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DESARROLLO Y VALIDACIÓN DE METODOLOGÍAS Y HERRAMIENTAS PARA LA GESTIÓN INTEGRAL DEL MEDIO ACUÁTICO PORTUARIO

PhD DISSERTATION

DEVELOPMENT AND VALIDATION OF METHODOLOGIES AND TOOLS FOR AN INTEGRATED MANAGEMENT OF AQUATIC HARBOR SYSTEMS

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Nomenclature

A	appearance description
AE	acute effect
AV	Average-value method
b	number of ERA scenarios
Bc	effect of the bacteriological pollution process
c	a specific cluster
Ch	effect of the chemical pollution process
Co	consequences
C_D	diffusion coefficient
d	product relative density
dt	distance
D	density scenario
DCS	diffuse contaminant sources
Dk	percentage of the product distilled at 180 °C
E	environmental risk analysis scenario
Ed	constant factor referred to the conditions of the operations' scenarios
ESE	ecological singular elements
Eu	effect of the eutrophication process
Ev	ecological value
Evp	percentage of specific pollutant liable to be evaporated
E_{global}	global effect
fc	frequency of occurrence
f_D	frequency of a product density in case a spill occurs
f_{Ew}	frequency of an ERA scenario
f_Q	frequency of a quantity category in case a spill occurs
f_{ST}	frequency of a spill type in case a spill occurs
f_{Vc}	frequency of a cluster
F	numbers of discharge points of a specific facility
f	frequency of an ERA scenario
g	constant gravity
g,h	a grid cell
H	hazardousness
HP	Hydromorphologycal pressure
i	a pollution incident
j	a specific quantity scenario
K	number of clusters
Kd	a correction factor to the estimation of diffuse sources' affected areas
Kw	kappa index
l	a spill type

$\mathbf{L_F}$	a discharge point
n	dimension of met-ocean variable data
N	number of pollution incidents
Na	naturalness
Nd	constant factor referred to materials' nature
o	number of quantity scenarios
p	number of percentile
P	percentage of specific pollutant
PA	Protected Areas
PI	Pollutant incident sources
PCS	Point contaminant sources
$\mathbf{PR_{g,h}}$	presence of product in a grid cell
q	discharge quantity
Q	quantity scenarios
$\mathbf{Q_{th}}$	quantity category
$\mathbf{r_{ini}}$	oil spill initial radius
R	risk
$\mathbf{R_W}$	risk determined by the worst case method
$\mathbf{RE_w}$	environmental risk of an ERA scenario
$\mathbf{RL_F}$	environmental risk for a discharge point
RT	recovery time
s	number of spill types
S	affected extension
ST	spill type vector
Su	susceptibility
SACs	special areas of conservation defined under Directive 92/43/EEC
SCIs	sites of community Importance defined under Directive 92/43/EEC
SPAs	special protected areas defined under Directive 2009/147/EC
t	density categories
T	temperature
Ta	time with adverse conditions
th	quantity percentile
$\boldsymbol{T}$	simulation time
$\boldsymbol{\tau}$	time in minutes
$\mathbf{U_a}$	advective velocity of currents
$\mathbf{U_c}$	superficial velocity of currents
$\mathbf{U_v}$	currents of superficial layers of water column generated by wind
V	meteorological or oceanographic variable
Vu	vulnerability
$\mathbf{V_v}$	wind direction
$\mathbf{V_c}$	a specific cluster vector

$\mathbf{V_{eta}}$	sea level
$\mathbf{V_{u}}$	wind velocity
w	a specific ERA scenario
WC	Worst-case method
WD	Weighted method
$\mathbf{W_{10}}$	wind velocity at 10 meters above the surface
ΔT	remaining simulation time
$\Delta \mathbf{x}$	diffusion turbulent process
$\Delta \mathbf{x}^2$	cuadratic displacement due to turbulent diffusion
$\Delta \mathbf{w}$	reduced gravity
ρ_w	water density
ρ_{oil}	spilled product density
ν	kinematic viscosity of water
$\emptyset$	diameter of a spill circumference due to spreading process
[x]	average concentration of a substance at cell level

RESUMEN

De acuerdo con la normativa de estudios de doctorado de la Universidad de Cantabria en relación a los requerimientos exigidos para aquellas tesis redactadas en un idioma diferente al español, aprobada por Junta de Gobierno de 12 de marzo de 1999 y actualizada a 18 de diciembre de 2013, a continuación se presenta un resumen en español "suficientemente extenso" del documento original redactado en inglés.

1. Introducción

Alrededor del 90% del comercio mundial se realiza a través del mar (ICS, 2016), siendo el transporte marítimo la columna vertebral del comercio internacional (IMO, 2013b). En términos de volumen, en Europa, el 75% de los intercambios europeos de mercancías con el resto del mundo se realiza a través de puertos. El peso bruto total de mercancías manipuladas en los puertos de la UE se estima que fue de 3.7 billones de toneladas en 2013 (ESPO, 2015). Para el año 2030 se espera un crecimiento del 50% del transporte marítimo de mercancías (European Commission, 2013b), lo que se traducirá, necesariamente, en una expansión de los puertos ya existentes, así como en la demanda de nuevas infraestructuras portuarias. A medida que el tráfico de carga de mercancías sigue creciendo, se incrementa también la preocupación de garantizar su sostenibilidad a largo plazo, orientando el debate actual sobre la globalización, el comercio y el medio ambiente hacia el desarrollo sostenible (UNCTAD, 2012a). Además, los puertos desempeñan un papel clave en la cadena de suministro, ya que conforman el eslabón central entre el transporte marítimo y terrestre, siendo en ellos donde se llevan a cabo la mayoría de las operaciones rutinarias relacionadas con el transporte de mercancías (Ng y Song, 2010). Por ello, en los últimos años, las autoridades portuarias de la Unión Europea han venido implementado sistemas de gestión para evaluar y mejorar su comportamiento ambiental (Asgari et al., 2015). El reglamento EMAS (European Commission, 2009b), el certificado ISO 14001, el "Self Diagnostic Method" (SDM) o el "Ports Environmental Review System" (PERS) son algunos ejemplos de estos sistemas.

Las zonas portuarias son consideradas sistemas complejos desde el punto de vista medioambiental, dada su localización en la zona costera y la gran variedad de mercancías que se manipulan en ellas (Darbra et al., 2004). En este sentido, la calidad del medio acuático se encuentra entre los 17 indicadores de estado utilizados en el diseño de las estrategias medioambientales portuarias (Peris-Mora et al., 2005), y ocupa la octava posición en la lista de las diez prioridades ambientales de los puertos europeos (ESPO-ECOPORTS, 2016). Además, las aguas portuarias se encuentran dentro del marco de aplicación de la Directiva Marco del Agua (DMA) - Directiva 2000/60/CE (European Commission, 2000a) - , habiéndose identificado, en Europa, un total de 583 masas de agua muy modificadas (HMWBs) por la presencia de puertos (Kampa y Laaser, 2009). La totalidad de estas masas, según la DMA, debe alcanzar un estado de calidad definido como "buen potencial ecológico". La legislación y el creciente interés socioeconómico por el desarrollo sostenible de estas áreas ha empujado a la comunidad científica a desarrollar herramientas y procedimientos que permitan aportar soluciones para el mantenimiento de la calidad del medio acuático portuario, sin menoscabo de la economía sobre la que se sustentan (Juanes et al., 2013).

En relación a los agentes que producen efectos perniciosos sobre la calidad del agua en zonas costeras, las emisiones difusas constituyen una fuente importante de contaminación (Preston, 2002; Gómez, 2010). Estas fuentes son especialmente relevantes en las áreas portuarias donde confluyen multitud de usos y actividades de especial interés social y gran relevancia económica (usos comerciales, logísticos, de almacenaje, industriales o incluso náutico-recreativos, etc.). La coexistencia de dichos usos puede conllevar a una afección ambiental negativa del medio acuático expuesto a múltiples contaminantes procedentes de una gran variedad de peligros ambientales (Darbra y Casal, 2004), entendidos éstos como aquellas fuentes de contaminación presentes en la zona de servicio portuario. Éstas, en el contexto de esta Tesis comprenden tanto las emisiones puntuales y difusas consecuencia de la actividad ordinaria del puerto, como las fuentes de episodios contaminantes causados por operaciones realizadas en condiciones desfavorables. En este sentido, cabe destacar que, la contaminación marina accidental derivada de las operaciones rutinarias que las embarcaciones realizan en puerto (carga y descarga de graneles líquidos, suministro de combustible, navegación, etc.) supone una importante amenaza para la calidad del medio acuático portuario (IMO, 1978). Dicha contaminación operacional puede conllevar efectos deletéreos, especialmente cuando se repite en el tiempo sin activarse acciones de respuesta (Ng y Song, 2010). En relación a la contaminación marina accidental, Darbra y Casal (2004) detectaron que, en las zonas portuarias, los derrames son los accidentes más habituales (51% del total de accidentes ocurridos), siendo los derrames de hidrocarburos los que se dan con mayor frecuencia (59%). En consecuencia, la contaminación difusa por derrames de hidrocarburos es uno de los problemas más comunes de las zonas portuarias.

Con el objetivo de aportar soluciones para una gestión adecuada de dichos riesgos se han desarrollado herramientas cuantitativas de gestión que permiten trasladar los datos científicos en información concreta sobre los efectos potenciales que las actividades portuarias tienen sobre el medio acuático. Estas herramientas se han centrado en un único contaminante o un único peligro (p.ej., Ronza et al., 2006; Castanedo et al., 2009; Abascal et al., 2010), no han abordado la integración de diferentes peligros (p.ej., Ondiviela et al., 2012; Juanes et al., 2013; Gómez et al., 2014c; 2015), han ignorado la variabilidad espacial y temporal de los contaminantes y sus receptores potenciales (p.ej., Trbojevic y Carr, 2000), no han tenido en cuenta las características ecológicas de los receptores del riesgo (p.ej., Bruzzone et al., 2000) o han considerado, únicamente, los impactos generados por derrames accidentales (p.ej., Grifoll et al., 2011). En definitiva, no existe un método estándar globalmente aceptado para el análisis del riesgo ambiental en zonas portuarias (Wooldridge et al., 1999; ESPO, 2007). Además, ninguna de las metodologías existentes considera la combinación de los efectos producidos por la contaminación marina accidental y la operacional. De manera general, se puede afirmar que, el análisis del riesgo ambiental es una herramienta que debería ser capaz de identificar y caracterizar los peligros, considerar las condiciones ambientales locales y definir el riesgo en términos espaciales y probabilísticos.

En el contexto de la gestión acuática portuaria, se plantean cuestiones de suma importancia, cuya correcta respuesta debe permitir asignar prioridades en la aplicación de medidas y acciones en la gestión del riesgo: ¿qué peligros están afectando en mayor medida al sistema acuático portuario?; ¿qué contaminantes están afectando a un área determinada de la zona de servicio portuario?; ¿en qué medida cada actividad o instalación contribuye al efecto global de la actividad portuaria? En este sentido, los mapas de riesgo ambiental deben permitir explorar la variabilidad espacial y temporal del mismo, así como la distribución de los factores determinantes del riesgo, las concentraciones de los contaminantes, los efectos derivados en el medio y la exposición a los diversos receptores. Para que dichos mapas permitan establecer prioridades ajustadas a los objetivos de la gestión ambiental de un puerto concreto, deben poderse adaptar tanto a su escala espacial (p.ej., una dársena determinada, una instalación concreta o la zona de servicio portuario) como a sus peligros específicos, así como a la estrategia ambiental del puerto.

La identificación de los peligros ambientales constituye una fase extremadamente importante en el proceso de análisis del riesgo ambiental. La calidad de los resultados de las etapas sucesivas en este proceso depende en gran medida de la calidad de esta fase inicial. Así, la caracterización de los derrames potenciales generados por emisiones difusas (cantidades de vertido, tipos de productos, etc.) es todo un desafío en el análisis del riesgo ambiental de este tipo de instalaciones. Diversos autores han desarrollado herramientas para la identificación de los peligros ambientales en zonas portuarias (Darbra et al., 2004; Darbra et al., 2005; Peris-Mora et al., 2005; Puig et al., 2015), pero ninguno de ellos define procedimientos para el establecimiento de escenarios de riesgo. Así pues, para el análisis del riesgo ambiental de derrames son utilizados, de manera generalizada, escenarios hipotéticos basados en el criterio de experto o en el *peor de los casos*. En el caso particular de las instalaciones de carga y descarga de graneles en áreas portuarias es necesario definir y seleccionar escenarios basados en datos reales, mediante procedimientos estandarizados. De esta manera, se podrán aplicar análisis estocásticos y probabilísticos que puedan reflejar la variabilidad espacial y temporal del riesgo ambiental asociado a dicha actividad.

Por otro lado, la estimación cuantitativa del riesgo ambiental de las emisiones contaminantes ha estado inevitablemente ligada a la utilización de modelos numéricos. Hoy en día, existen modelos numéricos calibrados que son ampliamente utilizados para la simulación de la trayectoria de derrames en el medio marino (p.ej., Mestres, 2002; Abascal et al., 2007; Azevedo et al., 2014). Estos modelos son capaces de interpretar, simular y predecir de una forma teórica las respuestas de los contaminantes en el medio acuático. Siempre y cuando hayan sido calibrados y validados adecuadamente, son herramientas muy valiosas para la predicción de los efectos de los contaminantes sobre los componentes del ecosistema (p. ej., Yuan et al., 2007). Sin embargo, en muchos casos necesitan ser manejados por técnicos expertos (Otero et al., 2015), requiriendo además un alto coste computacional (Roberts et al., 2010) y una detallada caracterización de la emisión y de las condiciones ambientales por parte del usuario que, en muchos casos, está sujeto a la disponibilidad de los forzamientos océano-meteorológicos detallados por parte de servidores externos. Por el contrario, las herramientas numéricas basadas en sistemas de información geográfica (SIG) son, de manera general, de fácil uso y permiten analizar las distribuciones espaciales de los derrames, proporcionando información decisiva en la toma de decisiones, siendo potencialmente utilizada no solo por usuarios expertos sino también por técnicos y gestores.

En la actualidad, existen herramientas basadas en SIG específicas para predecir el área potencial de afección de emisiones difusas (p.ej., Juanes et al., 2013). Los procesos de transporte considerados por estas herramientas son comunes a todos los tipos de materiales, ignorando los procesos físicos y químicos que se producen en el medio acuático. Sin embargo, es conocido que, dependiendo de las características de la sustancia o material liberado en el medio, existe una complejidad y diversidad de procesos físicos y químicos que afectan a su destino y transporte. Con el fin de dotar a los gestores de herramientas de bajo coste computacional, rápidas, efectivas y de fácil manejo, se considera necesario el desarrollo de herramientas basadas en sistemas de información geográfica que permitan obtener la variación espacial y temporal del riesgo ambiental de derrames de hidrocarburos en el medio acuático, incorporando las dinámicas o procesos de reacción necesarios.

Además del conocimiento de la evolución del derrame en el medio, la evaluación del riesgo ambiental pasa por el conocimiento de las consecuencias asociadas al mismo. Las consecuencias se definen como los efectos que puedan derivarse de los riesgos ambientales y están necesariamente relacionadas con las características de los productos derramados. Las metodologías existentes para la evaluación de las consecuencias producidas por derrames de hidrocarburos consideran como factor fundamental la llegada del producto vertido a zonas específicas que albergan determinados recursos biológicos (hábitats y/o especies) o destinadas a usos y servicios concretos (pesca, acuicultura, zonas turísticas, etc.). Sin embargo, las consecuencias derivadas de los derrames de hidrocarburos están relacionadas con características como la persistencia, la toxicidad o la bioacumulación de los productos vertidos. Por ello, se considera necesario el desarrollo de nuevas metodologías para evaluar el impacto potencial de las instalaciones de carga y descarga de hidrocarburos en áreas portuarias. Éstas deben considerar no solo la presencia de contaminantes, sino también los efectos derivados de los mismos en los diferentes compartimentos ambientales. En este sentido, cabe destacar que, en zonas portuarias, los sedimentos constituyen un compartimento ambiental esencial, siendo su calidad un indicador de la salud del ecosistema (Mali et al., 2016). Además, muchos compuestos orgánicos y contaminantes tóxicos y persistentes (p.ej., PCBs, HAP, metales pesados, etc.) son retenidos en este compartimento (Ondiviela et al., 2012).

Finalmente, como herramientas predictivas que son, los procedimientos de análisis del riesgo requieren contrastar las estimaciones efectuadas con datos de campo reales, tanto en lo que respecta a los niveles de contaminación transferidos al medio acuático, como a la comprobación del impacto deletéreo real que dicha contaminación provoca en los organismos. No obstante, es bien conocida la dificultad que entraña la cuantificación del impacto real que los contaminantes producen en el funcionamiento del sistema, dado que: i) normalmente la contaminación es una mezcla compleja de sustancias con diferentes niveles de toxicidad, persistencia y bioacumulación; ii) se pueden producir efectos aditivos y/o sinérgicos; iii) los efectos son diferentes en cada especie, grupo funcional o estadio de desarrollo; y, iv) los efectos subletales son difíciles de detectar y cuantificar, al menos, a nivel de población o comunidad. En este sentido, el método Weight of Evidence (WoE) es el procedimiento adecuado para sintetizar e interpretar un conjunto de pruebas que permitan obtener conclusiones, por ejemplo, con respecto a la relación entre una exposición a los contaminantes y el impacto ambiental que producen (Ågerstrand y Beronius, 2016). Así pues, la validación de las herramientas y metodologías para el análisis del riesgo debe integrar información sobre: i) el nivel de contaminación que se transfiere realmente a los diferentes compartimentos ambientales (agua, sedimento, biota); y, ii) el impacto de los agentes tóxicos en diferentes niveles de organización biológica (suborganísmico, individuo, comunidad).

En resumen, las metodologías existentes para la evaluación de riesgos ambientales, a nivel de puerto, se centran en contaminantes específicos introducidos por emisiones puntuales, sin integrar a las emisiones difusas o las fuentes de episodios contaminantes. En relación al riesgo ambiental producido por los derrames de hidrocarburos, las metodologías existentes hacen uso de escenarios hipotéticos y los resultados suelen basarse en modelos numéricos sofisticados, sin tener en cuenta las consecuencias específicas de los productos involucrados. Por otra parte, los métodos y las herramientas utilizadas para estimar los riesgos ambientales no suelen validarse mediante la cuantificación del impacto ambiental real a través de campañas específicas de toma de datos en campo. Esta Tesis Doctoral se centra en la propuesta de métodos y herramientas que permitan abordar estas limitaciones con el objetivo de gestionar el medio acuático portuario bajo un enfoque integral.

2. Objetivos

El objetivo general de esta Tesis es desarrollar herramientas y metodologías dirigidas al análisis cuantitativo del riesgo ambiental en áreas portuarias, que permitan mejorar la gestión integral del medio acuático en dichas zonas. Las aproximaciones desarrolladas en esta tesis están basadas en el análisis probabilístico o estocástico con el objeto de reflejar la variabilidad espacial y temporal del riesgo ambiental. Las metodologías propuestas son validadas mediante un caso de estudio real situado en el Mar Mediterráneo, en el Puerto de Tarragona.

Los objetivos específicos de la Tesis se centran en los siguientes aspectos:

1. Desarrollar una metodología para la integración del riesgo ambiental de los múltiples efectos producidos en los sistemas acuáticos como consecuencia de las actividades portuarias.
2. Desarrollar una metodología para la definición de escenarios de riesgo de emisiones difusas relacionadas con el manejo de hidrocarburos.
3. Desarrollar una herramienta basada en Sistemas de Información Geográfica para la estimación de la afección de derrames de hidrocarburos.

4. Desarrollar una metodología para la evaluación del riesgo ambiental de instalaciones de manejo de hidrocarburos.

3. Organización de la tesis

La Tesis está organizada de la siguiente manera:

En el *Capítulo I* se exponen los motivos por los cuales se ha realizado el presente trabajo de investigación y se presentan los objetivos específicos planteados.

En el *Capítulo II* se describe la zona de estudio y las escalas espaciales utilizadas en los diferentes estudios realizados en la tesis. Además, se muestran los datos físicos, datos de calidad ambiental y los datos relacionados con los peligros ambientales para cada una de las escalas utilizadas.

En los siguientes capítulos (III, IV, V y VI) se detallan los trabajos llevados a cabo para la consecución de los objetivos específicos de esta tesis. Cada uno de estos cuatro capítulos está compuesto por un resumen, una introducción, los objetivos específicos de cada estudio, un apartado de metodología, de implementación y de resultados y una discusión. De esta manera, cada capítulo es una versión editada de los artículos ya publicados o aceptados en revistas indexadas dentro del SCI.

En la Figura 1 se representa de manera gráfica la relación entre los objetivos específicos, los casos de estudio y los capítulos de esta Tesis.

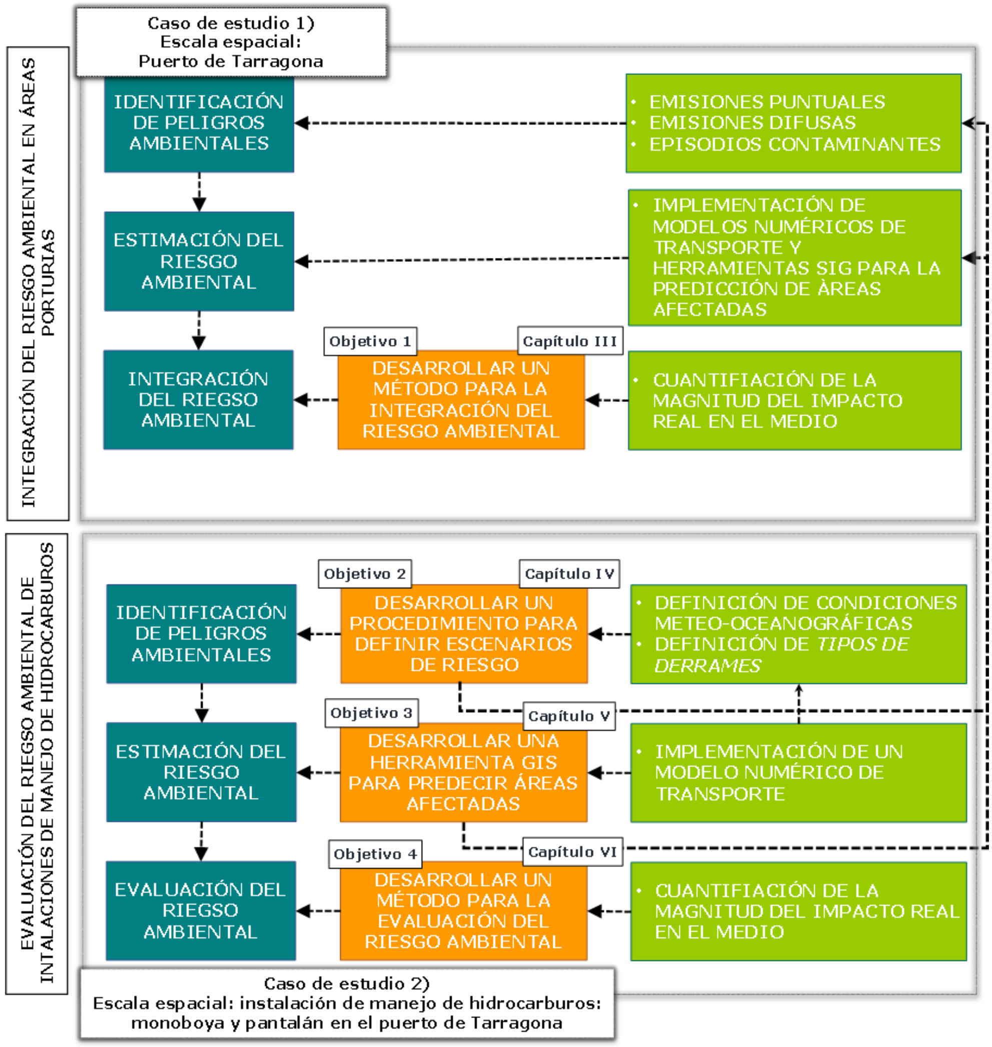


Figura 1. Resumen gráfico de la relación entre los objetivos específicos, los casos de estudio y los capítulos de esta Tesis.

En la Figura 2 se proporciona un resumen gráfico de los estudios desarrollados para dar respuesta a las cuestiones antes planteadas que han sido abordadas en esta tesis. Los estudios desarrollados son los siguientes:

- *Capítulo III*: *Método para la obtención de mapas de priorización en áreas portuarias*: en este capítulo se desarrolla una metodología para la elaboración de mapas de priorización mediante la integración del riesgo ambiental de los múltiples efectos producidos en los sistemas acuáticos como consecuencia de las actividades portuarias. A partir de los datos obtenidos de su implementación en el puerto de Tarragona, se lleva a cabo un estudio sobre la relación entre el impacto ambiental y el riesgo estimado.

- *Capítulo IV*: *Método para la definición de escenarios de riesgo de emisiones difusas: s*e presenta un método para la definición de escenarios en el análisis del riesgo ambiental de emisiones difusas. Este método se implementa en una instalación de manejo de hidrocarburos situada en el Puerto de Tarragona.

- *Capítulo V*: *Herramienta SIG para la evaluación del riesgo ambiental de derrames de hidrocarburos*: en este capítulo se presenta la herramienta SPILL Tool. Consiste en una herramienta SIG para la definición del área de afección potencial de instalaciones de manejo de hidrocarburos. La nueva herramienta se valida mediante la comparación entre los resultados obtenidos por la herramienta SPILL Tool y por un modelo numérico calibrado. La validación se realiza en el caso de estudio concreto de una instalación de manejo de hidrocarburos situada en el Puerto de Tarragona.

- *Capítulo VI*: *Método para la estimación del riesgo ambiental de derrames de hidrocarburos*: en este capítulo se propone una metodología para la definición espacial y temporal del riesgo ambiental de instalaciones de manejo de hidrocarburos mediante la incorporación del factor de consecuencias. Para ello, se lleva a cabo un estudio sobre la relación entre el impacto real medido y el riesgo estimado mediante la aproximación "Weight of Evidence" en una instalación de manejo de hidrocarburos en el Puerto de Tarragona.

Finalmente, en el *Capítulo VII* se enumeran las conclusiones generales y específicas de la tesis y se proponen futuras líneas de investigación.

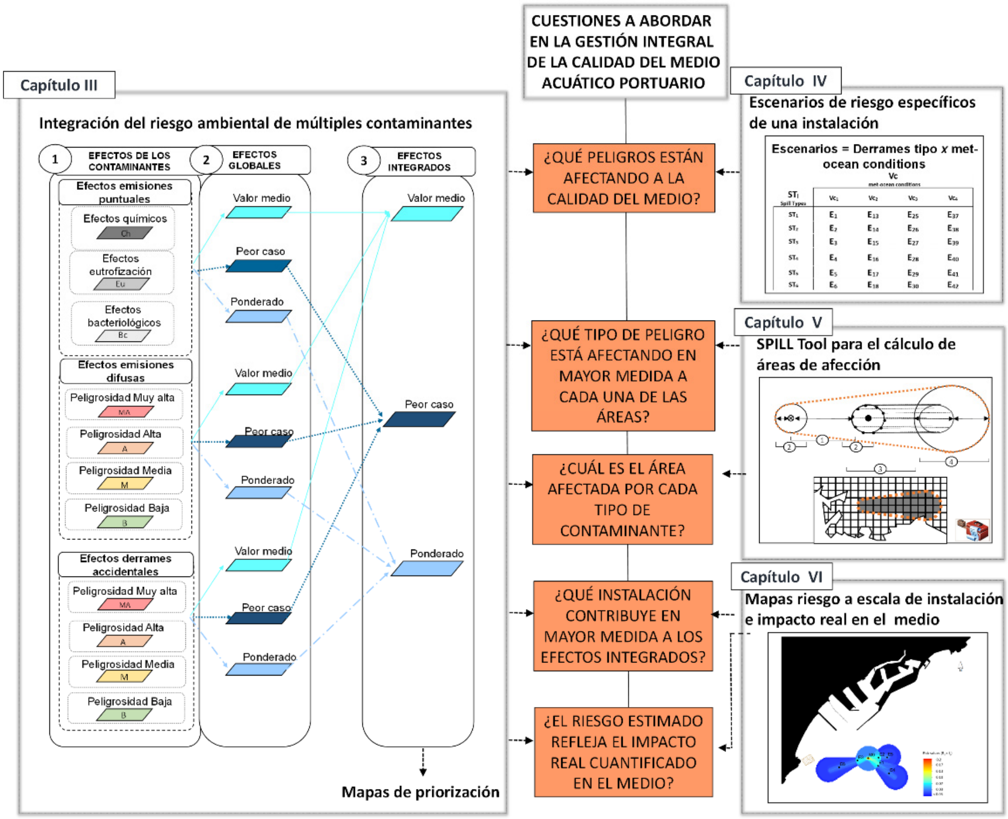


Figura 2. Resumen gráfico de los estudios desarrollados en el marco de esta Tesis para dar respuesta a las cuestiones planteadas.

4. Zona y escalas de estudio

Las metodologías y herramientas propuestas en esta Tesis se han desarrollado y validado a través de su implementación en el puerto de Tarragona. Para ello, se han definido dos escalas de trabajo espaciales: una escala global a nivel de puerto y una escala local a nivel de instalación. El capítulo III se desarrolla a escala portuaria mientras que los capítulos IV, V y VI se centran en una instalación específica de manejo de hidrocarburos del puerto de Tarragona. En la Figura 3 se muestra la localización del puerto de Tarragona y la instalación de manejo de hidrocarburos (monoboya y pantalán).

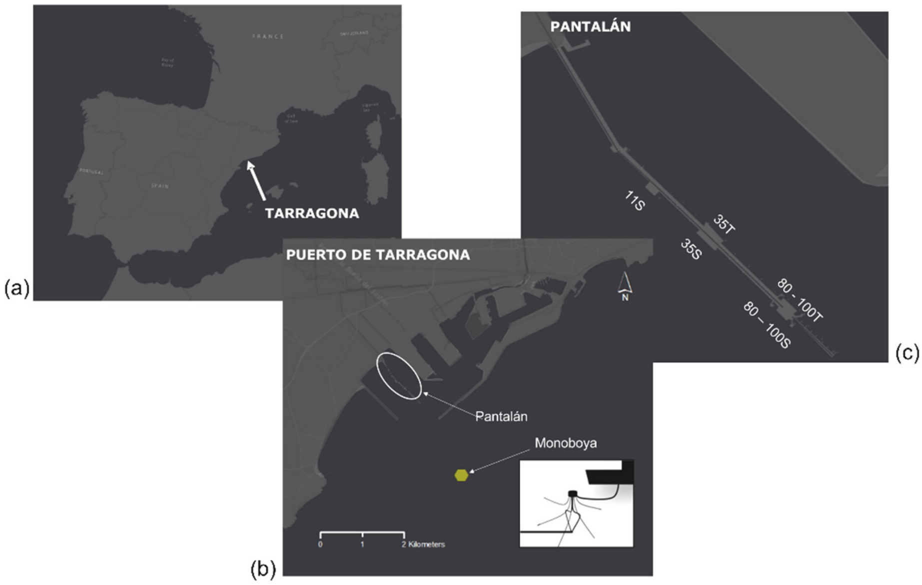


Figura 3. Localización de (a) Tarragona, (b) instalación de manejo de hidrocarburos (pantalán y monoboya) y esquema de la estructura de la monoboya y, (c) atraques del pantalán.

4.1 Escala portuaria: Puerto de Tarragona

El Puerto de Tarragona está localizado en el mar Mediterráneo, en el NE de la costa española (1º14'E, 41º05'N) (Figura 3). Es un puerto granelero industrial en cuyos alrededores se sitúa un gran complejo petroquímico que incluye una de las mayores refinerías de petróleo de España.

Los peligros ambientales considerados en los estudios desarrollados en esta tesis son las emisiones contaminantes y los episodios contaminantes. Las emisiones contaminantes se clasifican en puntuales o difusas según el modo en el que introducen los contaminantes en el medio acuático. Las *emisiones puntuales* son aquellas emisiones de sustancias o materiales contaminantes canalizadas por puntos fijos y predefinidos (escorrentías canalizadas, alivios de tormenta, vertidos puntuales, etc.) mientras que las *emisiones difusas* son aquellas emisiones de sustancias contaminantes o materiales no canalizadas (filtraciones, dragados, pérdidas, actividades de carga/descarga, etc.). Por otro lado, los *episodios contaminantes* son los derrames producidos de forma accidental y que puedan conllevar una reducción de la calidad del medio acuático (Juanes et al., 2013). En la

Figura 4 se muestran los peligros ambientales identificados en el puerto de Tarragona.

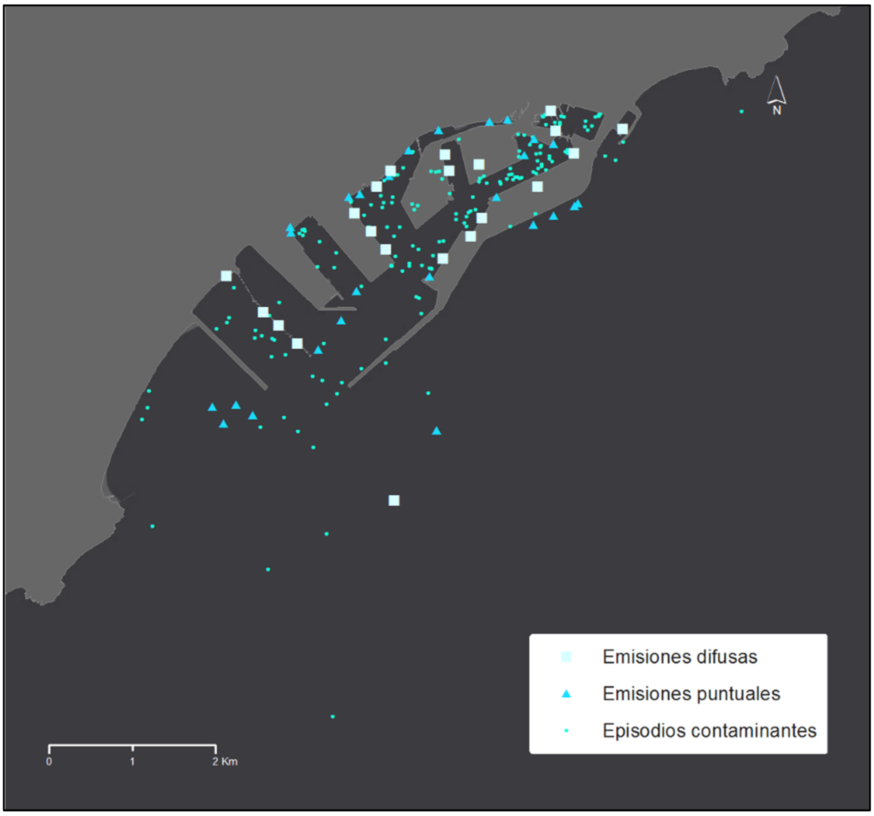


Figura 4. Localización de las emisiones puntuales y difusas identificadas y de los episodios contaminantes registrados en el Puerto de Tarragona (2007 -2015).

