicological parameters of tracer compounds of similar kinds to those tested in this study. Furthermore, the eco-toxicological data measured and reported in Paper II can be used in future ERAs of using these compounds offshore.

Paper III: Modeling the fate and transport of synthetic enhanced oil recovery polymers in the marine environment

Synthetic EOR polymers are widely used for increasing oil recovery from oil reservoirs through the process of polymer flooding (Standnes and Skjevraak, 2014). Currently, most polymer flooding projects are implemented in onshore oil reservoirs, with increasing interest in its application in offshore oil and gas reservoirs. Injected polymers are usually back-produced with the PW, which, for offshore applications, is usually discharged into the sea. These synthetic polymers show resistance to microbial degradation, unless the molecular weight is reduced to less than 3 kilodaltons (Guezennec et al., 2015). Chemicals with less than 20% microbial degradation over 28 days are categorized as red chemicals and are usually not allowed to be discharged on the NCS (Norwegian Oil and Gas Association, 2018). The main motivation for Paper III is to improve the understanding of the residual lifetime of polymers in the sea. Residual lifetime can be defined as the time needed for the discharged polymer to reach a molecular weight below which it becomes biodegradable in the marine environment (Opsahl et al., 2023).

The primary cause of polymer depolymerization is expected to be reactive oxygen species (ROS) of both biological and photocatalytic origin (Opsahl et al., 2023; Nomi et al., 2015; Ramsden and McKay, 1986; Vinu and Madras, 2008). Another project at the IOR Centre focuses on measuring photocatalytic depolymerization rates for a wide range of synthetic polymers. Using these depolymerization rates, in Paper III, a novel method is proposed to estimate the residual lifetime of synthetic polymers in the marine environment. The proposed method uses the DREAM model to estimate the concentration distribution of polymers in the sea over a long-term horizon. Simultaneously, the concentration distribution is linked with the depolymerization rate equation in an integrated way, to estimate the residual lifetime of synthetic polymers. The applicability of the method is demonstrated by estimating the residual lifetime of synthetic polymers discharged from

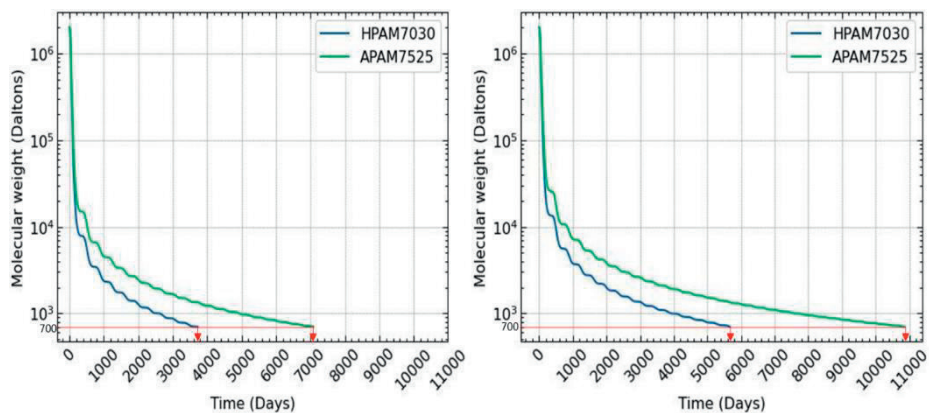


Figure 7: Estimated residual lifetime of two configurations of potential EOR polymer releases at average depths of 100 meters. Left: Residual lifetime for a single release site. Right: Residual lifetime for multiple release sites (Figure adopted from Vora et al., 2023a)

single and multiple oil fields on the NCS. Figure 7 shows the residual lifetime of two common configurations of synthetic polymers released from single and multiple release sites on the NCS. It shows that the polymer configuration HPAM7030 released from a single oil field will need 3727 days to reach a weight average molecular weight of 0.7 kilodaltons from an assumed weight average molecular weight of 2 megadaltons at the time of discharge. The molecular weight of 0.7 kilodaltons is assumed to be a biodegradability threshold. After reaching the biodegradability threshold, the polymer is expected to degrade in a comparatively shorter time than the residual time estimated in this study (Wennberg et al., 2017).

Paper III's primary contribution is a method to estimate the residual lifetime of synthetic polymers discharged from single/multiple oil fields offshore. The method is generic and can be used to estimate the residual lifetime of other polymer configuration/release scenarios as required. Hence, we believe that the proposed method and indication of the residual lifetime of polymers may be relevant to environmental authorities and the industry, in future revisions of the discharge regulations relating to polymers.

Paper IV: Exposure and effects of synthetic enhanced oil recovery polymers on the Norwegian Continental Shelf

Paper IV focuses on characterizing the environmental impact and risk of discharging synthetic polymers into the marine environment. A hypothetical case of implementing polymer flooding using anionic polyacrylamide (APAM) is assumed for the Brage field on the NCS. Environmental risk is characterized by EIF values resulting from simulating PW discharges containing back-produced APAM and other production chemicals, using the DREAM model. Two main scenarios are used in the characterization of environmental impact and risk. The first scenario estimates EIF values of APAM using short-term/near-field simulations (where the discharge point is placed within a 50*50-kilometer grid) of PW discharge into the sea. The second scenario is based on long-term/far-field simulations (where the discharge point is placed within a 1200*1800-kilometer grid), to assess polymer build-up due to the repeated discharge of polymers from multiple release sites over time.

The first scenario is based on estimating EIF values for different molecular weight fractions of APAMs, using short-term/near-field simulations. EIF values are routinely used to indicate environmental risk for discharging chemicals on the NCS (Johnsen et al., 2000). Aquatic toxicity data for different molecular weight fractions of APAM are used as a reference to determine the impact threshold (PNEC) values of APAM (Farkas et al., 2020; Hansen et al., 2019). Figure 8 shows the contribution to EIF values for two molecular weight fractions of APAMs, with and without the use of an AF. The estimated EIF values at expected discharge concentrations indicate low to moderate environmental impact from discharging APAMs on the NCS. This was the case both with and without AF. Although the EIF values suggest low/moderate environmental impact from APAMs, there is still uncertainty associated with this conclusion. Synthetic EOR polymers will undergo depolymerization after being discharged into the sea. The

toxic effects of intermediate compounds formed during the depolymerization process are unknown and thus contribute to uncertainty.

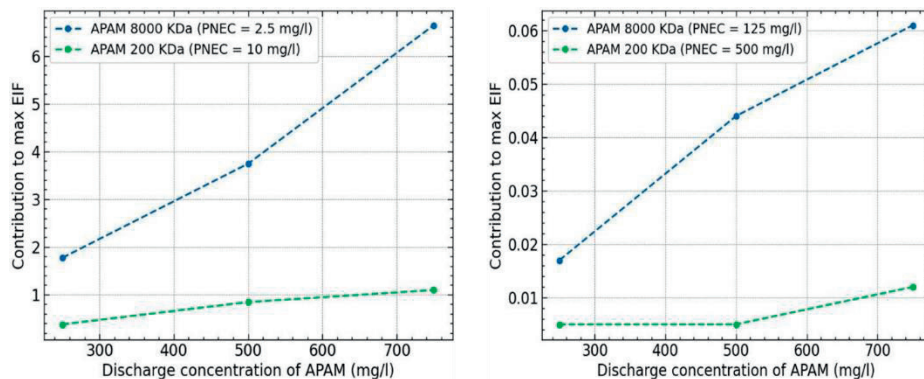


Figure 8: Contribution to maximum Environmental Impact Factor (EIF) values from 200 and 8000 kilodaltons molecular weight fraction of anionic polyacrylamides calculated at different discharge concentrations. Left: EIF values assessment factor of 50 is used. Right: EIF values with no assessment factor (Figure adopted from Vora et al., 2023b)

In the near-field simulation scenario, a traditional approach based on estimating the EIF values is used to assess the magnitude of the environmental impact of the polymers. The second scenario, based on far-field simulations, is primarily studied in addition because synthetic EOR polymers show resistance to microbial degradation. The persistent nature of the polymer may cause a build-up of polymers on the NCS if repeatedly discharged from multiple oil fields. The build-up of polymers may increase the concentration to a level that could be harmful to aquatic species. In the far-field simulations, polymers are repeatedly released annually over a 10-year period from seven arbitrarily chosen oil fields on the NCS. The highest 75 percentile concentration values during the first and tenth years of discharge are used in regression analyses against the amounts of polymer released each year (Figure 9). The 75 percentile values are used to avoid the inclusion of extreme artifactual values. The regression analyses suggest that polymers will not build up to harmful concentration levels within the simulation area at the expected mass of

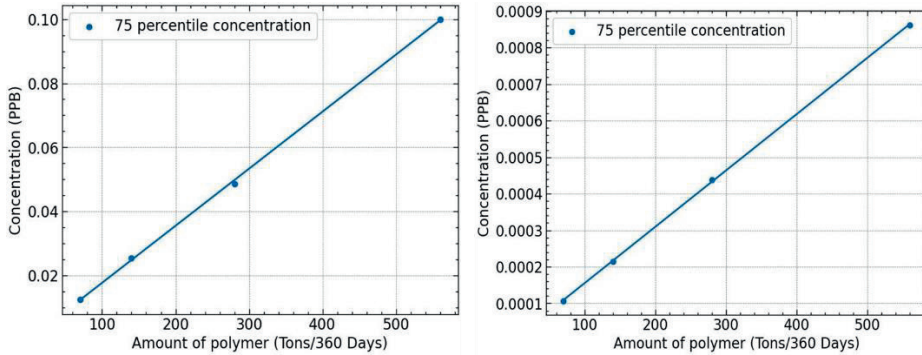


Figure 9: Linear regression results for polymer concentration against the amount of polymer discharged each year. Left: linear regression for the mass of polymer discharged each year and extracted highest values of 75 percentile concentrations during the first year of simulation. Right: similar linear regression as left but for concentration values extracted during the tenth year of simulation. Differences in the y-axes should be noted (Vora et al., 2023b)

polymers released each year. This is evident from Figure 9, as the 75 percentile concentrations calculated during the 10th year of simulation are significantly lower than the 75 percentile concentrations during the 1st year. One important reason is that ocean currents/winds constantly transport polymer mass outside the grid. There is a considerable margin of safety between the highest concentration values calculated by the model and the concentration at which harmful effects on aquatic species have been observed (in laboratory experiments).

We believe there is no reason to think there will be build-up to higher concentration levels outside the grid area, based on the assumption that polymers are dissolved in the seawater. Hence, the further fate in the ocean waters will be dominated by dilution and depolymerization. In addition to demonstrating that a non-standard use of the DREAM model can be used to simulate long-term exposures to and effects of multi-release scenarios for polymer releases to the sea, a contribution from the paper is that the regression equations can be used as a practical tool to roughly estimate indicative long-term concentrations from other amounts of polymer released each year in alternative scenarios on the NCS.

3.3 Risk-oriented framework for SSDs

Research question 3: How can uncertainties be addressed in a transparent manner when using SSDs in ERAs?

The third research question addresses the issue of uncertainties in relation to SSDs. Here, a risk-oriented framework is proposed for better understanding of risk and uncertainties while using SSD.

Paper V: Implementing a risk-oriented framework for addressing uncertainties in the species sensitivity distributions

The use of SSDs is based on fitting a statistical model to data on the sensitivity (e.g., toxicity data) of different species to a specific stressor. SSDs are typically used to determine the potentially affected fraction (PAF) of species at certain exposure concentrations and to determine threshold concentration (PNEC) values, above which unacceptable adverse effects on the group of species may occur. The PNEC values are typically used in the assessment of the environmental risk of a stressor. Although SSDs are widely used in regulatory frameworks and scientific applications around the world, some challenges exist in finding common ground on eco-toxicological, statistical, and regulatory issues. One such challenge is appropriately understanding the role of the SSD in the risk description, as well as addressing and treating uncertainties. This challenge was noticed while studying SSDs during the work on this thesis, and the main motivation for Paper V was to contribute to a better understanding of risk and uncertainties in relation to the use of SSDs for ERA. This is done by proposing a risk-oriented framework that bridges the gap between a concept (the SSD) and its (method of) use in traditional ERA and the risk conceptualization outlined in Section 2.1.2.

Paper V reviews existing literature to understand some common ways in which risk is defined and uncertainties are addressed when using SSDs. Numerous studies have made an effort to address the issue of uncertainties related to SSDs, but the emphasis has primarily been on the

stochastic aspect of uncertainty (Suter, 1990; Suter et al., 2002; Wigger et al., 2020). Although it has been acknowledged that uncertainties may also exist due to lack of knowledge, e.g., of complex ecological processes, this has not been explicitly addressed and included in the risk description. In Paper V, the conceptualization of risk and its description explained in Section 2.1.2 is applied when using SSDs.

Table 3 gives an overview of components and sub-components of the framework that can be used to describe risk and address uncertainties in a systematic manner when using SSDs. The framework explicitly distinguishes between two types of uncertainties when assessing consequences using SSDs. The first is aleatory uncertainty, i.e., due to inherent randomness, and the second is epistemic uncertainty, i.e., due to lack of knowledge. These uncertainties are assessed by using some measure of uncertainty. For example, probability is one of the commonly used measures of uncertainty, but other measures such as interval probability or qualitative measures also exist (Flage et al., 2014). The uncertainty measures are based on some background knowledge, which is understood as a combination of justified beliefs (assumptions) and evidence (Aven and Flage, 2022). The justified beliefs are interpreted as practical and theoretical assumptions underlying the concept of SSDs, as summarized by Forbes and Calow (2002), whereas evidence includes the toxicity or other effects data of any stressor available from laboratory studies. The assumptions are fixed conditions in the assessment that in reality may deviate to a greater or lesser extent (Khorsandi and Aven, 2017). Paper V includes a scheme for assessing bias in theoretical and practical assumptions underlying SSDs. The scheme is based on assessing the potential for deviation from the fixed conditions specified in the assumptions, the sensitivity of the risk metric (e.g., the HC₅) to deviations, and the strength of the knowledge supporting the deviation potential and sensitivity assessments. Using this scheme, different assumptions can be classified into specific assumption bias categories.

Table 3: Risk description components for species' sensitivity distributions (Table adopted from Vora et al., 2023c)

Main component	Sub-component	Example
Consequence specification (C')	Specified risk sources (RS')	Chemical
	Specified threat/events (A')	Release of the chemical into the ecosystem
	Specified effect/consequence metrics (C')	PAF using SSD
Uncertainty measure (Q)	Aleatory uncertainty measure	Confidence intervals
	Epistemic uncertainty measure	Traditional statistics: None (treated by making assumptions instead of characterization by an uncertainty measure) Bayesian methods: Subjective probability
Background knowledge (K)	Justified beliefs	Practical and theoretical assumptions underlying SSD
	Evidence	Data related to toxicity or other effects on the species Information, e.g., about the number of species present in the ecosystem Modelling, e.g., the use of a statistical distribution Testing, e.g., laboratory testing producing the toxicity or other effects data for estimating sensitivity of the species to stressor etc.

As described in Section 2.1.2, the background knowledge (combination of assumptions and evidence) and its strength (SoK) is an integral part of the risk description and should be highlighted when describing risk. Based on the classification of assumptions into different assumption bias categories, the framework in Paper V (Vora et al., 2023c) proposes three key points (listed below) to qualitatively characterize the strength of knowledge (e.g., data and information) supporting an SSD.

- “Keystone or other functionally important species are weighted more than other species in the SSD
- The proportion of species selected for input into the SSDs is a representative sample of the ecosystem of interest
- Interaction between the species is accounted for in the SSDs”

The SoK is considered strong if all the above points are addressed when using SSDs in an ERA. On the other hand, if none of the points is addressed, the SoK is considered weak. Cases in between can be considered as having medium SoK. The points included above are key for assessing SoK, but other criteria related to the effects of exposure to stressors at early life stages of species, number of species used in generating SSDs, type of ecological endpoint and distribution used could also be included in characterizing SoK. The inclusion of such criteria needs to be explicitly stated when defining the risk assessment’s goals.

Paper V’s main contribution is a risk-oriented framework that proposes how to address uncertainty due to lack of knowledge and includes the representation of such uncertainty in the risk description. Furthermore, the framework includes a scheme for assessing assumption bias and the set of criteria listed above to characterize SoK when using SSDs. The proposed framework is in line with the concept of risk and its description, as explained in Section 2.1.2, and should be applicable in future ERAs related to the use of SSDs in EOR solutions, as well as being of general interest in using SSDs for scientific applications.