4.2 Escala local: instalación de carga y descarga de hidrocarburos de Repsol Petróleo

La instalación considerada para los estudios desarrollados a esta escala es la terminal de hidrocarburos del puerto de Tarragona (Figura 3 (b)). Está compuesta por un pantalán y una monoboya en los cuales se lleva operando desde 1975. La instalación comprende 6 puntos de descarga: un pantalán de 1489 m con 5 atraques (11S, 35S, 35T, 80-100S y 80-100T, Figura 3 (c)) para buques de 11000, 40000 y 100000 tonelaje de paso muerto (TPM), y un muelle flotante (monoboya, Figura 3 (b)) para el amarre y carga/descarga de buques de entre 250000 y 325000 TPM. El calado en la monoboya es de alrededor de 40 m, mientras que en el pantalán la máxima profundidad es de alrededor de 15 m. Tanto el pantalán como la monoboya son puntos de carga y descarga activos con 6 y 4.2 millones de Tn de mercancías manejadas en 2014, respectivamente. La monoboya tiene dos mangueras flotantes para crudo y una manguera para repostaje de fuel oil (Figura 5).

Figura 5. Buque operando en la monoboya del Puerto de Tarragona.

En el pantalán, los buques hacen uso de dos tuberías para crudo con capacidad de 4800 – 10000 Tn^3/h, una tubería para nafta, una tubería para delastrar, 6 tuberías para fuel-oil, gas-oil gasolina y gas-oil. Además, en esta instalación se maneja queroseno, gasolina de pirólisis, propano, etileno, propileno, diésel, octano y butileno, butadieno, agua dulce y diversos gases.

A nivel de instalación los peligros ambientales considerados son los episodios contaminantes. La información sobre los episodios contaminantes se obtuvo mediante la consulta de: i) los informes de emergencia del centro de Coordinación de Salvamento Marítimo (CCS Tarragona) (1998-2011); ii) el registro de episodios contaminantes de la Autoridad Portuaria de Tarragona (1985-2012); y, iii) el registro de episodios contaminantes de Repsol Petróleo, S.A. (1997-2011). Se identificaron un total de 22 episodios contaminantes ocurridos en la monoboya y el pantalán en el periodo 1989 – 2012.

5. Método para la obtención de mapas de priorización en áreas portuarias

En este apartado se incluye una versión editada del artículo de investigación publicado, en la revista Marine Pollution Bulletin. 111: 57-67, por Valdor, P.F., Gómez, A.G., Ondiviela, B., Puente, A., y Juanes J.A., en 2016, con el título "Prioritization maps: the integration of environmental risk to manage water quality in harbor areas".

En este capítulo se propone una metodología para la elaboración de mapas de priorización mediante la integración del riesgo ambiental de los múltiples efectos producidos en los sistemas acuáticos como consecuencia de las actividades portuarias. El método desarrollado se estructura en cuatro fases que comprenden: i) la identificación de los peligros ambientales; ii) la estimación de las consecuencias (efectos integrados); iii) la estimación de la vulnerabilidad (características del medio); y, iv) la integración de los riesgos ambientales (mapas de priorización) (Figura 6).

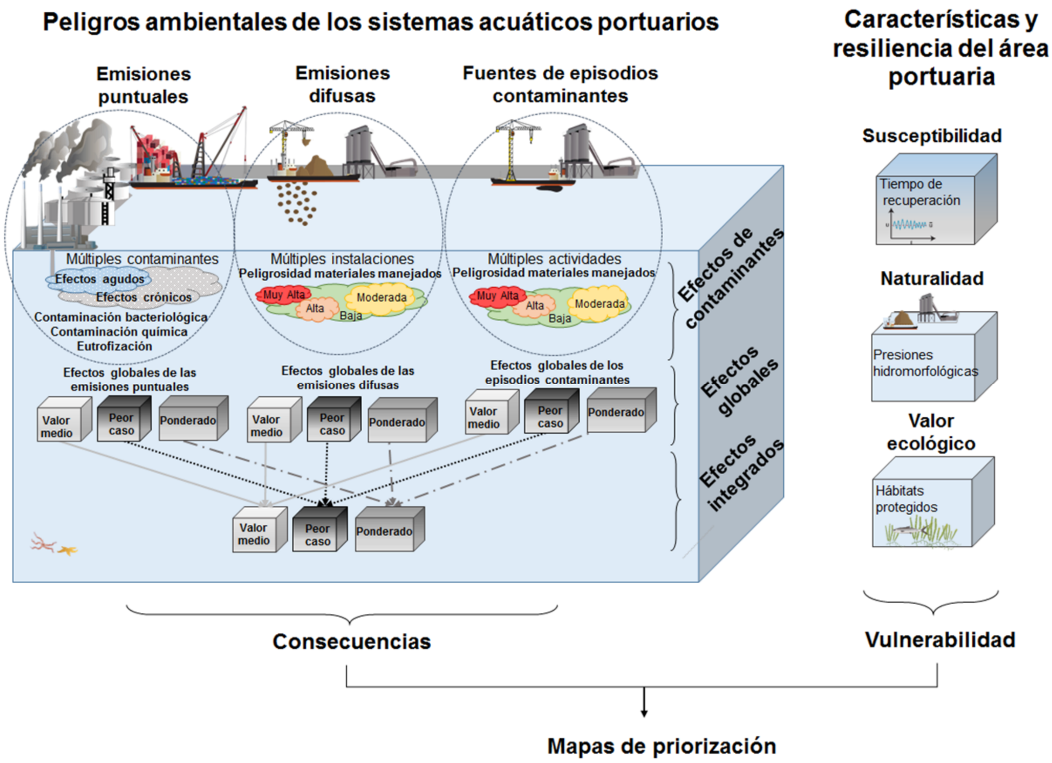


Figura 6. Resumen gráfico de la metodología propuesta para la elaboración de mapas de priorización para la gestión de sistemas acuáticos portuarios.

En primer lugar, para identificar los peligros ambientales, se localizan y caracterizan las emisiones puntuales, emisiones difusas y fuentes de derrames accidentales. Para caracterizar las emisiones puntuales y difusas es necesario recopilar información sobre su localización, contaminantes descargados o manejados, caudales (en el caso de las emisiones puntuales), cantidades manipuladas (en el caso de las emisiones difusas) y frecuencia de ocurrencia (en el caso de derrames accidentales). Para ello, se consultan diferentes fuentes de información como son las autorizaciones de vertido, el Registro Estatal de Emisiones y Fuentes Contaminantes (PRTR) y las bases de datos locales de episodios contaminantes (Gómez et al., 2015; Valdor et al., 2015).

En segundo lugar, se estiman los efectos de los peligros ambientales identificados. En este trabajo, los efectos integrados se definen como los producidos en el medio como resultado de la existencia de todos los peligros ambientales. La estimación de los efectos se realiza mediante 3 niveles sucesivos (Figura 7) que comprenden: i) el cálculo de los efectos de cada contaminante; ii) la estimación del efecto global asociado a cada peligro ambiental; y, iii) el cálculo del efecto integrado de todos los peligros ambientales presentes en la zona de estudio. Con el fin de adaptar los mapas de priorización a las peculiaridades de la zona de estudio así como a la escala espacial y al propósito de la gestión, se proponen tres métodos diferentes para la integración de los efectos: i) el método del Valor medio; ii) el método del Peor caso; y, iii) el método Ponderado. El método del Valor medio se basa en el concepto de "similar action" (Cedergreen et al., 2008) que presupone una acción similar de los componentes de una mezcla. El método del Peor caso se basa en el concepto de "independent action" que asume que en una mezcla de contaminantes no existe interacción física, química o biológica por lo que cada contaminante tendrá un efecto ambiental independiente del efecto producido por el resto de contaminantes que componen dicha mezcla (Spurgeon et al., 2010). Finalmente, el método Ponderado considera que, en áreas portuarias, la contaminación química conlleva a un mayor impacto ambiental, mientras que la eutrofización y la contaminación bacteriológica suponen un menor riesgo y estima el efecto global de cada peligro ambiental asignando pesos a los distintos procesos.

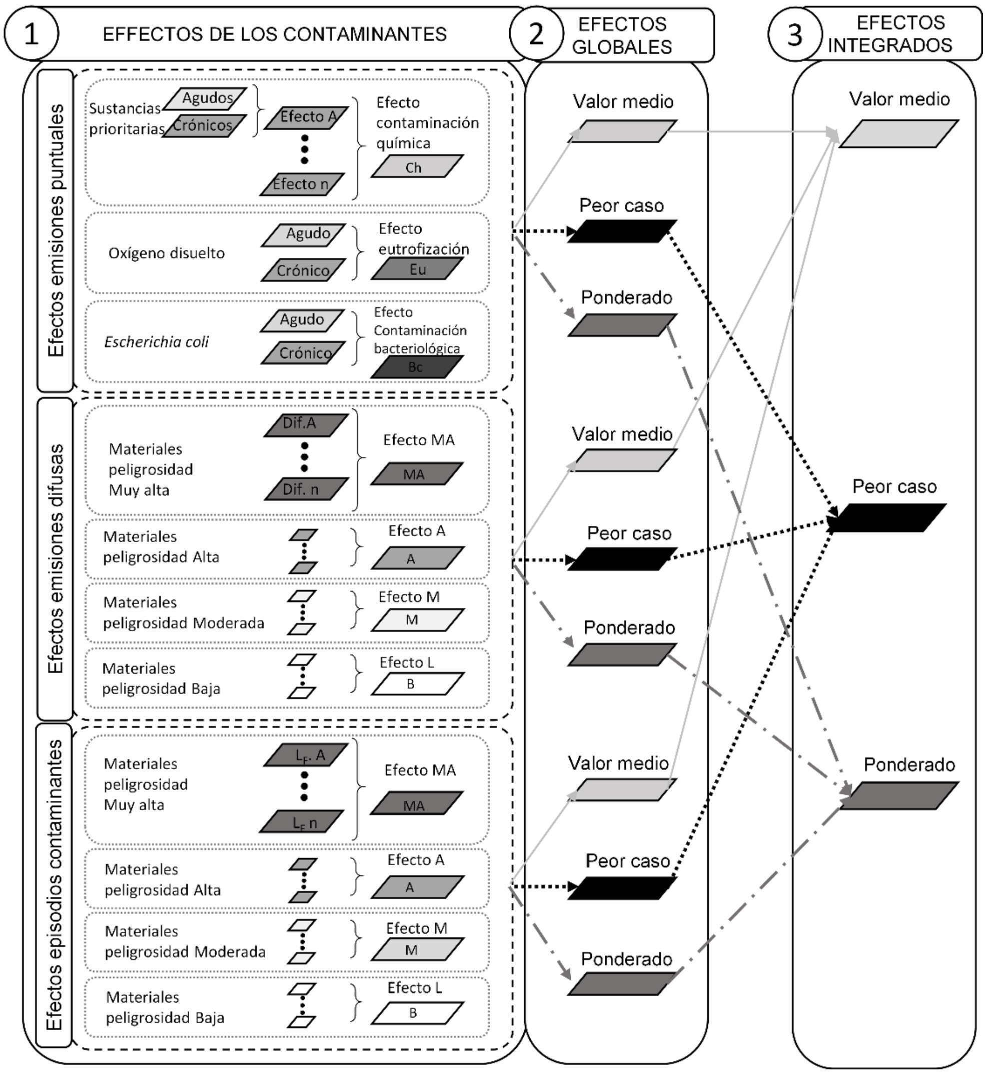


Figura 7. Resumen gráfico de la metodología para la obtención de efectos integrados.

En tercer lugar, se estima la vulnerabilidad del medio receptor considerando la susceptibilidad frente a posibles perturbaciones, su naturalidad y el valor ecológico de los potenciales receptores del medio. Para ello, se estima la capacidad de renovación del medio acuático mediante el cálculo del tiempo de recuperación (susceptibilidad) (Gómez, et al., 2014a), la alteración del medio producida por las presiones hidromorfológicas (naturalidad) (Gómez et al., 2014b) y la afección potencial de áreas sensibles según la Directiva 91/271/CEE (European Commission, 1991) y áreas incluidas en la Red Natura 2000 - Directiva 2009/147/CE (European Commission, 2009a); Directiva 92/43/CEE (European Commission, 1992) - (valor ecológico).

Finalmente, los efectos de los peligros ambientales y la vulnerabilidad del medio se combinan para obtener el mapa de priorización.

El método propuesto fue validado mediante su implementación en el puerto de Tarragona. Para ello, se identificaron y caracterizaron los peligros ambientales a los que está expuesto el medio acuático portuario en Tarragona: emisiones puntuales (26), emisiones difusas (21) y fuentes de episodios contaminantes (21). En segundo lugar, se calculó el área afectada por cada uno de los contaminantes asociados a los peligros ambientales identificados utilizando un modelo numérico 2D y herramientas SIG (Figura 7 (1)). Con ello, se estimaron los efectos agudos y crónicos de los contaminantes liberados por las emisiones puntuales, mediante modelado numérico, considerando tres tipos de procesos: i) contaminación química, producida por sustancias prioritarias - Directiva 2013/39/CE (European Commission, 2013a) - ; ii) eutrofización, medida como disminución de oxígeno disuelto; y, iii) contaminación bacteriológica, utilizando *Escherichia coli* como indicador (Gómez, 2010; Juanes et al., 2013). Los efectos contaminantes producidos por las emisiones difusas y los episodios contaminantes se estimaron mediante el uso de una herramienta SIG (Juanes et al., 2013) considerando la densidad y peligrosidad de los materiales manejados. Una vez conocidos los efectos de los contaminantes, se llevó a cabo su integración para estimar los efectos globales de cada peligro ambiental (Figura 7 (2)) mediante los tres métodos de integración. Finalmente, se llevó a cabo la tercera fase de integración (Figura 7 (3)) aplicando los mismos métodos de integración para la obtención de los efectos integrados.

Para estimar la susceptibilidad del medio, se llevó a cabo el cálculo del tiempo de recuperación a nivel de celda en toda el área de estudio (rango: 0-430 días). Para el cálculo de la naturalidad, se identificaron las presiones hidromorfológicas (52) mediante la planimetría proporcionada por la Autoridad Portuaria y fotografías aéreas y se estimó el área potencialmente alterada por cada una de ellas. El valor ecológico fue homogéneo para toda el área de estudio, ya que no se identificaron áreas protegidas dentro de la zona de servicio portuario. Finalmente, se combinaron los efectos integrados y la vulnerabilidad para obtener la variabilidad espacial del riesgo ambiental de la zona de servicio del puerto en cuatro categorías: bajo, moderado, alto y muy alto (Figura 8).

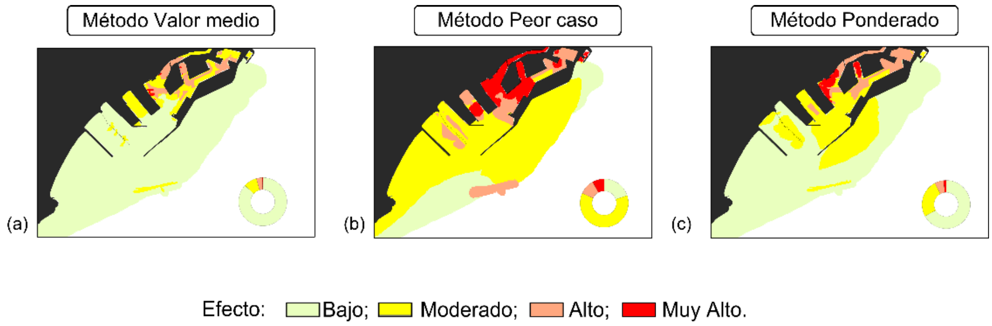


Figura 8. Representación de la variabilidad especial del riesgo ambiental obtenido mediante (a) método del Valor medio, (b) método del Peor caso y, (c) método Ponderado.

Como resultado se obtuvo que $1.9 \cdot 10^3$ Ha de la zona de servicio portuaria se encuentra bajo riesgo de afección por los peligros ambientales identificados en el puerto de Tarragona. Los valores más elevados del riesgo se localizaron en las áreas más confinadas, donde se identificaron la mayoría de las emisiones contaminantes. El método del valor medio mostró las estimaciones más permisivas, valorando el 84% del área total afectada con un riesgo ambiental bajo. Por el contrario, el método del peor de los casos arrojó las estimaciones más restrictivas, siendo el método que presentó mayor porcentaje de área afectada valorada con un riesgo ambiental muy alto (7%). Finalmente, el método ponderado mostró un 70% del área afectada con un riesgo ambiental bajo, mientras que únicamente el 1% presentó un riesgo muy alto.

Con el objetivo de analizar la correspondencia entre los valores de riesgo estimados y el impacto real sobre el medio, se consideraron datos tomados durante los años 2009, 2010 y 2011 de variables de agua medidas estacionalmente (invierno-verano-otoño-primavera) y variables de sedimento medidas anualmente en 9 estaciones de muestreo localizadas en la zona de servicio portuario (Figura 9). Las variables consideradas fueron nutrientes (amonio, nitratos, nitritos, fosfatos y silicatos), condiciones de transparencia (turbidez), condiciones de oxigenación (saturación de oxígeno), salinidad, metales pesados (plomo, níquel y zinc) y elementos biológicos (clorofila *a*) en agua. En el sedimento se consideraron nutrientes (nitrógeno total Kjeldahl, carbono orgánico total), metales pesados (arsénico, cobre, cromo total, plomo, mercurio, níquel y zinc) e hidrocarburos aromáticos policíclicos (benzo(b)fluoranteno, benzo(a)antraceno, benzo(a)pireno, benzo(ghi)perileno, criseno, fluoranteno, indeno(1,2,3-c,d)pireno y fenantreno).

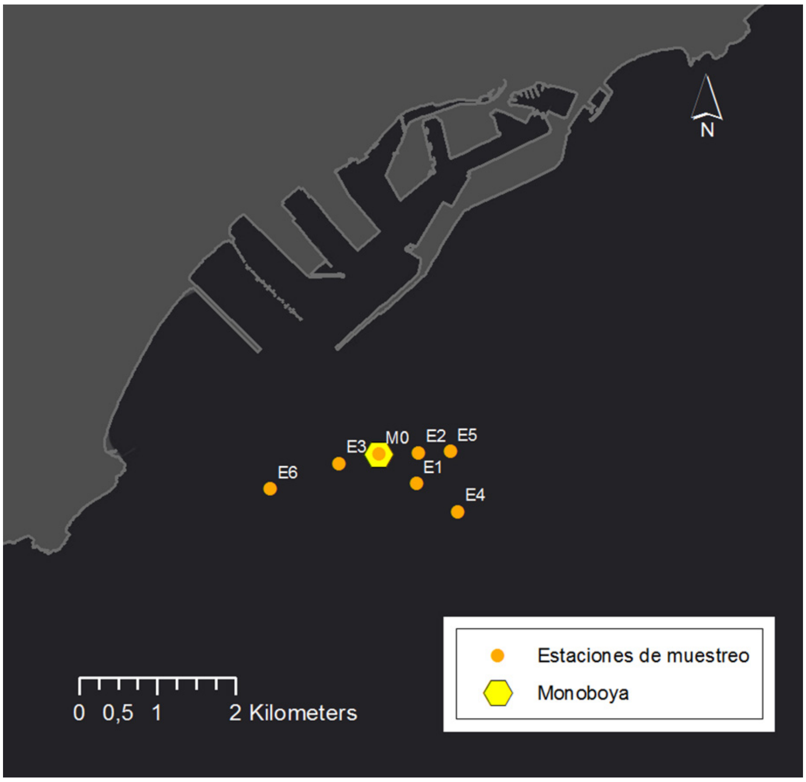


Figura 9. Localización de las estaciones de muestreo en la monoboya del Puerto de Tarragona.

La correlación obtenida fue significativa ($|r|>0.7$ y $p<0.05$) entre los valores del riesgo estimados mediante los tres métodos de integración y las variables clorofila *a* y nitratos en agua, y plomo en el sedimento. Los valores del riesgo estimados mediante los métodos del Valor medio y Ponderado obtuvieron correlaciones significativas con el carbono orgánico total en sedimento.

A partir de los resultados obtenidos en la implementación al Puerto de Tarragona se concluye que el método propuesto permite integrar las estimaciones de la variabilidad espacio-temporal de los contaminantes y sus efectos en áreas portuarias. Los mapas de priorización, fácilmente interpretables, son combinación de distintas fuentes de contaminación (puntual, difusa, episodios contaminantes), de varios impactos potenciales (contaminación química, eutrofización, contaminación bacteriológica) y de diferentes materiales (peligrosos o potencialmente peligrosos). Los métodos de integración planteados en este estudio se encuentran significativamente correlacionados con el impacto real sobre el medio. Por todo ello, se considera que los diferentes métodos de integración pueden ser utilizados indistintamente, pudiéndose adaptar a la escala de aplicación deseada y las peculiaridades de cada zona específica de estudio, así como al propósito de la gestión ambiental. La implementación de la metodología propuesta a un caso real confirmó su utilidad como herramienta para la toma de decisiones en la gestión integral de la calidad de los sistemas acuáticos portuarios.

6. Método para la definición de escenarios de riesgo de emisiones difusas

En este apartado se incluye una versión editada del artículo de investigación publicado, en la revista Marine Pollution Bulletin. 90 (1-2): 78-87, por Valdor, P. F., Gómez, A. G. y Puente, A., con el título "Environmental risk analysis of oil handling facilities in port areas. Application to Tarragona harbor (NE Spain)".

En este capítulo se propone una metodología para evaluar en términos espaciales y temporales el riesgo ambiental de instalaciones de manejo de hidrocarburos mediante la definición de escenarios de riesgo específicos de la instalación (*Derrames tipo)* y de la zona de estudio (*condiciones meteo-oceanográficas*). El método desarrollado se estructura en cuatro fases que comprenden: i) la identificación de los peligros ambientales; ii) la caracterización de las condiciones meteorológicas y oceanográficas; iii) la caracterización de los escenarios de riesgo; y, iv) la evaluación del riesgo ambiental.

En primer lugar, para definir los derrames tipo, se identifica la instalación y sus puntos de descarga potenciales. Con base en la información registrada sobre los episodios contaminantes ocurridos en la instalación objeto de estudio, se lleva a cabo una estimación de la cantidad, densidad del producto y frecuencia de ocurrencia de cada tipo de derrame potencial (Figura 10 (1)).

En segundo lugar, se definen las condiciones meteorológicas y oceanográficas más probables del área de estudio. Mediante la aplicación de la técnica estadística de clasificación k-medias a una base de datos meteorológica y oceanográfica suficientemente extensa (≥15 años), se obtienen grupos de condiciones ambientales. A partir de los centroides representativos de cada uno de los grupos se definen las condiciones meteo-oceanográficas más probables del área de estudio (Figura 10 (2)).

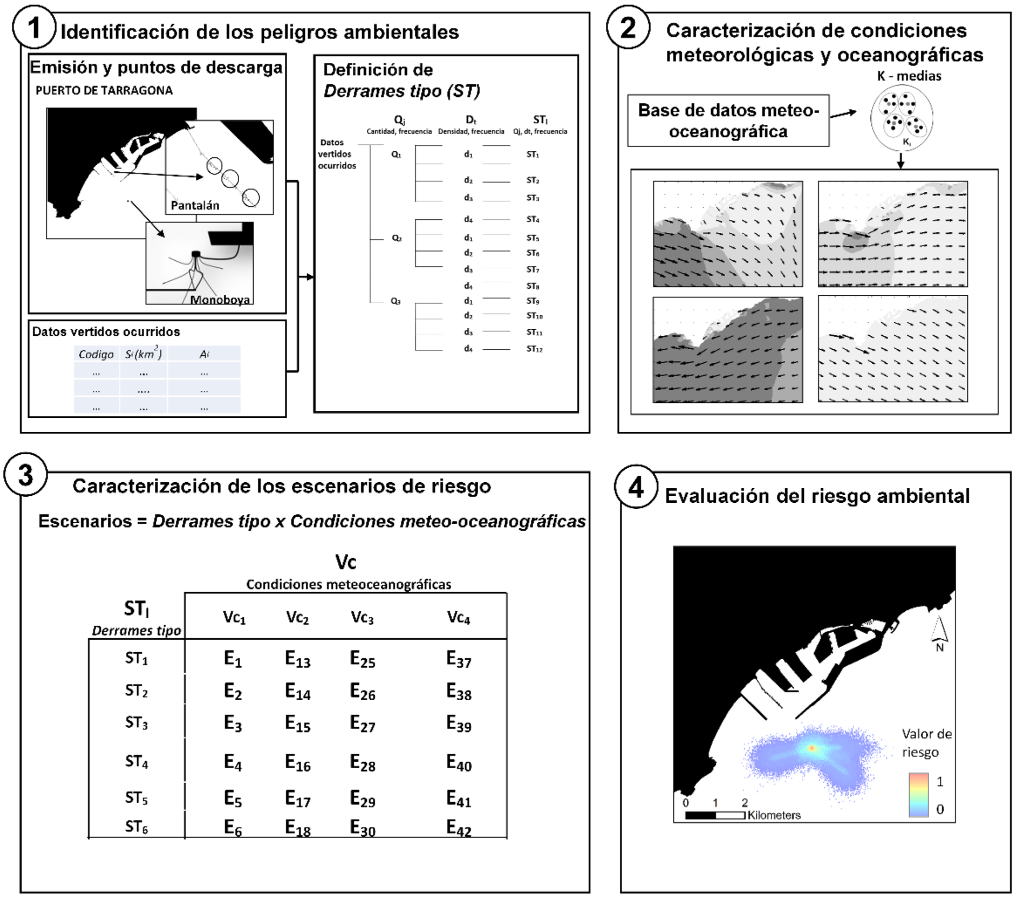


Figura 10. Resumen gráfico de la metodología para el análisis del riesgo ambiental de emisiones difusas por hidrocarburos y su implementación en Tarragona.

En tercer lugar, se definen los escenarios del riesgo específicos de la instalación objeto de estudio. Para ello, se lleva a cabo la combinación de los derrames tipo específicos de la instalación y las condiciones meteo-oceanográficas más probables de la zona de estudio. De esta manera, cada escenario estará asociado a la probabilidad de que, en caso de ocurrencia de un derrame, éste sea un *Derrame tipo* específico sometido a unas condiciones meteo-oceanográficas determinadas (Figura 10 (3)).

Finalmente, mediante el uso de modelos numéricos, se estima espacialmente el riesgo ambiental de cada escenario de riesgo para cada punto de descarga potencial de la instalación con una probabilidad asociada. Así, para obtener el riesgo ambiental espacial de cada punto de descarga, se realiza la integración del riesgo ambiental estimado para cada escenario a nivel de celda (Figura 11). El producto final es un mapa de riesgo ambiental de áreas potencialmente afectadas en términos espaciales y probabilísticos.

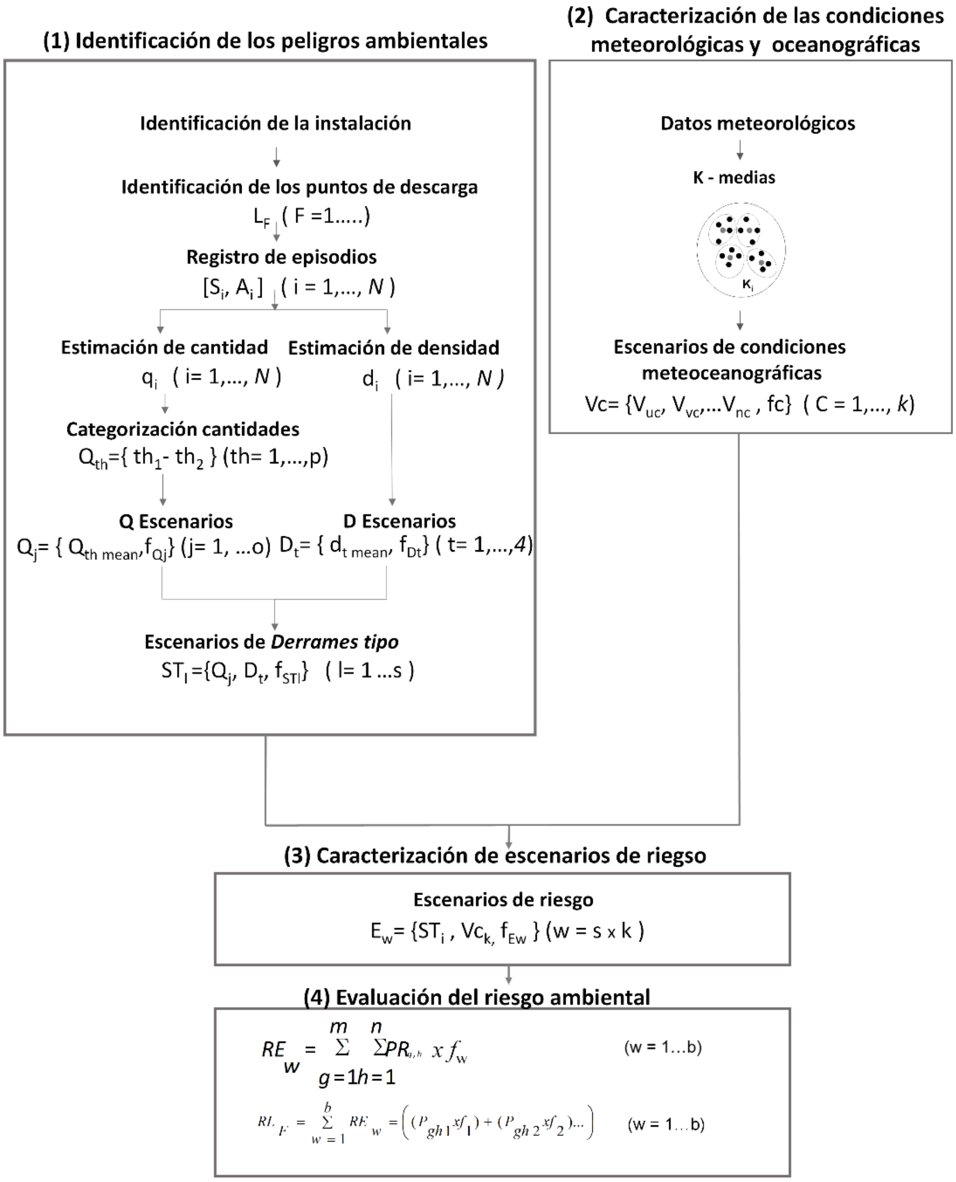


Figura 11. Esquema de la metodología propuesta para la definición de escenarios de riesgo de emisiones difusas relacionadas con el manejo de hidrocarburos.

El método propuesto fue validado mediante su implementación en la monoboya de Repsol Petróleo, S.A. del puerto de Tarragona. Se analizaron los datos registrados de episodios contaminantes ocurridos en la monoboya considerando la apariencia del derrame en el medio y la extensión del área afectada de cada uno de ellos. A partir del análisis de estos datos se establecieron 3 categorías de cantidades y 4 categorías de densidades de producto, de cuyo cruce se obtuvieron 12 *Derrames tipo* específicos de la instalación (Figura 11 (1)).

Por otro lado, para esta zona de estudio, se identificaron 4 condiciones meteo-oceanográficas representativas (Figura 11 (2)). A partir del cruce de los 12 Derrames tipo y las 4 condiciones meteo-oceanográficas se definieron 48 escenarios de riesgo característicos de la monoboya asociados a una probabilidad concreta (Figura 11 (3)). Los escenarios se utilizaron en la evaluación del riesgo ambiental de la instalación.

Para cada uno de los 48 escenarios de riesgo se calculó el transporte del hidrocarburo en el medio mediante un modelo numérico 2D con un tiempo de simulación de 2 horas. Los resultados de las diferentes simulaciones, a nivel de celda, comprendidos en valores de 0 a 1, fueron integrados obteniéndose un área total de afección potencial alrededor de la monoboya de 5.6 km^2 (Figura 12). El valor medio del riesgo fue de 0.1, presentado un valor máximo de 1 (localizado en las inmediaciones de la monoboya) y un valor mínimo de 0.003 (en las zonas más alejadas a la misma).

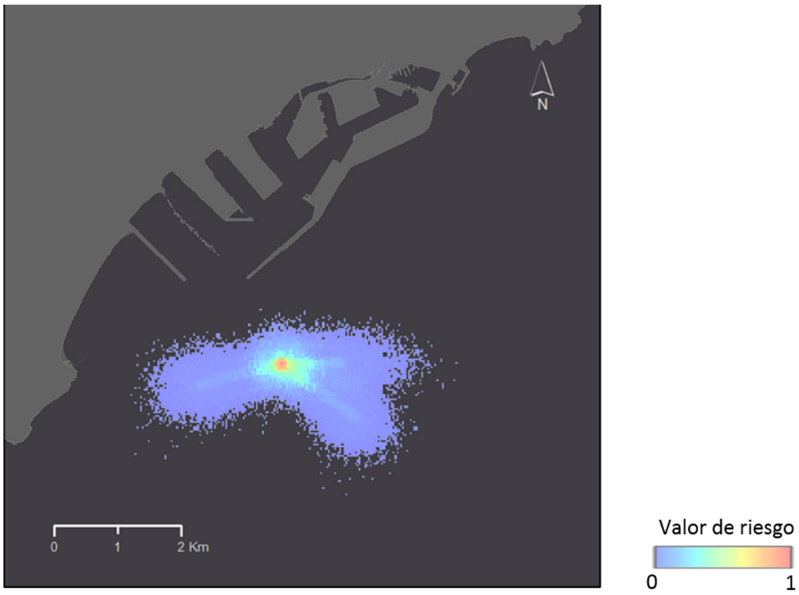


Figura 12. Representación espacial del riesgo ambiental de la monoboya del puerto de Tarragona.

A partir de los resultados obtenidos en la implementación al Puerto de Tarragona, se concluye que el método propuesto permite identificar y caracterizar los peligros ambientales de una instalación aun cuando no existe información detallada de los incidentes ambientales ocurridos. Además, los resultados cuantitativos obtenidos para la monoboya permiten afirmar que los productos vertidos no son transportados de manera lineal en el medio sino que las áreas afectadas forman conos o elipses a partir del punto de descarga cuya forma y extensión está determinada por la combinación de la cantidad y densidad del producto vertido en un escenario específico y por las condiciones ambientales. Por lo tanto, la consideración de escenarios específicos que definan las características de los productos susceptibles de ser vertidos, así como la consideración de las componentes espacial y temporal en el análisis del riesgo, son imprescindibles para llevar a cabo una descripción realista del área de afección potencial de las instalaciones de manejo de hidrocarburos.

Cabe destacar que, los resultados obtenidos mediante la aplicación del método propuesto podrían aplicarse en el diseño de programas de vigilancia ambiental para la evaluación del impacto de instalaciones de manejo de hidrocarburos. Además, la distribución espacial y temporal del riesgo obtenida podría permitir a los gestores identificar los potenciales conflictos ambientales entre la instalación objeto de estudio y los recursos económicos y ambientales cercanos (servicios y usos del área potencialmente afectada, infraestructuras, bienes ambientales, etc.). En consecuencia, el método presentado en este capítulo constituye una herramienta adecuada para la toma de decisiones en la gestión integral de la calidad de los sistemas acuáticos portuarios.

7. Herramienta SIG para la evaluación del riesgo ambiental de derrames de hidrocarburos

En este apartado se incluye una versión editada del artículo de investigación publicado, en la revista Journal of Environmental Management. 170: 105-115, por Valdor, P. F., Gómez, A. G., Velarde, V., y Puente, A., con el título "Can a GIS toolbox assess the environmental risk of oil spills? Implementation for oil facilities in harbors".

En este capítulo se describe la herramienta SPILL Tool, desarrollada para la evaluación espacial y temporal del riesgo ambiental de instalaciones de manejo de hidrocarburos en zonas cercanas a la costa (Figura 13).

La herramienta ha sido desarrollada en ArcGIS (10.1) usando la librería de Python para ArcGIS. SPILL Tool se carga de manera sencilla a través de la ventana de ArcToolbox de ArcGIS (ArcGIS 10.1 by ESRI^{TM}). Su uso es simple, intuitivo y está guiado a través de una interfaz gráfica amigable. Los procesos de cálculo de la herramienta pueden ser integrados bajo el geoprocesador de ArcGIS de manera que puedan ser fácilmente combinados con otros procesos en nuevos flujos de trabajo o modelos con *ModelBuilder*.

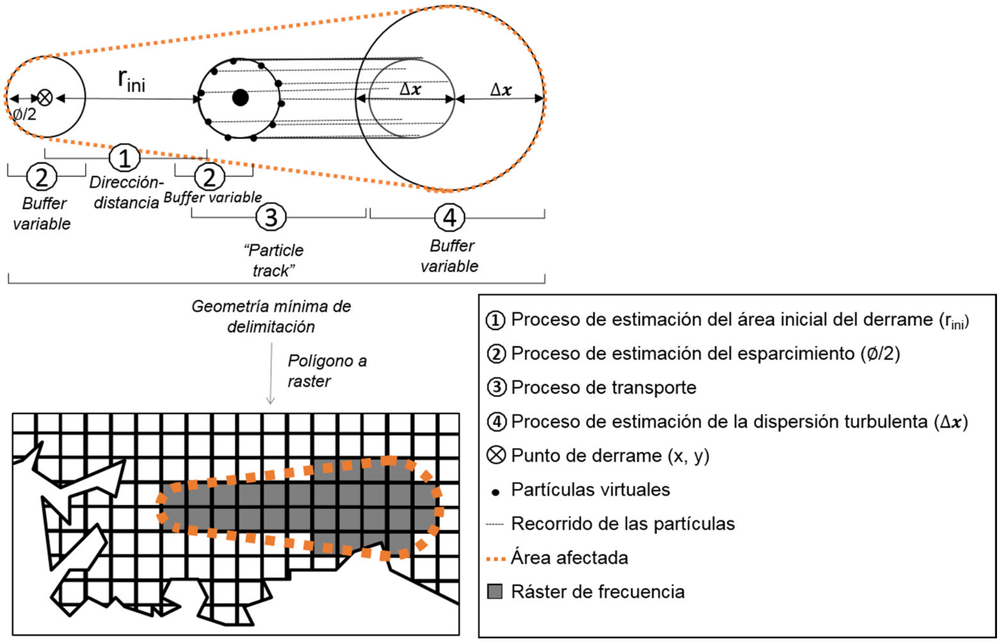


Figura 13. Resumen gráfico de los procesos de cálculo de la herramienta SPILL Tool.

Los procesos de cálculo de la herramienta están basados en cuatro etapas diferenciadas:

1. Área inicial del derrame: el cálculo del área inicial del derrame se estima en función de la cantidad de producto derramada y la densidad del mismo.
2. Esparcimiento: la estimación del esparcimiento del hidrocarburo en el medio se calcula considerando la cantidad y densidad del producto derramado y el tiempo de respuesta ante el derrame (tiempo de simulación).
3. Transporte: el transporte y trayectoria del hidrocarburo derramado se estima mediante el uso de una herramienta de transporte de partículas conservativas que calcula la dispersión virtual de las partículas para unas

condiciones hidrodinámicas específicas.

4. Dispersión turbulenta: el desplazamiento del derrame debido al proceso de dispersión turbulenta se calcula con base en el valor del coeficiente de dispersión y el tiempo que el producto derramado permanece en el medio.

Finalmente, SPILL Tool proporciona un ráster de salida que contiene el área potencialmente afectada para un escenario específico: un derrame tipo asociado a unas condiciones meteo-oceanográficas concretas (ver apartado 6).

La herramienta SPILL Tool se implementó en la monoboya y en los tres puntos de descarga (P11, P35 y P80-100) del pantalán de Repsol Petróleo S.A. en el puerto de Tarragona. Para ello, se consideraron los 48 escenarios de derrame tipo previamente definidos (ver apartado 6). A cada uno de los 4 puntos de descarga potenciales de dicha instalación se aplicaron los 48 escenarios, realizándose un total de 192 simulaciones (Figura 14).

Las áreas afectadas calculadas usando la herramienta SPILL Tool fueron comparadas espacialmente con los resultados obtenidos mediante la aplicación de un modelo numérico de transporte de hidrocarburos bidimensional calibrado: TESEO 2D (Abascal et al., 2007). Para cada una de las 192 simulaciones se consideró satisfactorio un porcentaje de coincidencia superior al 70% de la superficie afectada. Además, se llevó a cabo una evaluación estadística comparativa de los valores del riesgo estimados a nivel de celda, utilizando el RMSE (observación de la desviación estándar, RSR) (Bennett et al., 2013). Valores de $RSR \leq 0.70$ se consideraron resultados satisfactorios.

El 89.1% de las simulaciones realizadas obtuvieron porcentajes de coincidencia mayores del 70%. La mayoría de los casos con porcentajes menores (<70%) fueron derrames de productos de elevada densidad (0.96 and 0.98). Solo se obtuvieron porcentajes de coincidencia menores del 70% para dos escenarios de baja densidad (0.73 and 0.83). En cuanto a la evaluación estadística, el valor del índice RSR obtenido para la monoboya fue de 0.60. Para los puntos de derrame P35 y P80-100 del pantalán el valor del índice fue de 0.54, obteniéndose un valor de RSR de 0.51 para el punto de derrame P11.

Con base en los resultados obtenidos, pudo concluirse que la herramienta SPILL Tool es capaz de definir la variación espacial del riesgo ambiental asociado a una determinada instalación de manejo de hidrocarburos, siendo capaz de representar diferentes volúmenes y densidades de producto derramado, distintas localizaciones de los puntos de derrame y condiciones ambientales. Los resultados obtenidos en la implementación son satisfactorios, ya que muestran una buena correspondencia con los resultados obtenidos por un modelo numérico calibrado.

Por lo tanto, SPILL Tool es una herramienta precisa y adecuada para la gestión del riesgo ambiental de manejo de hidrocarburos. Sin embargo, su uso está limitado a zonas cercanas a la costa con un hidrodinamismo de menor magnitud que las aguas abiertas y a áreas en las que el derrame es rápidamente detectado y retirado, es decir, con tiempos de simulación cortos (alrededor de 2-4 horas). En zonas portuarias donde se cumplen estas condiciones, SPILL Tool constituye una herramienta útil para el análisis del riesgo de derrames de hidrocarburos que se caracteriza por ser rápida, simple y con posibilidades de ser manejada por una gran cantidad de usuarios potenciales “no expertos “.

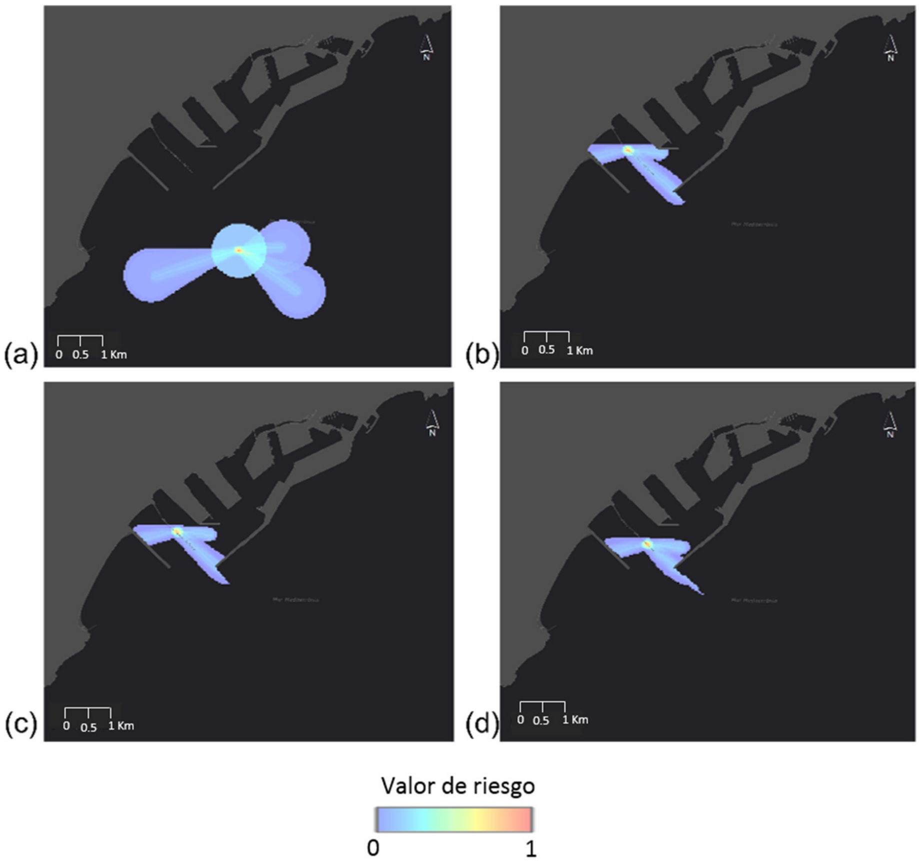


Figura 14. Representación espacial del riesgo ambiental y las áreas de afección potencial en (a) la monoboya y los puntos de descarga, (b) P11, (c) P35 y, (d) P80-100 del pantalán en el puerto de Tarragona.

8. Método para la estimación del riesgo ambiental de derrames de hidrocarburos

En este apartado se incluye una versión editada del artículo de investigación elaborado por Valdor, P. F., Puente, A., Gómez, A. G., Ondiviela, B. y, Juanes J.A., con el título "Are environmental risk estimations linked to the actual environmental impact? Application to an oil handling facility (NE Spain)" aceptado por la revista Marine Pollution Bulletin en septiembre de 2016.

Las instalaciones destinadas a la manipulación de hidrocarburos en áreas portuarias se caracterizan por la ocurrencia de derrames de pequeña magnitud, pero mantenidos en el tiempo, por lo que cabe esperar una respuesta del medio frente a este tipo de contaminación. Bajo esta hipótesis, en este capítulo se propone una metodología para la definición espacial y temporal del riesgo ambiental de instalaciones de manejo de hidrocarburos mediante la incorporación del término de las consecuencias ambientales.

Para validar la metodología desarrollada, en la monoboya de Repsol Petróleo, S.A. del Puerto de Tarragona se estiman las consecuencias y se cuantifica el impacto real sobre el medio mediante el análisis de contaminantes en el sedimento (contaminación), la respuesta a nivel de individuo (toxicidad) y los efectos a nivel de comunidad biológica (polución), siguiendo la aproximación "Weight of Evidence". Con ello, se lleva a cabo un estudio sobre la relación entre el impacto real y el riesgo ambiental estimado (Figura 15).

El cálculo del riesgo ambiental se estima considerando la presencia de producto derramado, la probabilidad asociada a cada escenario (ver apartado 6) y las consecuencias a nivel de celda. Las consecuencias se expresan en términos de persistencia en el medio de los productos derramados y su afección potencial. La persistencia se tiene en cuenta mediante: i) el porcentaje de contaminante de producto susceptible de causar un impacto en el medio; y, ii) el porcentaje de producto susceptible de ser evaporado una vez derramado. El riesgo ambiental a nivel de instalación se estima combinando el valor de riesgo en cada celda de los escenarios de riesgo previamente establecidos.

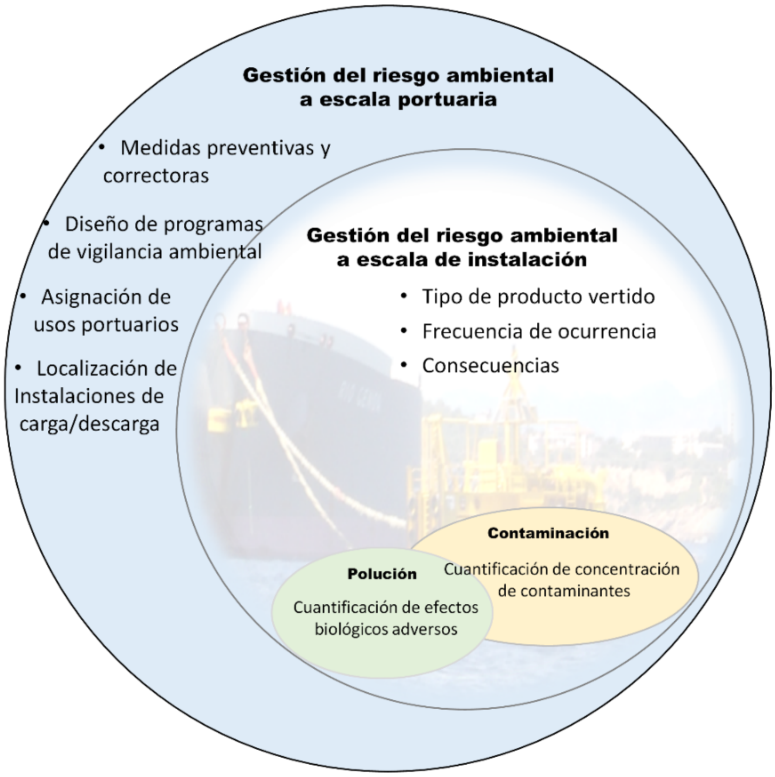


Figura 15. Representación gráfica de la aproximación seguida en el estudio llevado a cabo en la monoboya del puerto de Tarragona para la definición de un método para el análisis del riesgo de instalaciones de manejo de hidrocarburos.

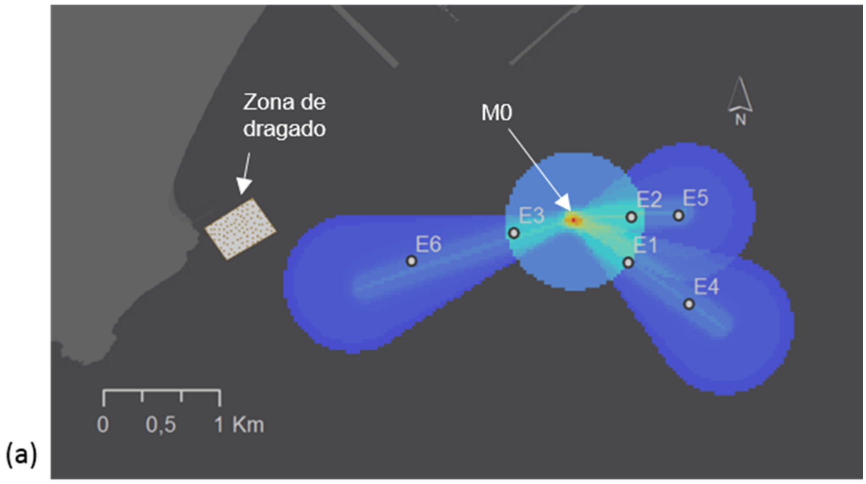
En el caso concreto de la monoboya, la presencia de producto se calculó mediante la herramienta SPILL Tool (ver apartado 7), de acuerdo con los derrames tipo definidos por los escenarios de riesgo específicos establecidos para esta instalación (ver apartado 6). El área total de afección estimada considerando las consecuencias fue 3.2 km^2 menor que el área total estimada considerando únicamente la presencia/ausencia de producto en términos probabilísticos. Además, los valores de riesgo medio, mínimo y máximo fueron menores cuando se consideraron las consecuencias (Figura 16).

Por su parte, las consecuencias se estimaron de acuerdo con aquellos contaminantes específicos detectados en el medio (HAP) que presentaron una variación espacial dentro del área potencial de afección de la instalación. Para ello, se tomaron muestras de 7 estaciones localizadas en el área potencial de afección de acuerdo con las trayectorias preferentes de los derrames tipo (Figura 15). Con el objetivo de cuantificar la contaminación en el sedimento y su impacto ambiental, se midió la concentración de contaminantes en sedimento (contaminación), la respuesta a nivel de individuo (test de toxicidad: inhibición de bioluminiscencia de *Vibrio fischeri* y desarrollo embrionario de *Paracentrotus lividus*) y los efectos a nivel de la comunidad biológica (macroinvertebrados) (polución).

Los resultados de los análisis realizados en los sedimentos mostraron que los contaminantes que contribuyen en mayor medida a la variabilidad espacial de la contaminación en el área potencial de afección de la monoboya de Repsol son los hidrocarburos aromáticos policíclicos, entre ellos: el benzo(a)antraceno, el benzo(a)pyreno, el criseno, el benzo(g,h,i)perileno, el benzo(k)fluoranteno, fluoranteno, indeno(1,2,3-cd)pireno y el antraceno. Por su parte, la comunidad de macroinvertebrados reflejó un impacto moderado en todas las muestras analizadas, no existiendo variabilidad entre estaciones, siendo dominantes las especies tolerantes a la materia orgánica de acuerdo con los grupos ecológicos definidos en el índice MEDOCC. Respecto a los test de toxicidad, los valores de toxicidad más elevados se detectaron en las estaciones M0 y E6.

Por último, se llevó a cabo un análisis de correlación de Spearman a nivel de estación entre los valores de riesgo obtenidos mediante la metodología propuesta y los indicadores de contaminación (concentración de contaminantes) e impacto (índices de comunidades bentónicas, test de toxicidad). Se encontraron correlaciones significativas ($|r|>0.7$) entre la concentración de benzo(a)antraceno y benzo(a)pireno y los valores de riesgo estimados. No se encontró correlación entre el riesgo y los indicadores de impacto analizados. Por lo tanto, los resultados del riesgo ambiental estimados considerando la persistencia y el efecto potencial se correlacionan significativamente con los niveles de contaminación, pero no con los efectos biológicos observados (polución).

De los análisis realizados en este estudio se puede concluir que, en términos generales, los resultados del riesgo ambiental estimados teniendo en cuenta la presencia/ausencia de contaminantes en el medio sobreestiman el impacto real de una fuente contaminante. Por ello, se deben considerar las consecuencias asociadas a los contaminantes específicos manejados en la instalación objeto de estudio para obtener una valoración del riesgo ambiental más realista.



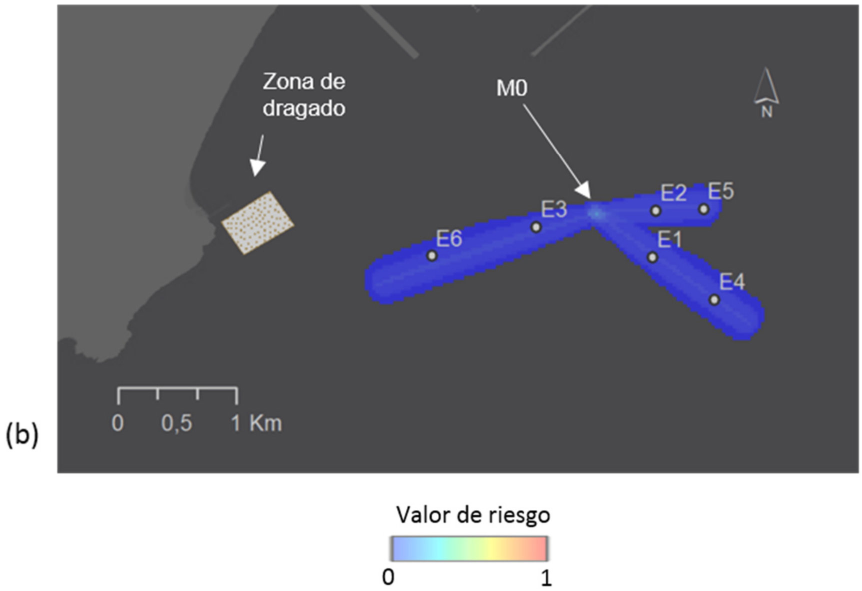


Figura 16. Representación de la variación espacial del riesgo ambiental en la monoboya estimado considerando (a) y no considerando (b) el término de Consecuencias.

9. Conclusiones generales y futuras líneas de investigación

En esta tesis se han desarrollado aproximaciones cuantitativas basadas en análisis estocásticos y probabilísticos para la evaluación del riesgo de los peligros ambientales en áreas portuarias. Los resultados obtenidos han aportado metodologías y herramientas para la gestión integral del medio acuático a una escala portuaria así como a una escala local a nivel de instalación.

9.1. Conclusiones

Los resultados obtenidos en esta tesis permiten obtener conclusiones específicas derivadas de cada procedimiento desarrollado:

- **Mapas de priorización:**

Los mapas de priorización resultado de la implementación de la metodología que se presenta en el Apartado 5 permiten calcular la variabilidad espacial y temporal de los contaminantes y sus efectos así como realizar la integración de los mismos, obteniendo mapas de riesgo fácilmente interpretables. La metodología propuesta para el desarrollo de mapas de priorización permite: i) identificar los peligros ambientales que afectan a las diferentes áreas del sistema acuático portuario; ii) identificar los contaminantes que afectan a la calidad del medio; y, iii) conocer la contribución de cada uno de ellos al efecto global de la actividad portuaria sobre el sistema.

- **Escenarios de riesgo de emisiones difusas:**

La metodología presentada en el Apartado 6 permite la definición de un reducido número de escenarios para la evaluación del riesgo ambiental de instalaciones de manejo de hidrocarburos en áreas portuarias. Los escenarios se basan en la combinación de *tipos de derrame* específicos de la instalación (cantidad y densidad) y las condiciones locales meteorológicas y oceanográficas más probables. La metodología permite seleccionar escenarios de riesgo aun siendo escasa la información de partida.

- **Herramienta SPILL Tool:**

La herramienta SPILL Tool presentada en el Apartado 7 constituye una herramienta útil para el estudio de la evolución de derrames de hidrocarburos durante las primeras 2-4h después del vertido. Permite definir la variación espacial del riesgo ambiental asociado a una determinada instalación de manejo de hidrocarburos, y es capaz de representar el riesgo asociado a diferentes volúmenes y densidades de producto derramado, distintas localizaciones de los puntos de derrame, así como diferentes condiciones ambientales. Se caracteriza por ser rápida, simple y con posibilidades de ser manejada por una gran cantidad de usuarios potenciales "no expertos".

- **Estimación del riesgo ambiental de instalaciones de manejo de hidrocarburos:**

El procedimiento presentado en el Apartado 8 permite la estimación del riesgo ambiental de instalaciones de manejo de hidrocarburos teniendo en cuenta las consecuencias de los contaminantes específicos manejados en las mismas. Las consecuencias son estimadas con base en la persistencia de los contaminantes en el medio acuático y en su efecto potencial. Este método permite conocer la contribución de una determinada instalación al efecto global de la actividad portuaria sobre el sistema acuático, lo cual facilita la definición de medidas preventivas y correctoras, el diseño de programas de vigilancia de la calidad ambiental, la asignación de usos a áreas específicas (p.ej., áreas recreativas) o incluso la ubicación o reubicación de instalaciones de manejo de mercancías.

9.2. Futuras líneas de investigación

Atendiendo a las preguntas planteadas en la introducción (ver Figura 2) en relación con la gestión de la calidad de los sistemas acuáticos portuarios, los estudios llevados a cabo en esta Tesis han revelado la existencia de ciertos aspectos que podrían ser mejorados en los procedimientos descritos.

A continuación, se resumen los aspectos más relevantes que deberían abordar futuras investigaciones.

1. La inclusión del enfoque "intensidad-duración-frecuencia (IDF)" en la estimación de los efectos de los peligros ambientales proporcionaría una estimación más realista de la variación espacio temporal del riesgo estimado por los mapas de priorización.

2. La inclusión de los servicios ecosistémicos en la estimación de la vulnerabilidad supondría una mejora en la metodología para la elaboración de los mapas de priorización.

3. La calibración del coeficiente de difusión y de los parámetros que determinan las condiciones que establecen una diferenciación en los

cálculos para estimar el proceso de difusión turbulenta, conllevaría a una mejora en la estimación de las áreas afectadas por la herramienta SPILL Tool. Para ello, deberían realizarse estudios dirigidos a la recopilación de información detallada y análisis de derrames de hidrocarburos en áreas portuarias.

4. El desarrollo de procedimientos para la estimación de las consecuencias considerando otro tipo de sustancias y/o materiales supondría un avance en la evaluación del riesgo ambiental de instalaciones de carga/descarga de mercancías. Para ello, las metodologías y la herramienta SPILL Tool desarrolladas en esta Tesis podrían ser adaptadas para el análisis del riesgo ambiental de sustancias nocivas y peligrosas (SNP).

Finalmente, la implementación de las metodologías y la herramienta desarrollada a casos de estudio reales ha confirmado su utilidad para la toma de decisiones en la gestión integral de los sistemas acuáticos portuarios. Sin embargo, se deberían llevar a cabo trabajos de validación mediante su implementación en un grupo heterogéneo de sistemas acuáticos portuarios. Este grupo debería estar formado por zonas de estudio representativas de la variabilidad potencial de escenarios en las áreas portuarias. Para ello, se deberían desarrollar estudios dirigidos a conocer la relación entre el impacto ambiental real y la evaluación del riesgo ambiental, considerando la presencia, persistencia, toxicidad, biodisponibilidad y los efectos biológicos potenciales de los contaminantes asociados al peligro.

SUMMARY

The general objective of this thesis is to develop methodologies and tools to improve the integrated management of aquatic harbor systems, by the advance in the knowledge of quantitative approaches to assess the environmental risk of hazards in harbor areas. These approaches are based on stochastic or probabilistic analysis to reflect the spatial and temporal variability of risk and are validated through field data. In order to achieve this general objective, a series of specific objectives were pursued through conducting four specific studies: i) to develop a methodology to integrate environmental risks of multiple contaminants from activities liable to generate negative effects on harbor areas; ii) to develop a procedure to define environmental risk scenarios of non-point oil sources; iii) to develop an easy-to-use GIS based tool to estimate the potential affected area produced by spills from oil handling facilities; and, iv) to develop a method to assess the environmental risk of oil handling facilities.

The methodology to integrate environmental risks of multiple contaminants from activities liable to generate negative effects on harbor areas was developed and implemented at Tarragona harbor. The method is based on Environmental Risk Assessment (ERA) procedure and integrates the effects produced by different contaminants coming from a range of environmental hazards. Consequences are considered as the effects derived from all identified hazards, while vulnerability is expressed in terms of functional relations between the environment susceptibility against a disturbance and the state of conservation related to the value of the receptors at risk. Consequences and vulnerability are integrated obtaining a spatial variation of risk: **prioritization maps**. Prioritization maps are made up of four main stages: i) the identification of environmental hazards; ii) the estimation of consequences (integrated effects); iii) the estimation of vulnerability (environmental characteristics); and, iv) the integration of environmental risks. In order to adapt prioritization maps to the peculiarities of the study area, three different methods of integrating the effects are proposed: Average-value, Worst-case and Weighted methods. The method has been tested by its application to Tarragona harbor. The results of risk were significantly correlated to water and sediment quality indicators.

Secondly, the procedure to define **environmental risk scenarios** of non-point oil sources is designed. The method is based on four stages: i) identification of environmental hazards; ii) characterization of meteorological and oceanographic conditions; iii) definition of environmental risk scenarios; and, iv) assessment of environmental risk. The method was tested by its application to a facility in Tarragona harbor. The method is capable of representing: i) specific local pollution cases (e.g., discriminating between products and quantities released by a discharge source); ii) oceanographic and meteorological conditions (selecting a representative subset data); and iii) potentially affected areas in probabilistic terms.

Thirdly, the easy-to-use GIS based tool to estimate the potential affected area produced by spills from oil handling facilities in near shore areas is developed. **SPILL Tool** is developed by using the ArcGIS (10.1) geographical Information system. The SPILL Tool is a custom script tool, fully integrated under ArcGIS Geoprocessing so it uses Python and ArcGIS scripting library building a non-ambiguous geoprocessing workflow. The SPILL Tool provides as a result a raster output of probabilistic potential affected area of a specific scenario. SPILL Tool was extensively tested by applying it to oil handling facilities at Tarragona harbor (NE Spain). SPILL tool showed a satisfactory correspondence with results obtained by means of a calibrated 2D numerical model.

Finally, the method to assess the environmental risk of oil handling facilities is developed. **Consequences** of **specific pollutants** are estimated considering its persistence and potential toxicity. The environmental risk of a specific isolated oil handling facility was estimated and the associated environmental impact was quantified based on ‘weights of evidence’ approach. The relationship between the environmental impact and the environmental risk assessment at the oil handling facility was studied. The contamination quantified at the potential affected area around the facility has proved to be related with environmental risk estimations. However, lines of evidences obtained do not allow us to assert that the activity developed at this facility had an environmental impact associated.

Developed studies at this Thesis provide a wide range of methodological procedures to improve the integrated management on water quality at harbor and

oil handling facility level. The implementation of these methods to a real case confirms their usefulness as decision-making tools to support water quality management in harbor areas.

Chapter I

Introduction and background to the research

CHAPTER I. INTRODUCTION AND BACKGROUND TO THE RESEARCH

1.1 Motivations for the research

Maritime transport is the backbone of international trade and a key engine driving globalization. Twenty-four hours a day and all year round, ships carry cargoes to all corners of the globe (IMO, 2013b). On account of this, seaports are very important facilities for a country's economy. Maintenance of the shipping industry's economic sustainability is crucial given its vital role. About 90% of world trade is transported through marine waters upon which the functioning of the world economy and its further development depends (ICS, 2016). As proof of this, the International Maritime Organization (IMO) has devoted the World Maritime Day of 2016 to the next theme: 'Shipping: indispensable to the world'.

In terms of volume, 75% of European freight exchanges with the rest of the world pass through the 1900 plus seaports in the maritime Member States of the European Union. Moreover, more than one third of goods being transported between EU Member States transits through seaports. The total gross weight of goods handled in EU ports was estimated at 3.7 billion tonnes in 2015 (Figure 1.1) (ESPO, 2015).

Seaborne trade is growing very fast – a 50% growth is predicted by 2030 (European Commission, 2013b). An ever-increasing growth in maritime commerce and traffic is demanding the development of more ports and the expansion of existing ones. It is not just the volume of traffic that is growing. Bigger ships, with much deeper drafts, are on their way: so even harbors will need deeper and larger channels, basins and docks to accommodate these new classes of vessels (Runhaar, 2016).

As freight cargo traffic continues to grow, the question of how to ensure their long-term sustainability is playing an increasingly important part in the policy debate on globalization, trade, development and environmental sustainability (UNCTAD, 2012a; 2012b). The UN Conference on Sustainable Development held in Rio de Janeiro in 2012, known as Rio+20, resulted in the outcome document entitled "The Future We Want". The document calls for a wide range of actions and also commits Governments to work towards a transition to a "green economy", evolving around the three, equally important, dimensions of sustainable development – i.e. the economic, social and environmental dimensions. In order to generate a license for growth, ports are increasingly embracing a more sustainable development approach (European Commission, 2011).

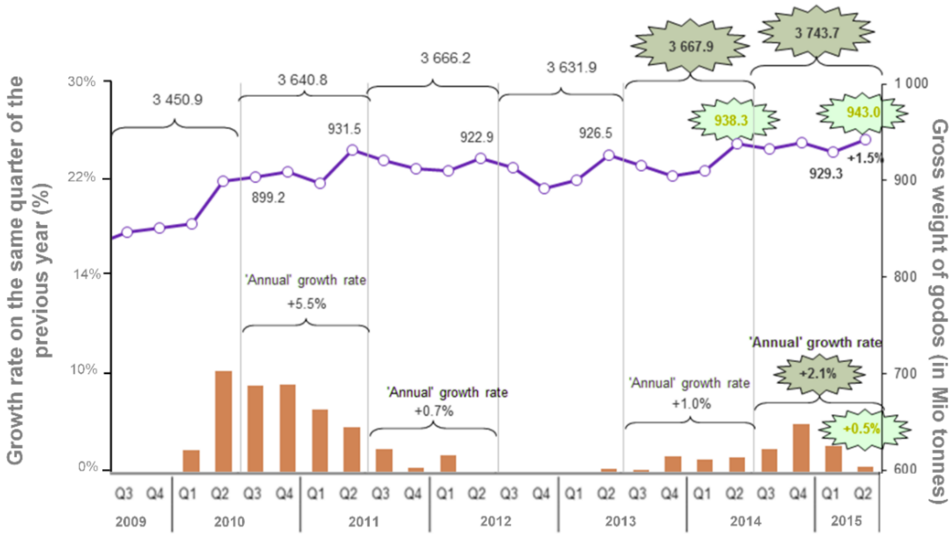


Figure 1.1 Gross weight of seaborne goods handled in EU-28 main ports (adapted from Eurostat - Maritime transport – Goods).