3.4 Discussion

The previous section summarized the scientific contributions made by the papers in this thesis. This section discusses the results from the papers. Broadly, the research conducted in this thesis aims to provide new data and methods that can be used for ERA of EOR solutions. Furthermore, the findings of this thesis can be used by relevant authorities to make key policy decisions concerning the use and discharge of synthetic polymers in the marine environment.

3.4.1 Traditional ERA procedures and recent risk concept

As explained in Section 2.1, in this thesis, risk is conceptualized as a duplet of the consequences (C) of an activity and the uncertainty (U) associated with the consequences, i.e., $\text{risk} = (C, U)$. Vulnerability, on the other hand, is interpreted as “conditional risk”, meaning consequences and associated uncertainties given (conditional on) a risk source (RS) or the occurrence of an event (A), i.e., $\text{vulnerability} = (C, U | \text{RS/A})$. PW discharges essentially fit into the definition of conditional risk, where a discharge of PW in the marine environment corresponds to the event A, which is certain to occur. The framework in Paper I is based on commonly used ERA procedures that propose to describe risk in terms of PEC/PNEC ratios of any stressor. In this thesis, we used the DREAM model to estimate the consequences associated with chemical discharges along with PW in terms of EIF values. The description of risk in terms of PEC/PNEC ratios or EIF values focuses on predicting the consequences for a certain stressor, i.e., on establishing a consequence prediction C^* conditional on a specified stressor exposure event A' , i.e., on establishing $C^*|A'$. However, other components of the risk description, as outlined in Section 2.1, i.e., uncertainty measures associated with the specified consequences and the background knowledge, are not widely addressed when applying existing ERA procedures. Both PEC and PNEC values have uncertainties

associated with them, and addressing these uncertainties in full will necessitate a significant scientific effort, which is beyond the scope of this thesis. However, a part of this thesis (Paper V) is focused on addressing uncertainties and strength of knowledge while using SSDs, which is a commonly used method to determine PNEC values.

EIF values predict the consequences of chemical discharges based on PEC/PNEC ratios during and immediately after discharge and for up to approximately 30 days. A higher EIF value means that a larger volume of water has the potential for environmental impact on 5% or more species due to the combined effect of all chemicals present in the PW. The contribution to EIF values from an individual chemical reflects the potential of that chemical to cause environmental impact within the volume calculated by the EIF. The EIF methodology is mainly used to study the extent of environmental impact and for comparing potential consequences among different chemicals, as well as for screening chemicals that have a lower environmental impact than others. Furthermore, if the EIF values are zero, the potential for environmental impact on the species may be less than 5%, and risk is commonly considered acceptable in this case. It is important to note that uncertainties associated with PEC and PNEC values are not commonly assessed (e.g., using probabilities and strength of knowledge classifications) while calculating (contribution to) EIF values from individual chemicals, and EIF values are used as the main metric to express and provide information about the environmental risk of chemicals. In this thesis, the EIF values are used to provide information about the environmental risk for tracers (Paper II) and synthetic polymers (Paper IV).

3.4.2 ERA of tracers and polymer flooding

Paper II estimates EIF values for seven tracer compounds. The results suggest contributions to the EIF values from tracers lower than 0.003 at expected concentrations, as these tracers are typically used in small

quantities. Once the discharge is stopped, the tracers are rapidly diluted in the sea, making the PEC/PNEC ratio less than 1, thus not contributing to the EIF values. However, challenges arise for chemicals (e.g., synthetic polymers) that are persistent in nature (Paper IV), as it may take a relatively long time for these chemicals to degrade. The persistent nature of synthetic polymers contributes to uncertainties related to the long-term fate and effects of discharging these compounds into the marine environment. Addressing these uncertainties through experimental studies may be challenging. As a result, the concepts of strength of knowledge, comprehending underlying assumptions and their bias may be useful in understanding uncertainties and providing decision support for approval of using these chemicals offshore.

Synthetic polymers show resistance to microbial degradation in seawater (El-Mamouni et al., 2002). Hence, environmental authorities express concerns about using and discharging these polymers into the sea. At present, the microbial degradation rate (biodegradation) is usually used to assess the degradation rate of chemicals in the marine environment on the NCS (OSPAR guidelines, 2020). Although photocatalytic degradation is mentioned in the ERA guidelines, it is rarely used in practice, due to complex testing procedures (ECHA, 2016b). In this thesis, a novel method for estimating polymer residual lifetime, based on photocatalytic depolymerization rates measured at the IOR Centre, has been proposed. The results show that the polymer's residual lifetime is primarily determined by the percentage composition of different monomer groups in the polymer. In addition, the location of the polymer in the water column is an important factor, as most of the incident solar irradiation attenuates within the top layer in the water column. Other key factors, such as the hydrolysis of polymers and biological ROS, may positively influence the depolymerization process. As a result, further research into the influence of these variables on the overall depolymerization rate may aid in reducing uncertainties and in obtaining more precise estimations of polymer residual lifetime in the sea.

Only a few other studies have attempted to understand other aspects of the fate and environmental transport of synthetic polymers in the marine environment (Brakstad et al., 2020, 2021). These studies mainly investigate the interaction/attachment of synthetic polymers with/to live/dead algal material and mineral particles. The conclusion from these studies suggests that synthetic polymers are not expected to interact/attach with/to algal material/mineral particles to any large degree at typical discharge concentrations and, thus, may not undergo sedimentation in the marine environment. Hence, it appears that, after discharge, the polymers will be mainly transported with water masses due to ocean currents and slowly depolymerize in the water column, according to the depolymerization rates used to estimate the residual lifetimes in Paper III.

Another factor contributing to uncertainties related to consequences is the effects of synthetic polymers on aquatic species. Paper IV uses available toxicity data of synthetic polymers to estimate the corresponding EIF values. The estimated EIF values suggest that synthetic polymers may cause low/moderate environmental impacts on the aquatic species. However, the polymers will depolymerize in the sea, and the toxicity values of intermediate compounds formed during the depolymerization process are not known. Although some studies have found a link between polymer chain length and toxicity (Bolto and Gregory, 2007), others have been unable to find a direct link (Beim and Beim, 1994; Hall and Mirenda, 1991). As synthetic polymers are persistent in the marine environment, Paper IV focuses on simulating the discharge of polymers from multiple release sites to investigate the possibility of polymer build-up on the NCS. With the multiple release sites and amounts specified in the study, the simulation results do not indicate an expected polymer build-up. Moreover, the discharged polymers are rapidly diluted to a concentration of a few parts per billion and will over time further dilute to even lower concentrations. At these extremely low concentrations, polymers are not expected to cause

harmful effects on aquatic species. The uncertainties in this study can lie in the PEC of polymers, due to the relatively long simulation duration of 10 years, as well as the lower spatial resolution used to determine polymer concentration. Additionally, the study assumes that discharged polymer does not degrade over the duration of the simulation. However, as discussed in Paper III, a certain proportion of the discharged polymers will eventually degrade after depolymerization within the simulation time. Despite these uncertainties, the study's findings are quantitatively indicative within its specified conditions, and the overall conclusion of insignificant expected polymer build-up on the NCS and insignificant harmful impacts of polymers on aquatic species still appears to be valid.

3.4.3 Risk and uncertainties in using SSD

At present, the uncertainty associated with the consequences estimated in terms of PAF using SSDs is mainly addressed through statistical approaches, i.e., by using confidence intervals. Another source of uncertainty, i.e., due to lack of knowledge, is usually not highlighted when using SSDs. The central idea of the framework in Paper V is that the strength of the background knowledge is key in risk assessments, and it needs to be included when describing risk. The framework in Paper V proposes a set of criteria for evaluating the SoK and a scheme for assessing bias in the assumptions underlying SSDs. Using such criteria to characterize the SoK and assumption bias helps in understanding risk and addressing uncertainties in a systematic and transparent manner when using SSDs. For instance, understanding biases in assumptions can help in shortlisting assumptions that have the potential to deviate in an unfavorable direction and, thus, in implementing necessary countermeasures. The characterization of SoK as strong or weak can aid in understanding the degree of uncertainty and in narrowing down research topics to reduce uncertainties when using SSDs in ERA.

4 Future research needs

As described in Section 3, the research conducted in all the papers in this thesis is closely related. Each paper highlights potential topics of future research related to the research described in the paper. This section presents some ideas for future research that were identified during the work conducted in the thesis.

4.1 Research needs related to ERA of tracers/polymer flooding and traditional ERA procedures

The standard testing methods were found to be applicable for measuring eco-toxicological parameters and for ERA of the kind of tracer compounds studied in this thesis, but this needs to be reverified for new kinds of tracers, e.g., nano-particle-based tracers. Eco-toxicological testing of such tracers might bring methodological challenges in testing the biodegradability and toxicity by standard methods.

Polymer flooding using synthetic polymers shows a significant potential for additional oil recovery and economic benefits on the NCS (Smalley et al., 2020). However, environmental authorities face a challenge in the question of allowing the use and discharge of synthetic polymers on the NCS, as there are uncertainties related to the residual lifetime of polymers in the sea and related to the formation of intermediate compounds during depolymerization and their effects on the aquatic species. The so-called NUSAP notational scheme (Funtowicz and Ravetz, 1990; 1991) can be used to deal with the uncertainty related to the fate and effects of synthetic polymers in the sea. NUSAP stands for Numerical, Unit, Spread, Assessment and Pedigree and is typically used to aid in the process of policy making based on scientific research and underlying uncertainties. The application of NUSAP, the concept of SoK as used in this study, or other similar schemes to evaluate the available

scientific information on the fate and effects of synthetic polymers could be a topic of future research. The output of such research could aid in policy decisions regarding the use and discharge of polymers on the NCS. An example of using the NUSAP scheme in relation to the uncertainty-based risk perspective presented in Section 2.1 is available in Berner and Flage (2016).

The method to assess environmental risk in terms of PEC/PNEC ratios, also known as the RCRs, is widely used in ERA and also proposed in Paper I. Some of the commonly used methods to determine PEC and PNEC are highlighted in Section 2. Each of these methods gives an uncertain estimate of PEC and PNEC, and these uncertainties are rarely addressed while conducting ERA. Paper V proposes a framework that addresses uncertainties in PNEC values (based on using SSDs) in a systematic and transparent manner. A potential topic of future research could be to extend and apply such frameworks and the underlying concepts of SoK and assumption bias to other methods of determining PEC and PNEC. The output of such research could be useful in making the ERA process more transparent.

4.2 Research needs related to ERA of other EOR solutions

Other EOR solutions, such as low salinity/smart water flooding, ASP flooding, and CO₂ flooding, could also be relevant for increasing oil recovery (Smalley et al., 2020). Implementing ASP flooding, for example, can lead to back-production of other chemicals, such as surfactants. As a result, if ASP flooding is chosen as an EOR solution, future research should focus on the ERA of chemicals injected during the ASP flooding. In addition to injected chemicals, the naturally occurring chemicals from the reservoir are back-produced with the PW. These naturally occurring chemicals from the reservoir also pose an environmental risk to the ecosystem. Hence, reducing the volume of back-produced water and its discharge into the sea may help in lowering

the overall environmental risk. A potential topic of future research could thus be to analyze the amount of back-produced water and corresponding oil recovery potential from different EOR processes and to shortlist the EOR process that has the minimum environmental risk.

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Part II

Paper I

An environmental risk assessment framework for enhanced oil recovery solutions from offshore oil and gas industry.

Authors: Mehul Vora, Steinar Sanni & Roger Flage

Published in: *Environmental Impact Assessment Review*, 88, 106512, 2021. <https://doi.org/10.1016/j.eiar.2020.106512>



Contents lists available at ScienceDirect

Environmental Impact Assessment Review

journal homepage: www.elsevier.com/locate/eiar

An environmental risk assessment framework for enhanced oil recovery solutions from offshore oil and gas industry

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ARTICLE INFO

Keywords:

Environmental risk assessment
Enhanced oil recovery
Polymer flooding
Marine pollution
Emissions to air
Produced water, drilling discharges

ABSTRACT

Environmental risk assessments are necessary to understand the risk associated with enhanced oil recovery (EOR) solutions and to provide decision support for choosing the best technology and implementing risk-reducing measures. This study presents a review of potentially relevant environmental/ecological risk assessment (ERA) guidelines and, based on this review, proposes an initial suggestion of an ERA framework for understanding the environmental impacts from EOR solutions. We first shortlist the important elements necessary for conducting an ERA of EOR solutions from the selected guidelines. These elements are then used to build the suggested ERA framework for produced water discharges, drilling discharges and emissions to air from EOR solutions, which is the primary objective of the present study. Furthermore, the emphasis is placed on identifying the knowledge gaps that exist for conducting ERA of EOR processes. In order to link the framework with the current best environmental practices, a review of environmental policies applicable to the marine environment around the European Union (EU) was conducted. Finally, some major challenges in the application of ERA methods for novel EOR technologies, i.e. uncertainties in the ERA due to lack of data and aggregation of risk from different environmental impacts, are discussed in detail. The frameworks suggested in this study should be possible to use by relevant stakeholders to assess environmental risk from enhanced oil recovery solutions.

1. Introduction

In 2018, the International Energy Agency (IEA) presented the World Energy Outlook (WEO), which predicts an increase in energy demand of around 25% by 2040, in order to meet the requirements of an increasing population. Fossil fuels – particularly oil and gas – will continue to account for the majority of the supply to meet this increase in energy demand. “Natural gas and oil continue to meet a major share of global energy demand in 2040, even in the sustainable development scenario. Not all sources of oil and gas are equal in their environmental impact” ((International Energy Agency (IEA), 2018), p. 5). Currently, offshore oil and gas production accounts for around 30% of the world’s energy production, and this share is expected to increase in the future (International Energy Agency (IEA), 2018; Zheng et al., 2016). Novel Improved Oil Recovery (IOR)/Enhanced Oil Recovery (EOR) technologies are currently being proposed as attractive solutions for increasing oil recovery efficiency from offshore oil and gas fields. However, these IOR/EOR solutions can

have adverse environmental impacts, due to discharges to the marine environment and emissions to air.

Muggeridge et al. (Muggeridge et al., 2014) write that most oil companies are focusing on maximizing the recovery factor (RF) from currently operational fields, as it is becoming increasingly difficult to discover new oil and gas reserves. The average RF from oil fields is between 20% and 40% (Muggeridge et al., 2014). Enhanced Oil Recovery (EOR) methods involve the use of different technologies, such as water alternating gas (WAG) injection, smart water injection, and polymer flooding, to increase oil recovery from existing fields (Muggeridge et al., 2014; Torrijos et al., 2018). Improved Oil Recovery (IOR), a term used at times as equivalent to EOR, also implies improving oil recovery but, instead, by intelligent reservoir management and advanced reservoir monitoring techniques. By using a combination of IOR and EOR technologies, it is possible to increase the RF by somewhere in the range of 50% to 70% (Muggeridge et al., 2014).

Improving the RF is not only economically beneficial as it helps to

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<https://doi.org/10.1016/j.eiar.2020.106512>

Received 6 April 2020; Received in revised form 9 September 2020; Accepted 3 November 2020

Available online 3 February 2021

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maintain the production rate, but it may also be environmentally favorable when compared to setting up an oilfield in a newly discovered reserve. However, there can still be potential environmental impacts resulting from novel EOR solutions, due to produced water discharges, drilling discharges and emissions to air (Bakke et al., 2013; Sanni et al., 2017; Stephens et al., 1977; Zheng et al., 2016). Additionally, there can be environmental risk due to accidents. However, this study is mainly focused on the environmental risk related to the operational discharges from EOR processes. To avoid unwanted environmental consequences, we need to address three important questions: What are the specific environmental threats from EOR processes? Do we have a detailed ERA framework to assess environmental risk from EOR processes? Do we need new tools to assess the environmental impacts?