Harbors play a key role in the maritime supply chain since they are located as the center link between land and sea transportation for international trade. The majority of routine shipping operations are developed on harbor areas, where releases of unwanted materials to the sea could occurs (Ng and Song, 2010). According to the European Maritime Policy, the capacity development of ports must mirror the growth of Europe's domestic and international trade and occur in a way that is compatible with related EU policy objectives, in particular its environmental and competitiveness goals (European Commission, 2011). Any significant improvement that can be achieved in their infrastructures and the quality of services will have a significant effect on the efficiency of maritime supply chains (Asgari et al., 2015).

The management of European seaports is in most cases devolved to a port authority, an entity which, regardless of ownership and other institutional features, assumes both public and economic responsibilities. This hybrid character makes port authorities were ideally placed to meet the various challenges that both market forces and society impose upon seaports (ESPO, 2015). This verifies the port authorities' inquisitiveness to improve their environmental performance and to achieve a better environmental management of the harbor area.

In the last several years there have been various proposals implemented by ports authorities to assess the sustainability of their performance. Three main environmental certifications have been used for this purpose: ISO 14001, EMAS, and EcoPorts (Asgari et al., 2015). ISO 14001 specifies the requirements for an environmental management system that an organization can use to enhance its environmental performance (Technical Commitee ISO/TC 207, Environmental management, 2015). On the other hand, EMAS is a EU Eco-Management and Audit Scheme developed by the European Commission for companies and other organizations to evaluate, report, and improve their environmental performance (European Commission, 2009b). Finally, EcoPorts Foundation (EPF) has designed and developed specific environmental management systems for ports: the Self Diagnostic Method (SDM) and the Ports Environmental Review System (PERS). These systems are mostly applied for ports in Europe (ESPO/EcoPorts) (Asgari et al., 2015) as ESPO (European Sea Ports Organization) promotes the use of EcoPorts Foundation's tools in its Environmental Code of Conduct (ESPO, 2003). These standards aim to assess, organize and reorganize towards a sustainable development in business organization. By its implementation specifically at port areas they constitute a tool to assist port managers to identify environmental risk and to establish priorities for action and promote continual improvements.

Given their position in coastal areas and the great variety of substances handled in harbor areas, they are considered as complex systems from an environmental point of view (Darbra et al., 2004). To identify main port environmental threats, Peris – Mora et al., (2005) analyzed a total of 63 forms of potential environmental impacts from different harbor activities, through a system of sustainable environmental management indicators. Water quality was selected as one of the 17 pressure/state indicators for a harbor environmental policy. From 1996, ESPO and EcoPorts regularly monitor the top environmental priorities of European port authorities. The outcome of 2016, built on data from 91 ports, reflects that water quality occupies the eighth position, gaining importance from the tenth position held in 2013 (ESPO-ECOPORTS, 2016).

Regarding water quality, harbors are under the scope of the Water Framework Directive (WFD) – Directive 2000/60/EC - (European Commission, 2000a), which establishes a framework for the protection of surface waters and groundwaters. Its main objective is to achieve a 'good ecological status' for all natural European water bodies and a 'good ecological potential' for heavily modified water bodies (HMWBs) until 2015 (Borja and Elliott, 2007; Gonçalves et al., 2013). Harbors are being acknowledged as uses of special economic and social relevance which activity is developed at HMWBs (European Commission, 2000a; Ondiviela et al., 2012). A total of 583 HMWBs were designated on account of harbor activities along Europe (Kampa and Laaser, 2009).

In addition to the EU legislation, a very important increase on the concern for improving the water quality in harbor areas has emerged among managers (ESPO-ECOPORTS, 2016). The scientific community has begun to provide sustainable solutions to maintain the quality of port waters, without undermining the economy on which the area is based. In that sense, the Environmental Risk Analysis (ERA) has become the quantitative tool worldwide used to assess, in probabilistic terms, the potential effect caused on the environment due to the exposure of contaminant agents (Gómez, 2010). ERA provides a framework to integrate scientists, policy makers, risk assessors and managers in addressing environmental problems (Eduljee, 2000) by conducting the processes of: i) hazard identification; ii) risk assessment; and, iii) risk management. Hazard identification provides a comprehensive list of all hazards and their characteristics. Environmental risk assessment supplies the description of hazards in terms of their nature and magnitude by determining the probability of occurrence, the vulnerability of the environment and the consequences derived from hazards. Risk management proposes preventive and corrective measures that should be applied to reduce such risk in a cost-effective manner (Gómez et al., 2015). At national level, the Spanish National Port Administration published the Recommendation for Maritime Works "ROM 5.1-13. Quality of Coastal Waters in Port Areas" (Revilla et al., 2007; Juanes et al., 2013). This Recommendation, based on WFD principles, defines the environmental strategy of national harbors through the environmental risk assessment at contaminant source level.

In that sense, several methodologies to assess the environmental risk associated to particular hazards in harbors have been developed considering various approaches and distinctive levels of complexity. Examples of these are approaches based on hydrodynamic models which relate water renewal of the harbor and risk of water quality degradation (Grifoll et al., 2010; Gómez et al., 2014c) or the development of multi-metric index to estimate the environmental risk of the individual discharges to the port jurisdiction area (PJA) by considering the probability, the consequences of hazards and the vulnerability of the system (Ondiviela et al., 2012; Gómez et al., 2015).

Harbor areas are characterized by a wide range of activities which could implicate point and diffuse sources. Industrial (related with oil terminals, chemical and petrochemical plants, etc.), navigation and shipping activities (loading and unloading of goods, oil jetties, dredging, etc.) are mainly related to non-point sources (Ronza et al., 2003). On many occasions, the interaction of many possible influences makes difficult to precisely identify the surrounding hazards and their multiple effects. On the other hand, the environmental effect of a combined group of substances will be different from the environmental effect of a single substance. Thus, managing complex and heterogeneous mixtures of contaminants with, in some cases, no defined origin, represents a problem for managers (De los Ríos et al., 2016). Despite the previous methodologies, the integration of environmental risk of different hazards affecting the same area is an actual dare in the ERA at harbor areas. The combination mechanism of the estimation of risk due to different hazards is crucial on aquatic systems subjected to a several number of pollution sources, as harbor areas (Gómez, 2010). It is thus necessary to implement an evaluation procedure that differentiates sources and effects to provide, with the highest possible certainly, the environmental risk resulting by the integration of all hazards and proceed with the most sustainable management (Gómez et al., 2015).

Environmental impacts generated by port activities, including shipping operations, have increasingly become an important research topic. Darbra and Casal (2004) reported that the most frequent accidents in port areas are releases (51% of total accidents occurred) and, the greatest proportion of accidents in ports (59%) are related to oil spills. Accordingly, non-point pollution by oil spills is one of the most widespread problems in port areas (loading and unloading of bulk liquid, fuel supply, navigation). Due to the difficulty to characterize non-point contaminant sources in harbor areas in general, and in oil handling facilities in particular, most potential impact assessment methods ignore the characteristics of the contaminants and evaluate hazards based on hypothetical scenarios, expert or worst case criteria (Gómez, 2010; Lahr and Kooistra, 2010). However, the consideration of agents’ characteristics is essential because the complexity and diversity of physical and chemical processes on the aquatic environment determine the fate and transport of the product. So, the more similar the scenarios used to the real cases occurred, the more representative of the real impact is expected to be the risk assessment. Therefore, there is a necessity to develop quantitative procedures based on real information to select scenarios for a realistic description of the potential effects at oil handling facility level.

The quantitative estimation of the environmental risk of oil spills has been inevitably linked to the use of numerical models. Numerical models are tools designed for predicting the evolution of contaminants so they are able to reproduce the environmental processes which contaminants are subjected to. These models are able to interpret, simulate and predict the responses of contaminants on aquatic environment in a theoretical way. As long as numerical models have been adequately calibrated and validated, they are invaluable tools for predicting effects on ecosystem components (e.g., Yuan et al., 2007). In most cases these models require expert users to interpret the output data as well as external servers of large databases to provide the model inputs. On the contrary, managers are demanding on these days, easy-to-use tools able to provide similar results to numerical models not limited by high spatial data resolution and not requiring web service managers or experienced users.

Beyond the potential affected areas by oil spills, to assess their environmental risk it is necessary to know their associated consequences. Consequences are defined as the effects on the environment that may result from environmental hazards and are necessarily related to characteristics of spilled product. Physical and chemical characterization is crucial to know the transport process and fate of the products. Existing methods to assess the consequences of oil spills are just based on the product arrival to biological resources or human-use areas (habitats and species protection areas, fishing, aquaculture, tourism areas, etc.). However, at harbor areas, where chronic contamination from operational pollution is expected and pollutant incidents are generally rapidly solved, persistence, toxicity or bioaccumulation should play an important role on the oil spills' consequences. Thus, methodologies to assess the environmental risk of oil handling facilities are needed in order to provide accurate information about consequences of potential spills.

Finally, it should not be ignored that numerical tools and methods used to estimate the consequences of specific discharge sources or the vulnerability of the system are predictive or based in assumptions. Uncertainty is associated with studies related with these kind of tools and methods. Thus, validation of methodologies and tools aimed to predict environmental risk should be developed in order to know if the estimated risk is related to the actual impact on the environment.

In summary, the environmental risk assessment methodologies at harbor level are focused on specific contaminants introduced by point contaminant sources, without integrating the contaminants introduced by diffuse sources and pollutant incidents. Once the environmental riks is focused on oil spills, scenarios are hipotetically defined and results are based on sophisticated numerical models, without considering the consequences of involved products. Moreover, methods and tools used to estimate the environmental risks are not usually validated with the real environmental impact through field data. These limitations have tried to be overcome in this Doctoral Thesis.

1.1.1 Integrating environmental hazards at harbor level

International Maritime Organization's (IMO) 1973 Convention considered that the operational pollution and the accidental pollution could pose big threats to the marine environment. In harbor areas, operational pollution is due to routine operations so it is likely to occur, causing an environmental impact specially if they agglomerate over time without response (Ng and Song, 2010). Operational marine pollution comes mainly from cargo handling activity. Handling of dry bulk cargo may cause release into water and dust emissions (air pollution) being possible the deposition on surface water. Handling of liquid bulks may require discharge through pipelines, which provides a potential risk for leaks, emissions and spillages. The release of cargo into the marine environment may have important environmental effects (European Commission, 2011). Thus, operational aspects of commercial shipping (waste handling, ballast water management, loading/unloading of goods, etc.) are subjected to national or international rules, regulations and conventions as MARPOL Convention for the prevention of pollution from ships (IMO, 1991), Ballast Water Management Convention (BWM) to manage the releases of ballast waters (IMO, 2004), International Maritime Solid Bulk Cargoes Code (IMSBC) (IMO, 2013a) or the International Maritime Dangerous Goods (IMDG) Code (IMO, 2014).

On the other hand, accidental pollution is an unlikely but a huge magnitude source of contaminants so a high impact is expected from pollutant incidents caused by shipping. The prevention and management of accidental marine pollution has been particularly focused on oil spills. Thus, in 1990, 15 States ratified the International Convention on oil pollution preparedness, response and cooperation, recognizing the high level of risk associated with accidental spills. However, legislation recently approved is not limited to oil spills. Nowadays, regulation includes all kinds of chemicals that could cause a deleterious effect on the environment. In this regard, the Decision 2850/2000/EC (European Commission , 2000b) established a community framework for cooperation in the field of accidental or deliberate marine pollution from discharges of hazardous substances into the marine environment, whatever their origin. The legislation related to the management of this type of events was completed with the Directive 2004/35/EC (European Commission, 2004), by which, based on the furtherance of the 'polluter pays' principle, an environmental liability framework was established with the primary objective of preventing and remedying environmental damage.

Despite the legislation approved, there are no standardized procedures for the analysis of integrated environmental risks considering operational (diffuse sources) and accidental (pollutant incidents) marine pollution (ESPO, 2007). An integrated management of harbor aquatic systems should provide a spatial description of environmental risk to allow managers addressing issues like the followings: i) is it possible to localize and characterize both point and non-point contaminant sources (hazards)?; ii) which contaminants are affecting the water quality on a specific port jurisdiction area?; iii) which is the area most affected by what kind of hazard?; iv) which is the area most affected by what kind of contaminant?; or, v) which facility is contributing the most to the integrated effects?. Based on this issues, the need to provide local maps of integrated environmental risk of multiple contaminants to port authorities arises. The definition of spatial and temporal risk based on stochastic or probabilistic analysis is essential for reflecting spatial and temporal variability (Castanedo et al., 2009; Abascal et al., 2010; Santos et al., 2013a) and for providing answers to the questions raised. Therefore, 'inventories and maps' reflecting spatial and temporal distribution of risk are essential results for risk management and to support best decision-making.

Methodologies aimed to define individual (due to one contaminant) and integrated risk (due to multiple contaminants) caused by point and diffuse sources (ordinary operations) as well as by pollutant incidents (accidental pollution) should be developed.

1.1.2 Characterizing non-point oil sources

Identification and characterization of environmental hazards constitute the first phase in the ERA process. This phase is extremely important as builds the grounds which supporting the consecutive stages of the process. The quality of all subsequent stages depends largely on the quality of this initial phase. When the origin of contaminants is delimited to a point source, the appropriate solution is to identify contamination causes and to treat emissions right at the origin (De Los Ríos et al., 2016). The main problem related to non-point sources (diffuse source and pollutant incidents) is the lack of information on discharge patterns.

As non-point pollution by oil spills is one of the most widespread problems in port areas, in the last years, scientific and technological advances in prevention of marine pollution have focused on developing techniques and procedures mainly aimed to oil spill management. Operational oceanography systems able to provide oil spill trajectory forecasting at local scale have been developed (Otero et al., 2015; Abascal et al., 2016). This kind of systems are undeniably usefulness in dealing with crisis involving dramatic environmental and socioeconomic impacts (Castanedo et al., 2006). When a spill occurs, real data can be rapidly process by operational systems and the best accurate results are expected to obtain. However, when prevention and contingency plans are designed, hypothetical spills are often established by expert criteria. This could yield to an introduction of a subjective element in the first phase of the ERA process leading to a lack of realism in this conventional procedures.

Characterization (e.g., pollution loads and pollutant diversity) is a challenge in the analysis of environmental risks for facilities where the loading and unloading of oil occurs. To overcome these limitations, researchers worldwide, focused on different disciplines, have started using innovative methods for selecting quantitative scenarios (Rotmans et al., 2000; Franco et al., 2016; Rico et al., 2016; Schweizer and Kurniawan, 2016). A better system understanding, the uncertainty analysis or the selection of a small set of local scenarios are some of the needs that must be overcome by these new methods. A method based on historical data from a specific oil handling facility should provide a set of concrete scenarios defining the reality of the system in order to answer the following questions: i) how many scenarios should be considered?; ii) what kind of characteristics should defined the scenarios?; iii) what are the most-probable spills' characteristics if spills do occur?. Although several methodologies allow to identify environmental hazards in harbor areas, no procedures have been developed to define scenarios in the ERA process. The environmental risk assessment of oil handling facilities should be based on the characterization of potential discharges through the definition of scenarios by means of a standardized and homogenous methodology.

In order to carry out stochastic and probabilistic analysis to reflect the spatial and temporal variability of risk, in the particular case of oil handling facilities in harbor areas, the definition and selection of a small set of real based scenarios is needed.

1.1.3 Predicting the trajectory of oil spills

The environmental risk assessment and management of oil spills is usually based on the study of their trajectories by means of numerical models. High resolution numerical models involve, in most cases, a huge computational cost (Roberts et al., 2010) and require a detailed characterization of contaminant sources and environmental conditions provided by external servers. For those which are embedded in local operational systems, meteorological forcing obtained from extensive databes (e.g., MYOCEAN) are required. In addition, a web service that manages the operational system need daily forecast of high resolution ocean variables (carried out, in turn, by other modelling systems) (Castanedo et al., 2014). As Otero et al. (2015) recognized, most of these numerical tools need to be run by a qualified technician (e.g., GNOME; MEDSLINK-II, De Dominicis et al., 2013; ROFF, Carr et al., 2008) providing outputs hard to understand by a non-expert (Roberts et al., 2010).

There is an increasing interest from managers to have easy-to-use tools capable to provide similar results to numerical models in quantifying affected areas from spills at local scales (as harbor areas). Based on simple input data and providing easily interpretable results, the numerical tools should allow to answer the following questions: i) is it possible to know this sources' contribution to the global environmental pollution for a specific area?; ii) where is the potential affected area located?; and, iii) where should the monitoring strategy be focused if an environmental monitoring program is conducted?.

Geographical Information Systems (GIS) provide significant contributions to environmental risk assessment in virtue of its intrinsic ability to analyze and display large amounts of spatial data. The powerful visualization of data and analysis of results are useful in decision-making processes (Debaine and Robin, 2012; Vafai et al., 2013; Lu et al., 2014). Nowadays, Open Source Geographic Information Systems are freely available and widely used. They are becoming an increasingly common procedure for the analysis of the spatial distribution of environmental risk and support for decision-making (e.g., Akbar et al., 2011), including managers and technicians from port authorities and stakeholders. Generalist GIS tools to obtain the extension of the potential affection of contaminant source have been developed (e.g., Juanes et al., 2013). These tools consider common transport processes to all types of products, ignoring the product characteristics and physical and chemical processes on the environment of substances or materials under study.

In order to provide fast, low computational cost and easy to use numerical tools, specific GIS tools gathering up particular product formulations are needed to predict the trajectories of oil spills.

1.1.4 Estimating the consequences of oil spills

Consequences are considered as the effects derived from an environmental hazard. Consequences of oil spills have been traditionally estimated in economic and environmental terms. Regarding the environmental characteristics, the arrival of the product to environmental resources has been usually considered (recreational areas, aquaculture areas, protected areas, etc.). Nevertheless, there are situations in which the spilled product do not reach economic or those specific environmental resources, but still have an impact on the environment by adhering to particulate organic matter and persisting in porous materials including muddy or sandy sediment. Sediments are an essential and dynamic part of the harbor; their quality and quantity are integral parts to ecosystem health (Mali et al., 2016).

Current methodologies aimed to assess environmental risk of oil handling facilities considering the presence/absence of product released in the water column, sea-

surface and shoreline (contamination). These methodologies do not have into account the sediment as potentially damaged compartment from spills.
On the other hand, and in order to assess the potential impact of oil handling facilities in harbor areas, it should be take into account not just the contamination (presence of contaminants on the environment) but also the pollution (effects derived from contaminants released), specially when chronic effects are studied. To do this, the persistence, toxicity and the bioaccumulation of products (pollution) should be considered.

New methods to assess the consequences of oil spills sources are required in order to answer the following questions: i) what is the potential impact on the environment of the oil handling facilities?; ii) where this impact is expected to be located?.

1.1.5 Validating environmental risk assessment

Environmental risk analysis on aquatic systems includes the evaluation of the likelihood that adverse ecological effects occur as a result of exposure to one or more contaminants. From a management point of view, a description of the relation between predicted environmental risk and measured real impact is essential to answer relevant issues related with harbor aquatic systems: i) what is the real impact on the environment?; ii) where this impact is located?; iii) what indicators should be used in a monitoring strategy?; vi) what are the ecological risks associated to a particular management option (e.g. for a specific facility)?. In order to correctly answer these questions the validation of ERA predictions must be performed (e.g., field works to assess the validity of decisions) (Chapman et al., 2002). On the other hand, synergic or additive effects between different contaminants from multiple hazards located in harbor areas could derive on a higher pollution effects than predicted. To avoid contaminants interactions and reduce uncertainty, validation of methodologies and tools should be developed at local scale for specific and isolated facilities.

Weight of evidence (WoE) evaluation is the processes of summarizing, synthesizing and interpreting a body of evidence to draw conclusions, e.g., regarding the relationship between a chemical exposure and adverse environmental effect (Ågerstrand and Beronius, 2016). A battery of indicators that integrates sediment quality, bioavailability of pollutants (by analysis of bioaccumulation) and biological effects resulting from exposure to pollutants at different levels of biological organization (cell level, individual, community) (Bebianno et al., 2015) are commonly used following WoE approach.

Consequently, the validation of the ERA methodologies requires to check if the risk estimations are reflecting the actual environmental impact by integrating quantitative data of contaminants and its consequences on the environment. Studies aimed to measure: i) contaminants ranges in water and sediment harbor aquatic systems; ii) ecological responses caused by the exposure to contaminants at individual level (toxicity); and, iii) the effects caused at biological community level should be developed at local scale to validate the new ERA methodologies developed for harbor areas.

1.2 Objectives of the thesis

The general objective of this thesis is to develop methodologies and tools to improve the integrated management of aquatic harbor systems, by the advance in the knowledge of quantitative approaches to assess the environmental risk of hazards in harbor areas. These approaches are based on stochastic or probabilistic analysis to reflect the spatial and temporal variability of risk and are validated through field data.

The specific objectives of this thesis are focused on the following aspects:

1) To develop a methodology to integrate environmental risks of multiple contaminants from activities liable to generate effects on harbor areas.

2) To develop a procedure to define environmental risk scenarios of non-point oil sources.

3) To develop an easy-to-use GIS based tool to estimate the potential affected area produced by spills from oil handling facilities.

4) To develop a method to assess the environmental risk of oil handling facilities.

1.3 Layout of thesis

The structure of the thesis is organized as follows:

In Chapter I the motivations for the research of the studied aspects are presented. The specific objectives designed to answer the questions raised are outlined and the structure of the thesis is described. In Chapter II, a detailed description of the study areas is presented. The following four chapters (III, IV, V, and VI) address the objectives of the thesis. Each of the chapters includes an abstract, a brief introduction, the developed methodology, the results obtained, a discussion and the conclusions sections. Chapters III, IV, V and VI has led to the publication of research articles in SCI journals. Finally, Chapter VII contains a detailed description of the thesis conclusions.

The relationship between chapter's objectives and study cases within the thesis are synthetized in Figure 1.2.

A brief summary of the studies conducted in each chapter is described as follows:

Chapter III. Prioritization maps: the integration of environmental risks to manage water quality in harbor areas: in this chapter, a method to integrate the environmental risk of multiple effects of uses and activities developed in harbor areas is presented. The method is based on Environmental Risk Assessment (ERA) procedure and integrates the effects produced by different contaminants coming from a range of environmental hazards. Consequences are considered as the effects derived from all identified hazards. Vulnerability is expressed in terms of functional relations between the environment susceptibility against a disturbance and the state of conservation related to the value of the receptors at risk. Consequences and vulnerability are integrated obtaining a spatial variation of risk: prioritization maps. Prioritization maps are made up of 4 main stages: i) an identification of environmental hazards; ii) the estimation of consequences (integrated effects); iii) the estimation of vulnerability (environmental characteristics); and, iv) the integration of environmental risks. In order to adapt prioritization maps to the peculiarities of the study area, three different methods of integrating the effects are proposed: average-value, worst-case and weighted methods. The implementation to a real case (Tarragona harbor, NE Spain) confirmed its usefulness as a risk analysis tool to communicate and support water quality management in harbors.

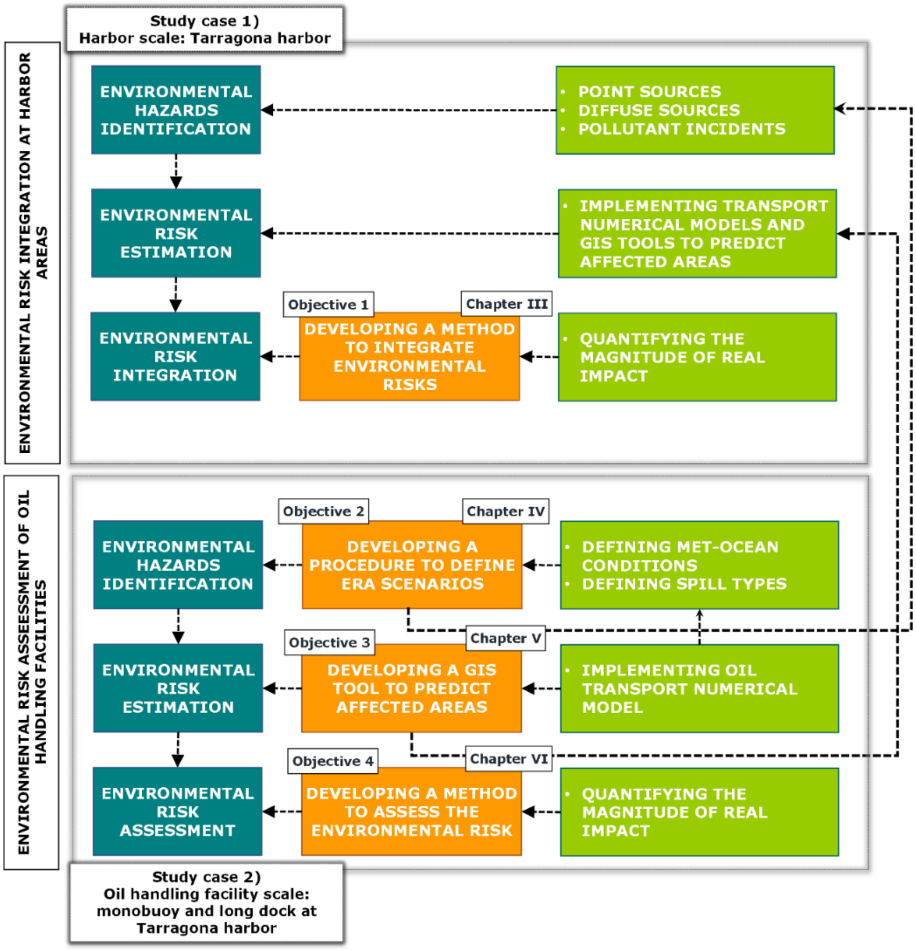


Figure 1.2 Relationship between chapter's objectives and study cases within the thesis.

Chapter IV. A method to define environmental risk analysis scenarios of non-point oil contaminant sources: in this chapter a new methodology to define the scenarios in order to assess the environmental risk of oil handling facilities in port areas is developed. The method is based on four stages: i) identification of environmental hazards; ii) characterization of meteorological and oceanographic conditions; iii) definition of environmental risk scenarios; and, iv) assessment of environmental risk. The method was tested by its application to a facility in Tarragona harbor. The results showed that the method is capable of representing: i) specific local pollution cases (i.e., discriminating between products and quantities released by a discharge source); ii) oceanographic and meteorological conditions (selecting a representative subset data); and, iii) potentially affected areas in probabilistic terms.

Chapter V. A GIS toolbox to assess the environmental risk of oil spills in harbors: in this chapter a new tool (SPILL Tool) to study the transport and fate of oils spills and to assess the environmental risk of oil handling facilities in near shore areas is developed by using the ArcGIS (10.1) geographical Information system. The SPILL Tool is a custom script tool, fully integrated under ArcGIS Geoprocessing so it uses Python and ArcGIS scripting library building a non-ambiguous geoprocessing workflow. The SPILL Tool provides a raster with the potential affected area of a specific scenario in probabilistic terms. SPILL Tool was extensively tested by applying it to oil facilities at Tarragona harbor (NE Spain) showing a satisfactory correspondence with results obtained by means of a calibrated 2D oil transport numerical model.

Chapter VI. A method to assess the environmental risk of oil handling facilities: in this chapter, a new method to assess the environmental risk of oil handling facilities is developed. The environmental risk of an specific isolated oil handling facility, considering the consequences of specific pollutants was estimated and the associated environmental impact was quantified based on 'weights of evidence' approach. The relationship between the environmental impact and the environmental risk assessment at the oil handling facility was studied. The contamination quantified at the potential affected area around the facility has proved to be related with environmental risk estimations. However, lines of evidences obtained do not allow us to assert that the activity developed at this facility has an environmental impact associated.

The relationship between the questions raised at the motivations for the research exposed in Chapter I and the specific studies carried out at the thesis are synthetized in Figure 1.3.

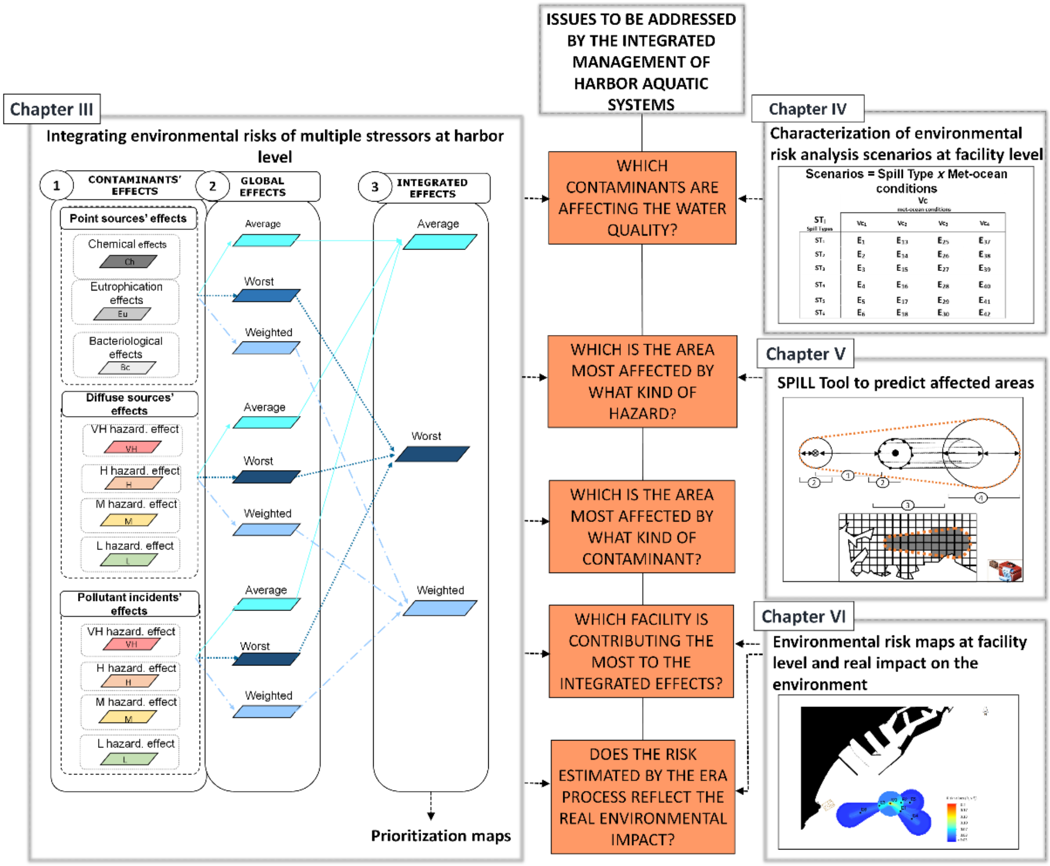


Figure 1.3 Graphical summary of the studies carried out to answer the questions raised.

1.4 Thesis contribution

1.4.1 Scientific projects

This thesis is part of the MarPort project (BIA2012-34123) founded by the National Plan for Research in Science and Technological Innovation from the Spanish Government 2008-2011 (Ministerio de Economía y Competitividad) (http://marport.ihcantabria.es/en/) and PREVEMAR project (BIA2015-67298-R, MINECO/FEDER, UE) founded by the National Plan for Research in Science and Technological Innovation from the Spanish Government 2013 – 2016 (Ministerio de Economía y Competitividad) (http://prevemar.ihcantabria.es/en/).

1.4.2 Scientific production

The work in this thesis translates in 3 published and 1 accepted scientific articles to SCI scientific journals:

1. Valdor, P. F., Gómez, A.G., Puente, A., 2015. Environmental risk analysis of oil handling facilities in port areas. Application to Tarragona harbor (NE Spain). Marine Pollution Bulletin. 90 (1-2): 78-87. doi: 10.1016/j.marpolbul.2014.11.018.
2. Valdor, P.F., Gómez, A.G., Velarde, V., Puente, A., 2016. Can a GIS toolbox assess the environmental risk of oil spills? Implementation to oil facilities in harbours. Journal of Environmental Management. 170: 105 – 115. doi: 10.1016/j.jenvman.2016.01.012.
3. Valdor, P.F., Gómez, A.G., Ondiviela, B., Puente. A., Juanes, J.A., 2016. Prioritization maps: the integration of environmental risks to manage water quality in harbor areas. Marine Pollution Bulletin. 111 (1-2): 57-67. doi: 10.1016/j.marpolbul.2016.07.028.
4. Valdor, P.F., Puente. A., Gómez, A.G., Ondiviela, B., Juanes, J.A., 2016. Are environmental risk estimations linked to the actual environmental impact? Application to an oil handling facility (NE Spain). Accepted for publication in Marine Pollution Bulletin.

Besides, the work offered in this thesis has been presented in several scientific congresses and conferences:

1. Valdor, P.F., Gómez, A.G., Juanes, J.A., Puente, A., Cárdenas, M., Abascal, A.J., Camus, P., Ondiviela, B. 2013. Environmental risk assessment of hydrocarbon diffuse emissions: application to the Tarragona's port monobuoy. *3rd Mediterranean Days of Coastal and Port Engineering*. Marseille, France. Jointly organized by The World Association for Waterborne Transport Infrastructure (PIANC).

2. Valdor, P.F., Puente, A., Gómez, A.G., de los Ríos, A., Juanes, J.A. 2015. Validating the environmental risk assessment. Application at Tarragona harbor. (In Spanish: Validación de la evaluación del riesgo ambiental. Aplicación en el puerto de Tarragona). *XIII Jornadas Españolas de Ingeniería de Costas y Puertos*, Avilés, Spain. Jointly

organised by several entities.

3. Valdor, P.F., Gómez, A.G., Puente A. 2015. Environmental risk analysis of oil handling facilities in port areas. Application to Tarragona harbor (NE Spain). 38th AMOP Technical Seminar on Environmental Contamination and Response, Vancouver, Canada. Jointly organised by Environment Canada (EC), Government of Canada.

4. Valdor, P.F., Gómez, A.G., Velarde, V., Puente, A. 2015. Can a GIS tool assess the impact of oil spills?. 38th AMOP Technical Seminar on Environmental Contamination and Response, Vancouver, Canada. Jointly organised by Environment Canada (EC), Government of Canada.

1.4.3 Tool Product

The features of the GIS tool developed in the framework of this thesis are described as follows:

Name: SPILL Tool
Developer: Environmental Hydraulics Institute of the University of Cantabria "IH Cantabria”
Year first available: 2015
Hardware required: ArcGIS 10.1 for Desktop system requirements
Software required: Python 2.4 or later; ArcGIS 10.1; FWTools (http://fwtools.maptools.org/)
ArcGIS extensions required: Spatial Analyst 10.1 ©1999-2012 Esri Inc.
Program languages: Python
Toolbox size: 191 KB
Availability: Download: http://marport.ihcantabria.es/en/descargas/

Chapter II

Study sites and data

CHAPTER II. STUDY SITES AND DATA

The methodologies and tools emerged from this thesis were developed and implemented at Tarragona harbor. Two spatial scales were used: harbor scale and oil handling facility scale. Chapter III is developed at harbor scale and chapters IV, V and VI are focused on a specific oil handling facility at Tarragona harbor (Figure 2.1).

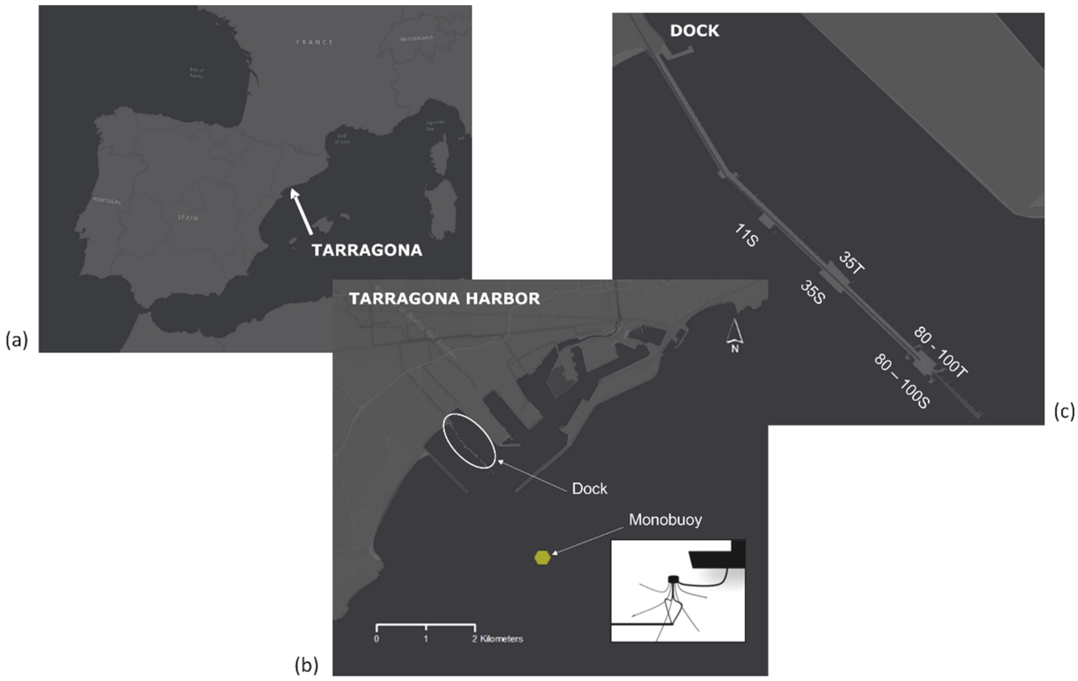


Figure 2.1 Location of (a) Tarragona, (b) Tarragona harbor and the oil handling facility (dock and monobuoy) and, (c) the moorings located at the dock.

A description of the Tarragona harbor and the oil handling facility are presented below.

2.1. Tarragona harbor

Tarragona Harbor is located in the Mediterranean Sea on the NE Spanish coast (1º14’E, 41º05’N) (Figure 2.1).

From the Port Jurisdiction Area (PJA), the total water surface occupies about 4120 ha and total terrestrial area is extended around 543 ha (Figure 2.2). Tarragona harbor has several facilities for maritime trade which comprise wharves and berths where the main uses and activities are carried out. These are distributed over a total length of 11,252 m of docks and 2,347 m of jetties. The harbor entrance is 450 m large and the maximum depth of water is 20 m at sheltered waters and 42.8 m at the monobuoy.

The plan for the use of harbor areas of Tarragona harbor (Spanish Government, 1994) delimits different areas to which harbor uses are assigned. At terrestrial area, 8 different areas are recognized: city–harbor border, commercial-industrial, dredging area, fishing area, logistic activity area, marinas, storage–allocation area, shipyard area, and finally, areas designated to other uses as road use (Figure 2.2). It is noteworthy the dimension of the industrial–commercial area which occupies almost the 58.8% of the total terrestrial surface and logistic activities which holds the 17.7%.

Within the PJA of Tarragona harbor, two kind of non-harbor recreational uses are developed: bathing and diving uses. Two bathing waters are located at the PJA: La Pineda, an urban beach of around 2.4 Km long localized on the coast line between the dike and Cap the Salou and El Miracle, a semi urban beach of 0.9 Km and located near the marina (Spanish Government, 2016). On the other hand, in the outer harbor breakwater there is an area intended for diving activity (Figure 2.2).

The economic structure of the hinterland of Tarragona harbor is based on two main axes: petrochemical industry and the agricultural and farming activity at the Ebro valley. This makes that bulk materials are the main cargo handled at Tarragona harbor. It is an industrial bulk carrier harbor surrounded by an extensive petrochemical cluster which includes one of the largest Spanish oil refineries and an advanced chemical complex.

The annual report of Tarragona harbor (Autoridad Portuaria de Tarragona, 2014) indicates that the total bulk traffic in 2014 was around $32{\cdot}10^6$ Tn managing mainly crude oil, energetic petroleum gases, fuel oil and naphtha (Table 2.1). Solid bulks reached the 30.3% of total bulks being the coal and coke the most abundant following by cereals and flours. General cargo was mainly represented by paper pulp and steel products with 0.9% of total bulks. Fruits and vegetables cargo reached the 0.3% followed by motor vehicles and automobile pieces, wood and cork and, scrap iron. Finally, at Tarragona harbor 148,638 TEUS (Twenty-foot Equivalent Units) were handled in 2014.

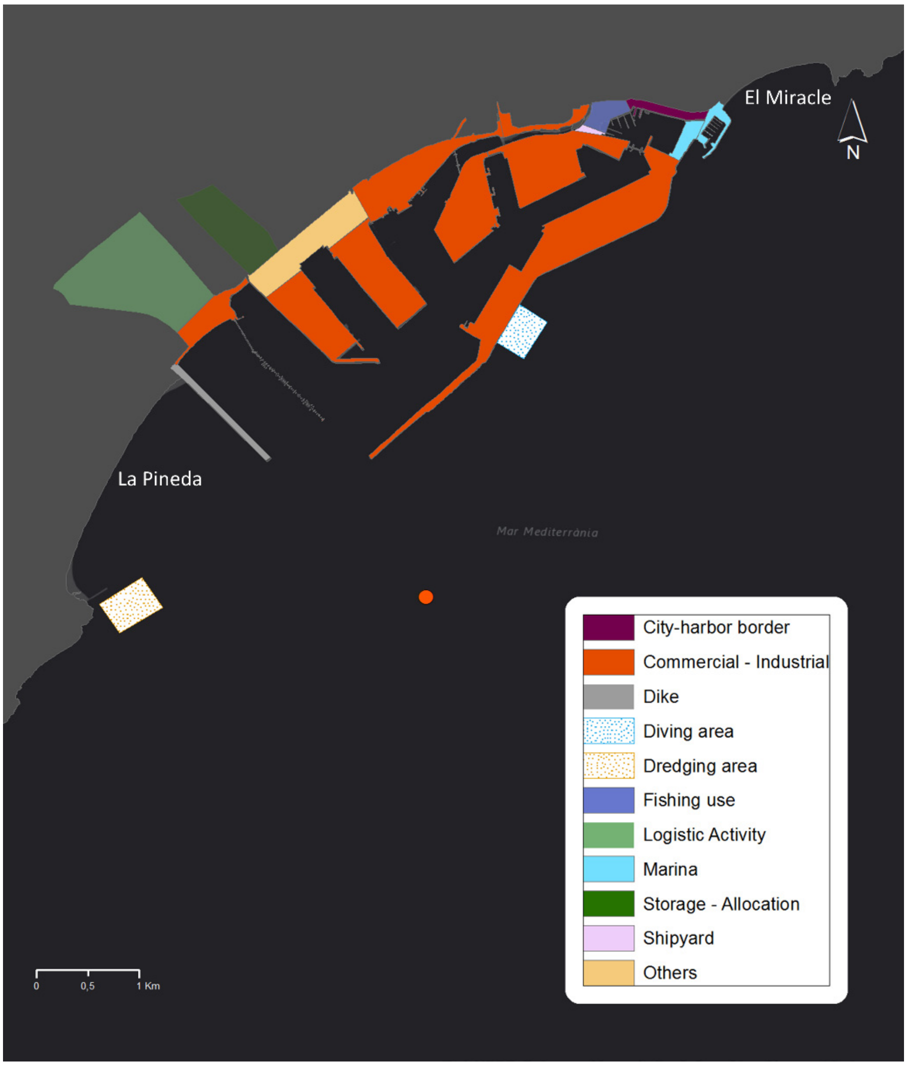


Figure 2.2 Location of port uses and non – harbor uses at Tarragona harbor.

Bulk	Millions of Tones
Crude oil	8.1
Coal and petroleum coke	4.5
Others petrol products	3.6
Fuel oil	3.2
Cereals and flours	3.0
Chemical products	2.2
Fodder	1.4
Energetic petroleum gases	1.1
Gasoil	0.8
Paper pulp	0.5
Steel products	0.4
Biofuels	0.3
Gasoline	0.3
Others	2.3

Table 2.1 Quantities of types of bulk handled at Tarragona harbor in 2014 according to their nature.

2.1.1. Environmental hazards

The environmental hazards considered at the studies developed in this thesis are: contaminant sources and pollutant incidents sources. Contaminant sources are any regular discharge of substances or energy liable to affect the water quality. Contaminant sources are classified into point and diffuse in function of the way in which they are introduced into the aquatic environment. *Point contaminant sources* are defined as the discharge of pollutant substances or materials channeled through predefined fixed points (channeled runoff waters, storm drains, and point-source discharge, etc.) while *diffuse contaminant sources* are the non-channeled discharge of pollutant substances or materials (filtrations, dredging, losses, handling activity, etc.). A *pollutant incident* is considered as any accidental discharge that may reduce the environmental quality, whether the reduction is punctual or occurs progressively (Juanes et al., 2013).

For the purpose of this thesis, point contaminants sources are characterized taking into account substances related with three quality processes:

i) chemical pollution, caused by priority substances - Directive 2013/39/EU (European Commission, 2013a) - ;

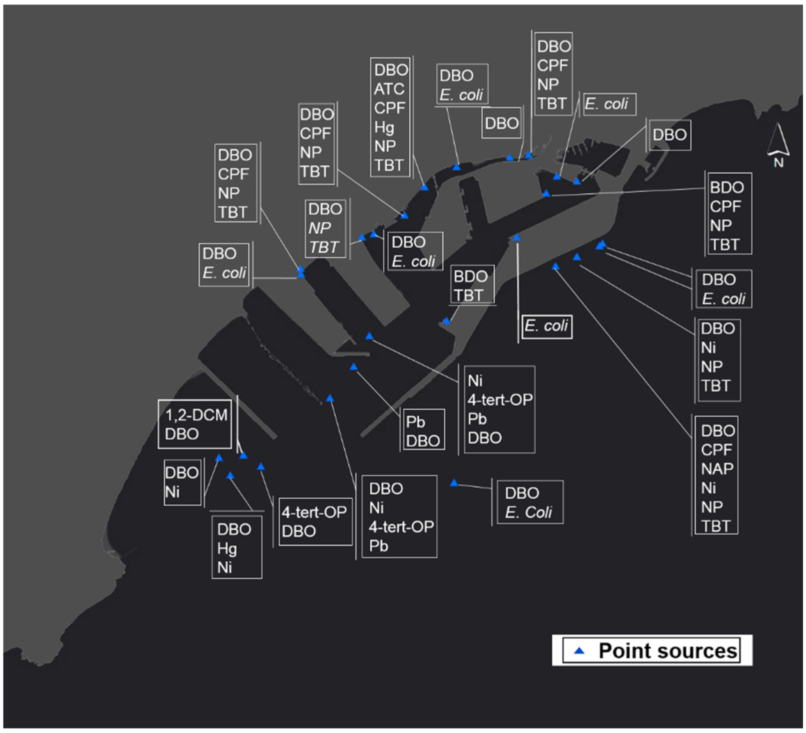
ii) eutrophication process, measured by the decrease of dissolved oxygen; and,
iii) bacteriological contamination, using *Escherichia coli* as indicator - Directive 2006/7/EC (European Commission, 2006a) -.

On the other hand, diffuse contaminant sources and pollutant incidents are characterized considering the hazardousness and density of substances or materials handled or spilled. The characterization of hazardousness of substances is based on the related legislation and considers:

i) *very high* hazardousness for priority hazardous substances established by Directive 2013/39/EU (European commission, 2013a);
ii) *high* hazardousness for priority substances established by the Directive 2013/39/EU (European commission, 2013a);
iii) *moderate* hazardousness for dangerous materials of IMDG Code; and,
iv) *low* hazardousness for potentially dangerous materials and other materials established at IMDG Code (IMO, 2014).

Information provided by the Port Authority of Tarragona allowed to identify 47 potential pollutant sources. From these, 26 are *point sources* mostly produced by industrial activity and urban wastes, which are liable to spill 10 different priority substances and *E. coli* into the water (Figure 2.3). For 23 of the 26 point contaminant sources the biological oxygen demand was characterized in order to know if they are liable to cause eutrophication process. The 21 identified *diffuse sources* are mainly produce by cargo terminals, vessel-port interfaces and MARPOL waste activities. 14 of the diffuse sources are liable to discharge very high hazardous materials into the water, 6 diffuse sources are liable to discharge high hazardous substances and only 1 could discharge moderate hazardous materials into water (Figure 2.4).

The port authority's local database contains a total of 227 pollutant incidents registered between 2007 and 2015. Basic information related to the pollutant incidents (e.g., discharge source, a description of the discharge's appearance in the water, and/or affected areas) were collected. A representation of the location of incidents occurred between 2007 and 2015 is shown in Figure 2.5.



ATC: Anthracene; CPF: Chlorpyrifos; 1,2-DCM: 1,2-Dichloroethane; Hg: Mercury; NAP: Naphthalene; Ni: Nickel; NP: Nonylphenol; 4-tert- OP: 4-tert- Octylphenol; Pb: Lead; TBT: Tributyltin; *E.coli: Escherichia coli; BDO*: biological oxygen demand.

Figure 2.3 Location of point sources at Tarragona harbor and discharged substances.

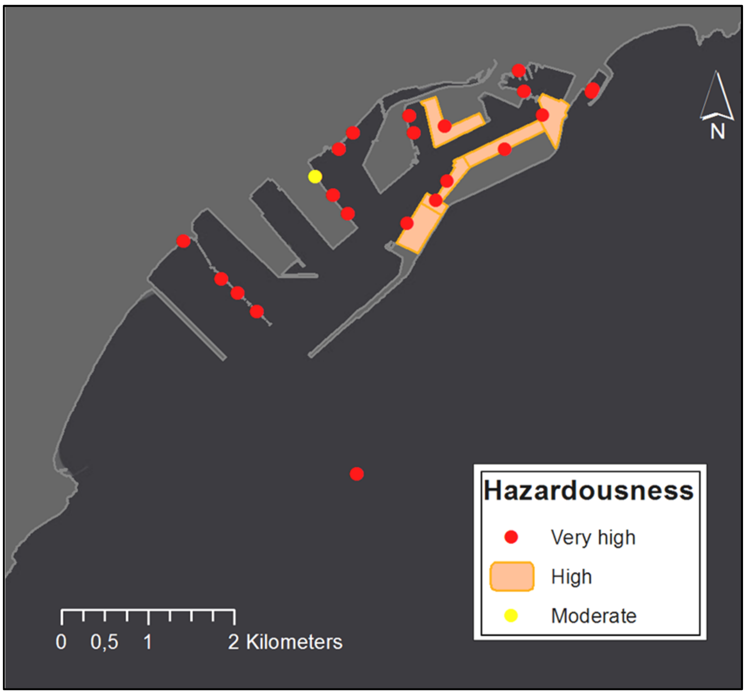


Figure 2.4 Location of diffuse sources at Tarragona harbor and its hazardousness.

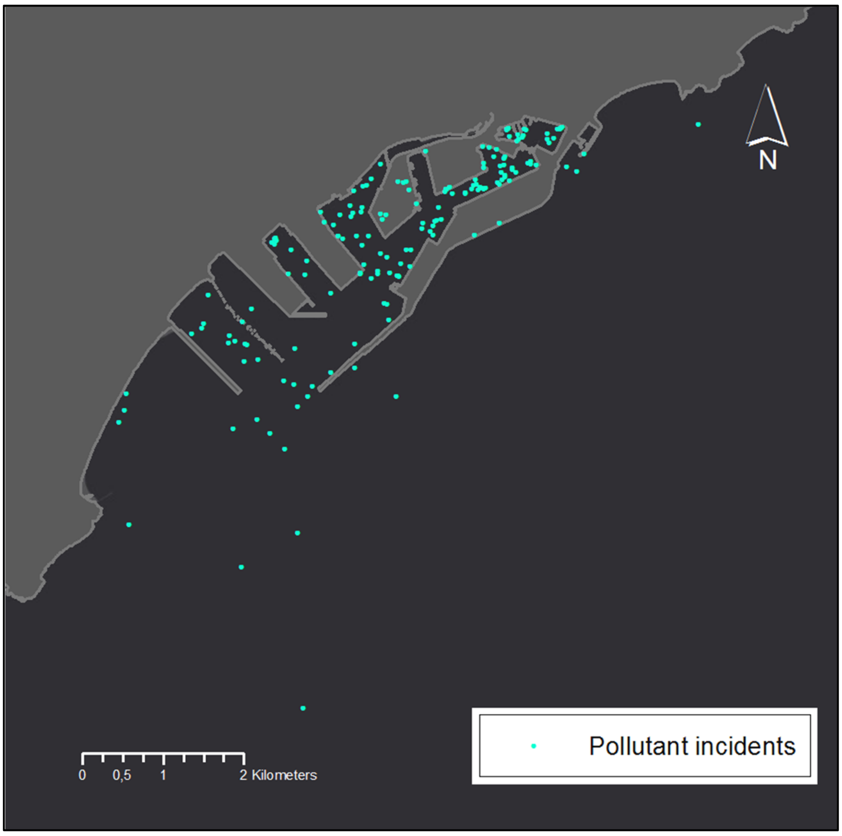


Figure 2.5 Location of pollutant incidents occurred between 2007 and 2015 at Tarragona harbor.

2.1.2. Physical data

Bathymetry data were obtained from the Port Authority of Tarragona. These data were interpolated using a TIN method into an ArcGIS 10.0. (ESRI™) geodatabase to obtain a finite element grid of regular square cells (Figure 2.6). A finite-difference grid of regular square cells (935x883, 30 m of edge) was obtained to carry out the prediction of the evolution of substances by numerical models.

Met-ocean conditions at Tarragona harbor were defined by three environmental variables: sea level (V_{eta}), wind velocity (V_u) and wind direction (V_v). Sea level data were obtained from the GOS re-analysis database of sea level for European waters (Abascal et al., 2010; 2011). Wind velocity and wind direction data were obtained from the SeaWind-ERA-Interim dataset of wind for North Europe waters and coastal seas (Menéndez et al., 2011; 2014). Met-ocean data were analyzed by applying K-means algorithm (MacQueen, 1967; Camus et al., 2011) and 49 representative met-ocean conditions were stablished (Figure 2.7).

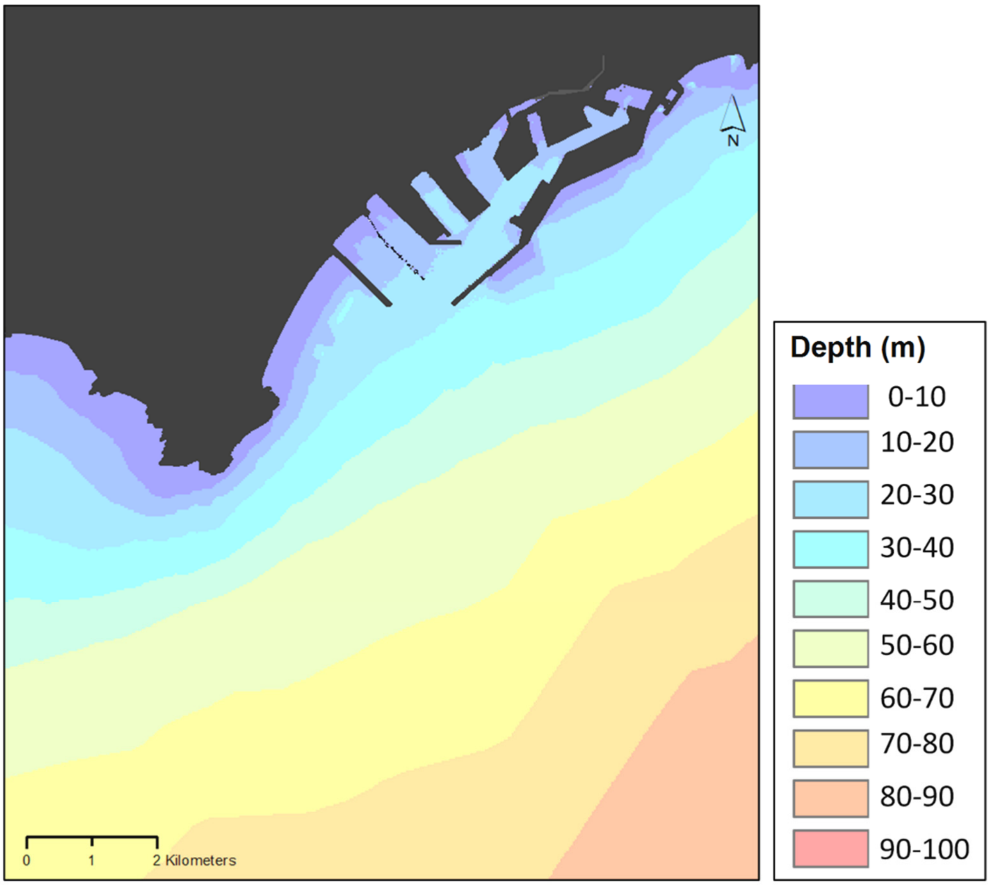


Figure 2.6 Representation of the bathymetry mesh grid at Tarragona harbor.

Wind-generated currents produced by the 49 most-probable hydrodynamic conditions were calculated using a quasi-three dimensional model (García et al., 2010). To do this, currents due to the Francolí River and astronomical tides were neglected since the study area is characterized by a micro tidal regime (centimeters of mean tidal range) and minor river inputs (usually low or null irregular river flows). A Friction Chezy coefficient of 55 $m^{1/2}\cdot s^{-1}$, a 1 $m^{2}\cdot s^{-1}$ Eddy viscosity coefficient, a Wind drag coefficient of 0.0026 were stablished from previous studies (Gómez et al., 2014a). Finally, a medium annual regime of winds was estimated in order to compute the affected area of the environmental hazards. To obtain a medium annual regime of winds, Monte Carlo method was applied to the 49 representative met-ocean conditions previously selected, taking into account constant wind conditions in periods of 8 h and the probability of occurrence of each wind component (Gómez at al., 2014a).

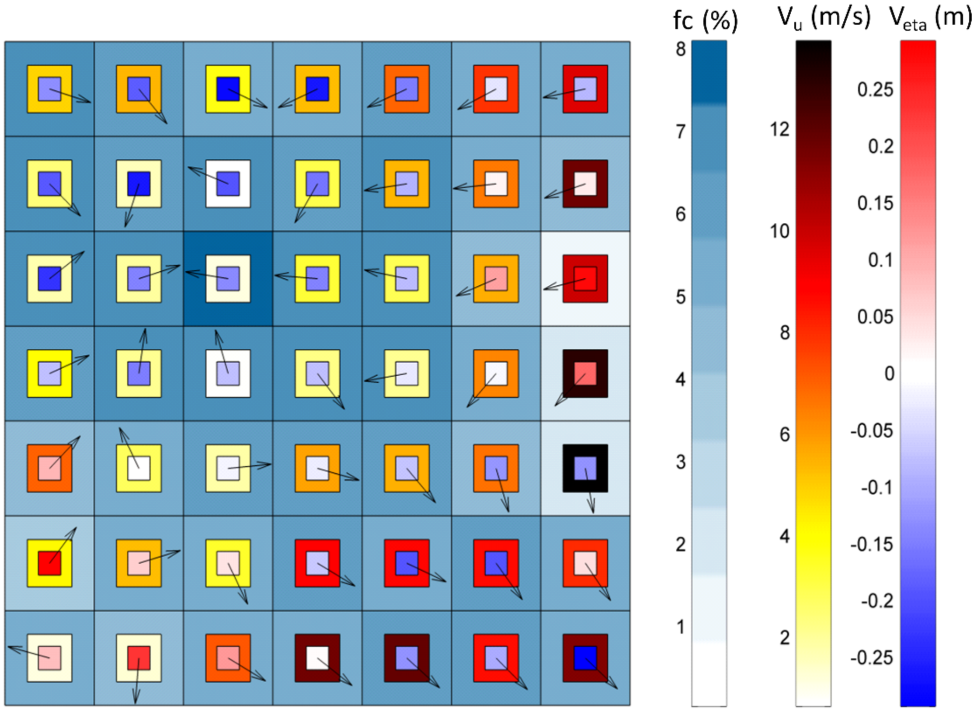


Figure 2.7 Representation of the 49 centroids selected by statistic k- means technique. V_{eta}(m): sea level, W_s(m/s): wind velocity and, fc (%): occurrence percentage. The arrows indicates wind direction.

2.1.3. Environmental quality data

Environmental quality data of Tarragona harbor was compiled from the Environmental Quality Monitoring Program of Tarragona Port Authority. Water and quality data seasonally collected (campaigns in winter-summer-autumn-spring) and sediment data annually collected during 2009, 2010 and 2011, at 9 sampling sites, were used (Figure 2.8).

Figure 2.8 Location of sampling sites at Tarragona harbor.

Biological elements, oxygenation conditions, transparency, salinity, nutrients and specific pollutants (metals and organic compounds) were analyzed in water samples (Table 2.2). Water column samples were collected using a 5 l Niskin at surface, medium depth and bottom. Samples were stored in plastic (for metal analysis) or glass bottles (for nutrients and organic compounds analysis) and adequately refrigerated during sample collection works. Once in the laboratory, the samples were freeze at -5°C. Chlorophyll a, dissolved oxygen, turbidity and salinity were measured by means of CTD (conductivity-temperature-depth) multiparameter probe.

Water quality variables	
Biological elements	Chlorophyll a
Oxygenation conditions	Dissolved oxygen
Transparency	Turbidity
Salinity	Salinity
Nutrients conditions	Ammonium
	Nitrates
	Nitrites
	Phosphate
	Silicate
Metals	Arsenic
	Cadmium
	Chromium
	Copper
	Lead
	Mercury
	Nickel
	Zinc
Organic compounds	1,2,4-Trichlorobenzene
	1,2-Dichloroethane
	4-tert-octilfenol
	Acenaphthene
	Anthracene
	Benzene
	Benzo(a)pyrene
	Benzo(b)fluoranthene
	Benzo(ghi)perylene
	Benzo(k)fluoranthene
	Fluoranthene
	Fluorene
	Hexachlorobutadiene
	Hydrocarbons Total
	Indeno(1,2,3-cd)pyrene
	Naphthalene
	Pyrene
	Tributyltin

Table 2.2 Water variables measured in samples collected at Tarragona harbor.

Sediment samples were collected by a 600 cm^2 Van Veen grab sampler. Physico-chemical variables and specific pollutants (metals and organic compounds) were analyzed in sediment samples (Table 2.3). Sediment samples were stored in Pyrex glass bottles (for organic pollutants) and zip plastic bags (for metals analysis) and adequately refrigerated during sample collection works. Once in the laboratory, both the glass bottles and plastic bags were freeze at -5°C and -20°C, respectively.

Sediment quality variables	
Physico-chemical indicators	Total Kjeldahl nitrogen
	Total organic carbon
Metals	Arsenic
	Chromium Total
	Copper
	Lead
	Mercury
	Nickel
	Zinc
Organic compounds	4-nonylphenol
	Benzo (b) fluoranthene
	Benzo(a)anthracene
	Benzo(a)pyrene
	Benzo(ghi)perylene
	Benzo(k)fluoranthene
	Chrysene
	Fluoranthene
	Indeno(1,2,3-c,d)pyrene
	PCB 101
	PCB 118
	PCB 138
	PCB 153
	PCB 180
	PCB 28
	PCB 52
	Phenanthrene
	Polycyclic aromatic hydrocarbons total
	Pyrene

Table 2.3 Sediment variables measured in samples collected at Tarragona harbor.

Analytical methods of water and sediment variables followed normalized Standard Methods (APHA, 2004) and U.S. Environmental Protection Agency methods (US EPA).

2.2 Oil handling facility

The oil terminal considered as a facility case study is located at Tarragona harbor (Figure 2.1(b). The facility consists of a dock and a monobuoy, which has been operating at the harbor since 1975. The dock (1,489 m length) has 5 moorings (11S, 35T, 35S, 80-100T, 80-100S, Figure 2.1(c) for vessels of 11,000, 40,000 and 10,0000 deadweight tonnage (DWT). The floating dock (monobuoy, Figure 2.1(d) allows for mooring and unloading vessels of up to 250,000 DWT under normal conditions and up to 325,000 DWT and 40 meters draught in special conditions. Both, the long dock and the monobuoy are highly active sites, with 8 and 4.2 millions of Tons of goods traffic in 2014, respectively.

The monobuoy has two floating pipelines for crude, and different connection for bunkering fuel oil to the vessels (Figure 2.9).

Figure 2.9 A vessel operating at the monobuoy of Tarragona harbor.

The long dock has two pipelines for petroleum crude with a capacity of 4,800 - 11,000 Tm^3/h. Vessels make use of other different pipelines for handling naphtha and deballasting, fuel oil, vacuum diesel gasoline and diesel, kerosene and pyrolysis gasoline (PYGAS), propane, ethylene and propylene, diesel, octane and butylene, butadiene, fresh water and several gases.

2.2.1. Environmental hazards

At oil handling facility scale, pollutant incidents were considered as environmental hazards. As mentioned before, a pollutant incident is any discharge that may reduce the environmental quality, whether the reduction is punctual or occurs progressively (Juanes et al., 2013).

Data on pollution incidents at the long dock and the monobuoy were extracted and compiled from:

i) general emergency reports (1998-2011) from the Coordination Centre of Sea Rescue and Marine Pollution of Tarragona (CCS Tarragona);
ii) a database of pollution incidents recorded by the Tarragona Port Authority from 1985 to 2012; and,
iii) pollution incident reports from Repsol Petróleo, S. A. during the period 1997-2011.

For the specific case of the monobuoy and the dock at the port of Tarragona, 22 accidental spills were identified from 1989 to 2012, 7 of which occurred at the monobuoy and 15 at the dock. These records did not contained detailed information about the spilled product neither the quantity, but a description of the spill's appearance and the extent of the affected area were recorded for each spill.

2.2.2. Physical data

As mentioned at harbor scale description, a finite-difference grid of regular square cells (452x371, 30 m of edge) obtained from interpolation of bathymetric data provided by Port Authority of Tarragona by means of ArcGIS 10.0. (ESRI^{TM}) was obtained (Figure 2.6).

Regarding met-ocean conditions, three dimensional data of sea level (GOS re-analysis, Abascal et al., 2010; 2011), wind direction and wind intensity (SeaWind-ERA-Interim dataset, Menéndez et al., 2011; 2014) was analyzed by applying K-means algorithm (MacQueen, 1967; Camus et al., 2011) and four representative met-ocean conditions were stablished at oil handling facility scale with different frequency of occurrence (fc) (Figure 2.10):

i) Vc_1: northwest winds (312º, 5.6 m/s) and -0.09 m of sea level (fc=0.18);

ii) Vc_2: west winds (277º, 2.6 m/s) and -0.05 m of sea level (fc=0.20);

iii) Vc_3: east winds (79º, 5 m/s) and 0.04 m of sea level (fc=0.16); and

iv) Vc_4: calm conditions (301º, 0.1 m/s) and -0.14 m of sea level (fc=0.46).

Wind-generated currents produced by the 4 most-probable hydrodynamic conditions were calculated using a quasi-three dimensional model (García et al., 2010). As it was mentioned before, currents due to the Francolí River and astronomical tides were neglected. A Friction Chezy coefficient of 55 $m^{1/2}\cdot s^{-1}$, a 1 $m^2\cdot s^{-1}$ Eddy viscosity coefficient, a Wind drag coefficient of 0.0026 were stablished from previous studies (Gómez et al., 2014a).

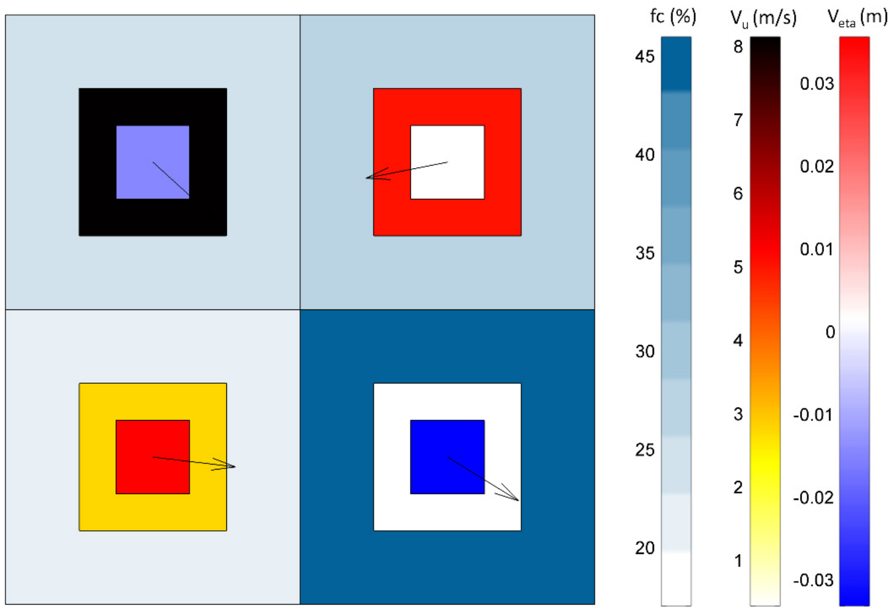


Figure 2.10 Representation of the 4 centroids selected by statistic k- means technique. V_{eta}(m): sea level, W_s(m/s): wind velocity and, fc (%): occurrence percentage. The arrow indicates the wind direction.