Let us consider an example of polymer flooding as a potential EOR process, to address the above-listed questions. Polymer flooding is usually carried out with anionic polyacrylamide (APAM) or partially hydrolyzed polyacrylamide (HPAM) (Brakstad et al., 2020). The recent study performed to assess the acute and sub-acute toxic effects on Atlantic cod from APAM polymers showed low or negligible toxic effects at concentrations lower than 150 mg/l (Hansen et al., 2019). However, the PAM polymers are persistent in the marine environment at higher molecular weights (El-Mamouni et al., 2002), and there is a lack of knowledge about the chronic toxic effects of these polymers. In order to have a solid ERA, it is important to understand the complete degradation pathway of PAM polymers and the associated toxicity of the degraded polymers. To understand this in further detail, there is a study ongoing on the depolymerization process of PAM polymers and the formation of their degradation products (Opsahl & Kommedal, 2021a,b), unpublished results). In addition, a cytotoxicity study using degraded PAM polymers on rainbow trout gill cells is being conducted (Opsahl & Kommedal, 2021c), unpublished results). Moreover, the monomer generated as a part of the degradation process is known to be toxic (Xiong et al., 2018). Despite the low or negligible acute toxic behavior of PAM polymers at a concentration of less than 150 mg/l, it is important to examine the environmental risk associated with the fate, possible accumulation over a long time and the degradation products of PAM polymers in the marine environment. Similarly, chemical compounds used as a part of an alkaline-surfactant-polymer (ASP) EOR process could also be a threat to the marine environment (Tackie-Otoo et al., 2020).

Another EOR process based on capture and injection of carbon dioxide (CO₂) offers a promising alternative for enhancing oil recovery and at the same time mitigating climate change by permanently sequestering CO₂. (Dai et al., 2014; Mac Dowell et al., 2017). Even though uncertainty in the oil prices make CO₂ – EOR less attractive, there are cases in which CO₂ – EOR could still be economically viable (Ampomah et al., 2017; Dai et al., 2016; Mac Dowell et al., 2017). A detailed study of both environmental and economic risk and benefits is therefore recommended before screening and implementing a particular EOR process for a given oil and gas reservoir.

More recently, the human induced seismicity due to anthropogenic activities has become a concern and may also pose significant environmental and economic risk. More than 100 instances of such seismic events are recorded due to conventional oil and gas operations and hydraulic fracturing (Foulger et al., 2018). Such seismic events during EOR processes may pose significant environmental and economic risk. However, the scope of current paper is to mainly consider the environmental risk from operational discharges or emissions occurring specifically related to the EOR processes or products (not related to possible accidental effects) and therefore risk due to induced seismicity is not discussed further.

To assess the environmental impacts, current ERA guidelines around the world can be an important reference point. ERA guidelines from different countries/regions present a generic ERA framework that can form a basis for conducting an ERA of EOR solutions. For EOR processes, the ERA framework from Smit et al. (2006a) (Environmental Risk

Management System (ERMS) Report No. 3) presents a framework for drilling discharges. However, a holistic ERA framework for produced water discharges, drilling discharges and emissions to air from EOR solutions for offshore application is currently lacking. In the present study, we shortlist the important elements necessary for conducting an ERA from potentially relevant ERA guidelines around the world. These elements are then used to make an initial suggestion regarding an ERA framework for produced water discharges, drilling discharges and emissions to air from offshore EOR solutions, which is the main objective of the present study. Similar studies suggesting an ERA framework for different areas of application are available in the literature, for instance a framework from Skinner et al. (Skinner et al., 2016), which presents a detailed ERA framework based on an expert elicitation process. More specific ERA frameworks exist, for example from Landquist et al. (Landquist et al., 2013), presenting an ERA framework for polluting shipwrecks; from Lamorgese and Geneletti (Lamorgese & Geneletti, 2013), providing a framework for urban planning.

To understand current best environmental practices (BEP) and tools used for assessing environmental impact, a review of environmental policies applicable to the marine environment around the European Union is carried out. The guidelines from the Oslo and Paris Commission (OSPAR) are the most comprehensive in the context of ERA of EOR solutions. The model system Dynamic Risk and Effect Assessment Model (DREAM) is proposed as one of the suitable tools for an ERA of produced water and drilling discharges (Department of Energy and Climate Change, 2014). However, the applicability of the DREAM or similar model for the chemicals used in the EOR processes could be limited. In the case of the limited applicability of currently available simulation tools, there are opportunities to develop a novel tool for assessing the environmental impact from EOR processes. Finally, challenges involved in the application of the suggested ERA frameworks for novel EOR technologies are discussed. These challenges include uncertainty assessments and joint aggregation of risk from produced water discharges, drilling discharges and emissions to air. The uncertainties are mainly due to the lack of data regarding the use of polymers on a large scale and their degradation and toxic behavior in the marine environment.

The paper is organized as follows: ERA guidelines are reviewed, and the shortlisting of important elements necessary for conducting ERA is explained in Chapter 2. In Chapter 3, the ERA framework for produced water discharges, drilling discharges and emissions to air from EOR solutions is proposed. Also, a review of environmental policies for the marine environment around the EU is presented. In Chapter 4, there is a discussion about the ERA framework, knowledge gaps in conducting ERA and the challenges involved in the ERA of novel EOR solutions. Chapter 5 highlights the main conclusions.

2. Approaches for environmental risk assessment (ERA)

2.1. Scope of review

An ERA is a process of identifying and assessing the potential adverse effects on organisms, populations or communities mainly as a result of exposure to chemical and non-chemical stressors from industrial activities (Government of Canada, 2012; US Environmental Protection Agency (US-EPA), 1998). In this study, four guidelines for assessing risks to the environment are selected and reviewed. The criteria for selecting these guidelines are language, i.e. English, representation of the different geographical areas and relevance to the EOR context. The selected guidelines are generic and could form as a basis for ERA of any anthropogenic activity. The group of countries representing these guidelines contributes to around 30% of the world's oil and gas production (United States Energy Information Administration, 2019). All documents related to the guidelines, regulations and policies are collected through online resources. The selected guidelines in the present paper are assigned an identifying letter, to simplify subsequent comparison (Table 1). The research paper from Skinner et al. (Skinner

Table 1
Overview of selected Environmental Risk Assessment guidelines for review and comparison.

Geographical region	Document reviewed	Comments	Identifying letter
United States of America (USA)	US EPA (US Environmental Protection Agency (US-EPA), 1998)	The methodology is broad in scope and includes three key phases: problem formulation, analysis and risk characterization.	A
Canada	Government of Canada (Government of Canada, 2012)	The methodology is for ecological risk assessment of contaminated sites in Canada. The framework includes four key phases: problem formulation, exposure assessment, effects assessment and risk characterization.	C
Europe	(European Chemical Agency (ECHA), 2016; European Chemical Agency (ECHA), 2008a; European Chemical Agency (ECHA), 2008b) & European Chemical Agency (ECHA), 2012 (R.6, R.10, R.16 & R.19)	The EU methodology is mainly intended for the assessment of chemicals and is focused on four key phases: hazard identification, exposure assessment, dose-response assessment and risk characterization.	E
United Kingdom (UK)	(Department of Environment, Food and Rural Affairs (DEFRA), 2011)	ERA framework in UK has four key phases: formulate problem, assess risk, appraise options, address risk.	U
Note: The article listed below is used as a reference for shortlisting important elements in the key phases of ERA.			
Not applicable	(Skinner et al., 2016)	The methodology from Skinner et al. is developed as a part of the expert elicitation process and consists of four key phases: hazard identification, exposure assessment, effects assessment, and risk characterization.	S

et al., 2016) presents a generic ERA framework based on an expert elicitation process. The important components from this framework are shortlisted and used as a reference point for comparison among different guidelines. Since definitions of environmental and ecological risk assessment overlap to a large extent, ERA is used as an abbreviation for both environmental and ecological risk assessment.

2.2. Evaluation

To investigate the key elements in the selected ERA guidelines, the four key phases of the common ERA scheme are followed (Government of Canada, 2012; Skinner et al., 2016) (Fig. 1).

- **Problem formulation:** This is the first step in any ERA process where information about goals, hazard sources, contaminants of concern, assessment endpoint and methodology for characterizing exposure and effects is collected for an explicitly stated problem.
- **Exposure Assessment:** It is a process of measuring or estimating the exposure in terms of intensity, space and time in units that can be combined with effects assessment to characterize risk.
- **Effects Assessment:** The purpose of the effect's assessment is to characterize the adverse effects by a contaminant under an exposure condition to a receptor.
- **Risk characterization:** The process of estimating the magnitude of adverse ecological impacts based on the information collected from exposure and effects assessment.

In this study, important elements in these key phases are identified and compared with respect to the level of details covered about that particular element in the different guidelines (Table 1). A three-step scale is defined for this purpose, viz. *considered in substantial details, considered in limited details and not considered*. This exercise is useful in shortlisting important elements necessary for conducting an ERA and to refer such elements in a specific guideline for further information.

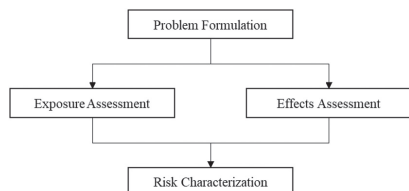


Fig. 1. Key phases in Ecological/Environmental Risk Assessment

2.3. Findings

Overall, no single guideline covers substantial details of all four phases in the ERA process. Most of the elements in the problem formulation and risk characterization are covered in substantial detail by guidelines A and C. All the guidelines have good theoretical coverage of exposure and effects assessment, and the guidance document on chemical safety assessment from the EU (E) prescribes specific equations to calculate exposure and no-effect concentration of chemical compounds in the receiving environmental media. (Table 2)

2.3.1. Problem formulation

Problem formulation is a key phase of any ERA process, and two guidelines (A and C) dominate the details covered for all shortlisted elements in the problem formulation phase. On a broad level, the ERA process is driven by overall site management goals and regulations that set the expectations for the desired condition of the ecosystem and its components, in the context of future site use. In guidelines A and C, examples are explained to assist in framing management goals for any site, in conjunction with local/national/international regulations. The baseline site investigation carries considerable weight in any ERA process, as it gives information about current contaminant sources, distribution, transport pathways and ecological condition of the site, which is explained in detail by guideline C.

The contaminants of concern (COCs) are the compounds selected for evaluation in the ERA process, due to their inherent properties of causing damage to the ecosystem. Guideline C explains key points in understanding sources and the selection of COCs in detail. The sources of COCs that could be of interest include on-site point sources (e.g., historical spills), on-site non-point sources (e.g., contaminated groundwater), underground artificial conduits (e.g., sewers, pipelines), natural pathways (e.g., fractures in geological structures) and significant off-site sources. COCs are controlled by several factors affecting their fate and transport in the environmental media. Guidelines C, E, and S cover considerable details about the processes that control the fate and transport, viz. the physical (hydrolysis, photolysis, etc.), chemical (adsorption, volatilization, etc.), and biological (biodegradation, excretion etc.) characteristics of COCs, along with properties of the receiving environmental media (pH, air pressure, soil density, etc.).

The receptors of concern (ROCs) are any non-human individual species, population, community, etc. that is potentially at risk of exposure to a COC (Government of Canada, 2012). Detailed information about ROCs, such as identification of receptor type and criteria for selection, is covered in guideline C. The conceptual model describes a graphical representation of a relationship between the contaminant sources, exposure pathways, and receptor, details about which are

Table 2
Comparisons of important elements in different ERA guidelines (the letters in this table refer to specific ERA guidelines; see Table 1).

	Important Elements of ERA	Guideline				
		A	C	E	U	S
Problem Formulation	Management goals	■	■	■	■	■
	Regulatory context	■	■	■	■	■
	Review of existing site information	■	■	■	■	■
	Contaminants of potential concern	■	■	■	■	■
	Factors controlling the stressors	■	■	■	■	■
	Receptors of concern	■	■	■	■	■
	Assessment endpoints	■	■	■	■	■
	Measurement endpoints	■	■	■	■	■
	Conceptual model	■	■	■	■	■
	Lines of evidence	■	■	■	■	■
	Data quality objectives	■	■	■	■	■
	Uncertainties	■	■	■	■	■
Exposure Assessment	Stressor information, distribution, release, etc.	■	■	■	■	■
	Exposure media information	■	■	■	■	■
	Receptor information	■	■	■	■	■
	Calculations procedure of contaminant concentration in media	■	■	■	■	■
Effects Assessment	Types of effects assessment measures	■	■	■	■	■
	Stressor - Response Analysis	■	■	■	■	■
	Linkage of measures of effect to an assessment endpoint	■	■	■	■	■
	Calculation procedure for no-effect concentration	■	■	■	■	■
Risk Characterization	Approaches for risk estimation	■	■	■	■	■
	Risk description	■	■	■	■	■
	Risk evaluation	■	■	■	■	■
Legend: Level of Detail Covered						
Considered in substantial detail		■				
Considered in limited detail		■				
Not considered		■				

explained in all guidelines. Lines of evidence consider any pairing of exposure and effect measures that provides evidence for the evaluation of a specific assessment endpoint; guideline C has explained this in detail. The three main outcomes of the problem formulation phase are as follows (US Environmental Protection Agency (US-EPA), 1998):

- Assessment endpoint reflecting management goals and regulatory considerations.
- Conceptual model explaining key relationships between stressor and assessment endpoint.
- Analysis plan to characterize exposure and effects assessment.

2.3.2. Exposure assessment

Any substance or process that can have an adverse impact on the ecosystem is termed a 'stressor' (Government of Canada, 2012). To assess the exposure of any stressor, it is important to identify the physical (density, state, etc.), chemical (solubility, toxicity, etc.) and biological (protein structure, biodegradation, etc.) properties of the stressor, which are explained in detail by guidelines A and E. Once the properties of stressors are known, the next step is to understand the characteristics of the receiving environmental media. These characteristics include certain parameters of the receiving environmental media that may affect the fate and transport of the stressor, the details about which are covered in guidelines C, E and S. The next important element is properties of the receptor, details about which are mostly covered by guidelines C and S. To estimate the concentration of the contaminant/stressor in the receiving environmental media, guideline E proposes the necessary mathematical equations. These equations can be used to calculate the concentration of the contaminant/stressor in the environmental media, once the stream containing the contaminant is discharged into the receiving media.

2.3.3. Effects assessment

For characterizing effects of stressors, approaches based on site-specific toxicity/biological studies and indirect toxicity/biological information are considered in substantial detail by guideline C. The next important element is to analyze the response of a receptor to a particular stressor; guidelines A, C and S explain this concept in detail. To create an accurate stressor-response profile, sound and explicit linkages between assessment endpoint and measures of effects are needed. These linkages are based on professional judgment or empirical or process models; details about these approaches are covered by guideline A.

Another important element in effects assessment is an approach for deriving the predicted no-effect concentration (PNEC) of any contaminant/stressor. The PNEC is defined as a threshold concentration, above which harmful effect to the species will most likely occur. Guideline E describes two main approaches to derive the PNEC. The first is based on using assessment factors to establish the no-effect concentration. Assessment factors are used to compensate for the uncertainty associated with extrapolating the toxicity data obtained from the laboratory studies to the field environment (European Chemical Agency (ECHA), 2008b). The PNEC is calculated by dividing the toxicity test data by an appropriate assessment factor. The value of assessment factors changes, depending on the toxicity test data available for a number of species and short-/long-term toxicity test data. The second approach uses a cut-off value of a species sensitivity distribution (SSD), based on chronic toxicity data on different species. The SSD method can be used when large data sets from long-term toxicity tests for different taxonomic groups are available. Guidelines A and C have also mentioned these approaches; however, guideline E prescribes the use of specific values of assessment factors, depending on the availability of acute/chronic toxicity data and corresponding environmental media.

2.3.4. Risk characterization

The risk characterization process involves the use of various approaches to characterize risk. These approaches include use of hazard

quotient, comparisons of stressor response to exposure curve, field observation, etc. Risk description includes a weight of evidence evaluation that considers each line of evidence for exposure and effect, to render a conclusion regarding the probability and magnitude of adverse ecological impacts. In risk evaluation, uncertainty in the risk estimation is evaluated. Risk evaluation also covers the significance of risk in terms of the acceptable level under regulations, stakeholders' interests, etc. Guidelines A and C explain these approaches in substantial detail.

3. A generic ERA framework for EOR solutions

The framework described here outlines the four key phases of an ERA process, as explained in the selected ERA guidelines. In each of these phases, the elements shortlisted from the comparison of ERA guidelines in the previous chapter are used to suggest the ERA framework for produced water and drilling discharges to the sea and emissions of greenhouse gases (GHG) to the air. A literature search was conducted, to identify possible stressors that may have an environmental impact, due to produced water, drilling discharges and emissions to air. These stressors are then considered in describing an ERA framework for produced water, drilling discharges and emissions to air.

All chemicals (tracers, polymers, etc.) used during the implementation of EOR solutions will be a part of produced water that is to be discharged into the marine environment. As a result, produced water discharges have the greatest potential for environmental impact from the EOR solutions. However, it is also important to consider drilling discharges in an ERA of an EOR process. During the implementation of EOR solutions, such as smart water/polymer flooding, there might be a need to drill new wells. Drilling new wells generates drilling waste that adds up to the total environmental risk of implementing EOR solutions. Furthermore, producing smart water on an oil platform, the injection of polymers and the re-injection of produced water into the reservoir increase the emissions to air. Therefore, emissions to air need to be considered in the ERA framework.