2.2.3. Environmental quality data

A specific sampling work was designed in the framework of this thesis in order to collect environmental quality data around the monobuoy. Sediment samples were collected in July 2014 at seven sampling sites in the area around the monobuoy (Figure 2.11). The location of the sampling sites was established based on the preferred trajectories of potential spills. These trajectories were calculated for the four most representative met-ocean conditions and scenarios based on the specific local pollution cases (calculated on Chapter IV).

The depth of sampling sites was about 40 m, ranging from 35.5 m of sampling site E6 to 48 m of sampling site E4.

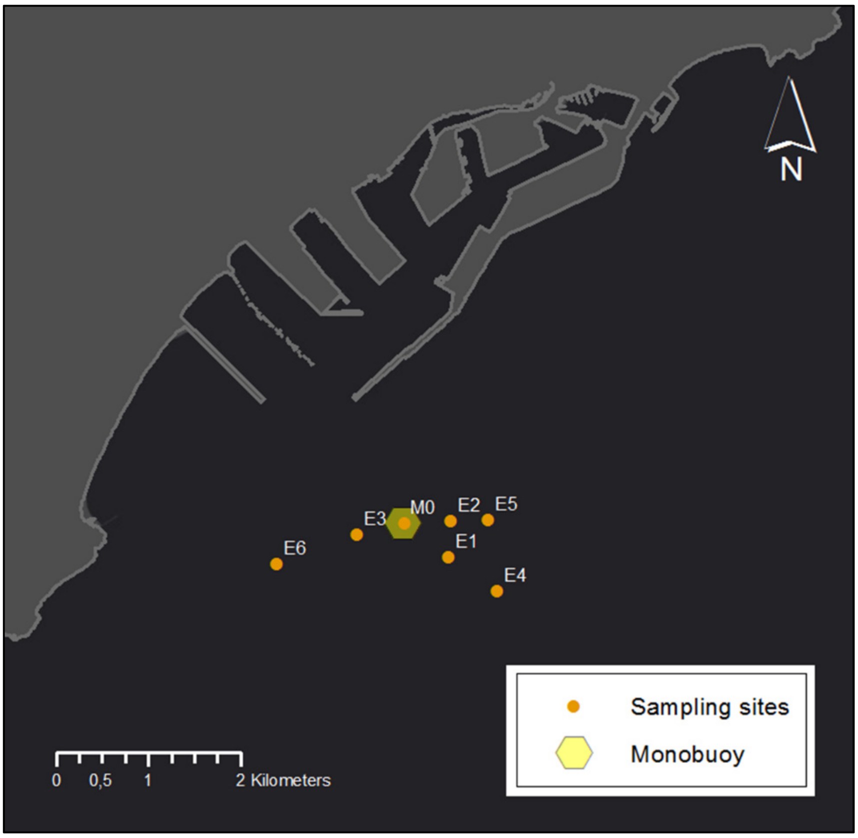


Figure 2.11 Location of sampling sites at the monobuoy of Tarragona harbor.

Sediment samples were collected by a 0.04 m^2 Van Veen grab sampler. Five samples were collected. One sample was destinated to physicochemical and specific pollutants analysis (Table 2.4), two samples were aimed at toxicity bioassays (*Vibrio fischeri* bacteria luminescence inhibition test and sea urchin embryology test) and two samples were destinated for macrobenthic community composition determination.

Samples for physicochemical, specific pollutants and toxicity bioassays were stored in ice storage refrigerators during sampling work and subjected to freeze-dried at the laboratory. Macrobenthic community samples were sieved *in situ* by using a sieve of 1 mm screen. The retained material was stored in plastic bottles with a mixture of seawater and 4% formaldehyde. 24 hours later the formaldehyde was replaced by a mixture of sea water and 70% ethanol for preservation until the identification process.

Granulometry was determined by dry sieving following the Wentworth scale. The organic matter was estimated from dried sediments (65 ºC, 48 h) as loss on ignition in a muffle furnace up to 550 °C for 6 h.

Benthic macrofauna was identifying at lower taxonomical level possible. Specific abundance (number of individuals/m^2), species richness (number of species/m^2) and diversity (Shannon Index) was calculated for each sample. The relative abundance of ecological groups considered in the Mediterranean Occidental index (MEDOCC) (Pinedo et al., 2015) to assess the ecological status (ES) according to WFD requirements was calculated.

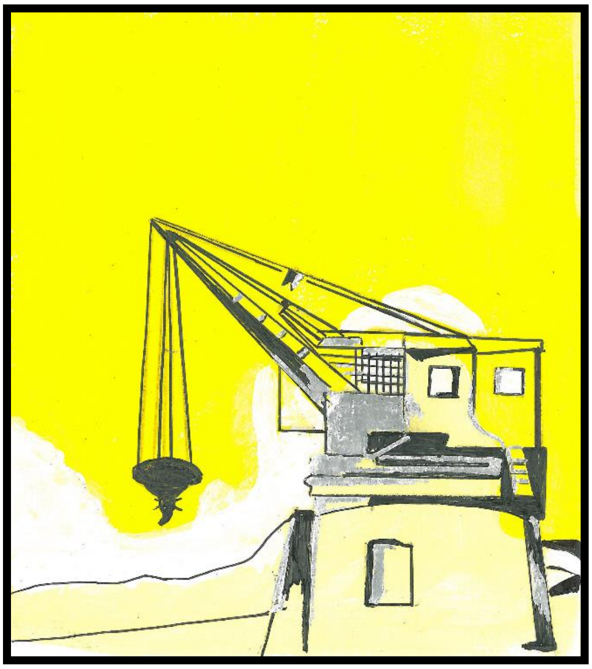
Polycyclic aromatic hydrocarbons were determined by high-resolution gas chromatography (HRGC-HRMS). Metals analytical methods followed normalized Standard method of U.S. Environmental Protection Agency methods EPA 6020 (US EPA, 2007a).

Pore water was extracted from sediment samples destined to *V. fischeri* toxicity analysis by the use of 0.47 µm filter paper filtration coupled to vacuum. The organic extract was obtained followed the EPA 3546 method (US EPA, 2007b) and filtrated by a 0.47 µm filter paper. Finally, *Basic test* for organic extract and 90*% Basic test* for aqueous extract were performed by a Microtox 500 Analyser (SDI, USA).

Sea urchin toxicity test was analysed followed normalized Standard method of the Studies and Experimentation of Public Works Center of the Ministry of Agriculture, Food and Environment of the Spanish Government (CIEM, 2015).

Sediment quality variables	
Physico-chemical indicators	Total organic matter
Biological elements	Macrobenthic community composition
Bioassays	*Vibrio fischeri* luminescence inhibition test
	Sea urchin embryology test
Metals	Arsenic
	Cadmiun
	Chrome
	Cobalt
	Copper
	Lead
	Mercury
	Nickel
	Vanadium
	Zinc
Organic compounds	Acenaphthene
	Acenaphthylene
	Anthracene
	Benzo(a)anthracene
	Benzo(a)pyrene
	Benzo(b)fluoranthene
	Benzo(g,h,i)perylene
	Benzo(k)fluoranthene
	Chrysene
	Dibenzo(a,h)anthracene
	Fluoranthene
	Fluorene
	Indeno(1,2,3-cd)pyrene
	Naphthalene
	Phenanthrene
	Pyrene

Table 2.4 Sediment quality variables measured in samples collected at the monobuoy of Tarragona harbor.

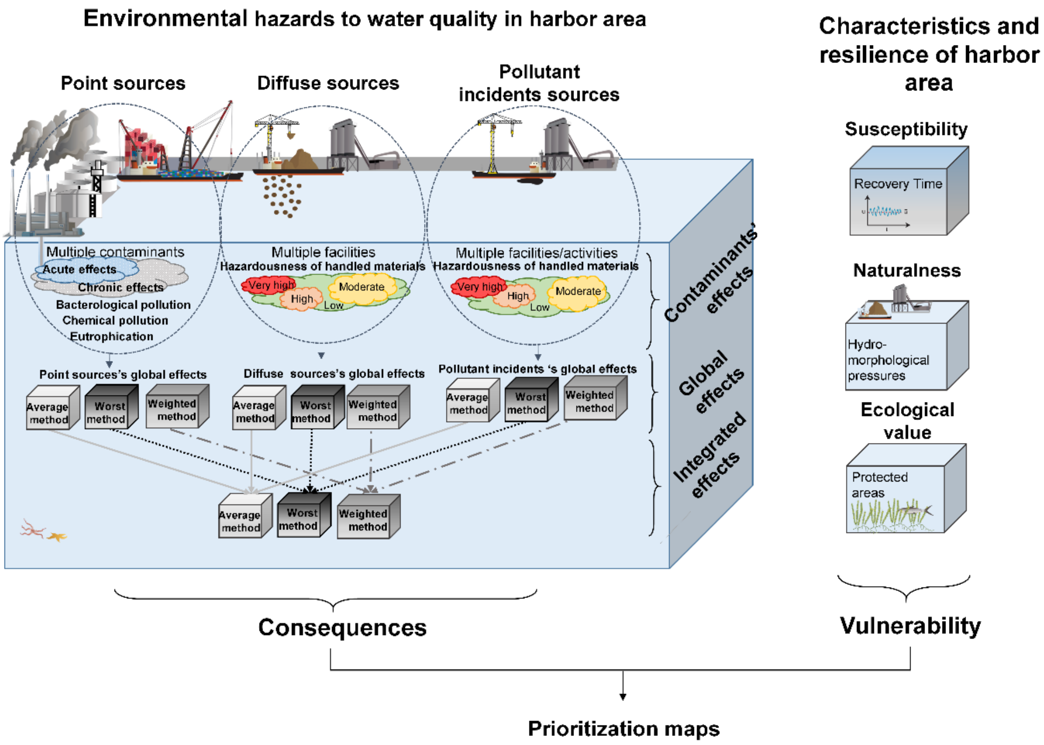


Chapter III

Prioritization maps

CHAPTER III. PRIORITIZATION MAPS: THE INTEGRATION OF ENVIRONMENTAL RISKS TO MANAGE WATER QUALITY IN HARBOR AREAS

*This chapter is an edited version of the research article published in the journal Marine Pollution Bulletin. 111: 57-67 by Valdor, P.F., Gómez, A.G., Ondiviela, B., Puente, A. and Juanes J.A. with the title '*Prioritization maps: the integration of environmental risk to manage water quality in harbor areas*'.*



The chart symbols are courtesy of the Integration and Application Network (ian.umces.edu/symbols).

Figure 3.1. Graphical abstract.

Abstract

In this chapter, a method that integrates the environmental risk of the multiple effects of the uses and activities developed in harbor areas is presented. The method is based on the Environmental Risk Assessment (ERA) procedure and

integrates the impacts caused by various contaminants coming from a range of environmental hazards. Consequences and vulnerability are integrated obtaining a spatial variation of risk: prioritization maps. Consequences are considered as the effects derived from all identified hazards. Vulnerability is expressed in terms of functional relations between environmental susceptibility against a disturbance and the state of protection of the receptors at risk. Prioritization maps are made up of 4 main stages: i) an environmental hazard identification; ii) the estimation of the consequences (integrated effects); iii) the estimation of vulnerability (environmental characteristics); and, iv) the integration of environmental risk. In order to adapt prioritization maps to the peculiarities of the study area, three different methods for the integration of the effects are proposed: average-value, worst-case and weighted methods. The implementation to a real case (Tarragona harbor, NE Spain) confirms its usefulness as a risk analysis tool to communicate and support water quality management in harbors. Prioritization maps at Tarragona harbor are significantly related to water and sediment quality indicators.

3.1 Introduction

Activities and uses developed in harbor areas have been widely recognized as services of special economic and social relevance. Commercial, nautical-recreational, logistic and storage uses, among others, are developed all together in the surrounding harbor area. Such coexistence of uses in harbor environments has had negative effects on the aquatic environment (Darbra and Casal, 2004) that can be perceived both spatially and temporally. Harbor areas are affected by multiple contaminants coming from a great variety of environmental hazards. Adequate tools to estimate the impact of multiple hazards and contaminants on harbors are required.

The effects of environmental hazards on water quality caused by ordinary activities (e.g., Ondiviela et al., 2012; Gómez et al., 2015) as well as uncontrolled spills in harbor areas (e.g. Grifoll et al., 2010; Mestres et al., 2010; Ondiviela at al., 2012) have been widely studied and procedures to provide sustainable solutions without undermining the economy on which the harbor area is sustained have been proposed (e.g., Ondiviela et al., 2012; Juanes et al., 2013; Gómez et al., 2015). But such studies have only focused on a unique contaminant (e.g., Gudimov et al., 2010) or hazard (e.g., Ronza et al., 2006; Castanedo et al., 2009; Abascal et al., 2010; Valdor et al., 2015), have obviated its integration (Gómez et al., 2014a; 2015), have ignored the spatial-temporal variation of receptors and agents (e.g., Trbojevic and Carr, 2000), have avoided the ecological characteristics of the receptors at risk (e.g., Bruzzone et al., 2000) or have considered only the impacts generated by accidents (e.g., Grifoll et al., 2011).

Previously developed methods have mainly focused on point contaminant sources deriving from ordinary activities. None of the actual methodologies combine the effects of regular contaminant sources with accidents. European guidelines and legislation promote the inclusion of specific information on the anticipated effects of accidental spills in management tools (IMO, 1991; 2000; 2010; European Commission, 2013a; 2014). Pollutant incidents due to operational deficiencies, as well as diffuse contaminant sources, should be incorporated in the environmental risk process. This way, all environmental hazards would be considered and best-decision measures could be ensured.

Several national and international institutions have recognized the need to evaluate risk from mixtures and multiple contaminants (NRC, 1994; Mileson et al., 1999; US EPA, 2003; WHO, 2009). While an individual hazard assessment outcome may not result in excessive effects on its own, a combination of the outcomes may cause significant adverse impacts (European Commission, 2010). This combined effect from various contaminants on the environment differs from the effect of a single contaminant (Velleux et al., 2008). Risk assessment of single contaminant need to be adapted and extended to deal with the specific challenges posed by mixtures (Løkke et al., 2013). Therefore, the overall effect of the various hazards must combine the effects of each of the contaminants (Lahr and Kooistra, 2010).

The different integration models (e.g. similar action, independent action) provide a heterogeneous assessment. In a regulatory perspective addressing the integrated effect of co-occurring chemicals is the first and most important step in providing a more realistic hazard assessment of chemical cocktails in both man and environment (Cedergreen, 2014). The integration method is a crucial aspect in the calculation of integrated environmental risk (Gómez, 2010), and must be adapted to the purpose of managing: What hazards are affecting the most port aquatic systems?; What contaminants are affecting a specific area of the harbor?; How much each facility contributes to the integrated effect?. Answering these questions will allow managers to prioritize the various hazards, contaminants and facilities in order to apply specific corrective and preventive measures.

The estimation of spatial-temporal environmental risk involves the estimation of: i) the consequences; and, ii) the environmental vulnerability (Gómez, et al., 2015). Consequences are considered as the effects derived from all identified hazards. The estimation of the spatial-temporal effects requires the study of the contaminants spilled from hazards to calculate their trajectory and the potential area affected (Valdor et al., 2015). Calibrated numerical models or tools in Geographical Information Systems are extensively used to simulate the evolution of contaminants (Wania and Mackay, 1999; Horiguchi et al., 2006; Yamamoto et al., 2009; Gómez, 2010; Valdor et al., 2016). On the other hand, vulnerability should be addressed in terms of functional relationships between the physical characteristics of the system (extrinsic vulnerability) and the state of protection (inherent vulnerability) (Kværner et al., 2006; Gómez, 2010; Gómez et al., 2014b; 2015). By means of the integration of consequences and vulnerability, prioritization maps would serve as reference for the development of contingency plans (Abascal et al., 2010; Santos et al., 2013b), designing environmental monitoring programs and management of environmental hazards as a whole.

This study is based on the hypothesis that activities and uses developed in harbor areas generate integrated effects caused by multiple contaminants which are introduced by point and diffuse contaminant sources (ordinary operations) as well as by pollutant incidents. Accordingly, the environmental management of these areas must be carried out in an integrated manner. To overcome these limitations, the study showed in this chapter focuses on developing a methodology to integrate the environmental risk of multiple effects from various hazards on harbor aquatic systems. The method as a whole was tested by application to the Tarragona harbor (NE Spain), analyzing the relationship between environmental quality indicators and risk values.

3.2 Methodology proposed

Prioritization maps are made up of 4 main stages: i) an environmental hazard identification; ii) the estimation of the consequences (integrated effects); iii) the estimation of the vulnerability (environmental characteristics); and, iv) the integration of environmental risks (prioritization maps).

3.2.1 Identification of environmental hazards

The identification of hazards comprises their systematic location and characterization. This way, the contaminants that are likely to cause deleterious effects to water quality are recognized. Environmental hazards to be considered are: point contaminant sources (predefined fixed points), diffuse contaminant sources (non-challenged discharges) and, pollutant incident sources (accidental spills).

Point and diffuse contaminant sources are characterized by gathering the necessary information (location, substances or materials discharged, flows, quantities handled, etc.) by consulting different sources (discharge authorization, Pollutant Release and Transfer Register (PRTR) and emission factors and local database of accidental spills, among others) (Gómez et al., 2015).

Potential pollutant incident sources are selected from the analysis of local databases of accidental spills. To do this, the next steps should be followed: i) the hazard level (hazardousness) of the substances or materials handled at each facility is defined (Table 3.1); ii) a frequency of occurrence is estimated to each facility. (Table 3.1); iii) both factors (the highest hazardousness of material or substances handled and the frequency) are combined as is shown in Table 3.1; and, iv) discharge points with significant frequency of incidents and relevant hazardousness are identified as potential pollutant incidents sources following the Table 3.1 assessment criteria.

	Frequency		
Hazardousness	High (>1 incident/month)	Medium (>1 incident/year)	Low (<1 incident/year)
Very High*	✔	✔	✔
High*	✔	✔	✔
Moderate*	✔	✔	✖
Low*	✔	✖	✖

✔ : Discharge points identified as potential pollutant incidents' sources.
✖ : Discharge points not considered as potential pollutant incidents' sources.
Very high*: Priority hazardous substances (Directive 2013/39/EU)
High*: Priority substances (Directive 2013/39/EU)
Moderate*: Dangerous materials (IMO, 2014)
Low*: Potentially dangerous materials and other materials (IMO, 2014).

Table 3.1 Identification of discharge points liable to cause pollutant incidents.

3.2.2 Estimation of integrated effects: consequences

The consequences (Co_{gh}) are defined as the integrated effects on the environment that may result from all environmental hazards. A mesh grid is created with the desired cell resolution comprising the study area. Effects are estimated at cell level obtaining a spatial variation. The integration is made up of 3 levels of integration (Figure 3.2): i) the effect of single contaminant; ii) the global effects of each type of hazard; and, iii) the integrated effects caused by all hazards.

Contaminants' effects

The *effects of contaminants* introduced by the various environmental hazards are estimated. The effects of the contaminants introduced by point contaminant sources are estimated in terms of ecological effects of three processes: i) chemical pollution process, caused by priority substances; ii) eutrophication process, measured by the decrease of dissolved oxygen; and, iii) bacteriological contamination process, using *Escherichia coli* as indicator (Gómez, 2010; Juanes et al., 2013). The spatial and temporal evolution of each contaminant introduced by a single point contaminant source is calculated by means of numerical models through one year of simulation (Thomann and Mueller, 1987).

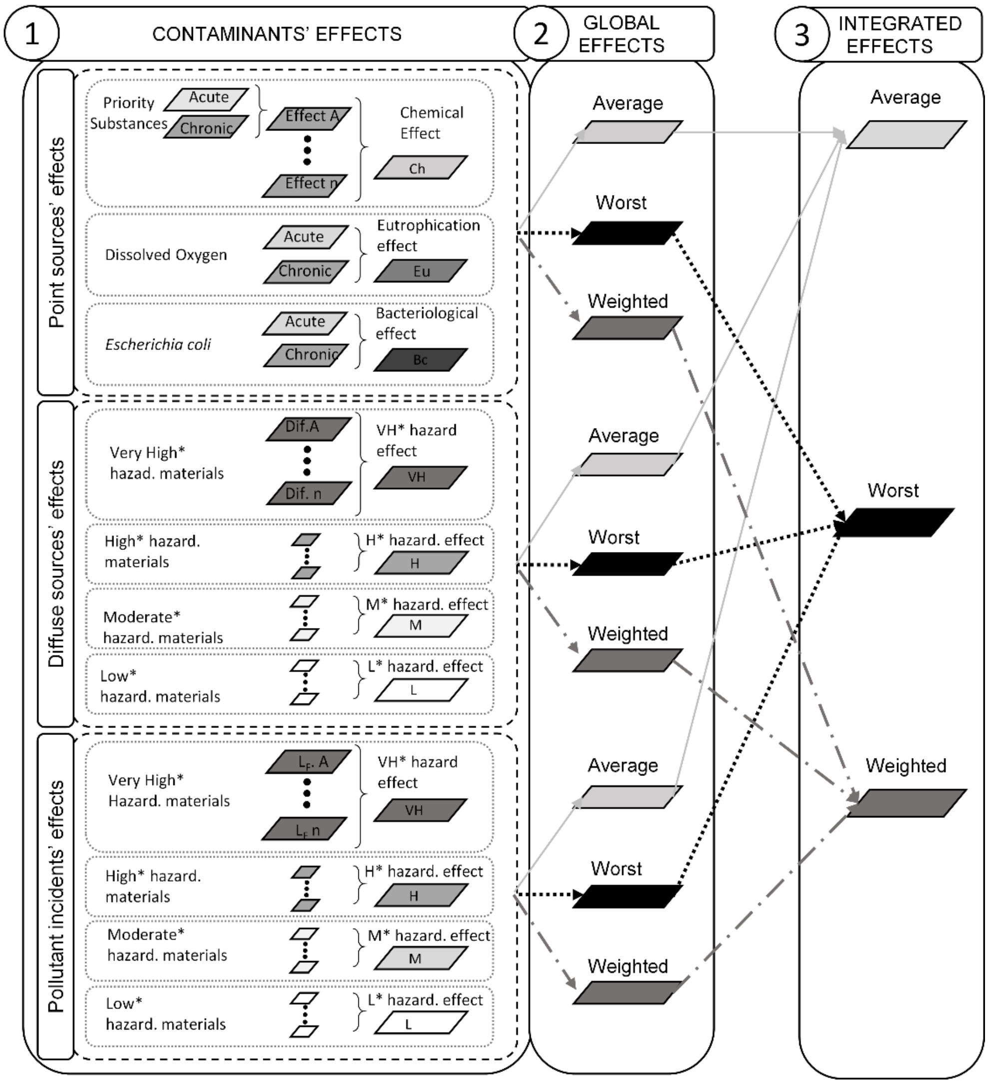


Figure 3.2 Graphic representation of main stages to obtain integrated effects.

For every contaminant, acute and chronic effects are computed at cell level (Gómez et al., 2014b):

- Acute effects: $$AE_{gh}=\frac{T_{adevserse\ conditions_{gh}}}{T_{total}} \times 100 \qquad \text{Eq. (3.1)}$$

Where, AE_{gh} is the percentage of time during which unacceptable conditions on the environment are recorded, $T_{adevserse\ conditions_{gh}}$ is the time at which the Maximum Allowable Concentration (MAC) of the contaminant is exceeded at cell level, and T_{total} is the time of the simulation (8760 hours).

- Chronic effects: $HQ_{gh} = \frac{[\bar{x}]_{gh}}{\mathrm{AA-EQS}}$; $HQ_{gh} = \frac{AA-EQS}{[\mathbf{OD}]_{gh}}$ Eq. (3.2)

Where, HQ_{gh} is the hazard quotient, $[\bar{x}]_{gh}$ is the annual average concentration of the specific chemical or bacteriological contaminant at cell level (g,h), $[\overline{\mathrm{OD}}]_{gh}$ is the annual average concentration of dissolved oxygen at cell level and AA-EQS is the Annual Average-Environmental Quality Standard.

Finally, the effect from each process is obtained by combining acute and chronic effects of the contaminant through a double entry matrix (Table 3.2). The effect of the chemical pollution process, which involves more than one contaminant (priority substances), is estimated by means of consideration of the worst case of all the effects (Gómez, 2010) (Figure 3.2).

	Acute effects			
	N	L	M	H
Chronic effects	($AE_{gh} < 0.1$)	($0.1 \leq AE_{gh} < 1.0$)	($1.0 \leq AE_{gh} < 3.0$)	($AE_{gh} \geq 3.0$)
N ($HQ_{gh} < 1$)	N (0)	L (1)	L (1)	M (2)
L ($1 \leq HQ_{gh} < 30$)	L (1)	L (1)	M (2)	M (2)
M ($30 \leq HQ_{gh} < 100$)	L (1)	M (2)	M (2)	H (3)
H ($HQ_{gh} \geq 100$)	M (2)	M (2)	H (3)	VH (4)

VH: Very high; H: High; M: Moderate; L: Low; N: Null

Table 3.2 Double entrance matrix for assessing the effect of each process of point contaminant sources (Gómez, 2010).

The effects due to contaminants introduced by diffuse contaminant sources or pollutant incidents' sources are estimated by calculating the potential affected areas using GIS tools (Gómez, 2010; Juanes et al., 2013). The potential affected area of each contaminant is the covering surface of the virtual particles' paths located in the perimeter of an area around the facility at a given constant distance Eq. (3.3).

$$\mathrm{dt} = kd \; x \; \frac{Nd \; x \; Ed}{D} \qquad \text{Eq. (3.3)}$$

Where, kd, Nd and Ed are constant factors; dt is the constant distance around the facility, kd is 100 kg/m^2, Nd is 1 for liquid materials and 5 for solids, D is the density of the less dense substance or handled material by the environmental hazard in kg/m^3, Ed is 0.1 for diffuse contaminant sources (by considering normal operations), while Ed is 1 for pollutant incidents' sources (by considering operations under completely unfavorable conditions) (Juanes et al., 2013).

The paths of the virtual particles are calculated during a two-hour period. The cells inside the potential affected area of each facility obtain the numerical value corresponding to the most hazardous substance or handled material (Table 3.1). By spatial superposition, four potential areas are obtained; one for each level of hazardousness (Figure 3.2).

Global effects

Global effects of each type of environmental hazard (point sources, diffuse sources and pollutant incident sources) are calculated using three different methods (Figure 3.2): i) Average-Value Method (AV), estimates the global effect of each type of environmental hazard by calculating the average value at cell level; ii) Worst-Case Method (WC), estimates the global effect of each type of environmental hazard by considering the highest value at cell level; and, iii) Weighted Method (WD), estimates the global effect at cell level by applying a weighting factor to each contaminant Eq. (3.4) and Eq. (3.5). By considering that, chemical pollution has greater impact on the environment while eutrophication or bacteriological pollution acquires a gradually smaller importance at harbor areas (Gómez, 2010). The formula for point sources is Eq. (3.4):

- Point sources: $WD\ \{PCS_{gh}\} = 0.8 \times Ch_{gh} + 0.15 \times Eu_{gh} + 0.05 \times Bc_{gh}$ Eq. (3.4)

Where, $WD\ \{PCS_{gh}\}$ is the global effect of point sources estimated by the weighted method, Ch_{gh} is the effect of the chemical pollution process (0 to 4), Eu_{gh} is the effect of the eutrophication process (0 to 4) and, Bc_{gh} is the effect of the bacteriological pollution process (0 to 4) at cell level (g,h).

On considering that, the contaminants' hazardousness is directly proportional to the impact caused. The formula for diffuse sources is Eq. (3.5):

- Diffuse sources: $WD\ \{DCS_{gh}\} = 0.5 \times Very\ High^*_{gh} + 0.3 \times High^*_{gh} + 0.15 \times Moderate^*_{gh} + 0.05 \times Low^*_{gh}$ Eq. (3.5)

Where *WD* $\{DCS_{gh}\}$ is the global effect of the diffuse sources estimated by weighted method, Very High$^*_{gh}$ is the effect caused by very high hazardousness materials (4 or 0), High$^*_{gh}$ is the effect caused by high hazardousness materials (3 or 0), Moderate$^*_{gh}$ is the effect caused by moderate hazardousness materials (2 or 0), Low$^*_{gh}$ is the effect caused by low hazardousness materials (1 or 0) at cell level (g,h). The applicable formula for the weighted method for pollutant incident sources is equivalent to Eq. (3.5).

The results obtained by the average and weighted methods are categorized into 5 levels according to ranges defined by the 80th, 60th and 20th percentiles of the potential range of effects obtained by the hypothetical combinations of the effect values at cell level (Table 3.3).

Integrated effects

The *integrated effects* of all the environmental hazards are obtained by considering the same integration methods: i) Average-Value Method (AV, Eq. (3.6)); ii) Worst-case Method (WC, Eq. (3.7)); and, iii) Weighted Method (WD, Eq. (3.8)). The integration is done by combining the results of the prior stage using the same method of integration (Figure 3.2).

- Average-value method:

$$Co_{AVgh} = 1/3\ [AV\ \{PCS_{gh}\} + AV\ \{DCS_{gh}\} + AV\ \{PI_{gh}\}] \qquad \text{Eq. (3.6)}$$

Where, Co_{AVgh} are the consequences of all hazards at cell level (g,h) estimated by the average-value method, AV $\{PCS_{gh}\}$, AV $\{DCS_{gh}\}$ and AV $\{PI_{gh}\}$ is the global effect at cell level of point, diffuse and pollutant incident sources, respectively, using the average method.

- Worst-case method:

$$Co_{WCgh} = WC\ [WC\ \{PCS_{gh}\},\ WC\ \{DCS_{gh}\},\ WC\ \{PI_{gh}\}] \qquad \text{Eq. (3.7)}$$

Where, Co_{WCgh} are the consequences of all hazards at cell level (g,h) estimated by the worst-case and method, WC $\{PCS_{gh}\}$, WC $\{DCS_{gh}\}$ and WC $\{PI_{gh}\}$ is the global effect at cell level of point, diffuse and pollutant incident sources, respectively, using the worst-case method.

- Weighted method:

$$Co_{WDgh} = 0.5 \text{ x } WD\ \{PCS_{gh}\} + 0.3 \text{ x } WD\ \{DCS_{gh}\} + 0.2 \text{ x } WD\ \{PI_{gh}\} \qquad \text{Eq. (3.8)}$$

Where, Co_{WDgh} are the consequences of all hazards at cell level (g,h) estimated by the weighted method, WD {PCS_{gh}}, WD {DCS_{gh}} and WD {PI_{gh}} is the global effect at cell level of point, diffuse and pollutant incident sources, respectively, using the weighted method.

The results obtained by the average and weighed methods are categorized into 5 levels. The threshold values for each assessment category are based on the 80^{th}, 60^{th} and 20^{th} percentiles of the potential range of the effects obtained by the hypothetical combinations of the effect values at cell level (Table 3.3).

3.2.3 Estimation of the environmental characteristics: vulnerability

Vulnerability is expressed in terms of the functional relations between the environment susceptibility against a disturbance and the state of protection related to the value of the receptors at risk (Eq. (3.9)) (Gómez, et al., 2014b):

$$\mathrm{Vu_{gh}} = \frac{1}{3}\left(2\ x\ Su_{\mathrm{gh}} + \frac{1}{3}\ \left(Na_{\mathrm{gh}} + 2\ x\ Ev_{\mathrm{gh}}\right)\right) \qquad \text{Eq. (3.9)}$$

Where, $\mathrm{Vu_{gh}}$ is the vulnerability, Su_{gh} is the susceptibility, Na_{gh} is the naturalness and, $Ev_{\mathrm{gh}}$is the ecological value at cell level (g,h).

Susceptibility is associated to the flushing capacity of aquatic systems and it is calculated by the estimation of the recovery time (Gómez, et al., 2014b). Recovery time is defined as the time required reducing a homogenous concentration of tracer to a 0.1% in a cell. Recovery time is computed using depth average numerical models (Table 3.4). The status of protection is defined as the combination of naturalness and ecological value. Naturalness evaluates the presence of physical anthropogenic modifications, by calculating buffer areas around hydromorphologycal pressures (HPs) using Buffer tool in ArcGIS. The buffer area is calculated by considering the length of the pressure and its continuity (Gómez et al., 2014b). Ecological value is defined as the presence of flora and fauna species at a certain area affected by environmental hazards. Ecological value is estimated based on the affection of sensitive areas recognized under Directive 91/271/EEC (European Commission, 1991), and protected areas included in the Natura 2000 network - Directive 2009/147/EC (European Commission, 2009a); Directive 92/43/EEC (European Commission, 1992) - (Table 3.4).

Effects	Method	Hazard	Assessment category	Assessment criteria
Global effects	Average	Point sources	N (0)	x = 0.00
			L (1)	0.00 < x < 1.33
			M (2)	1.33 ≤ x < 2.00
			H (3)	2.00 ≤ x < 3.00
			VH (4)	x ≥ 3.00
		Diffuse and pollutant incident sources	N (0)	x = 0.00
			L (1)	0.00 < x < 0.50
			M (2)	0.50 ≤ x < 1.33
			H (3)	1.33 ≤ x < 2.33
			VH (4)	x ≥ 2.33
	Weighted	Point sources	N (0)	x = 0.00
			L (1)	0.00 < x < 0.84
			M (2)	0.84 ≤ x < 2.37
			H (3)	2.37 ≤ x < 3.16
			VH (4)	x ≥ 3.16
		Diffuse and pollutant incident sources	N (0)	x = 0.35
			L (1)	0.00 < x < 0.35
			M (2)	0.35 ≤ x < 2.05
			H (3)	2.05 ≤ x < 2.90
			VH (4)	x ≥ 2.90
Integrated effects	Average		N (0)	x = 0.00
			L (1)	0.00 < x < 1.33
			M (2)	1.33 ≤ x < 2.33
			H (3)	2.33 ≤ x < 2.67
			VH (4)	x ≥ 2.67
	Weighted		N (0)	x = 0.00
			L (1)	0.00 < x < 1.20
			M (2)	1.20 ≤ x < 2.40
			H (3)	2.40 ≤ x < 2.80
			VH (4)	x ≥ 2.80

VH: Very high; H: High; M: Moderate; L: Low; N: Null

Table 3.3 Criteria used to assess the global and integrated effects estimated by average and weighted methods.