3.1. ERA of produced water discharges

To quantify the risk to the marine environment from produced water discharges, we suggest the use of the framework described in Fig. 2. The main stressor considered for produced water discharges is the toxicity of the chemical compounds used during the implementation of EOR processes. Other parameters, such as bio-degradation and the bio-accumulation potential of chemical compounds, also contribute to the risk. The chemical compounds could be tracers, polymers, surfactants etc., used as a part of the EOR process. The main compartment for exposure pathways of contaminants in the produced water discharges is the water column of the marine environment. Species present in the water column might be at risk of being affected by the toxicity of chemical compounds present in the produced water discharges.

The concentration of these chemicals, defined as predicted environmental concentration (PEC), in the marine environment can be determined using an approach explained by the ECHA, 2016. As discussed previously, the PNEC can be estimated by two methods recommended by the ECHA (European Chemical Agency (ECHA), 2008b). In a case where no toxicity data is available for certain chemical compounds, the PNEC can be estimated using a quantitative structure-activity relationship (QSAR) (European Chemical Agency (ECHA), 2008a). The ECHA, 2012 defines risk characterization by the ratio PEC/PNEC. The ratio is related to the extent of the damage specific compounds can cause to the marine environment. Environmental risk is assessed by a comparison of exposure (PEC) of contaminants in produced water discharge to the sensitivity of the marine species (PNEC) for these contaminants. The higher the ratio, the higher the chemical hazard, and a higher percentage of marine species might be at risk of being affected.

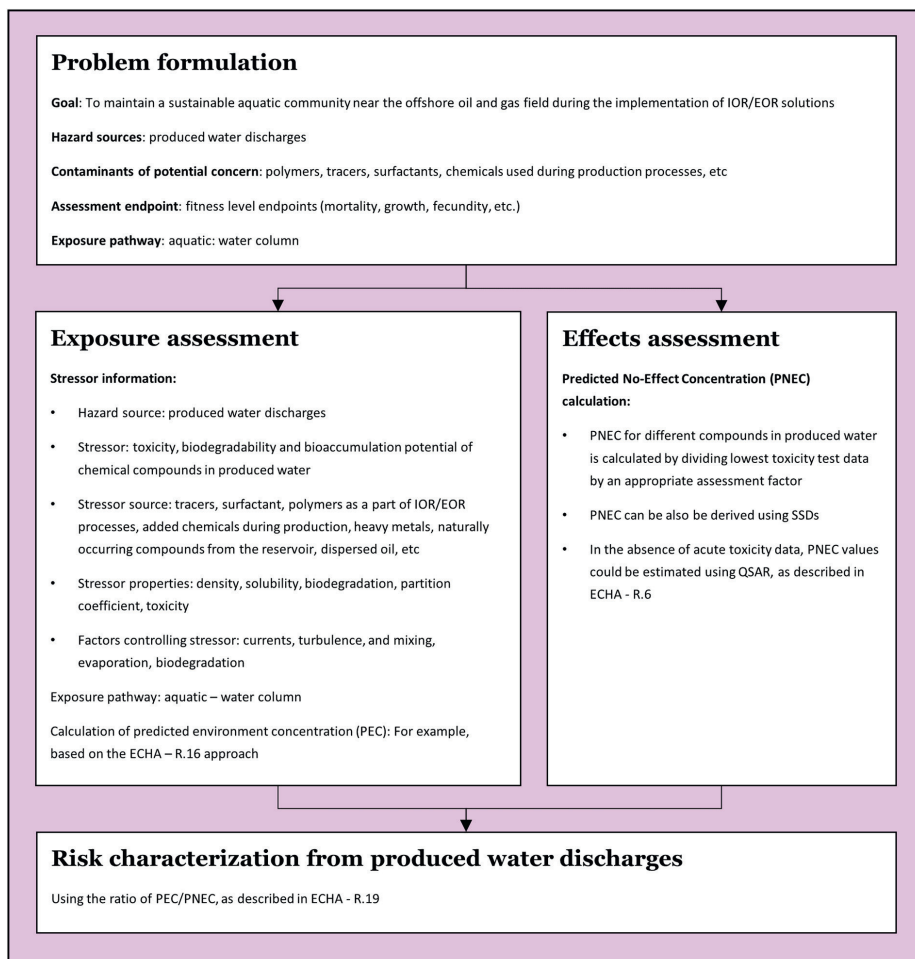


Fig. 2. Framework for ERA of produced water discharges from EOR solutions

3.2. ERA of drilling discharges

Drilling discharges may occur as a result of drilling new injection wells, as a part of operational strategies for EOR processes. The drilling discharges can have an environmental impact, through exposure in the water column, as well as on the seafloor sediments. For assessing environmental risks associated with these impacts, we have derived the framework in Figs. 3 and 4 respectively. In the water column, the concentration of toxic components and suspended matter concentration can be considered as the stressors. The toxic components can be a result of added chemicals during the drilling process, metals and naturally occurring compounds in the reservoir (Altin et al., 2008). The source of suspended particles is mainly the cuttings and the weighting agent added during the drilling process (Smit et al., 2006b; Smit et al., 2009). In sediments, toxic component concentration, oxygen depletion, change in grain size distribution and burial of organisms could be considered as the stressors (Smit et al., 2006(a), Smit et al. (Smit et al., 2006c). The

approach to characterize risk remains the same, i.e. by using the ratio of PEC and PNEC. However, for non-toxic stressors, the PEC and PNEC are redefined as predicted environmental change and predicted no-effect change, respectively (Rye et al., 2006). The PEC values for different stressors in the water column and sediments can be calculated based on the (European Chemical Agency (ECHA), 2016) (R.16) and Smith et al. (Smith et al., 2006) approach.

3.3. ERA for emissions to air

The increase in emissions to air stems from an increase in energy production needed to produce smart water, injection of polymers, reinjection of produced water, etc. during the implementation of EOR processes. Increase in energy production increases emissions to air of carbon dioxide (CO₂), methane (CH₄), non-methane volatile organic carbon (nmVOC), nitrogen-oxides (NO_x), sulfur-oxides (SO_x), etc. (Norwegian Oil and Gas Association, 2019). These gaseous compounds

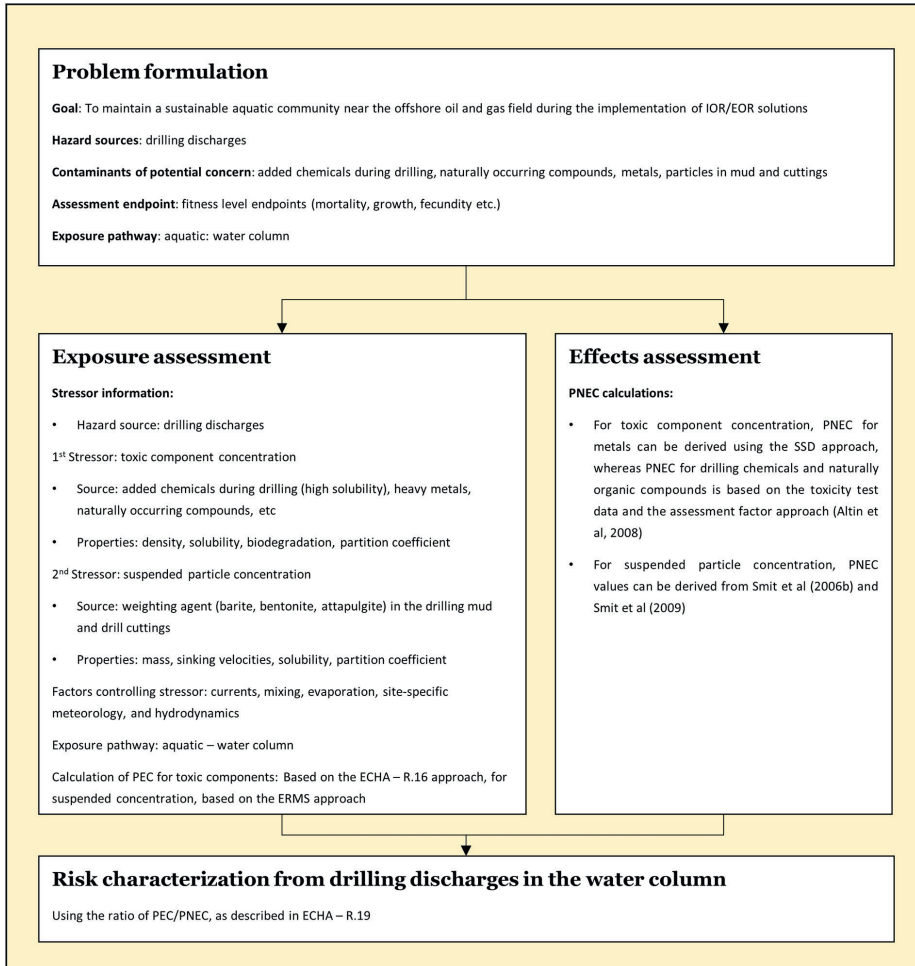


Fig. 3. Framework for ERA of drilling discharges in water column.

are emitted offshore and therefore they are not exposed to or pose a risk to the marine environment, wildlife or human populations directly. However, (GHG) emissions such as CO₂ and CH₄ increase global warming and cause several adverse effects, as a result of climate change (Interagency Working Grp. on Soc. Cost of Carbon, 2010). Therefore, in this study, mainly CO₂ and CH₄ emissions are considered, while assessing environmental risk from EOR solutions.

Increase in GHG emissions is known to have several adverse effects, like changes in agricultural productivity, ocean acidification, mass bleaching of corals, coastal destruction, etc., due to their global warming potential (Interagency Working Grp (Interagency Working Grp. on Soc. Cost of Carbon, 2010); Interagency Working Grp (Interagency Working Grp. on Soc. Cost of Greenhouse Gases, 2016)); (Marten & Newbold, 2012; Veron et al., 2009)). One major challenge in assessing environmental risk due to emissions to air is to derive PNEC values for GHG emissions. This is because there are several effects on the land and in the ocean from these emissions, far from the local emission locations, and it

involves a highly complex carbon cycle to evaluate the contribution of a particular GHG to each of these effects. A certain threshold has been established in terms of the global concentration of CO₂ (450 ppm), above which coral reefs around the world will start declining (Veron et al., 2009). However, the contribution of emissions from EOR processes to this global threshold will be mostly negligible. At present, it seems that there is no direct way to assess the environmental risk of specific consequences on the land and in the ocean from GHG emissions.

There is a methodology, called the social cost of carbon (SCC), to assess some of the impacts caused by GHG emissions on land and specifically to the human population (Interagency Working Grp (Interagency Working Grp. on Soc. Cost of Carbon, 2010); Interagency Working Grp (Interagency Working Grp. on Soc. Cost of Greenhouse Gases, 2016)). SCC is an estimation of economic damage associated with an increase in carbon emissions each year (Interagency Working Grp. on Soc. Cost of Carbon, 2010). SCC is calculated by integrated assessment models, considering net changes in agricultural productivity, human

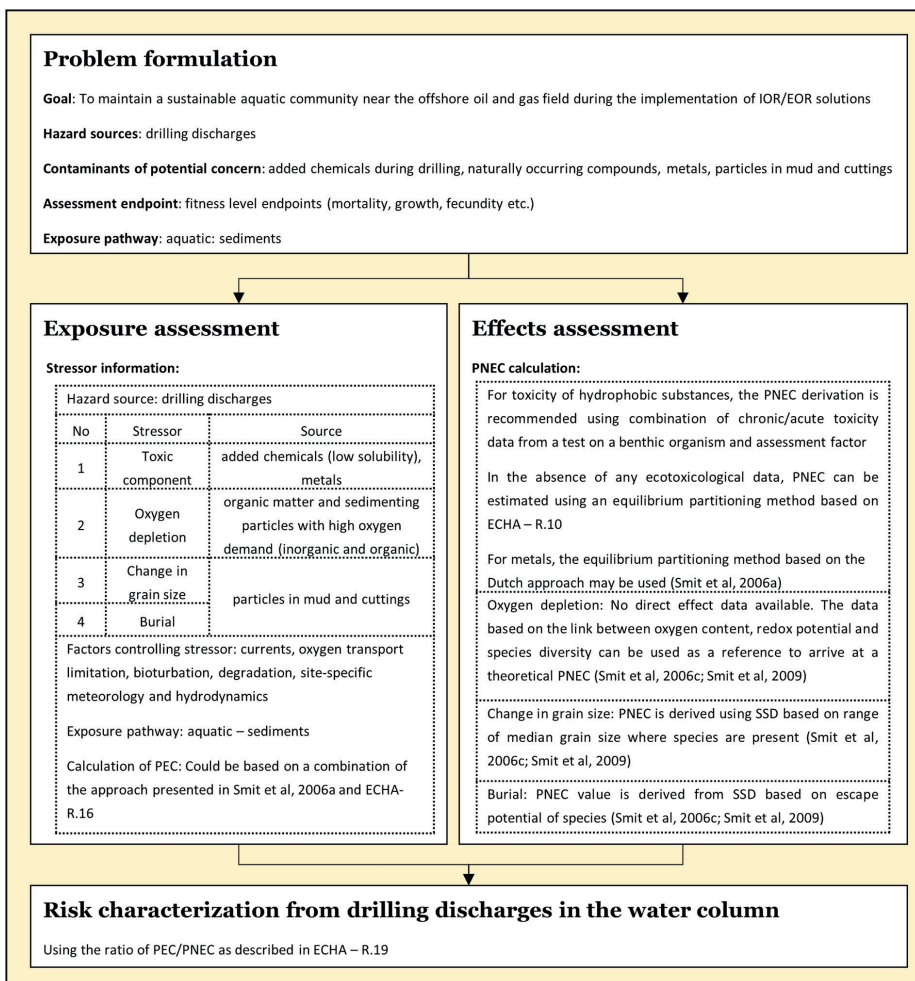


Fig. 4. Framework for ERA of drilling discharges in sediments

health, property damage from increased flood risk, etc. due to global warming (Interagency Working Grp. on Soc. Cost of Carbon, 2010). Therefore, we suggest an approach to quantify risk in terms of SCC, as described in Fig. 5. Emissions to air, mainly CO₂ and CH₄, can be quantified (PEC) using a method based on the use of an emission factor. The emission factor method uses a factor that can be multiplied with the volume and type of fuel combusted, to quantify different emissions. Guidelines available from the GHG protocol can be used to quantify these emissions (Gillenwater, 2005).

3.4. Compliance with policies for the marine environment in the European union

Environmental policies usually provide guidelines about the best environmental practices for assessing and reducing environmental impacts from anthropogenic activities. In recent years, the EU has emerged

as being in the forefront in advocating and implementing various multilateral environmental agreements (Kelemen & Kniewel, 2015; Le Cacheux & Laurent, 2015). Therefore, environmental policies applicable to the marine areas of the EU have been reviewed. Table 3 provides an overview of international conventions that are currently in practice for the protection of the marine environment around Europe (Regional Sea Convention (RSC), 2019). These conventions, along with other EU regulations, such as the Common Fisheries Policy (CFP) and Water Framework Directive (WFD), protect the marine environment from specific sources of pollution (European Union (EU) Coastal and Marine Policy, 2019). For instance, CFP regulates fisheries, while WFD regulates the flow of nutrients and chemicals into the sea (Smit et al., 2007).

Of all the conventions mentioned in Table 3, OSPAR provides the most comprehensive guidelines for assessing environmental risks and reducing pollution from offshore oil and gas activities. OSPAR is a collaboration between 15 governments and the European Union (EU), to

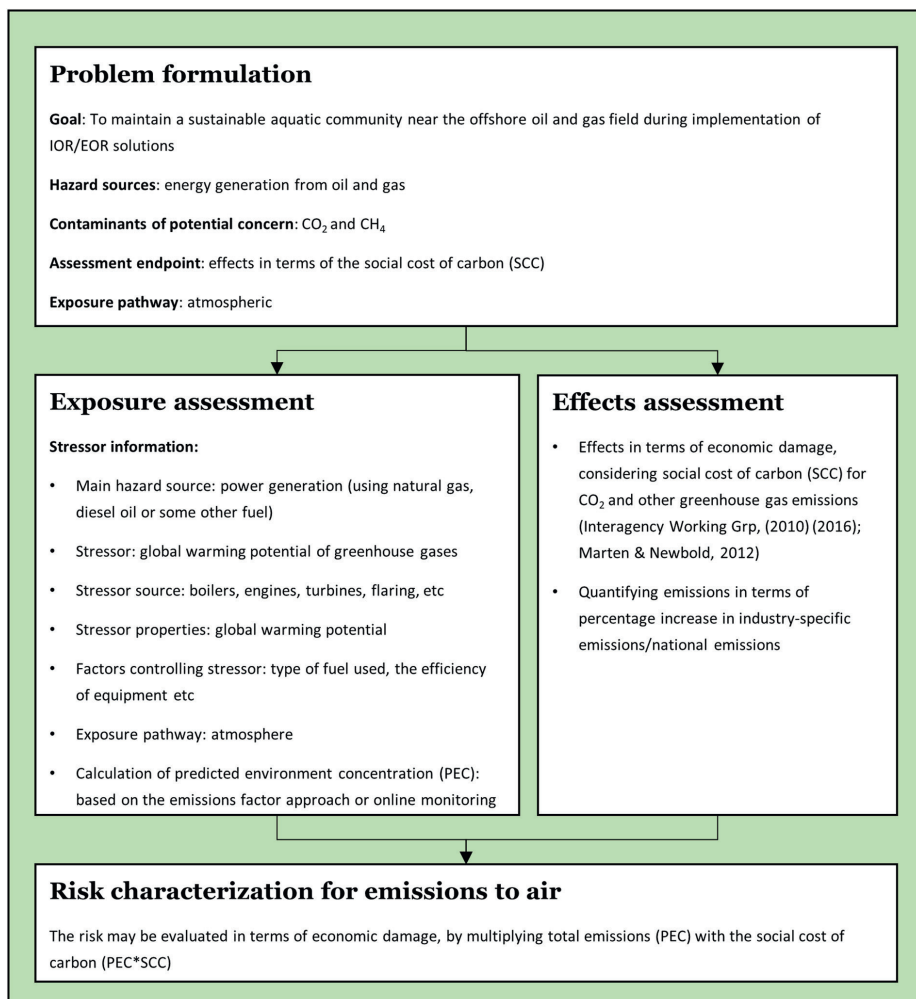


Fig. 5. Framework for ERA of emissions to air.

protect the marine environment of the North-East Atlantic. The OSPAR Commission provides guidelines for produced water management, drill cuttings' management, and the use of chemicals for offshore oil and gas operations (Oslo and Paris Commission (OSPAR), 2019).

- Produced water discharges: OSPAR lays down the procedure for implementing a Risk-Based Approach (RBA) to manage produced water discharges from offshore oil and gas installations.
- Drilling discharges: OSPAR has provided guidelines for the use of drilling fluids and the disposal of drill cuttings' residue, according to BEP.
- Use of chemicals: OSPAR has adopted a harmonized mandatory control system (HMCS) for using chemicals for offshore operations. The HMCS requires the data on parameters such as biodegradability, bioaccumulation and toxicity, for chemicals to be used offshore.

Chemicals that are above a certain threshold of these parameters are not permitted to be used in offshore operations.

Those countries that are part of the OSPAR agreement have their own program for implementing the above-mentioned guidelines from the OSPAR Commission (Department of Energy and Climate Change, 2014; de Vries & Tamis, 2014). These implementation programs recommend the use of an internationally recognized simulation tool for the ERA of oil and gas activities. In the UK's implementation of OSPAR's RBA, simulation tools such as DREAM, PROTEUS and MIKE are mentioned for conducting ERAs (Department of Energy and Climate Change, 2014). In the Dutch implementation program, DREAM and DELF3D are mentioned for conducting ERAs (de Vries & Tamis, 2014).

A comparison study by (de Vries & Karman, 2009) of all the above-mentioned simulation tools suggests the DREAM model to be the most

Table 3
Main international agreements for the protection of the marine environment in and around Europe.

Convention	Geographical area protected	Main sources of pollution addressed
HELCOM (Helsinki Commission)	Baltic Sea marine environment	agriculture, fisheries, industrial release, marine litter, shipping, etc.
OSPAR (Oslo and Paris Commission)	North-east Atlantic marine environment	hazardous substances, offshore oil and gas, offshore wind, shipping, aquaculture, radio-active substances' discharge, etc.
The Barcelona Convention	Mediterranean Sea marine environment	pollution from land-based sources, dumping protocol from ships and aircraft, pollution from ships, offshore exploration, etc.
The Bucharest Convention	Black Sea marine environment	chemical pollution from land-based sources and maritime transport, achieving sustainable management of marine living resources.

comprehensive tool for assessing environmental risk from produced water discharges. “*The DREAM model currently provides a convenient way of determining the extent of potential effects*” ((de Vries & Karman, 2009), p. 30). The stressors described in the framework for produced water and drilling discharges in this study are defined, and their effect can be estimated, in the DREAM model. To quantify the risk associated with produced water and drilling discharges, a risk-based environmental management tool, called an environmental impact factor (EIF), is incorporated within DREAM (Johnsen et al., 2000; Reed & Hetland, 2002; Smit et al., 2007; Smit et al., 2011). A detailed description of the methodology and EIF calculations for produced water discharges is available from Johnsen et al. (Johnsen et al., 2000); for drilling discharges, it is available from Smith et al. (Smith et al., 2006).

4. Discussion

A comparison of ERA guidelines shows that the information about shortlisted elements in the problem formulation and risk characterization phases are largely covered by guidelines from the US and Canada. The details about calculation procedures for assessing the exposure of contaminants (PEC) and the procedure for calculating no-effect concentration (PNEC) in effects assessments is covered by the ECHA guidelines. Based on the shortlisted elements from the guidelines, the ERA framework is suggested for produced water, drilling discharges and emissions to air. The procedure described in the framework can be used for assessing risk to the environment from the implementation of EOR solutions. Moreover, according to a recent study, the highest number of contaminants discharged in the sea comes from offshore oil and gas industry, followed by shipping, mariculture, dredging and dumping activities, offshore renewable energy devices, shipwrecks and seabed mining (Tornero & Hanke, 2016). The ERA framework suggested in this study could also form a basis and can be applicable for assessing environmental risk from other anthropogenic activities mentioned above.

Most of the polymer flooding projects around the world have shown promising results in increasing the oil recovery (Standnes & Skjevrak, 2014). However, until now, the majority of these projects were implemented onshore. Therefore, limited knowledge is available regarding the amount of back produced polymer, their treatment and if discharged their behavior in the marine environment, if these polymer floods are to be implemented offshore (Standnes & Skjevrak, 2014; Thomas et al., 2012). Some of the most commonly used polymers for EOR processes are acrylamide-based polymers that are shown to have a low degradation in the environment (Guezennec et al., 2015). These polymers exhibit low toxicity at environmentally relevant concentrations in the marine environment, however, their low degradation rate could be a challenge (Farkas et al., 2020; Hansen et al., 2019). Currently available simulation

tools such as DREAM focus on toxicity of chemicals for assessing environmental risk (Johnsen et al., 2000; Smit et al., 2007; Smit et al., 2011). Therefore, risk related to low degradation rates of polymers will not be captured by these tools. In this case, alternative methods to assess environmental risk from polymers needs to be adopted. These could include the use of ocean modelling tools such as Opendifr to track the trajectory of polymers in the marine environment (Dagestad et al., 2018). Along with this, improved knowledge and model expressions regarding de-polymerization and bio-degradation of polymers need to be developed for predicting the time for which polymers will stay in the marine environment before complete degradation.

It is important to emphasize that there are knowledge gaps regarding conducting a solid ERA of polymers. These knowledge gaps can provide opportunities for further research. As discussed previously, the behavior of polymers in the marine environment is a complex phenomenon that depends on biotic and abiotic factors contributing to the degradation. The degradation process involves the formation of different chemical compounds with varying toxicity before complete degradation. There is a study ongoing to bridge the knowledge gap of polymer degradation and the acute toxicity of degraded compounds in the marine environment ((Opsahl & Kommedal, 2021a) (a) (b) (c), unpublished results). Despite this study, the impacts from the accumulation of polymers in the marine environment over a long-time scale and the chronic toxicity of the degraded compound are currently unknown.

If these polymers are to be accepted for offshore use in the countries that are part of OSPAR commission, data about bio-accumulation, bio-degradation and aquatic toxicity needs to be submitted and approved by the relevant national competent authorities (Oslo and Paris Commission (OSPAR), 2019). For instance, in Norway, the regulation on offshore chemicals expands beyond the requirements of the OSPAR commission. Based on the eco-toxicological data, chemicals are categorized into black, red, yellow and green category, with black chemicals posing significant risk to the environment (Petroleum Safety Authority Norway, 2020). Although polymers used in the EOR process exhibit low toxicity, they will most likely fall into the red category due to their low degradation rate. If these polymers are to be approved for offshore use, a comprehensive risk assessment needs to be presented and approved by the relevant environmental authorities. Therefore, results from ERA done on the suggested framework in the current study coupled with the new method adoptions mentioned is of crucial importance. This is due to growing interest by stakeholders for implementing polymer flooding offshore, considering the significant economic potential in terms of oil recovery. Approved use of polymers offshore will likely have to be based on positive outcome of adequate risk assessment, and to achieve this it seems necessary beforehand that the process of polymer flooding is optimized to inject minimum amount of polymers in the reservoir, that the majority of the back-produced polymers are re-injected and only small amount are released in the marine environment.

For emissions of GHG, there is no standard methodology available to assess the environmental risk to the ecosystem. Although the global GHG concentration directly affects ocean acidification and coral reefs (Hooijdonk et al., 2016; Veron et al., 2009), we have been unable to find an existing methodology for estimating the PNEC for GHG emissions. The reason could be that the global concentration of CO₂ is the result of a highly complex carbon cycle, and several processes within the carbon cycle need to be modeled to arrive at conclusions regarding environmental effects. In this study, an approach, based on SCC, is described that mainly considers the impacts of GHG emissions on the human population. However, further work needs to be done to assess the risk to the ecosystem from GHG emissions.

Finally, there are challenges in conducting an ERA of EOR processes while using the framework suggested in this study. These challenges are related to dealing with uncertainties in the risk assessment and aggregation of total risk. In the section below, these challenges are elaborated in further detail.

4.1. Uncertainties in ERA

One major challenge that exists in an ERA of EOR processes is assessing and treating uncertainties at each stage of the process. The uncertainties exist in exposure assessment while estimating the PEC, and in effect assessment while estimating the PNEC. Uncertainties can lie in the estimation of the PEC for degradation products formed during the depolymerization of polymers in the marine environment. For estimation of the PNEC, the uncertainties can be due to varying toxic behavior of different compounds formed during the polymer degradation process. In order to have a concrete understanding and confidence in the ERA results, it is important to identify and address uncertainties scientifically. When uncertainties are assessed, efforts can be made to reduce the uncertainties through improved studies and knowledge generation. The ECHA has provided a guidance document on uncertainty analysis for chemical safety assessment (European Chemical Agency (ECHA), 2012) that is quite relevant in the context of the ERA of EOR processes. As per the ECHA's guidance document, the uncertainties can be categorized into three main types (European Chemical Agency (ECHA), 2012).

- **Scenario uncertainty:** Scenario uncertainty can be due to the accuracy of the described scenario. For instance, in assessing risk from produced water discharge, the assumption regarding the volume of discharge or concentration of polymers in the discharge can add to the uncertainties.
- **Model uncertainty:** This type of uncertainty can be due to the suitability of the model used for assessing environmental risk. For instance, the results from the DREAM model discussed in this paper are also subjected to uncertainty. This uncertainty can be a result of issues of accuracy in ocean currents data, wind data and algorithms used for the simulation of produced water or drilling discharge.
- **Parameter uncertainty:** Parameter uncertainty can be a result of errors in measurement, in the extrapolation of data, etc., for instance errors in the analytical methods used to estimate biodegradation, toxicity of polymers that are planned to be used as part of the EOR process.

The uncertainties discussed above can be due to lack of knowledge or inherent randomness within the system (European Chemical Agency (ECHA), 2012). For instance, as part of EOR processes, there will be new chemical compounds (polymers, tracers) that are planned for offshore use. There will be uncertainty about the behavior of new chemicals in the marine environment, as they have not been tested on a large scale in situ. Moreover, the degradation of polymers is a slow process, and the degradation products might be toxic (Al-Moqbali et al., 2018). There is limited knowledge about the toxicity of compounds that are formed at different stages during the degradation cycle of polymers. It is indeed a challenge to account for this type of uncertainty. Examples of inherent randomness include extrapolation of data from laboratory scale to field scale, variability in ocean currents, etc. The ECHA guidance document prescribes ways in which the uncertainty can be handled (European Chemical Agency (ECHA), 2012). Details about the procedure for handling uncertainties are not within the scope of this study.

4.2. Aggregation of risk

Another challenge in the ERA of EOR solutions is to aggregate the total environmental risk from produced water, drilling discharges and emissions to air. The risk from emissions to air is inversely related to the risk of produced water discharges. For instance, if produced water is re-injected or treated, the emissions to air will increase, due to the increase in power requirement for running pumps and the treatment units for produced water. If not re-injected/treated and discharged to the marine environment, the risk to the marine environment will increase. It is also difficult to compare risk from produced water and from drilling discharges, as they do not have similar units of expression. The risk from

drilling discharge on sediment is usually assessed based on the area impacted, while the risk from produced water discharge is assessed based on the volume of water impacted. Moreover, the risk from produced water discharge can be of a relatively short-term nature because of the biodegradation and dilution of chemicals in the water column. The risk from drilling discharges on sediments tends to be long-term, in most cases, as it might change the sediment structure and other properties for a longer period of time. Furthermore, the discharge of produced water and of drilling waste differ in time and space. One alternative for aggregating risk could be an evaluation of different impacts, assessing their severity and finding a way to combine them by expert judgements. However, the comparison and aggregation of risk from produced water discharges, drilling discharges and emissions to air is a complex issue and needs further work.

5. Conclusion

Currently, a comprehensive framework for the ERA of EOR solutions is lacking. In this study, the main objective is to contribute towards an initial suggestion for such a framework. The framework is suggested by describing the shortlisted elements from a comparison of a set of existing ERA guidelines. The suggested framework is set to be used for an ERA of produced water, drilling discharges and emissions to air from EOR solutions. For the ERA of emissions to air, mainly GHG, currently no standard methodology is available to determine the PNEC values for GHG emissions. We suggest a methodology, based on the social cost of carbon, that considers impacts in terms of the cost to society from emissions of GHG to the atmosphere. The risk assessment framework suggested in this study could also be considered for assessing environmental risk from other anthropogenic activities in the marine environment.

It seems like currently available simulation tools might not be able to assess environmental risk from discharge of polymers in the marine environment. In this case, new tools need to be developed to assess the environmental risk of polymers. One of the challenges in assessing the total environmental risk of EOR processes is the aggregation of environmental risk from produced water, drilling discharges and emissions to air. Another challenge is uncertainties in the assessment. To have better ERA accuracy, it is important to address and treat uncertainties. One such treatment is to reduce them through improved studies and data, which has relevance for the identification of research and development tasks to develop better EOR solutions. This is particularly relevant for our main purpose, which is to guide the research and technological development priorities for more environmentally friendly EOR processes. A second purpose following this is to support decision-making for the implementation of risk-reducing measures such as the re-injection/treatment of produced water or drilling discharges etc.

Funding

The project is funded by the Research Council of Norway, project code (grant number): 230303.

Declaration of Competing Interest

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

Acknowledgement

The authors acknowledge the Research Council of Norway and the industry partners, ConocoPhillips Skandinavia AS, Aker BP ASA, Vår Energi AS, Equinor ASA, Neptune Energy Norge AS, Lundin Norway AS, Halliburton AS, Schlumberger Norge AS, and Wintershall DEA, of The National IOR Centre of Norway for support.

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Paper II

Environmental risk assessment of inter-well partitioning tracer compounds shortlisted for the offshore oil and gas industry.

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Published in: *Energy Exploration & Exploitation*, 40(6), 1743–1759, 2022.