Parameter	Indicator	Assessment category	Assessment criteria
Susceptibility (Su_{gh})	*Recovery time (RT_{gh})*	VH (4)	RT_{gh} > 30 d
		H (3)	7 d< RT_{gh} ≤ 30 d
		M (2)	1 d < RT_{gh} ≤7 d
		L (1)	RT_{gh} ≤1 d
Naturalness (Na_{gh})	*Alteration by hydromorphologycal pressures (HP)*	VH (4)	Not altered by HP
		L (1)	Altered by HP
Ecological value (Ev_{gh})	*Affection of protected areas (PA)*	VH (4)	PA affected
		L (1)	PA not affected

VH: Very high; H: High; M: Moderate; L: Low; N: Null; d: days

Table 3.4 Indicators, metric and assessment criteria to estimate each parameter in the vulnerability estimation (adapted from Gómez et al., 2014b).

A protected area will be significantly affected depending on the pollution process considered. A sensitive area can be just affected by the eutrophication process, while Natura 2000 network areas can be affected by chemical and eutrophication processes. Protected areas cannot be significantly affected by bacteriological processes (Table 3.5).

	Protected areas		
Pollution process	Sensitive areas[1]	SPAs[2]	SCIs/SACs[3]
Chemical (Ch)	✖	✔	✔
Eutrophication (Eu)	✔	✔	✔
Bacteriological (Bc)	✖	✖	✖

✔ : Affected flora and fauna.
✖ : Non affected flora and fauna
[1]: sensitive areas defined under Directive 91/217/EEC; [2]: special protected areas (SPA) defined under Directive 2009/147/EC and; [3]: sites of community importance (SCI) and special areas of conservation (SAC) defined under Directive 92/43/EEC.

Table 3.5 Criteria to establish the affection of flora and fauna on protected areas by chemical, eutrophication and bacteriological processes.

3.2.4 Integration environmental risks: prioritization maps

A prioritization map is obtained by the combination of two components: the consequences of all hazards and contaminants and the vulnerability of the environment (Eq. (3.10)).

$$R_{gh} = Co_{gh} \times Vu_{gh} \qquad \text{Eq. (3.10)}$$

Where, R_{gh} is the environmental risk, Co_{gh} are the consequences and Vu_{gh} is the vulnerability at cell level (g,h).

Environmental risk values are categorized into 5 levels (Table 3.6). Threshold values for each assessment category are based on the 80th, 60th and 20th percentiles of the risk values obtained by the hypothetical combinations of the potential consequences and potential vulnerability values at cell level.

Assessment category	Assessment criteria
N (0)	$x = 0.00$
L (1)	$0.00 < x < 2.51$
M (2)	$2.51 \leq x < 5.60$
H (3)	$5.60 \leq x < 8.0$
VH (4)	$x \geq 8.0$

VH: Very high; H: High; M: Moderate; L: Low; N: Null

Table 3.6 Criteria used to assess the environmental risk.

3.3. Implementation of prioritization maps at Tarragona harbor

To test the method proposed, prioritization maps of all environmental hazards and contaminants at the Tarragona harbor were obtained and a study of the correspondence between risk values and environmental data was performed.

The Tarragona harbor is located in the Mediterranean Sea on the North Eastern Spanish coast (1º14'E, 41º05'N) (Figure 2.1). It is an industrial bulk carrier port surrounded by an extensive petrochemical cluster (*see Chapter II for more information*).

3.3.1 Data and methods

A finite-difference grid of regular square cells (391 x 426, 30 m of edge) was obtained by interpolating bathymetrical data from the Port Authority using a TIN method (ArcGIS 10.1 by ESRI™) (Figure 2.6). Hydrodynamic currents were estimated. The currents due to the Francolí River and the astronomical tides were neglected since the study area is characterized by a micro-tidal regime (centimeters of mean tidal range) and minor river inputs (usually low or null irregular river flows). Wind-generated currents caused by the 49 most-probable hydrodynamic conditions were calculated using a quasi-three dimensional model (MacQueen, 1967; Camus et al., 2011; García et al., 2010; Valdor et al., 2015) (Figure 2.7). The medium annual regime of winds was obtained using the Monte Carlo method, taking into account constant wind conditions for periods of 8 h and the probability of occurrence of each wind component (Gómez et al., 2014a). A Friction Chezy coefficient of 55 $m^{1/2}\cdot s^{-1}$, a 1 $m^2\cdot s^{-1}$ Eddy viscosity coefficient, a Wind drag coefficient of 0.0026 were stablished from previous studies (Gómez et al., 2014a).

In order to assess consequences, all environmental hazards were identified (Figure 3.3). The affected area of each environmental hazard was computed using 2D numerical models or GIS tools (ArcGIS 10.1 by ESRI™). The Maximum Allowable Concentration (MAC-EQS) considered for the acute effects of contaminants were those established by Directive 2013/39/EU (European Commission, 2013a) for priority substances, 4.8 mg/l for dissolved oxygen and 50000 UFC/100 ml for *E. coli*. For chronic effects, the Average Annual-Environmental Quality Standards (AA-EQS) considered were Directive 2013/39/EU (European Commission, 2013a) for priority substances, 2.3 mg/l for dissolved oxygen and 5000 UFC/100 ml for *E. coli* (US EPA, 2002; Gómez, 2010).

Integrated and global effects maps considering the three integration methods were represented and compared using the Kappa index (Cohen, 1960) to establish similarities and differences between the values obtained by different methods.

To assess vulnerability, the recovery time was calculated at cell level. Naturalness was computed by means of GIS software (ArcGIS 10.1 by ESRI™). Hydromorphologycal pressures were identified from aerial photographs and the corresponding buffer areas were calculated (Figure 3.3). In the same way, 2 bathing waters were identified: La Pineda, an urban beach of around 2.4 Km length and El

Miracle, a semi-urban beach of 0.9 Km (Spanish Government, 2016).

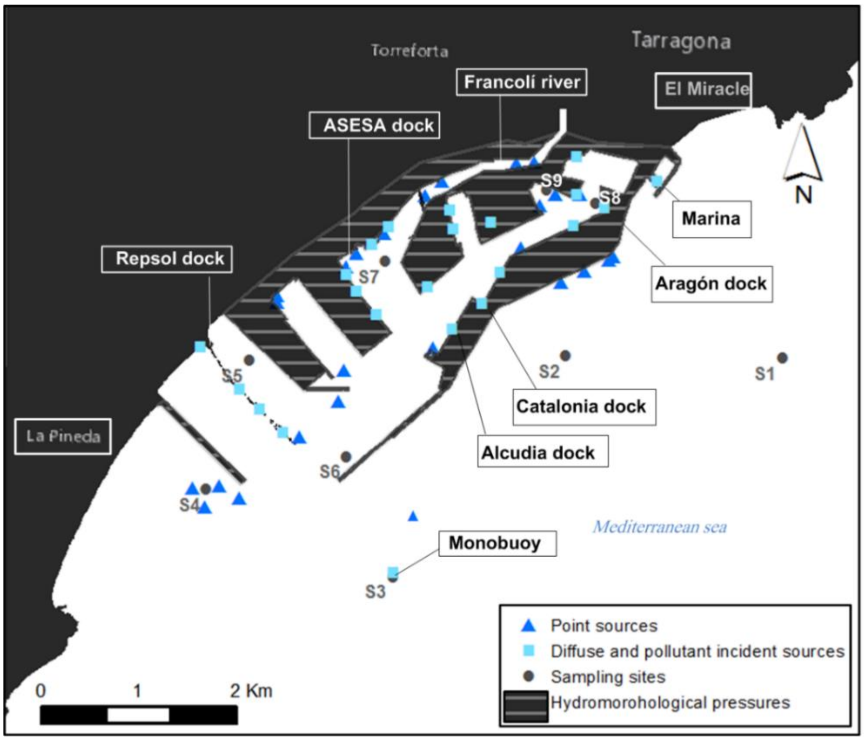


Figure 3.3 Location of sampling sites, point, diffuse and potential incident sources, hydromorphologycal pressures at Tarragona harbor.

Finally, prioritization maps considering the three integration methods were represented and compared using the Kappa index (Cohen, 1960) in order to perceive similarities and differences between the values obtained by different methods.

The risk values obtained by each integration method were obtained at sampling station level (S1 to S9) (Figure 3.3). Each sampling station was geographically related to a cell in the finite element grid. The representative risk value for a sampling station was obtained by calculating the average of risk values in the related cell and the eight adjacent cells.

In order to analyze the correspondence between risk values and environmental data, water quality data seasonally collected (campaigns in winter-summer-autumn-spring) (Table 2.2) and sediment quality data annually collected (Table 2.3) during 2009, 2010 and 2011, at the nine sampling sites, was used (Figure 3.3). Those variables with concentrations below the quantification limit of the analytical technique were rejected. Thus, nutrients conditions (ammonium, nitrates, nitrites, phosphate and silicate), biological elements (chlorophyll a), transparent (turbidity), oxygenation conditions, salinity and some metals (lead, nickel and zinc) were considered. Sediment variables selected are shown in Table 3.7.

Redundant variables were discarded using a Spearman's rank correlation analysis ($|r|>0.8$ at $p<0.01$) (Table 3.8 and Table 3.9). Average values for each selected variable integrated in time and depth were calculated for each sampling station. To identify spatial patterns in terms of environmental data a Principal Component Analysis (PCA) was performed. The spatial distributions of water and sediment variables were analyzed separately. Finally, a Spearman's rank correlation analysis between environmental data and risk values was performed.

Sediment variables
Arsenic
Benzo (b) fluoranthene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(ghi)perylene
Chromium Total
Chrysene
Copper
Fluoranthene
Indeno(1,2,3-c,d)pyrene
Lead
Mercury
Nickel
Total Kjeldahl Nitrogen
Total Organic Carbon
Phenanthrene
Pyrene
Zinc

Table 3.7 Sediment variables selected at sampling sites of the Tarragona harbor.

	Ammonium	Chlorophyll a	Cu	Oxygen	Pb	Ni	Nitrates	Nitrites	Oxygen Saturation	Phosphate	Salinity	Silicate	Turbidity
Ammonium	-												
Chlorophyll a	0.36	-											
Cu	-0.36	-0.26	-										
Dissolved oxygen	0.18	0.02	0.45	-									
Pb	0.01	-0.41	0.61	0.32	-								
Ni	-0.27	-0.43	0.67	0.35	0.78	-							
Nitrates	0.23	0.46	0.11	0.29	-0.24	-0.18	-						
Nitrites	0.17	0.57	0.18	0.34	-0.23	-0.14	**0.88**	-					
Oxygen Saturation	0.20	-0.12	0.25	0.64	0.16	0.33	0.20	0.10	-				
Phosphate	-0.01	0.18	-0.38	-0.45	-0.46	-0.54	0.18	0.06	-0.25	-			
Salinity	-0.03	-0.04	0.50	0.70	0.46	0.48	0.15	0.20	0.36	-0.73	-		
Silicate	0.00	0.43	0.24	0.00	-0.19	-0.08	0.76	0.74	-0.14	0.23	0.05	-	
Turbidity	0.31	0.71	-0.17	-0.03	-0.44	-0.42	0.62	0.66	-0.19	0.26	-0.15	0.55	-
Zn	-0.12	-0.17	0.04	-0.30	0.30	0.32	-0.60	-0.52	-0.19	-0.22	-0.13	-0.45	-0.37

In bold, correlations >0.8 at $p<0.001$

Cu: copper; Pb: lead; Ni: nickel; Zn: zinc.

Table 3.8 Correlation coefficients amongst water variables.

	As	BbF	BaA	BbPyr	BghiPer	Cr	Chr	Cu	Fl	I123cdPyr	Pb	Hg	Ni	TKN	TOC	Phe	Pyr
As	-																
BbF	0.16	-															
BaA	0.19	**0.97**	-														
BbPyr	0.13	**0.99**	**0.95**	-													
BghiPer	0.22	**0.96**	**0.96**	**0.95**	-												
Cr	0.21	0.07	-0.05	0.12	0.06	-											
Chr	0.09	**0.92**	**0.87**	**0.93**	**0.87**	0.21	-										
Cu	0.32	-0.18	-0.24	-0.13	-0.16	0.72	-0.07	-									
Fl	0.18	**0.95**	**0.94**	**0.95**	**0.93**	0.06	**0.93**	-0.12	-								
I123cdPyr	0.15	**0.95**	**0.98**	**0.93**	**0.94**	-0.12	**0.84**	-0.32	**0.91**	-							
Pb	0.40	-0.26	-0.33	-0.22	-0.22	**0.81**	-0.17	**0.89**	-0.23	-0.41	-						
Hg	-0.23	0.04	-0.02	0.05	0.09	0.31	0.11	0.36	0.08	-0.08	0.31	-					
Ni	0.17	-0.08	-0.18	-0.03	-0.09	**0.84**	0.06	0.67	-0.08	-0.22	0.73	0.24	-				
TKN	0.31	0.08	0.03	0.09	0.11	0.38	0.16	0.44	0.11	-0.02	0.42	0.12	0.41	-			
TOC	0.24	0.27	0.21	0.33	0.34	0.42	0.41	0.34	0.29	0.15	0.30	0.29	0.41	0.16	-		
Phe	0.21	**0.94**	**0.94**	**0.94**	**0.95**	0.03	**0.90**	-0.12	**0.99**	**0.92**	-0.24	0.08	-0.11	0.12	0.31	-	
Pyr	0.20	**0.99**	**0.97**	**0.97**	**0.95**	0.07	**0.90**	-0.15	**0.96**	**0.95**	-0.24	0.04	-0.08	0.09	0.25	**0.95**	-
Zn	0.35	-0.12	-0.19	-0.07	-0.08	**0.84**	0.01	**0.93**	-0.08	-0.27	**0.93**	0.38	0.75	0.51	0.40	-0.08	-0.10

In bold, correlations >0.8 at $p<0.001$

As: arsenic; BbF: Benzo(b)fluoranthene; BaA: Benzo(a)anthracene; B(b)Pyr: Benzo(b)pyrene; BghiPer: Benzo(g,h,i)perylene; Cr: chromium; Chr: Chrysene; Fl: Fluoranthene; I123cdPyr: Indeno(1,2,3-cd)pyrene; Pb: lead; Hg: mercury; Ni: nickel; TKN: total Kjeldahl nitrogen; TOC: total organic carbon; Phe: Phenanthrene; Pyr: Pyrene; Zn: zinc.

Table 3.9 Correlation coefficients amongst sediment variables.

3.3.2 Identification of environmental hazards

A total of 47 contaminant sources were identified in the Tarragona harbor. From these, 26 were *point sources* (Figure 3.3), mostly caused by industrial activity and urban waste. These contaminant sources were liable to spill 10 different priority substances. The 26 point sources were liable to cause eutrophication problems, and 8 of them to cause bacteriological contamination. A total of 21 *diffuse sources* were identified mainly caused by cargo terminals, vessel-port interfaces and MARPOL waste activities (Figure 3.3). From these, 14 diffuse sources handled very high hazardous materials or substances, 6 presented high hazardous materials and just 1 proved moderate hazardousness.

A total of 159 pollutant incidents registered between 2007 and 2012 in the port authority's local database were analyzed (Figure 2.5). A total of 21 discharge points were identified as potential *pollutant incidents' sources* (↑ frequency; ↑ hazardousness, Table 3.1).

3.3.3 Estimation of consequences

The area affected by the *integrated effects* of hazards identified at the Tarragona harbor represented 44% of the port jurisdiction aquatic area (Figure 3.4). The affected area was mainly located inside the confined waters, where most of the pollutant sources were identified (Figure 3.2). Differences between the three integration methods were found. The average method provided less restrictive estimations with the 91% of the affected area showing low effects. The worst-case method was the most restrictive of all, presenting the highest percentage (about 12%) of cells with very high effects (Figure 3.4). Kappa index values indicated that the consequences estimated through the worst-case method agreed only very low with the average-value method (kw = 0.14, 21% in agreement), and low (kw =0.33, 37%) with the weighted method. The agreement between the average and the weighted methods was moderate (kw= 0.40, 75%).

Following an analysis of the results by type of environmental hazard*, global effects of point sources* presented an affected area of $1.7 \cdot 10^3$ Ha, 95% of the total area affected (Figure 3.4). 4% of the affected area presented moderate effects using average value method estimations, against 53% when the worst-case and the weighted method were applied. High and very high effects were shown only through the worst-case and weighted methods (Figure 3.4). The average-value method had a low agreement with the worst-case and the weighted methods (Kw= 0.15, 36%). There was total agreement (Kw= 1, 100%) between the worst-case and the weighted method.

Regarding the *global effects of diffuse contaminant sources*, just 100 ha were affected (Figure 3.4). Only the worst-case method showed very high effects. The agreement between pairs of methods was null in all the cases (Kw<0.05).

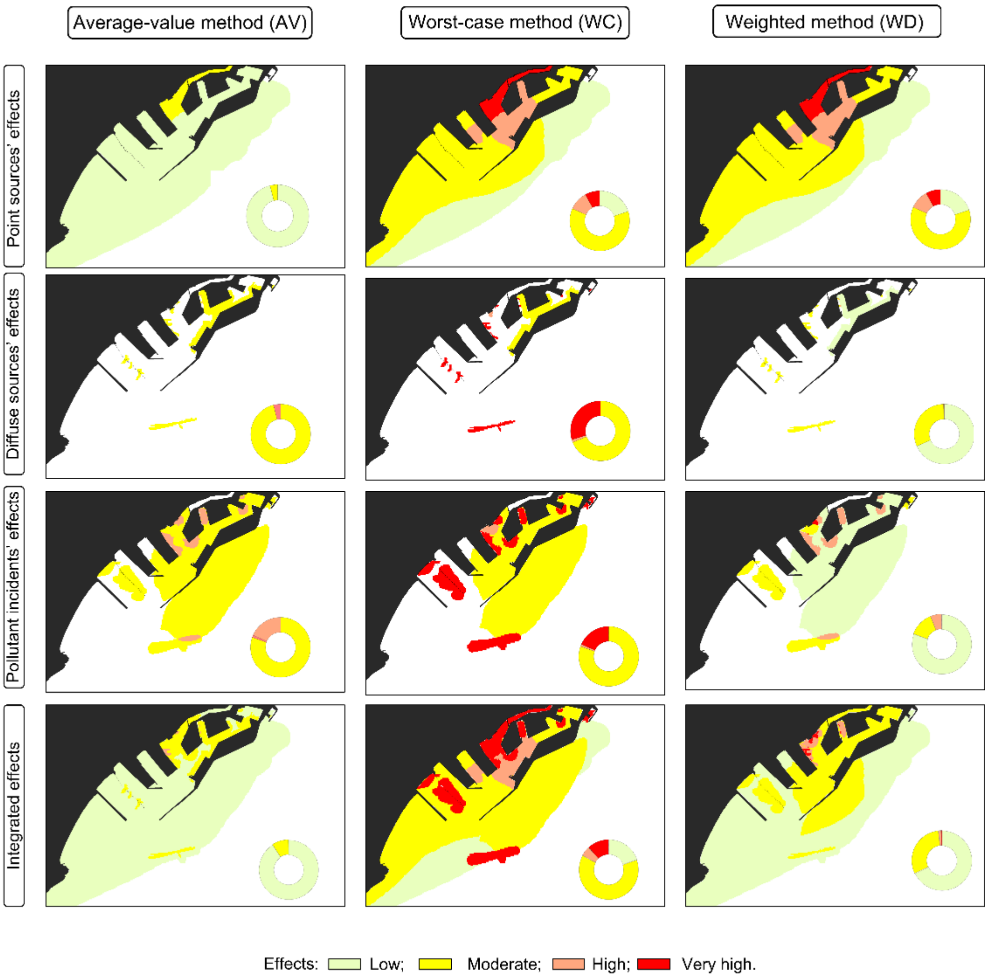


Figure 3.4 Spatial variability of global effects of point, diffuse and pollutant incident sources and integrated effects considering the three methods of integration: average-value method, worst-case method and weighted method.

Finally, a total of $0.9 \cdot 10^3$ ha were affected by *pollutant incidents' sources* (Figure 3.4), representing about the 50% of the total affected area. The 93% and 80% of the affected area presented moderate effects using the average and the worst-case methods, respectively. The 81% of the area affected by pollutant incidents showed low effects when the weighted method was used (Figure 3.4). The agreement between pairs of methods was low in all the cases (0.2 > Kw < 0.4).

3.3.4 Estimation of vulnerability

Vulnerability was higher in confined waters where the flushing capacity was lower (Figure 3.5). Recovery time (RT) values showed a marked spatial gradient, from < 1 day to values over 430 days. Higher values (> 1 day, moderate to very high susceptibility) were located at confined areas. Lower values (< 1 day, low susceptibility) were found in natural waters, far away from port infrastructures or natural geographical features (Figure 3.5(a)). Buffer areas of 52 hydromorphologycal pressures were computed to assess naturalness, affecting an area of $0.7{\cdot}10^3$ ha (Figure 3.5(b)). Hydromorphologycal pressures were mainly located around the harbor area, resulting from low naturalness. Ecological value was low for the whole spatial domain.

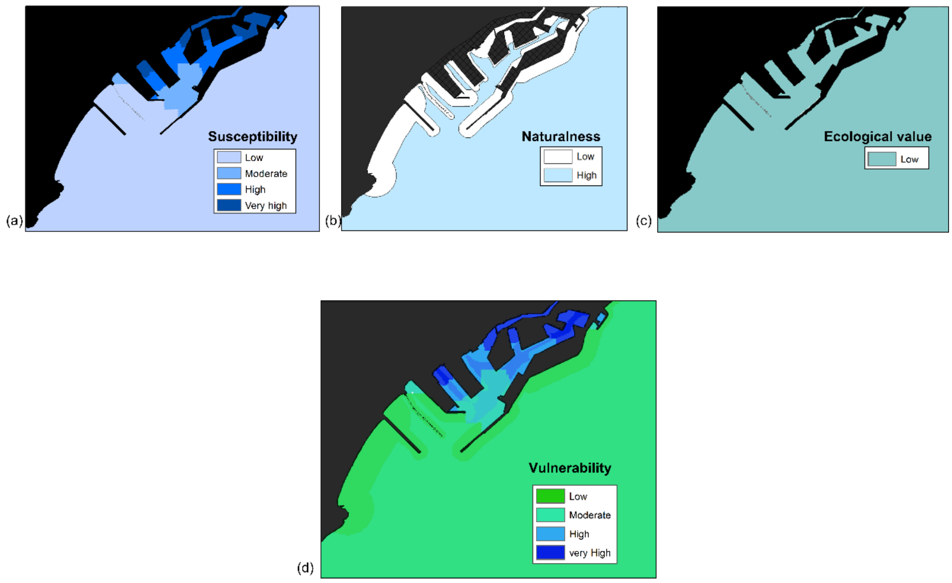


Figure 3.5 Spatial variability of (a) Susceptibility, (b) Naturalness, (c) Ecological value and, (d) Vulnerability at the Tarragona harbor.

3.3.5 Prioritization maps representation

At the Tarragona harbor, about $1.9 \cdot 10^3$ ha were at risk of being affected by the identified environmental hazards (Figure 3.6). Risk estimations showed the higher values in confined waters where most of the pollutant sources were identified, providing a marked spatial gradient (Figure 3.6). The average method provided less restrictive estimations showing low risk at the 84% of the total affected area. The worst-case method was the most restrictive of them showing the highest quantity (7%) for very high-risk values. The weighted method showed 70% of the affected area under low risk and 1% with very high risk (Figure 3.6). The average-value method had a low agreement with the worst-case method (kw = 0.29, 22% in agreement), and good agreement (Kw= 0.68, 76%) with the weighted method. The agreement between the worst-case and the weighted methods was moderate (kw= 0.51, 41%).

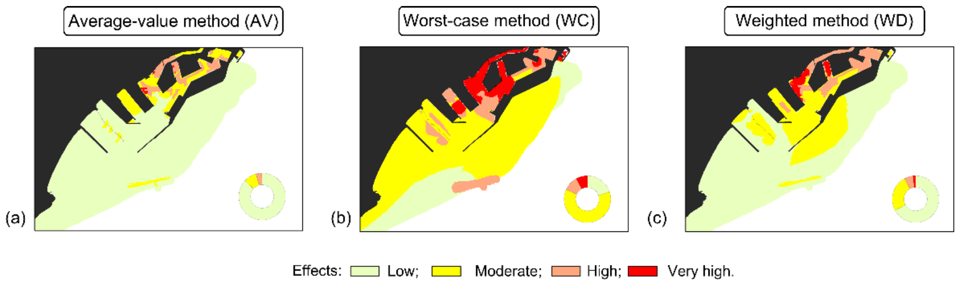


Figure 3.6 Prioritization maps at the Tarragona harbor estimated by the three methods (a) average-value method, (b) worst-case method and, (c) weighted method.

3.4 Correlation between environmental risk values and environmental data

Estimations of integrated risk at sampling stations of the Tarragona harbor presented a range from low (0.00) to very high risk (4.00) (Table 3.10). Higher risk values were registered at confined areas (S7, S8 and S9) while null assessment values were found in natural waters (S1).

	R_{gh}		
Sampling site	R_{AVgh}	R_{WCgh}	R_{WDgh}
S1	0.00	0.00	0.00
S2	1.00	2.00	1.00
S3	1.77	3.00	1.77
S4	1.00	2.00	1.00
S5	1.00	2.00	1.55
S6	1.00	2.00	1.55
S7	2.00	4.00	2.00
S8	3.00	3.00	3.00
S9	2.00	3.00	3.00

Table 3.10 Risk values estimated at each sampling site calculated using the average - value (R_{AVgh}), the worst-case (R_{wcgh}) and the weighted methods (R_{WDgh}) at the Tarragona harbor.

Regarding environmental data, a PCA analysis indicated that the first two principal components explained 74% and 69% of the total variance of water and sediments, respectively (Table 3.11).

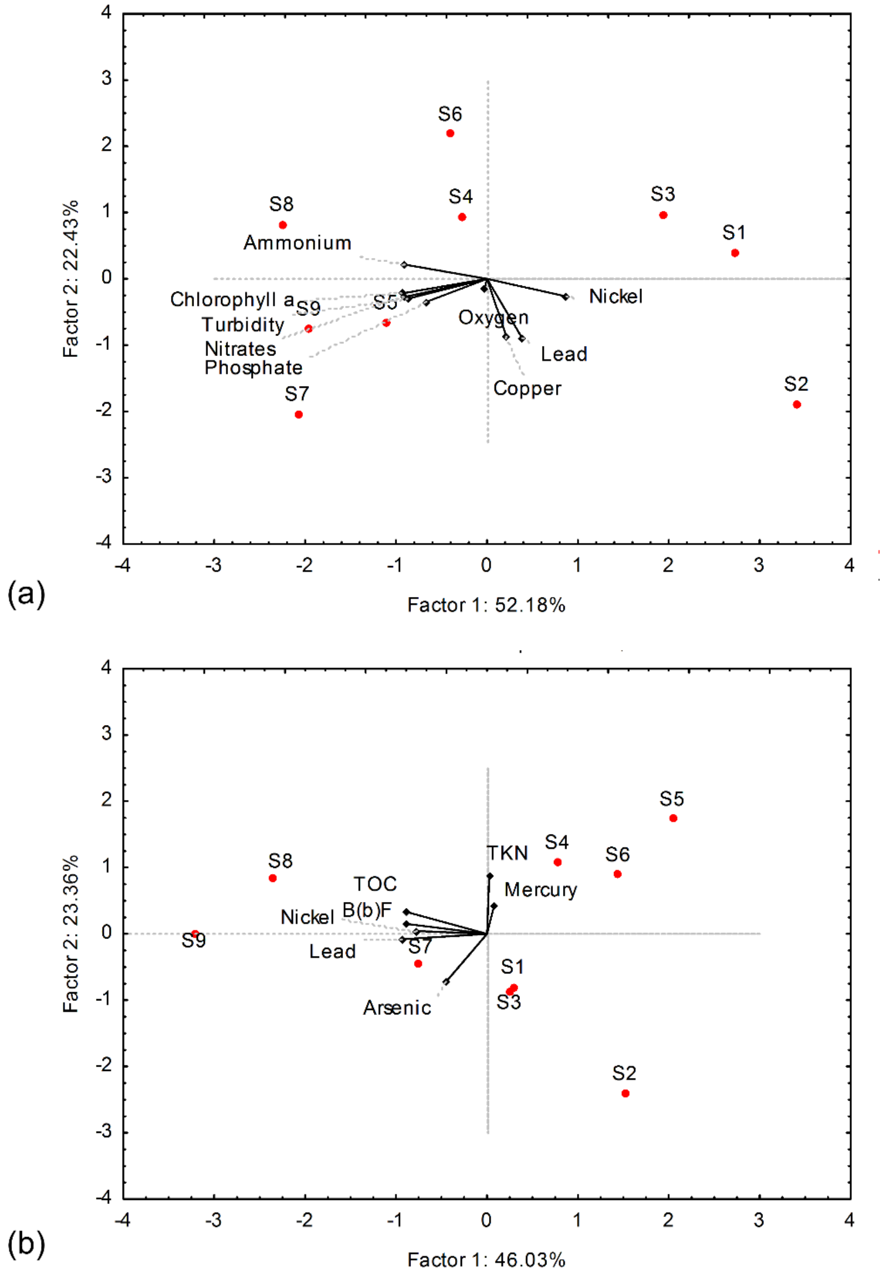
	Factor	Eigenvalue	Total variance (%)	Cumulative variance (%)
Water	1	4.69	52.18	52.18
	2	2.02	22.43	74.61
Sediment	1	3.22	46.03	46.03
	2	1.63	23.36	69.38

Table 3.11 Eigenvalues, total and cumulative percentages of variance related with the main components of the water and sediment variables analyzed at the Tarragona harbor.

The spatial plot of the two-dimensional space defined by the water variables (Figure 3.7 (a)) showed that sampling sites can be clustered into three groups: i) confined areas (S7, S8 and S9); ii) natural waters (S1, S2 and S3); and, iii) confined waters close to natural waters (S4, S6 and S5). Confined waters (S7, S8 and S9) were arranged according to the negative sector of the first axis (Factor 1), mainly defined by chlorophyll a, nitrates, ammonium and turbidity in water. However, S1, S2 and S3 were on the positive sector of factor 1 related with nickel. Factor 2 was related with lead and copper. Thus, the eutrophication process seems to predetermine the distribution of sites along the axis 1, with those located in really confined areas distributed in the most negative part of axis 1. By contrast, sites located in natural waters, near the area where handling activities take place, occupied the positive side of that axis which was more related to higher levels of certain heavy metals.

The two-dimensional space defined by the sediment variables (Figure 3.7 (b)) showed that confined waters were arranged on the negative sector of the first axis (Factor 1) mainly defined by lead, total organic carbon, benzo(b)fluoranthene and nickel in sediment. Factor 2 is related with total Kjeldahl nitrogen (TKN) and arsenic. So, pollution by total organic carbon (TOC), benzo(b)fluoranthene (BbF) and metals would predetermine the distribution of sites along axis 1, with sites located in really confined areas distributed in the negative part of the axis. On the contrary, sites located in natural waters (S1, S2 and S3) occupied the positive side of that axis.

These results were in agreement with the correlation with risk values obtained by the three integration methods which presented a high significant correlation ($|r|>0.7$ at $p<0.05$) between risk values and chlorophyll a and nitrates in water and lead in sediments (Table 3.12). The average-value and the weighted methods also showed high significant correlation with total organic carbon in sediments.



B(b)F: Benzo (b)fluoranthene
TOC: Total organic carbon
TKN: Total Kjeldahl nitrogen

Figure 3.7 Location of sampling sites of water (a) and sediment (b) variables with respect to the two-dimensional space defined by the first two principal components related to water and sediment variables.

	Variables	Average	Worst-case	Weighted
Water	Oxygen	-0.69	-0.60	-0.62
	Turbidity	0.47	0.39	0.60
	Ammonium	0.59	0.59	0.53
	Chlorophyll a	**0.79**	**0.75**	**0.83***
	Copper	0.09	0.28	-0.03
	Lead	-0.16	0.00	-0.23
	Nickel	-0.29	-0.36	-0.42
	Nitrates	**0.75**	**0.70**	**0.77**
	Phosphate	0.64	0.47	0.54
Sediment	Arsenic	0.38	0.28	0.23
	Nickel	0.66	0.66	0.62
	Lead	**0.74**	**0.71**	**0.71**
	Mercury	0.25	0.18	0.28
	Total Kjeldhal Nitrogen	0.24	0.12	0.35
	Total organic carbon	**0.72**	0.59	**0.73**
	Benzo(b)fluoranthene	0.40	0.19	0.44

in bold, correlation ≥0.7 significant correlation at $p<0.05$
*significant correlation at $p<0.001$

Table 3.12 Spearman rank correlations between water and sediment variables and risk values obtained by the average-value, the worst-case and the weighted methods at the Tarragona harbor.

3.5 Discussion

Risk maps such as prioritization maps help scientists, managers and experts explore the spatial variability of risk and the spatial distribution of contaminants' concentrations, exposure and effects (Lahr and Kooistra, 2010). Prioritization maps allow obtaining a synthetic interpretation of complex interactions of individual risks at the desired scale (Pistocchi et al., 2011). The methodology proposed can provide prioritization maps which reflect the spatial and temporal variability of: i) each contaminant; ii) different contaminants from a particular facility; iii) specific hazards; and, finally, iv) the potential water quality at harbor areas. The selection of uses, activities, hazards or contaminants to be included in the ERA process is subject to the objective of the analysis to be performed. Prioritization maps are useful tools for risk analysis and risk communication in order to define strategic actions to manage port water quality. This flexible and versatile tool provides managers with an instrument to establish preventive measures, allocate economic resources and identify the type of strategies to be implemented.