<https://doi.org/10.1177/01445987221097999>

Environmental risk assessment of inter-well partitioning tracer compounds shortlisted for the offshore oil and gas industry

Energy Exploration & Exploitation
2022, Vol. 40(6) 1743–1759
© The Author(s) 2022
DOI: 10.1177/01445987221097999
journals.sagepub.com/home/eea



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Abstract

Quantifying residual oil saturation (S_{OR}) in the inter-well region of oil and gas reservoirs is key for successfully implementing EOR solutions. Partitioning inter-well tracer tests (PITTs) has become a common method for quantifying S_{OR} . A new group of seven chemicals – pyridine, 2,3-dimethyl pyrazine, 2,6-dimethyl pyrazine, 4-methoxybenzyl alcohol, 3,4-dimethoxybenzyl alcohol, 4-chlorobenzyl alcohol, and 2,6-dichlorobenzyl alcohol – have been proposed as potential partitioning tracers for quantifying S_{OR} . Using these tracers can lead to their environmental release in the marine environment through produced water discharges, with currently limited knowledge on impacts in the marine ecosystem. The primary objective of the present study is to assess the environmental risk of discharging the tracer compounds in the marine environment. We investigated the fate and effect of these tracers in the marine environment. Biodegradability in seawater was measured to understand the fate of tracers in the marine environment. The acute toxicity of tracers was measured in terms of the percent cell viability of a rainbow trout gill cell line (RTgill-W1) and growth inhibition of the algae *Skeletonema costatum*. The ecotoxicological information obtained from these experiments was used in the dynamic risk and effects assessment model (DREAM) to calculate the tracers' contribution to the environmental impact factor (EIF). The results from the DREAM simulations suggest no contribution towards EIF values from any of the tracers at the expected back-produced concentrations. Results from simulations at higher concentrations suggest that both pyrazines have the lowest environmental risk, followed by 3,4-dimethoxybenzyl alcohol, 4-methoxybenzyl alcohol, and pyridine; while both chlorobenzyl alcohols show the highest environmental risk.

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Keywords

Environmental risk assessment, oil and gas industry, partitioning tracers, toxicity, biodegradability

Introduction

The implementation of enhanced oil recovery (EOR) solutions is essential for continued oil production from existing oil and gas reservoirs (Smalley et al., 2018; Wever et al., 2011). Quantifying residual oil saturation (S_{OR}) in the inter-well region of oil and gas reservoirs is key for successfully implementing EOR solutions (Sanni et al., 2018). First introduced by Cooke (1971), the use of oil-water partitioning tracers in partitioning inter-well tracer tests (PITTs) has become a common method for quantifying S_{OR} (Cooke, 1971; Tang & Harker, 1991; Viig et al., 2013).

In a recent study, seven chemical compounds from three chemical families (benzyl alcohols, pyrazines, pyridines) were shortlisted for their potential use as oil-water partitioning tracers in PITTs (Silva et al., 2018, 2019, 2021a, 2021b). The use of tracers in PITTs from offshore installations usually results in their operational (e.g. with produced water) discharges in the marine environment. If discharged into the sea, the tracer compounds may pose an environmental risk to the marine ecosystem. (Beyer et al., 2020; Sanni et al., 2017b). The three important parameters for assessing the environmental risk of any chemical compound in seawater are the octanol-water coefficient, biodegradation potential, and toxicity of the compound (Oslo and Paris Commission (OSPAR), 2012). The octanol-water coefficient values were available from the literature for all seven tracers (Silva et al., 2018, 2019, 2021a, 2021b). However, the biodegradability and toxicity data for most of the tracers considered in the current study are not available. The potential tracer compounds to be used for offshore application are shortlisted based on their ability to remain stable at high reservoir temperature, pressure, and salinity (Silva et al., 2019). Considering their stability at extreme reservoir conditions, further research to understand the biodegradation potential and toxicity become especially important from environmental risk assessment and regulatory perspectives.

The primary objective of the current study is to generate key data i.e., biodegradability and toxicity of newly shortlisted tracer compounds. Once these key data are available, the environmental risk of these compounds can be estimated for operational as well as accidental releases into the sea. The secondary objective is to compare the environmental risk of seven tracer compounds and, subsequently, rank them to give insights regarding the compounds that are more environmentally friendly than others. Although the accidental releases will presumably have a higher environmental impact due to the release of pure substance, the probability of such an event is assumingly low compared to the operational discharges of tracers along with produced water. Moreover, the ranking of these compounds in terms of environmental risk concluded from operational release would remain the same for the same amount of accidental release. Therefore, we mainly focus on estimating the environmental risk from operational discharges of the tracer compounds in the marine environment.

The environmental risk was evaluated based on the data obtained from laboratory experiments and simulation modelling of environmental fate and impact upon release in a known produced water discharge on the Norwegian Continental Shelf (NCS). A modelling tool called dynamic risk and effects assessment model (DREAM) was used to simulate the produced water discharges for assessing the environmental risk of tracers in the marine environment (Reed & Hetland, 2002;

Johnsen & Frost, 2011). The environmental risk in the DREAM model is expressed in terms of the environmental impact factor (EIF). EIF is a specified volume of water where the ratio of environmental concentration to no-effect concentration for a particular chemical is greater than 1, thereby posing an environmental risk to the ecosystem. Other chemicals used in similar offshore applications are proven to contribute to EIF values and pose unacceptable environmental risks to the marine environment (Beyer et al., 2020; Johnsen & Frost, 2011).

To assess environmental risk, the toxicity of chemicals in the produced water is usually measured according to the standard methods suggested by European Chemical Agency (ECHA) and the OSPAR Commission (ECHA, 2008b; OSPAR, 2021). In this study, to strengthen the ERA results, a combination of standard laboratory test methods and an alternative method was chosen to measure the toxicity of tracers. A standard method for measuring toxicity to algae-*Skeletonema costatum* as recommended by the OSPAR commission was chosen as one of the methods. Along with this, a recently introduced method for measuring the acute toxicity of pollutants to fish gill cell lines was included in the study (Dayeh et al., 2013). The chemicals in the produced water are at present not normally tested for toxicity using fish gill cell lines. Therefore, the combined results from these two methods will help in understanding the variation in the toxicity of tracers to two different species and thereby strengthening the basis and results for ERA.

We conducted three sets of experiments to measure the biodegradability and toxicity values of seven tracer compounds. The first set of experiments was conducted to measure the biodegradability of tracers in seawater following Organization for Economic Co-operation and Development (OECD) guidelines (OECD, 1992). These experiments were aimed to understand the fate and exposure of tracer compounds once discharged into seawater. The second set of experiments was conducted to measure the acute toxicity of tracers in a rainbow trout gill cell line (RTgill-W1) (Dayeh et al., 2013). In this study, the cellular function of RTgill-W1 cells exposed to tracers was evaluated using Alamar Blue as an indicator dye. The third set of experiments was conducted to measure the growth inhibition of the algae *Skeletonema costatum* when exposed to tracers following the guideline from ISO 10253 (ISO 10253, 2016). Finally, the ecotoxicological information obtained from these experiments was used in a numerical dispersion and environmental risk assessment model to quantify the environmental impact related to operational discharges of the tracers compounds in the marine environment (Reed & Hetland, 2002).

Materials and methods

Chemicals and reagents

In this study, seven chemicals shortlisted as potential tracers are tested for their biodegradability and acute toxicity (Table 1). The following are chemicals and reagents used in the biodegradability studies: Aniline (CAS: 62-53-3), sodium acetate (CAS: 127-09-3), and other chemicals used to make the nutrient stock solution as prescribed in OECD 306 guidelines. For cytotoxicity studies, these were as follows: Leibovitz's L-15 Medium (catalog number-11415064) supplied by ThermoFisher scientific; Fetal bovine serum (FBS) supplied by Biowest, France; Penicillin Streptomycin & Phosphate buffered saline (PBS) supplied by Life Technologies; trypsin-EDTA and hydrogen peroxide supplied by Merck-Norway; Alamar Blue (resazurin) supplied by Alfa Aeser-Germany; and Dimethyl sulfoxide (DMSO, CAS: 67-68-5) supplied by AppliChem GmbH, Germany. For algae growth inhibition experiments, the stock solution for Z8 growth medium was supplied by the Norwegian institute of water research – Norway, and CO₂ was supplied by Nippon Gases-Norway.

Table 1. List of tracers tested in this study.

Tracer tested	Chemical abstract number (CAS)	Purity	Supplier origin	Acronym used in the article
2, 3-Dimethyl pyrazine	5910-89-4	>98%	TCl, Japan	23MPRZ
2, 6-Dimethyl pyrazine	108-50-9	>98%	TCl, Japan	26MPRZ
4-Chlorobenzyl alcohol	873-76-7	99%	Alfa Aeser, Germany	4BZOH
2, 6-Dichlorobenzyl alcohol	15258-73-8	>98%	TCl, Japan	26BZOH
4-Methoxybenzyl alcohol	105-13-5	98%	Acros Organics, India	4METBZOH
3, 4-Dimethoxybenzyl alcohol	93-03-8	96%	Acros Organics, India	34METBZOH
Pyridine	110-86-1	>99%	Alfa Aeser, Germany	PYR

Biodegradability experiments

The biodegradation of tracers in seawater was measured using a closed bottle method following OECD-306 test guidelines (OECD, 1992). In a closed bottle method, a pre-determined amount of test substance is dissolved in the test medium, and the consumption of dissolved oxygen (DO) is monitored over 28 days. A total of 8 closed bottles were used for each tracer compound and DO was measured on days 0, 5, 15 and 28 (i.e. duplicates for each day). Different sets of bottles were used each day to avoid the issue of possible oxygen loss during the measurement. A set of 8 blank bottles with no test substance were included to determine the oxygen demand of seawater alone. The difference in oxygen depletion between blank and test substances is then compared with the theoretical oxygen demand (ThOD) of the test substance to determine the biodegradation potential of the test substance. The amount of test substance added in each bottle was calculated based on the theoretical oxygen demand of 50% of the oxygen available in the test medium on day zero. This was done to avoid oxygen being a limiting factor for biodegradation. Seawater was collected at an 80 m depth in Byfjorden (59.03 °N, 5.63 °E) and then aged at room temperature for 4-5 days to overcome the high uptake value of dissolved oxygen in the blank bottle over 28 days. The test medium was prepared by adding 1 milliliter (ml) of mineral nutrient stock solution per liter of seawater as prescribed in OECD-306. The experiments were carried out in 300 ml biological oxygen demand (BOD) bottles. The amount of DO in the test medium was measured using a multimeter MU 6100 L with pHenomenal® OXY-11 probe, both from VWR – Germany. The test bottles were incubated at a constant temperature of $20 \pm 2^\circ\text{C}$ in a Liebherr Lovibond-TC 445 incubator.

Toxicity experiments: Exposure of chemicals to the RTgill-W1 cell line

Cell culture and growth media. The RTgill-W1 cells (ATCC; CRL-2523), derived from rainbow trout (*Oncorhynchus mykiss*), were routinely maintained at $20 \pm 1^\circ\text{C}$ in a 75 cm² tissue culture flask in 10 ml of a Leibovitz-15 (L-15) medium, with 10% FBS and 2% penicillin streptomycin. The growth media was changed three times a week. Cells were examined under an inverted phase-contrast microscope (Olympus CKX41) for growth and confluency. Once around 90% confluency was reached (around 7-10 days) in the original flask, cells were washed with PBS and dissociated

with trypsin-EDTA for subculturing and experiments. All experiments related to the culturing of cells and exposure of chemicals to cells were performed under a laminar flow hood in a sterile environment in the bio-safety cabinet.

Cytotoxicity studies. The cytotoxicity experiments using the RTgill-W1 cell line followed procedures described in Dayeh et al., 2013. The cytotoxicity of potential tracer compounds to RTgill-W1 cells was measured using Alamar Blue dye (Dayeh et al., 2013). Alamar Blue is a commercial product derived from the dye resazurin that has low fluorescence. Alamar Blue is reduced to a product called resorufin by the enzymes of living cells. Resorufin is highly fluorescent, and the amount of resorufin produced is directly proportional to the number of living cells. Hence, measuring fluorescence makes it possible to conclude about the number of living cells. Screening experiments were conducted for all tracers to determine the potential concentration range and value of a 50% loss in cell viability (EC50). Table 2 summarizes the entire setup of experiments carried out for the cell viability of RTgill-W1. Two sets of screening studies were conducted to narrow down the final concentration ranges for four tracers: 23MPRZ, 26MPRZ, 34METBZOH, and PYR. For the remaining three tracers, final experiments were conducted after the first set of screening experiments. Three tracers – 4METBZOH, 4BZOH, and 26BZOH – showed a clear indication of concentration ranges for a 50% loss in cell viability after the first set of screening experiments. There was therefore no need for these three tracers to undergo an additional screening experiment.

$$\% \text{ Cell Viability} = \frac{\text{FSU}_{\text{cells exposed to tracers}} - \text{FSU}_{\text{exposure without cells}}}{\text{FSU}_{\text{control cells}} - \text{FSU}_{\text{control without cells}}} \times 100 \quad (1)$$

The stock solution for the other five tracers, apart from 4BZOH and 26BZOH, were prepared by directly dissolving a pure chemical in L-15 growth media. Stock solutions were then diluted with L-15 growth media to make lower concentration solutions for exposures. 4BZOH and 26BZOH were found to be poorly soluble in water and growth media; therefore, DMSO was used as a solvent carrier for these two compounds. The 96-well tissue culture plates were used to seed the cells and for exposure to tracers. RTgill-W1 cells were seeded in a 96-well plate at a density of 40,000 cells in 200 microliters (μl) of medium per well. The plates with seeded cells were incubated at 20°C for 24 h for cells to attach and form a monolayer. After 24 h, the growth media was replaced by the tracer solutions in the growth media at different concentrations (triplicate for each concentration). A 100 micromolar hydrogen peroxide solution was used as a positive control. The plate was then incubated again at 20°C for 48 h. Tracer exposures were removed after 48 h, and a 484 micromolar Alamar Blue solution in the growth media was added to each well before incubating the plate for 4 h. The results were obtained as relative fluorescence units (RFU) at the excitation and emission wavelength pairs of 530-590 nanometer (nm) in a SpectraMax Paradigm Microplate Reader (Molecular devices – USA). The percentage of cell viability was calculated using equation 1 (Dayeh et al., 2013), and the percentage of cell viability for each tracer was used to fit four parameter log-logistic equations using drc package in R program (Ritz et al., 2015). The dose-response curves were plotted, and EC50 values were calculated using drc package in R program.

Toxicity experiments: The marine algae growth inhibition test

The marine algae growth inhibition test utilized *Skeletonema costatum* as the test species and followed the procedure described in ISO guideline 10253. The *S. costatum* strain NIVA-BAC 1 and

Table 2. Information about concentration ranges for screening and final experiments on the cell viability of a RTgill-W1 cell line and growth inhibition of *Skeletonema costatum*.

		Cell viability experiments				Algae growth inhibition experiments			
		Screening experiments - I		Screening experiments - II		Final experiments		Final experiments	
Tracer tested	Concentration range (mg/l)	Number of concentrations	Concentration range (mg/l)	Number of concentrations	Concentration range (mg/l)	Number of concentrations	Concentration range (mg/l)	Number of concentrations	Number of concentrations
23MPRZ	0.1-10,000	6	0.050-8368	24	100-9749	14	200-7689	10	10
26MPRZ	0.1-10,000	6	0.002-5157	24	100-12,525	14	75-6799	10	10
4BZOH	0.1-10,000	6	-	-	0.002-5157	24	0.10-510	15	15
26BZOH	0.1-10,000	6	-	-	0.002-5157	24	0.50-467	15	15
4METBZOH	0.1-10,000	6	-	-	0.050-8368	24	10-5120	10	10
34METBZOH	0.1-10,000	6	0.050-8368	24	100-11,991	14	200-7689	10	10
PYR	0.1-10,000	6	0.050-8368	24	100-12,525	14	100-10,103	10	10

stock solutions for growth medium were acquired from the Norwegian Institute of Water Research (NIVA). The Z8 growth medium was prepared using these stock solutions by following the procedure described in Kotai, 1972. This growth medium was used to maintain the algae strain and for growth inhibition experiments. The NIVA-BAC 1 algae strain was transferred into the growth media and grown under steady conditions of $15 \pm 1^\circ \text{C}$ in the incubator with 12 h light/dark cycle. A pre-culture of NIVA-BAC 1 at a cell density of 5000 cells/ml was started in a 100 ml growth medium under the direct exposure of light for 24 h and at a temperature of $20 \pm 2^\circ \text{C}$. This pre-culture was used to plot the calibration curve. The algae cells were counted under the microscope using a counting chamber and the corresponding fluorescence was measured at the excitation and emission wavelength pairs of 430–671 nm with a SpectraMax Paradigm Microplate Reader. The fluorescence units obtained from the calibration curve were used to calculate the cell density in growth inhibition experiments.

The experiments were carried out in 250 ml Erlenmeyer flasks under direct exposure to light with 6500 Luminex (lx) light intensity. The EC50 concentration values from RTgill-W1 tests were used as a reference for determining the concentration ranges for the algae growth inhibition tests. The range and number of concentrations tested for each chemical are summarized in Table 2. Appropriate amounts of pure test substances were directly added into the growth medium to achieve the final concentration needed in the exposure. DMSO was used as a solvent carrier and control for 4BZOH and 26BZOH. For all other chemicals, a blank control was used.

A pre-culture with a cell density of 5000 cells/ml was started by incubating cells from an algal stock culture 2-3 days before the exposure experiments. The required volume from the pre-culture was added to the test flask to create initial cell densities of 5000 cells/ml for the exposure experiments. The test flasks and control were then exposed under direct exposure to light for 3 days at a temperature of $20 \pm 2^\circ \text{C}$. Fluorescence was measured in a 24 well plate using a 1 ml test solution daily for 3 days (72 h) starting from day 0. The cell density is calculated from these fluorescence units using a calibration curve. Cell density was used to calculate the average specific growth rate (μ) using equation 2, where N_L and N_0 are the measured cell densities after specified time t_L and initial time t_0 , respectively (ISO 10253, 2016). The percentage growth inhibition ($I_{\mu i}$) was calculated based on the difference between the average specific growth rate in control and exposures using equation 3, where μ_c and μ_i is the average growth rate of the algae in the control flask and in the exposed tracer flask, respectively (ISO 10253, 2016). The pH of the test solution was measured before and after the exposure experiments. Test flasks were shaken manually once a day during the exposure period.

$$\mu = \frac{\ln(N_L) - \ln(N_0)}{t_L - t_0} \quad (2)$$

$$I_{\mu i} = \frac{\mu_c - \mu_i}{\mu_c} \times 100 \quad (3)$$

Modeling of tracer release with produced water

The dynamic risk and effects assessment model (DREAM) was used to assess the fate and effects of the tracer compounds discharged in the seawater (Reed and Hetland, 2002). The model calculates the environmental impact factor (EIF) values for produced water discharges in the sea. The EIF unit is defined as a water volume of 10^5 m^3 where the ratio of environmental concentration to no-effect concentration is greater than 1 (Reed and Hetland, 2002). A typical produced water stream from the Brage field on the Norwegian Continental Shelf (NCS) containing naturally occurring oil

components and production chemicals was used as a representative case for produced water discharge. The produced water discharge rate was 15,572 m³/day released at a depth of 17 m below the sea surface. The expected concentration range of tracer in the produced water was chosen based on the available literature data (Viig et al., 2013). Even though the expected tracer concentrations are lower, simulations with higher concentrations were included to understand the relationship between concentration and potential contributions to EIF from tracers. Default ocean currents and wind data available from the model for the month of May-1990 were used for simulation. The ocean currents and wind data for any month/year can be used for simulation. This will presumably not influence the calculation of EIF values. The simulation time span and discharge duration of produced water was kept at 30 days. A centrally located produced water discharge site with the coordinates 3°2.0' East and 60°32' North in a 50*50 kilometers habitat grid was used in the simulation.

Data treatment

All statistical analysis for plotting dose-response curves and calculation of EC50 values was done using 'drc' package in R program (<https://cran.r-project.org/web/packages/drc/drc.pdf>) (Ritz et al., 2015). Different models such as 4 parameter log-logistic, 2 parameter log-logistic, lognormal, weibul, etc., were tested to shortlist the model that best fits the toxicity data. The four-parameter log-logistic model was found to be the best fit for all chemicals, both for cell viability and growth inhibition data. The calculation of EC50 values and fitting of dose-response curves was done using the four-parameter log-logistic model by applying maximum and minimum restrictions as 1 and 0, respectively. For toxicity experiments, the significance level was set at $p < 0.05$, and hypotheses testing was done using a general linear hypotheses test (glht).

Results and discussion

Bio-degradability experiments

The biodegradability of tracers was measured indirectly as a function of oxygen consumption. Net oxygen consumption in the test bottles was calculated by subtracting the oxygen consumption in the blank bottle from the oxygen depletion recorded in the test bottles. The percentage of biodegradation over 28 days was then determined by comparing net oxygen consumption in the test bottles with the theoretical oxygen demand of the test chemical (OECD 306, 1992). Results in terms of percentage biodegradation for all tracers are summarized in Figure 1 and Table 3. Out of all the tested tracers, 4METBZOH and PYR show the highest potential for biodegradation over 28 days at 100% and 91%, respectively. The tracers that showed the lowest biodegradation were 23MPRZ, 4BZOH, and 26BZOH at 22%, 25%, and 32%, respectively. The remaining tracers, 26MPRZ and 34METBZOH, showed biodegradation at intermediate levels (49% and 45%, respectively).

The measurement of biodegradability using the OECD 306 method is largely dependent on the composition of microorganisms in the seawater used for the test. Seawater from another area or depth may have a different composition of microorganisms, which could give different biodegradation readings. It should be noted that there could be interference in oxygen uptake due to nitrification (OECD-306, 1992). However, the use of blanks in the experiments will presumably nullify such possible interference. Moreover, a biodegradation percentage of, say, 30% for a particular chemical means that microorganisms were able to degrade 30% of the chemical over 28 days. This value of 30% may increase with time due to the extended lag phase involved in the degradation process. Although quite similar in structure, a reasonable difference in biodegradability is observed

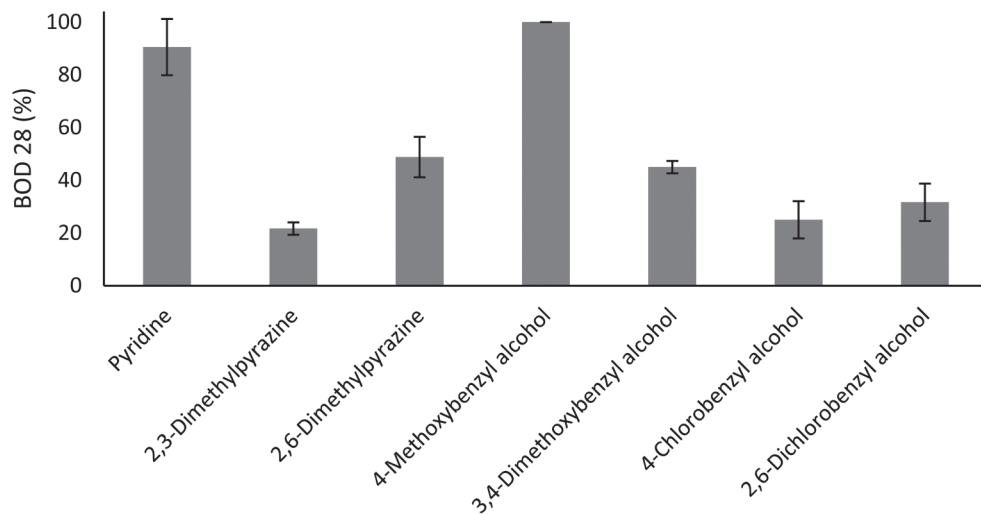


Figure 1. Comparison of biodegradation potential of all PITT tracers.

Table 3. Summary of biodegradability and toxicity results for the tracers tested. Numbers in brackets indicate 95% confidence intervals (min-max).

Tracer tested	% Biodegradation in 28 days	Toxicity studies	
		RTgill-W1 (48-h EC50 (mg/L))	<i>Skeletonema costatum</i> (48-h EC50 (mg/L))
23MPRZ	22	1743 (1506-1979)	1106 (1015-1196)
26MPRZ	49	756 (678-832)	754 (655-853)
4BZOH	25	43 (38-48)	71 (64-79)
26BZOH	32	50 (42-58)	77 (65-90)
4METBZOH	100	734 (624-844)	317 (292-341)
34METBZOH	45	1940 (1724-2156)	540 (480-600)
PYR	91	1883 (1647-2119)	347 (314-380)

between 23MPRZ and 26MPRZ. This could be due to an extended lag phase in 23MPRZ compared to 26MPRZ. One reason for an extended lag phase could be a lower rate of growth in microorganisms. More accuracy in determination of the tracer degradation might have been achieved by chemical analyses, however, this was beyond the scope of the study. It is also important to note that multiple degradation processes other than biodegradation may influence the overall degradation of a chemical in the marine environment. These processes include hydrolysis of chemicals, aquatic photodegradation, etc. (Hughes et al., 2020).

Cell viability experiments

The EC50 based on the metabolic activity in RTgill-W1 cells was determined after 48 h of exposure to all the tracer compounds at different concentrations. A progressive decline in cell viability of RTgill-W1 cells with the increase in tracer concentrations was measured using Alamar Blue dye.

Dose-response curves showing the effect of all tracers on the cell viability of RTgill-W1 cells after 48 h of exposure are shown in Figure 2. Table 3 summarizes EC50 values for all tracers when exposed to RTgill-W1. Among all tracers, both chlorobenzyl alcohols were observed to have the lowest concentrations at 50% cell viability (EC50). The lowest EC50 values were 43 mg/l and 50 mg/L for 4BZOH and 26BZOH, respectively. Almost 100% loss in cell viability was observed around 100 mg/l for both chlorobenzyl alcohols. The EC50 values for 26MPRZ and 4METBZOH were observed to be 755 mg/L and 734 mg/L, respectively. The remaining three tracers, 23MPRZ, 34METBZOH, and PYR, were within a high range of similar EC50 values (1743–1939 mg/L). The dose-response curves for 4METBZOH, PYR, and 23MPRZ deviate from the common s-shaped sigmoidal curve, exhibiting almost a linear relationship over a large range of higher exposure concentrations. Comparison of cytotoxicity data measured for the group of chemicals in the current study is difficult due to a lack of published data.

Marine algae growth inhibition tests

Growth inhibition of the algae *Skeletonema costatum* was determined after 48 h of exposure to all the tracer compounds at different concentrations (Table 3). A gradual increase in growth inhibition was observed with higher tracer concentrations. A decline in growth rate was observed in the control cultures in the last 24 h. During this time the exposed algae continued to be in a delayed exponential growth phase. The comparison of control and exposure at this stage may lead to a possibly incorrect conclusion concerning the decreased growth-inhibiting effect. To avoid this and obtain more consistent calculations, these were instead based on the last measurement within the exponential growth period after 48 h of exposure in both control and exposure cultures. Dose-response curves showing the effect of all tracers on growth inhibition after 48 h of exposure are shown in Figure 3. During the experiments, the cell density in the control group increased by a factor of more than 16, and the pH of the test medium did not increase by more than 1, fulfilling both validity criteria laid out by ISO 10253.

Comparing the results from toxicity experiments to RTgill-W1 and *Skeletonema costatum*, we observed that *S. costatum* was slightly more sensitive to tracers than RTgill-W1 cells. Similar to the results for cell viability experiments, both chlorobenzyl alcohols showed the lowest EC50 values for growth inhibition experiments. The EC50 values for 4BZOH and 26BZOH were 71 mg/l and 77 mg/L, respectively, which were slightly higher than the EC50 values for cell viability studies which were 43 mg/l and 50 mg/l, respectively. Almost 100% growth inhibition was observed at around 150 mg/L for both these compounds. The EC50 values of 4METBZOH and PYR for growth inhibition experiments were observed to be in the same range, 317 mg/L and 347 mg/L, respectively. The highest EC50 value of all tracers for growth inhibition experiments was 1106 mg/L for 23MPRZ, followed by 754 mg/L for 26MPRZ and 540 mg/L for 34METBZOH. Compared to the other tracers, a considerable difference in EC50 values for PYR, 23MPRZ, 4METBZOH and 34METBZOH was observed between growth inhibition and cell viability experiments. The EC50 values measured for growth inhibition of algae were lower than the cell viability of RTgill-W1. A possible reason for this could be that the assessment endpoint is inhibition of growth in the case of algae whereas for RTgill-W1 the endpoint is the mortality of cells. It would perhaps take higher concentrations to cause mortality, but growth could be inhibited at lower concentrations. Moreover, each chemical has a distinct toxic mode of action on different species. This may also influence the difference in EC50 values recorded for algae and Rtgill-W1. If more than 1 toxicity value is available for a particular chemical, the lowest value is selected for conducting ERA (ECHA, 2008b). Therefore, the lower EC50 value measured among cell viability and

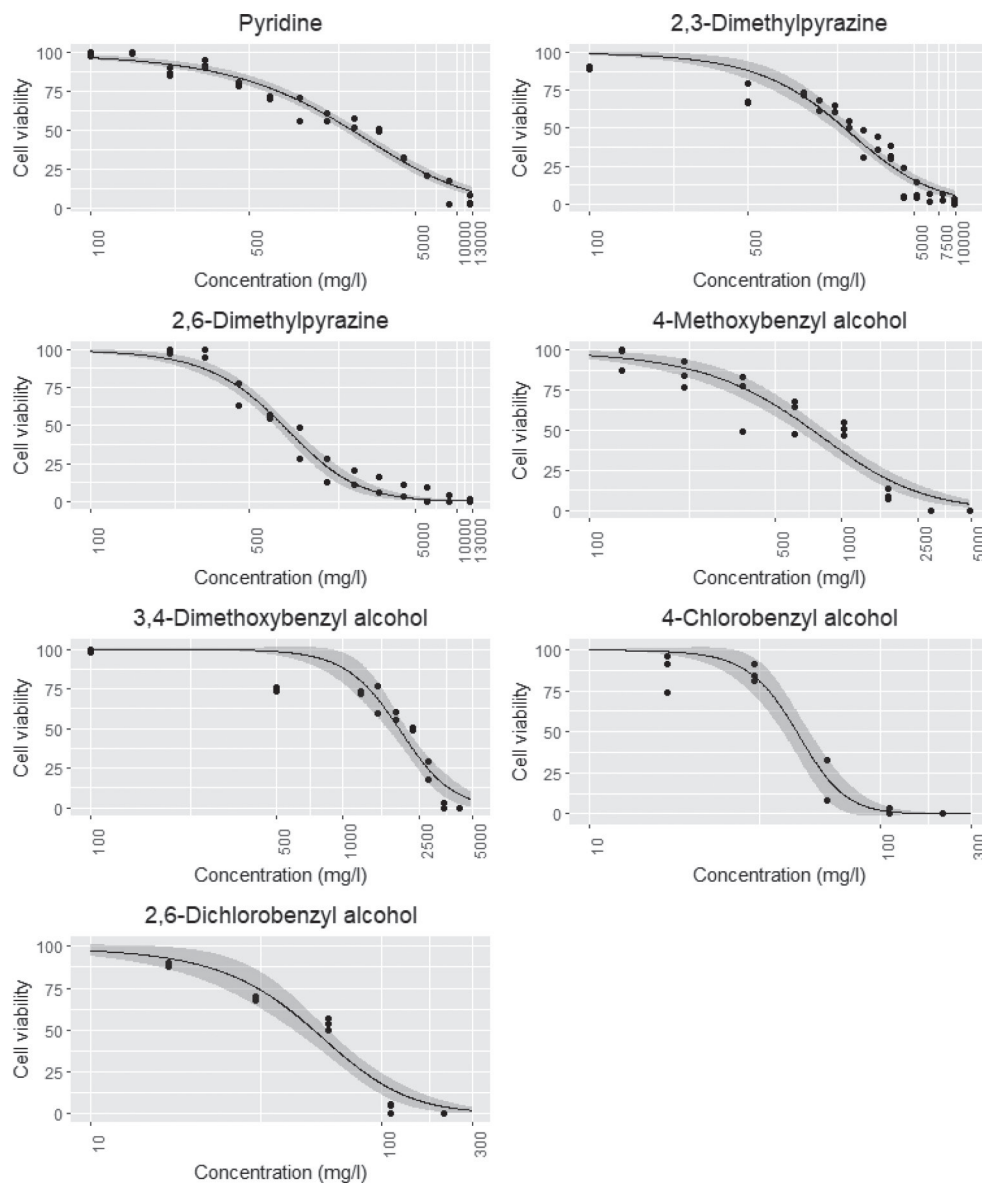


Figure 2. Cell viability of RTgill-W1 cells compared to control after 48 h of exposure to 7 tracers. Data are fitted using a four parameter log-logistic equation, and the ribbon around the dark line indicates a 95% confidence interval. Number of replicates: Three for each concentration ($p < 0.05$).

growth inhibition experiments was chosen to calculate EIF using the DREAM model. The lower EC50 values for tracers 4BZOH and 26BZOH was measured for cell viability experiments. For all other tracers, the lower EC50 value was measured for growth inhibition experiments. The inclusion of two different laboratory methods in this study thus strengthened the basis for the ERA and contributed to available literature data on toxicity by fish cell method comparative to the standard OSPAR recommended algal test.

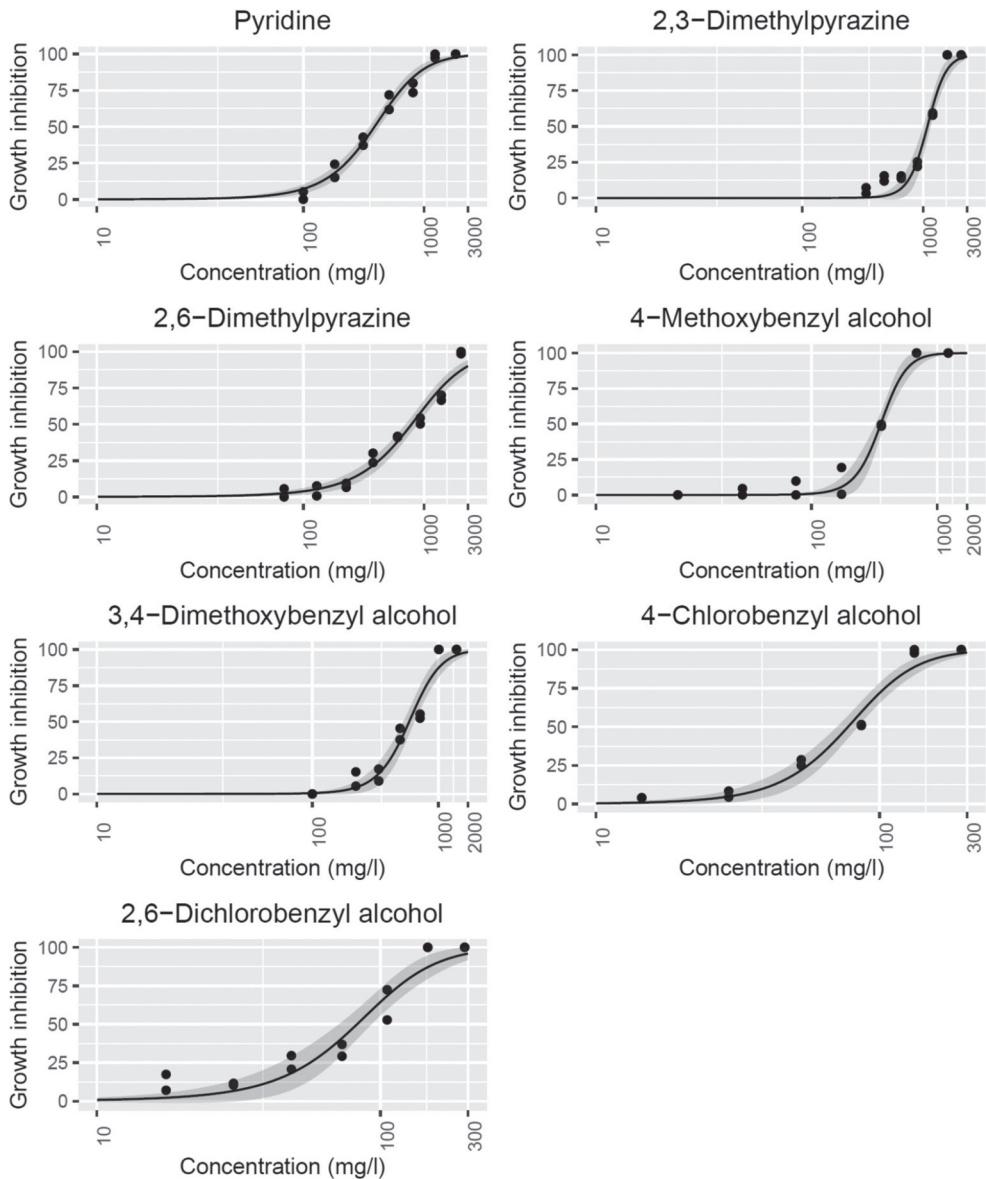


Figure 3. Growth inhibition of *Skeletonema costatum* compared to control after 48 h of exposure to 7 tracers. Data are fitted using a four parameter log-logistic equation, and the ribbon around the dark line indicates a 95% confidence interval. Number of replicates: Two for each concentration ($p < 0.05$).

Simulation of tracer release using the DREAM model

The contribution to environmental impact factors from different chemicals in the DREAM model is mainly dependent on the concentration of a chemical and corresponding ecotoxicological data. There is limited data available on the expected concentrations of tracers in the produced water stream. A report from Viig et al. (2013) suggests that the expected concentrations could be in

the range of a few micrograms per liter. However, the expected concentrations may vary based on the specific field applications and a group of tracers. This study uses the produced water release profile containing naturally occurring compounds and production chemicals from the Brage field on the NCS as a representative case for a typical produced water discharge in the North Sea. Tracers from the current study are added to this produced water stream, and the contribution to the time-averaged EIF from each tracer is calculated independently at different concentrations. A time-averaged EIF is an EIF value measured and averaged throughout the simulation (Reed and Hetland, 2002). The lowest EC50 values from cell viability and algae growth inhibition experiments were used to simulate tracers. An assessment factor of 1000 was used to account for uncertainties as recommended by the European Chemical Agency guidance document (ECHA, 2008b). Biodegradability values measured from this study are used, whereas octanol-water coefficient values are taken from the literature (Silva et al., 2018, 2019, 2021).

Table 4 and Figure 4 summarize the contribution to the time-averaged EIF from all tracers at different concentrations. The contribution to EIF remains zero at the expected concentration of a few micrograms per liter for all tracers. This is because the produced water stream is rapidly diluted in the marine environment, and the actual exposure concentrations will be significantly lower than the back-produced concentration of tracer in the produced water. The measured acute toxicity of tracers from this study is not high enough to contribute to EIF at such low concentrations. It is important to note that the assessed risk is based on the EC50 values obtained from acute toxicity experiments. To extrapolate from acute toxicity to chronic toxicity, an assessment factor of 100 is usually used for most of the chemicals (May et al., 2016). Moreover, the actual sub-lethal effects on marine species interpreted by different biomarkers may start at very low concentrations (Sanni et al., 2017a). This concentration might alternatively also be used as a criterion for assessing environmental risk (Sanni et al., 2017b). Data on sub-lethal effects for the group of chemicals in this study is lacking. To account for sub-lethal effects and other uncertainties, an assessment factor of 1000 is recommended by the European Chemical Agency (ECHA) (ECHA, 2008b). An assessment factor of 1000 is also used for other chemicals in the produced water release profile from the Brage field. Therefore, to have consistency and comparable assessment among all chemicals, an assessment factor of 1000 was used for tracers (ECHA, 2008b; May et al., 2016).

A minor contribution to EIF of 0.003 is seen for 4BZOH and 26BZOH at a concentration 10 times higher than the reported tracer concentration. This means that at 0.03 mg/L of 4BZOH and 26BZOH, the ratio of environmental concentration to no-effect concentration is greater than 1 in

Table 4. Summary of contributions to time-averaged Environmental Impact Factor (EIF) from all tracers at different concentrations.

Tracer	Contribution to EIF at different concentrations in mg/L					Ranking tracers from low to high contribution to EIF
	0.003	0.03	0.3	3	30	
23MPRZ	0	0	0	0.021	0.24	1
26MPRZ	0	0	0.003	0.033	0.46	2
34METBZOH	0	0	0.003	0.049	0.69	3
4METBZOH	0	0	0.003	0.054	0.74	4
PYR	0	0	0.003	0.072	0.98	5
26BZOH	0	0.003	0.055	0.766	9.1	6
4BZOH	0	0.003	0.068	0.915	11	7

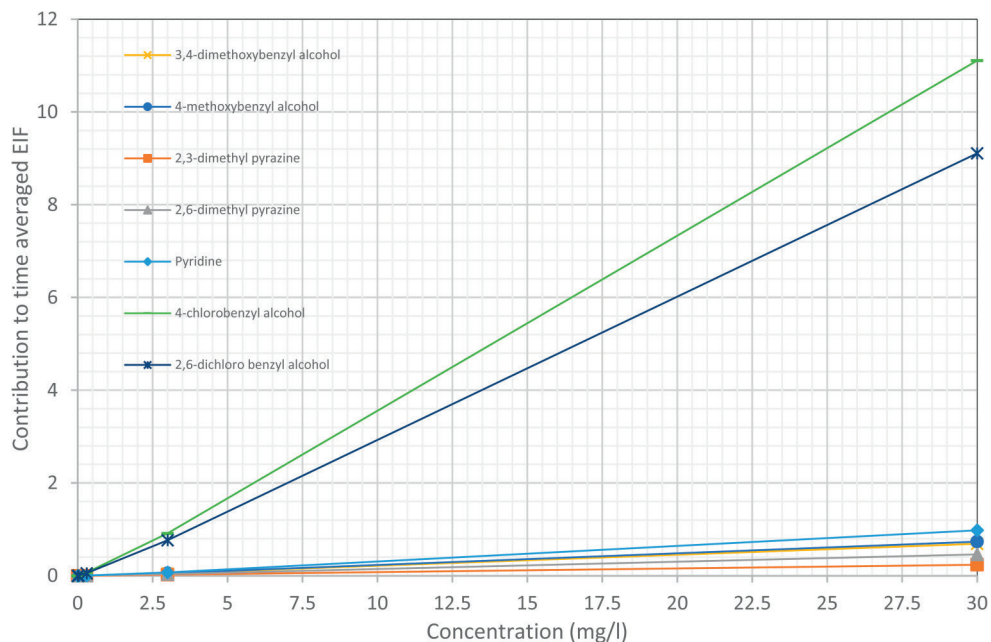


Figure 4. Contribution to time-averaged EIF from all tracers at different concentrations.

300 m³ of water (Reed and Hetland, 2002). At unrealistically high concentrations of 3 mg/L and 30 mg/L, all tracers show some contribution to the EIF. In Table 4, all tracers have been ranked based on their contribution to EIF at different concentrations. The lower-ranked tracers, 23MPRZ and 26MPRZ, show considerably lower contributions to the EIF compared to other tracers. It is important to note that tracers are ranked based on their contribution to EIF at unrealistically high concentrations in the produced water. At the expected concentrations of a few micrograms/liter, none of the tracers shows any contribution to the EIF.

A harmonized pre-screening scheme is usually followed for permitting the use of chemicals offshore in the countries that are part of the Oslo and Paris Commissions (OSPAR, 2019). According to the pre-screening scheme, the chemicals with biodegradability of less than 20% are usually not allowed to be used and discharged offshore. From our study, 23MPRZ, 4BZOH and 26BZOH show biodegradability between 20% and 35% over 28 days, but none of the chemicals shows biodegradability less than 20% over 28 days. For chemicals showing biodegradability greater than 20%, if two of the following three conditions are met, the chemicals are usually not allowed to be used offshore: biodegradation less than 60% over 28 days, bioaccumulation potential ($\log Pow$) ≥ 3 and $LC50/EC50 < 10$ mg/L. Of all the tracers tested in this study, only PYR and 4METBZOH show a biodegradability greater than 60%. However, one of the other two conditions, i.e., bioaccumulation potential ($\log Pow$) ≥ 3 and toxicity ($LC50/EC50 < 10$ mg/L), is not fulfilled for the tested chemicals. The low biodegradability (between 20% and 60%) measured for most of the tracers suggests that it may take more than 28 days for these compounds to completely bio-degrade. In addition to biodegradation, there are several other factors such as chemical hydrolysis, aquatic photodegradation, etc., that influence the overall degradation of a substance (Hughes et al., 2020). The amount of tracers used and discharged in the marine environment is usually quite low (Viig et al., 2013), and with the relatively low measured biodegradability, it seems therefore reasonable to consider that

only a minor amount of these compounds will potentially be accumulated in the marine environment over time. Of all the tested tracers, 4BZOH and 26BZOH show low biodegradability and high toxicity compared to other tracers. These two tracers are the most environmentally sensitive, and with all other factors being equal, these two might be given less priority in selections of tracers for offshore application. The acute toxicity based on EC50/LC50 values between 100–1000 mg/L and higher are classified as practically non-toxic (Patin, 1999). The toxicity of five of the tested tracers, apart from 4BZOH and 26BZOH, falls within this range. Therefore, any of these five tracers might be prioritized for offshore applications.

In this study, the primary focus was on assessing environmental risk from operational discharges of newly shortlisted tracer compounds in the marine environment. These tracers are usually transported in more concentrated form in the form of slugs to the offshore platform. There is a possibility of accidental release of these slugs into the sea during transportation and/or injection. The accidental release of these compounds in their pure form or together with other solvents will presumably result in higher environmental impacts than those associated with operational discharges. However, the frequency and probability of these accidental releases can be assumed as relatively low compared to the operational discharges of the tracers. In the event of accidental release, the predicted environmental concentrations (PEC) based on release amounts will be proportional to calculated operational releases in this paper, and the environmental risk will be reflected by assessed operational impact, PEC/PNEC (PNEC = threshold value), multiplied by the frequency (probability) of it occurring.

Conclusions

In this study, we measured the biodegradability and acute toxicity of seven chemical compounds that are shortlisted as potential tracers for quantifying residual oil saturation. All tracers showed some potential for biodegradation, with PYR and 4METBZOH showing over 90% biodegradation potential in 28 days. For toxicity tests, among all tracers, both chlorobenzyl alcohols displayed higher sensitivity towards RTgill-W1 and *Skeletonema costatum* and had the lowest EC50 concentration. All remaining tracers, barring 26MPRZ, showed a higher sensitivity towards *S. costatum* compared to RTgill-W1. Overall, the EC50 values for all tracers were in the range of 43–1940 mg/L. The ecotoxicological data obtained from this study can be used to assess the environmental impact and risk of using these chemicals in other anthropogenic activities.

We used this ecotoxicological data in the physical/chemical fate and effects modelling program to assess the environmental impact from the operational discharge of these tracers on the NCS. Out of all seven tracers, 4BZOH and 26BZOH were found to have the highest toxicity and contribution to EIF. The remaining five tracers were found to be practically non-toxic with reasonable biodegradability over 28 days. Therefore, these five tracers could be preferred over 4BZOH and 26BZOH for offshore application. At the same time, it is important to note that none of the tracers showed any contribution to EIF at the expected concentrations in the produced water. Moreover, the group of tracers in this study has achieved the limit of quantification in the range of nanograms/per liter using different analytical techniques (Silva and Bjørnstad 2020). The low limit of quantification means that a lesser quantity of these tracers could be used in the injection, which may reduce the expected concentrations in the produced water. In this case, the expected concentrations of tracers might reduce to levels even below micrograms per liter. It seems unlikely that these groups of tracers could pose an environmental risk at such low concentration ranges. Environmental risk of accidental release of tracer compounds can be calculated in a similar manner as in the case of operational releases, but with different release characteristics dependant on the case.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.


Acknowledgment

We thank Prof. Daniela M Pampanin and PhD candidate Giovanna Monticelli at University of Stavanger for training and guidance on conducting cytotoxicity experiments. We also thank Ms. Emily Lyng (Norwegian Research Centre) for training and guidance in running EIF simulations.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: The authors acknowledge the Research Council of Norway and the industry partners ConocoPhillips Skandinavia AS, Aker BP ASA, Vår Energi AS, Equinor ASA, Neptune Energy Norge AS, Lundin Norway AS, Halliburton AS, Schlumberger Norge AS, and Wintershall DEA, of The National IOR Centre of Norway, for their support. This work was supported by the Research Council of Norway (grant number 230303).

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Supplemental material

Supplemental material for this article is available online.

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Paper III

Modelling the fate and transport of synthetic enhanced oil recovery polymers in the marine environment.

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Draft ready for submission. Not included in the Brage repository.

Paper IV

Exposure and effects of synthetic enhanced oil recovery polymers on the Norwegian Continental Shelf.

Authors: Mehul Vora, Steinar Sanni, Emily Lyng & Roger Flage

Submitted to Regional Studies in Marine Science Journal.

Not included in the Brage repository.

Paper V

Implementing a risk-oriented framework for addressing uncertainties in species sensitivity distributions.

Authors: Mehul Vora, Roger Flage & Steinar Sanni

Submitted to Integrated Environmental Assessment and Management Journal.

Not included in the Brage repository.