In terms of managing, prioritization maps provide the answer to many questions: which contaminants are affecting water quality?; which is the area most affected by what kind of hazards?; Which facility is contributing the most to the integrated effects?, among many others. As an example, from the results obtained at the Tarragona harbor, we may conclude that chemical pollution affects 49% of the total Port Jurisdiction Area (PJA), while eutrophication and bacteriological pollution do not have any effects. The Francolí river mouth and the area around the chemical dock are affected by priority substances, while hydrocarbons are mainly affecting the monobuoy, the Repsol dock and the ASESA dock areas. On the other hand, solid bulks handled and stored at Catalonia, Alcudia, Navarra and Aragón docks are affecting the inner part of the harbor, but also the anchoring area (Figure 3.4). Point sources register the greatest effects in terms of extension and magnitude. As specific management measures derived from prioritization maps at the Tarragona harbor, the most suitable places to set up the equipment to remove liquid products from water could be stablished at the chemistry dock area. The equipment to respond to solid bulks' incidents should be placed at Alcudia or Catalonia docks. Finally, the marina could be an appropriate place to set up a boat with the equipment necessary to solve the pollution incidents.

Integration of hazards and contaminants are the key points in prioritization maps. Conceptual differences exist between the different integration methods of effects used in this work. The average method is based on the similar action model (SA), where the interaction of agents differs only in power and may be considered to the mixture, as a joint dilution of the contaminants (Cedergreen, 2008). On the other hand, the worst-case method is based on the independent action model (IA). The IA model assumes that contaminant mixture does not interact physically, chemically or biologically, i.e. each contaminant affects the environment independently by behaving differently (Spurgeon et al., 2010). Finally, the weighted method is not based on a classic model of mixture of agents. The method allocates greater importance to specific contaminants, processes or hazards, based on expert criterion. Estimations of the consequences at the Tarragona harbor showed that regardless of the integration method used, the same extension was occupied by the affected areas. These areas are mainly located around the confined waters where most of the pollutant sources are located. The agreement between the risk values estimated using the average-value and the worst-case methods was low, whilst it was good with the weighted method. The differences between methods are clearly evident when the degree of agreement between the estimation of the effects at hazard level are analyzed. This is low or null between pairs of methods for all the hazards (point and diffuse sources of contaminants and pollutant incidents' sources). Accordingly, the initial hypothesis that stated that the integration method is a crucial aspect for the calculation of integrated environmental risk is further confirmed.

The study of the correspondence between the environmental risk estimations and the environmental data could allow us to select the best integration method. But, risk assessments using the three integration methods at the Tarragona harbor presented a significant correlation with the spatial distribution of the same water and sediment quality environmental indicators. This enabled the integration method to be chosen based on the management objective and the peculiarities of the study area. It should be based on: i) the available data at the identification stage; and, ii) the purpose of managing the risk. Prioritization maps using the average value and the weighted methods should only be used when all environmental hazards can be well identified. In that sense, the identification stage requires a great effort to be made in order to gather all the information for the characterization of discharges, which is not always possible. On the other hand, the worst-case method could be used if the goal was to locate the best places for emergency plan materials, while, the weighted method could be the right choice if the main goal was to design an environmental monitoring program. However, it should be taken into account that the methods of risk analysis are predictive tools and should be validated through the study of the relationship between the predicted environmental risk and the measured real impact. Studies purporting to find out the existing relationship between the environmental risk and the real environmental impact caused by specific hazards should be carried out.

The inclusion of point and diffuse sources, as well as pollutant incidents' sources is a novel aspect in the creation of prioritization maps. From the implementation of the methodology to the Tarragona harbor we can confirm that the integration of diffuse sources is relevant when the ERA process is developed at lower scale (facility or activity level). On the other hand, the potential effects of pollutant incidents may occupy a great extension (Figure 3.4), overlapping with effects from other hazards and contributing to the spatial heterogeneity of risk maps. So, pollutant incidents' sources should be integrated as an environmental hazard in the ERA process, since they are crucial if the objective of the management is to decide where to place the material to remove products from water, but also to design a program to monitor the environmental hazards as a whole.

Finally, further research should be conducted to include the intensity-duration-frequency (IDF) approach to the estimation of the acute effects (Van de Vyver, 2015) and to consider the ecosystem services in the vulnerability assessment. Regarding the acute effects, the number of times (frequency) that an area has been affected by pollutant incidents of a specific hazardousness (intensity) could provide a more real effect estimation. In the same way, contaminants introduced by point contaminant sources could be estimated considering the number of times (frequency), how much (intensity) and for how long (duration) the threshold (Maximum Allowable Concentration (MAC)) is exceeded. On the other hand, vulnerability is expressed from an environmental point of view based on the absence of anthropogenic changes on ecosystems (naturalness) and on the protection of ecosystems (ecological value) (Gómez, 2010). However, beyond protected areas, the ecosystems also provide services to people, which are life-sustaining and contribute to human health and well-being (Rock, et al., 2005; UN, 2016). Therefore, vulnerability could integrate parameters to include the affection on ecosystem services. The assessment criteria could take into account the affection of bathing waters - Directive 2006/7/EC (European Commission, 2006a) - or other kind of water bodies designated as recreational waters, shellfish waters - Directive 2006/113/EC (European Commission, 2006b) - and areas designated for the abstraction of water intended for human consumption or coastal protection, among others.

3.6 Conclusions

The methodology presented at this chapter is capable of integrating the estimation of spatial-temporal variability of the contaminants and their effects by combining potential impacts of multiple process: chemical pollution, eutrophication, bacteriological contamination and other dangerous and potentially hazardous materials, and obtaining easily interpretable prioritization maps. To adapt prioritization maps to the peculiarities of the study area, three methods of integrating the effects are proposed: the average-value method, the worst-case method and the weighted method. The methodology is flexible enough to be adapted to the available data at the study area and the purpose of managing the risk. The prioritization maps obtained at the Tarragona harbor (North Eastern Spain) were significantly related to water and sediment quality indicators. The implementation to a real case confirms its usefulness as a decision-making tool to support water quality management in harbors.

Chapter IV

Scenarios of non-point oil sources

CHAPTER IV. A METHOD TO DEFINE ENVIRONMENTAL RISK ANALYSIS SCENARIOS OF NON-POINT OIL CONTAMINANT SOURCES

This chapter is an edited version of the research article published in Marine Pollution Bulletin. 90 (1-2): 78 – 87 by Valdor, P.F., Gómez, A.G., Puente, A. with the title 'Environmental risk analysis of oil handling facilities in port areas. Application to Tarragona harbor (NE Spain)'.

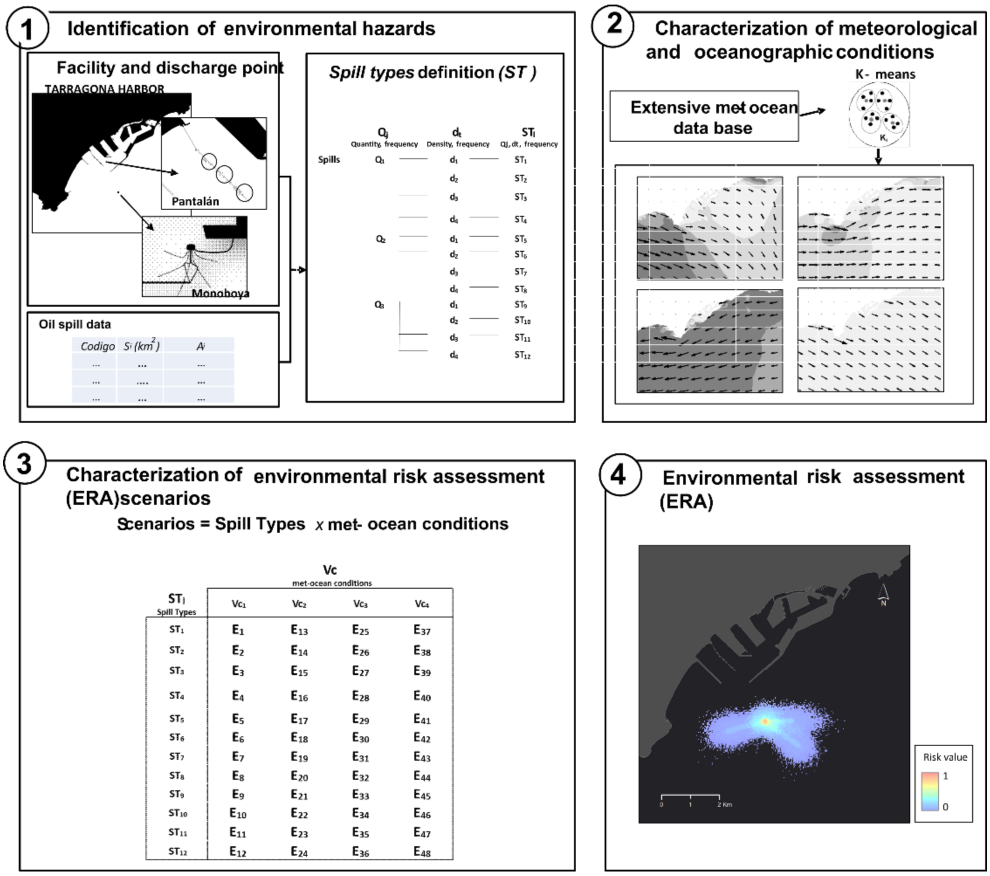


Figure 4.1 Graphical abstract.

Abstract

Non-point pollution from oil spills is a widespread problem in harbor areas (as a result of fuel supply, navigation and loading/unloading activities). In this chapter, a method to define the scenarios to assess the environmental risk of oil handling facilities in harbor areas is presented. The method is based on: i) identification of environmental hazards; ii) characterization of meteorological and oceanographic conditions; iii) characterization of environmental risk scenarios; and, iv) assessment of environmental risk (Figure 4.1). The procedure was tested by the application to the Tarragona harbor. The results showed that the method is capable of representing: i) specific local pollution cases (i.e., discriminating between products and quantities released by a discharge source); ii) oceanographic and meteorological conditions (selecting a representative subset data); and, iii) potentially affected areas in probabilistic terms. Accordingly, it can inform the design of monitoring plans to study and control the environmental impact of these facilities, as well as the design of contingency plans.

4.1 Introduction

Maritime transport is the backbone of international trade and a key driver of globalization. Approximately 80% of global trade by volume and over 70% by economic value is carried by sea and is handled by ports worldwide (UNCTAD, 2012a). As freight cargo traffic continues to grow, the question of how to ensure the long-term sustainability of such growth is playing an increasingly important role in the policy debate on globalization, trade, development and environmental sustainability (UNCTAD, 2012b). In terms of maritime transport, harbor areas are characterized by a wide range of activities: from industrial (e.g., activities related to oil terminals, chemical and petrochemical plants) to port-vessel interface activities (e.g., loading and unloading of goods, oil jetties, and dredging) (Ronza et. al, 2003). Furthermore, given their position in coastal areas and the great variety of substances handled there, ports are markedly complex systems from an environmental standpoint (Darbra et al., 2004). In that sense, Peris – Mora et al. (2005) identified accidental spills as the main cause of water pollution and Darbra et al. (2004) reported that the most frequent accidents in harbor areas are releases (51% of total accidents occurred). Also, the greatest proportion of accidents in ports (59%) are related to oil spills. Accordingly, non-point pollution, especially by oil spills, is one of the most widespread problems in port areas (loading and unloading of bulk liquid, fuel supply, navigation).

To address this issue, the IMO (International Maritime Organization) requires its state members to plan and prepare for oil incident responses by developing national systems for pollution response (IMO, 1995). Moreover, the Oil Pollution Preparedness, Response and Co-operation international convention (OPRC) requires States to establish a national system for responding to oil and Hazardous Noxious Substances (HNS) pollution incidents (IMO, 1991; 2000). Accordingly, site-specific (e.g., ports, oil and chemical facilities), local and regional contingency plans need to be defined. These must include an assessment of potential pollution risks based on meteorological, oceanographic and environmental conditions, as well as spill characteristics (IMO, 2010). In that sense European guidelines (IMO, 1991; IPIECA, 2008; European Commission, 2013a; 2014) suggest that oil spill risk analysis should focus on: i) a specific spatial context and specific hazard; and, ii) proper scientific data, allowing for more accurate and reliable results representing the best environmental risk assessment approaches (Santos et al., 2013a).

Environmental risk analysis (ERA) comprises the estimation of the likelihood of a spill's occurrence and the likely extent of adverse effects due to exposure to one or more stressors under certain circumstances (US EPA, 1998; Gómez, 2010). Moreover, ERA is a requirement of a proper spatial planning process (Greiving et al., 2006) which includes the development of 'inventories and maps' to support contingency planning, as well as environmental monitoring design, decision-making and risk management (Castanedo et al., 2009; Abascal et al., 2010; Santos et al., 2013b). Currently, there is no globally accepted standard method to be applied in ERA (Wooldridge et al., 1999; ESPO, 2007). Nonetheless, it should be taken into account that ERA method for oil handling facilities should provide tools to identify environmental hazards, to consider local environmental conditions and to obtain the spatial risk analysis in probabilistic terms.

Regarding identification of hazards, ERA of an oil handling facility should provide specific scenarios based on the characteristics of its spills. Identification of hazards is addressed in the first stage of the ERA to determine how exposure to stressors is likely to occur (Hope, 2006). Several tools have been developed to identify environmental hazards in harbor areas, but none specify how to define spill types in the ERA process (Darbra et al., 2004; 2005; Peris-Mora et al., 2005). Databases from accidental spills are often used for this purpose. Most of these databases, such as the FACTS database (TNO, 2012), have been refined as a result of international conventions (OPRC) (IMO, 1991) but mainly report large spills. However, small and medium sized spills account for 95% of all incidents recorded, many of which occur in harbors and oil terminals, during loading and discharging operations (40% and 29%, respectively) (ITOPF, 2013). These incidents are commonly reported in local databases (maintained by port authorities or maritime rescue societies). Analysis records in databases provide information about accidents related to a particular facility and its origins, causes and consequences (Darbra et al., 2004). Although most of these databases are not accurate enough to support a proper characterization of hazards, they usually contain some basic information (e.g., discharge source, a description of the discharge's appearance in the water, and/or affected areas), which can be very useful to characterize pollution incidents.

On the other hand, the ERA process of an oil handling facility should provide a representative local meteorological and oceanographic (met-ocean) conditions in order to define ERA scenarios. Port-specific ERA tools do not normally include a representative (met-ocean) variability of the study area or the spatial component of risk (Grifoll et al., 2010; Mestres et al., 2010; Ondiviela at al., 2012). The consideration of local met-ocean conditions to estimate the area affected by spills in coastal and offshore areas has been widely addressed by different authors (e.g., Cucco et al., 2012). These methodologies are based on forecasting systems since they have been applied in an operational way (e.g., Sotillo et al., 2008; El-Fadel et al., 2012). However, contingency plan processes require consideration of prevention. Reliable statistical results to define met-ocean scenarios, combining the effects of waves, winds and currents, are needed (Abascal et al., 2010).

Finally, a definition of spatial and temporal risk based on stochastic or probabilistic analysis is essential for reflecting spatial and temporal variability (Castanedo et al., 2009; Abascal et al., 2010; Santos et al., 2013b). For this reason, ERA requires the study of the evolution of oil in the marine environment in order to calculate the spill's trajectories and the final potential affected areas. To obtain precise results, a numerical transport model must be capable of simulating the movement of oil by calculating the trajectory of particles moving independently via wind, surface currents and turbulent diffusion. It must also consider the spreading and degradation processes that affect hydrocarbons (evaporation, emulsion and changes in rheological properties) (e.g., Mestres et al., 2002; Abascal et al., 2007;

Azevedo et al., 2014).

In this study, we focus our attention on the development of an ERA method at the oil handling facility level, including: i) identification of environmental hazards to establish spill types; ii) establishment of probabilistic meteorological and oceanographic conditions; iii) definition of ERA scenarios; and, iv) calculation of the probabilities for potentially affected areas. The overall method was applied to the monobuoy discharge point in the oil handing facility at the Tarragona harbor.

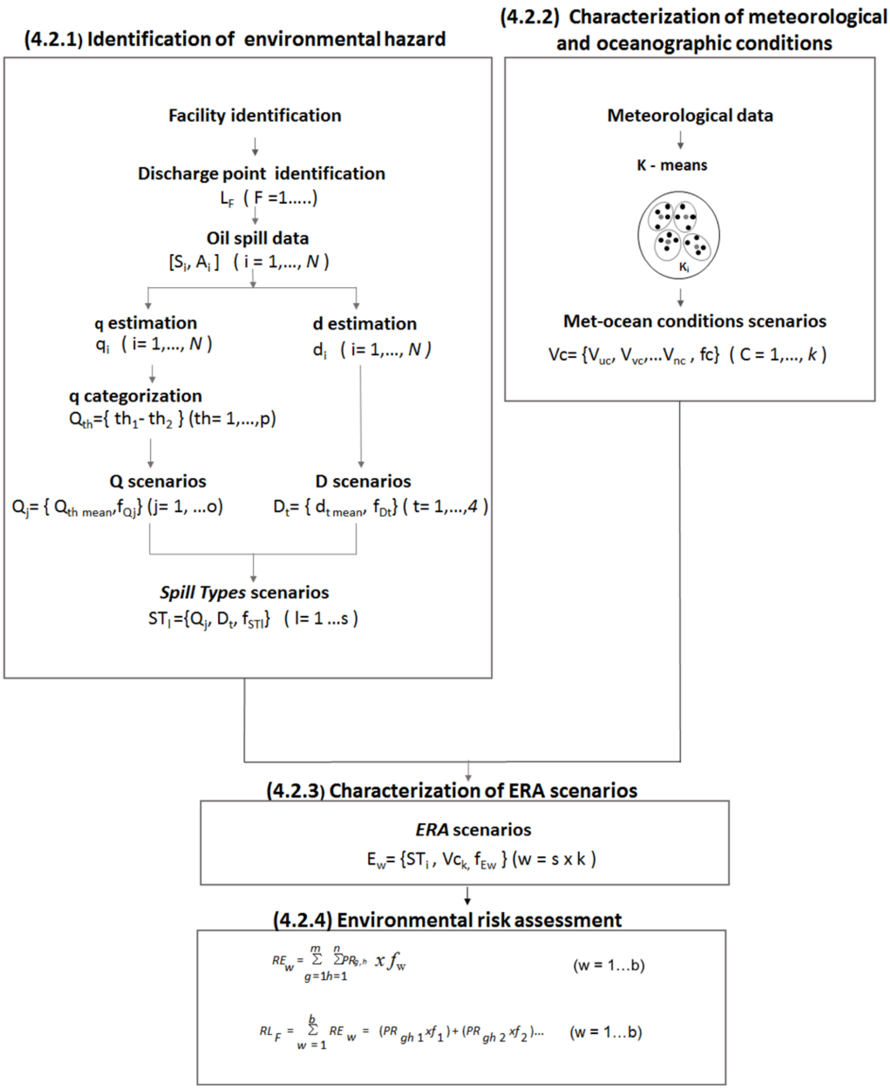
Following, the proposed methodology is described and results of its application to oil facility at the Tarragona harbor are presented.

4.2 Environmental risk analysis method and application to Tarragona oil facilities

There are four steps in the method (Figure 4.2): i) identification of environmental hazards; ii) characterization of meteorological and oceanographic conditions; iii) characterization of ERA scenarios; and, iv) assessment of environmental risk. Data related to pollution incidents at the long dock and the monobuoy at the Tarragona harbor were used as a basis for the development of the identification of the environmental hazard phase. The method as a whole was tested by its application to the monobuoy of Repsol Petróleo, S.A. at the Tarragona harbor (*see Chapter II for more information*).

4.2.1 Identification of environmental hazards

A facility is defined as a building or place that provides a particular service or is used for a particular industry. Locations where loading and unloading activity occurs are potential discharge points (L_F) for oil spills. Discharge points are identified as environmental hazards (pollutant incidents' sources of oil handling facilities). Every registered oil spill at each discharge point needs to be characterized in quantitative terms, including discharge quantity (q), product density (d) and frequency (f). From this information, characteristic spill types for oil handling facilities are defined.



$$RE_w = \sum_{g=1}^{m} \sum_{h=1}^{n} PR_{g,h} \; x \; f_w \qquad (w = 1\ldots b)$$

$$RL_F = \sum_{w=1}^{b} RE_w = (PR_{gh\,1} x f_1) + (PR_{gh\,2} x f_2)\ldots \qquad (w = 1\ldots b)$$

Figure 4.2 Schematic of the environmental risk analysis method for oil handling facilities in harbor areas.

Discharged quantity (q)

Discharge quantity (q) is estimated using the system established by the Bonn Agreement Oil Appearance Code (BAOAC) (Lewis, 2007). This system defines the relationship (based on experimental evidence) between the appearance of an oil spill in the sea, the thickness of the layer formed on the surface and the amount spilled (m^3/km^2). Thus, for a number of pollution incidents (i= 1,…, N) for which data exist on the appearance of the hydrocarbon (A_i) and the affected extension (S_i), the quantity discharge for each incident (q_i) is estimated by the BAOAC "base case" (Table 4.1). As specified by the BAOAC, the maximum estimate must be used to determine any response action. From the q_i estimate, categories of potential discharged quantities (Q_{th}) are established based on the percentile system.

Categorization of q_i is based on selected percentiles from a frequency distribution analysis. The most suitable percentiles are selected as threshold values (th). Once quantity categories Q_{th} = {th_1, th_2, … } (th= 1,…, p) are defined, the mean value of incidents registered between the th ranges ($Q_{th\ mean}$) is selected as the representative value. Each quantity scenario has an associated category and a probability (f_{Qj}) defined as the number of recorded incidents for each selected category, Q_j= {$Q_{th\ mean}$, f_{Qj}} (j= 1,…, o).

A_i	S_i. min. (m^3/km^2)	S_i. max. (m^3/km^2)	Vol. min. (m^3)	Vol. max. (m^3)
Shining (silver / gray)	0.04	0.3	0.01	0.06
Rainbow	0.3	5	0.06	1
Metallic	5	50	1	10
Discontinuous hydrocarbon color	50	200	10	40
Continuous hydrocarbon color	>200	>200	>40	>40

1 km^2 shed for each category 20% of occupied area each

Table 4.1 BAOAC ‘base case’.

Following the BAOAC guidelines (Table 4.1), q_i was estimated from the A_i and S_i data for each of the 22 spills registered at the Repsol facility in Tarragona harbor (Figure 4.3). Threshold values for each quantity category were taken from the 50^{th}, 90^{th} and 95^{th} percentiles of the estimated values for the quantity discharged.

Product density (d)

In local databases, appearance (A_i) data consist of a description of the semblance and type of hydrocarbon (distinguishing frequently between gas oils, fuel oils and crude oil as a generic classification). Due to the difficulty of knowing specifically the spilled product type and source of crude oils from which it derives, a generic classification to determine the relative density of spilled material in a landfill is established (IMO, 2005). Using the generic description of the product found in spill databases, the classification in Table 4.2 allows for estimation of the d_i value of the product spilled. To define spill types, the average value of each product type is taken, D_t = {$d_{t\ mean}$, f_{Dt}} (t=1,..., 4). This method considers that all product types handled in a facility have the same associated probability, so f_{Dt} will be the same value for each product considered (f_{Dt}= 0.25).

A_i	D_t
Gasoil and Kerosene	0.68 to 0.78
Diesel Fuel	0.81 to 0.85
Fuel oil*	0.925 to 0.926
Crude oil	0.95 ≤ 1.00

*light, medium and heavy fuel oil

Table 4.2 Product and relative density value classification.

According to this method, d_t for the 22 spills registered in the Tarragona harbor was estimated (Figure 4.3) yielding the four types of densities described in Table 4.2, with a f_{Dt} =0.25 for each type.

Definition of *spill types* (ST)

The combination of Q_j and D_t factors determines the definition of the spill types (ST) for a specific facility, ST_l= {Q_j, D_t, f_{STl}} (l=1,...s). The results do not predict the probability of a spill but rather the most-probable size distributions if spills do occur (f_{STl}). It is based on product density (f_{Dt}) and discharge quantity (f_{Qj}) frequencies. At the Repsol Petróleo, S.A. facility, 12 spill types were defined based on the 3 discharge quantity categories and the 4 product densities (Figure 4.3).

4.2.2 Characterization of meteorological and oceanographic conditions

To define the most-probable hydrodynamic conditions, an extensive meteorological and oceanographic database provided by state-of-the-art oceanic and atmospheric models is needed. Given a database of n dimensional vectors (e.g., surface sea level, wave period, and wind velocity), the K-means technique (KMA) is applied to obtain groups defined by a prototype or centroid of the same dimension as the original data (MacQueen, 1967; Camus et al., 2011). The number of clusters (k) is selected considering a manageable number of scenarios, and they are justified according to the minimum Davies Bouldin Index (DBI) (Davies and Bouldin, 1979; Negnevitsky, 2002). Each centroid is characterized by multidimensional environmental variables for a frequency of occurrence -V_C = {V_{uC}, V_{vC},…V_{nC}, f_{Vc}} (C= 1,…, k) representing the local hydrodynamic conditions.

Three dimensional data of sea level (GOS re-analysis, Abascal et al., 2010; 2011), wind direction and wind intensity (SeaWind-ERA-Interim dataset, Menéndez et al., 2011; 2014) was analyzed by applying K-means algorithm (MacQueen, 1967; Camus et al., 2011;) and four representative met-ocean conditions were stablished at oil handling facility scale with different frequency of occurrence (fc) (*see Chapter II for more information*):

i) Vc_1: northwest winds (312º, 5.6 m/s) and -0.09 m of sea level (fc=0.18);
ii) Vc_2: west winds (277º, 2.6 m/s) and -0.05 m of sea level (fc=0.20);
iii) Vc_3: east winds (79º, 5 m/s) and 0.04 m of sea level (fc=0.16); and
iv) Vc_4: calm conditions (301º, 0.1 m/s) and -0.14 m of sea level (fc=0.46).

	Quantity discharge $Q_j=\{Q_{thmean}, fq_j\}$	Product density $d_t=\{D_t, fD_t\}$	Spill types $ST_l=\{Q_j, D_t, f_{STl}\}$	Met-ocean conditions $Vc=\{V_{uc}, V_{vc}, V_{etac}, f_c\}$ Vc_1={5.6,312,-0.09,0.18}	Vc_2={2.6,277,0.04,0.20}	Vc_3={5,76,-0.05, 0.16}	Vc_4={0.1,301,-0.14 0.46}
Facility spills (22)	[0.1, 0.50]	[0.73, 0.25]	ST_1={0.1,0.73,0.12}	E_1={ST_1,Vc_1,0.0216}	E_{13}={ST_1,Vc_2,0.0240}	E_{25}={ST_1,Vc_3,0.0192}	E_{37}={ST_1,Vc_4,0.0552}
		[0.83, 0.25]	ST_2={0.1,0.83,0.12}	E_2={ST2,Vc_1,0.0216}	E_{14}={ST_2,Vc_2,0.0240}	E_{26}={ST_2,Vc_3,0.0192}	E_{38}={ST_2,Vc_4,0.0552}
		[0.96, 0.25]	ST_3={0.1,0.96, 0.12}	E_3={ST_3,Vc_1,0.0216}	E_{15}={ST_3,Vc_2,0.0240}	E_{27}={ST_3,Vc_3,0.0192}	E_{39}={ST_3,Vc_4,0.0552}
		[0.98, 0.25]	ST_4={0.1,0.98,0.12}	E_4={ST_4,Vc_1,0.0216}	E_{16}={ST_4,Vc_2,0.0240}	E_{28}={ST_4,Vc_3,0.0192}	E_{40}={ST_4,Vc_4,0.0552}
	[35, 0.45]	[0.73, 0.25]	ST_5={35,0.73, 0.11}	E_5={ST_5,Vc_1,0.0198}	E_{17}={ST_5,Vc_2,0.0220}	E_{29}={ST_5,Vc_3,0.0176}	E_{41}={ST_5,Vc_4,0.0506}
		[0.83, 0.25]	ST_6={35,0.83,0.11}	E_6={ST_6,Vc_1,0.0198}	E_{18}={ST_6,Vc_2,0.0220}	E_{30}={ST_6,Vc_3,0.0176}	E_{42}={ST_6,Vc_4,0.0506}
		[0.96, 0.25]	ST_7={35,0.96,0.11}	E_7={ST_7,Vc_1,0.0198}	E_{19}={ST_7,Vc_2,0.0220}	E_{31}={ST_7,Vc_3,0.0176}	E_{43}={ST_7,Vc_4,0.0506}
		[0.98, 0.25]	ST_8={35,0.98,0.11}	E_8={ST_8,Vc_1,0.0198}	E_{20}={ST_8,Vc_2,0.0220}	E_{32}={ST_8,Vc_3,0.0176}	E_{44}={ST_8,Vc_4,0.0506}
	[163, 0.10]	[0.73, 0.25]	ST_9={163,0.73,0.02}	E_9={ST_9, Vc_1,0.0036}	E_{21}={ST_9,Vc_2,0.0040}	E_{33}={ST_9,Vc_3,0.0032}	E_{45}={ST_9,Vc_4,0.0092}
		[0.83, 0.25]	ST_{10}={163,0.83,0.02}	E_{10}={ST_{10},Vc_1,0.0036}	E_{22}={ST_{10},Vc_2,0.0040}	E_{34}={ST_{10},Vc_3,0.0032}	E_{46}={ST_{10},Vc_4,0.0092}
		[0.96, 0.25]	ST_{11}={163,0.96,,0.02}	E_{11}={ST_{11},Vc_1,0.0036}	E_{23}={ST_{11},Vc_2,0.0040}	E_{35}={ST_{11},Vc_3,0.0032}	E_{47}={ST_{11},Vc_4,0.0092}
		[0.98, 0.25]	ST_{12}={163,0.98,0.02}	E_{12}={ST_{12},Vc_1,0.0036}	E_{24}={ST_{12},Vc_2,0.0040}	E_{36}={ST_{12},Vc_3,0.0032}	E_{48}={ST_{12},$Vc_4$0.0092}

Figure 4.3 General event tree of spill types, met-ocean conditions, and their relative probabilities of occurrence at the Repsol Petróleo, S.A. facility in the Tarragona harbor.

4.2.3 Characterization of environmental risk analysis scenarios

The combination of spill types and met-ocean conditions determines the ERA scenarios for a specific facility. Each ERA scenario is defined by a potential spill type (ST_l) and a representative met-ocean condition (V_C). Each scenario is also associated with most-probable size distributions if spills do occur (f_{STl}) and the frequency of a met-ocean condition's occurrence (f_{Vc}), E_w= {ST_l, V_{ck}, f_{Ew}} (w =1,…, s x k). This set of hypothetical scenarios should be used to assess the environmental risk of the facility.

The four probabilistic environmental scenarios selected at the Tarragona harbor were integrated with the spill types previously defined, yielding a set of 48 standardized spills, which will be the basis of the environmental risk assessment (Figure 4.3).

4.2.4 Environmental risk assessment

The environmental risk for a specific discharge point (L_f) and a selected ERA scenario (E_w) is estimated using numerical models and a 3 step process: i) obtaining the finite element grid; ii) calculating the hydrodynamic currents generated by met-ocean conditions; and, iii) calculating the transport and spillage spreading surface. The transport simulation time is defined by the resolution time. The resolution time is defined, based on registered spill information, as the period between the detection and the response to an oil spill (with equipment designed specifically to remove the product).

From the transport model results, the environmental risk of a specific ERA scenario (RE_w) is estimated considering the presence/absence of oil in each grid cell ($PR_{g,h}$ = 1 or 0) and its associated probability (f_w) (Eq. (4.1)).

$$RE_w = \sum_{g=1}^{m} \sum_{h=1}^{n} PR_{gh} \times f_w \qquad \text{Eq. (4.1)}$$

where m, n is the number of cells in the grid calculation, and g,h is a specific grid cell.

The environmental risk for each discharge point (RL_f) is the integration of all RE_w, and it is calculated with the following equation:

$$RL_F = \sum_{w=1}^{b} RE_w = [(PR_{gh1} \times f_1) + (PR_{gh2} \times f_2)...] \qquad (w=1...b) \qquad \text{Eq. (4.2)}$$

In the Tarragona harbor, oil transport and the spillage spreading surface for each of the 48 ERA scenarios were calculated for a specific discharge point (monobuoy).

The water elevation and velocity fields generated by the tides and winds were calculated using a quasi-three dimensional model (García et al., 2010). A Friction Chezy coefficient of 55 $m^{1/2}$ s^{-1}, an Eddy viscosity coefficient of 1 m^2 s^{-1}, and a wind drag coefficient of 0.0026 were used (Gómez et al., 2014a). For transport simulations, the TESEO model (Abascal et al., 2007) was used assuming a 25 m/s^2 diffusion coefficient. The simulation time (resolution time) was estimated to be 2 hours (Mestres et al., 2010).

Environmental risk was calculated using Geographical Information System software (ArcGIS 10.1 by ESRI™). The position of the oil particles every 600 s during the simulation time was mapped in a regular square grid (30 m edge). Affected areas and environmental risk for the 48 ERA scenarios were computed. From these results, the potentially affected area and the environmental risk for each met-ocean condition were calculated (Figure 4.4 (a), (b), (c), (d)). Met-ocean conditions Vc_1 (Figure 4.4 (a)) and Vc_2 (Figure 4.4 (b)) displayed a similar range of risk values (from 0.004 to 0.180 and from 0.004 to 0.200, respectively). In contrast, met-ocean condition Vc_3 (Figure 4.4 (c)) displayed lower risk values (from 0.003 to 0.160), and the calm met-ocean condition (Vc_4, Figure 4.4 (d)) displayed higher risk values (from 0.051 to 0.460). Although higher values were recorded for Vc_4 (calm conditions), the potentially affected area, concentrically located around the monobuoy, occupied only 1.3 km^2. The potentially affected areas of met-conditions Vc_1, Vc_2 and Vc_3 were greater, affecting 2.1 km^2, 2.3 km^2 and 2.1 km^2, respectively. These potentially affected areas stretched out along the three axes defined by their respective wind directions: south-east (Vc_1, Figure 4.4 (a)), east (Vc_2, Figure 4.4 (b)) and west south-west (Vc_3, Figure 4.4 (c)).

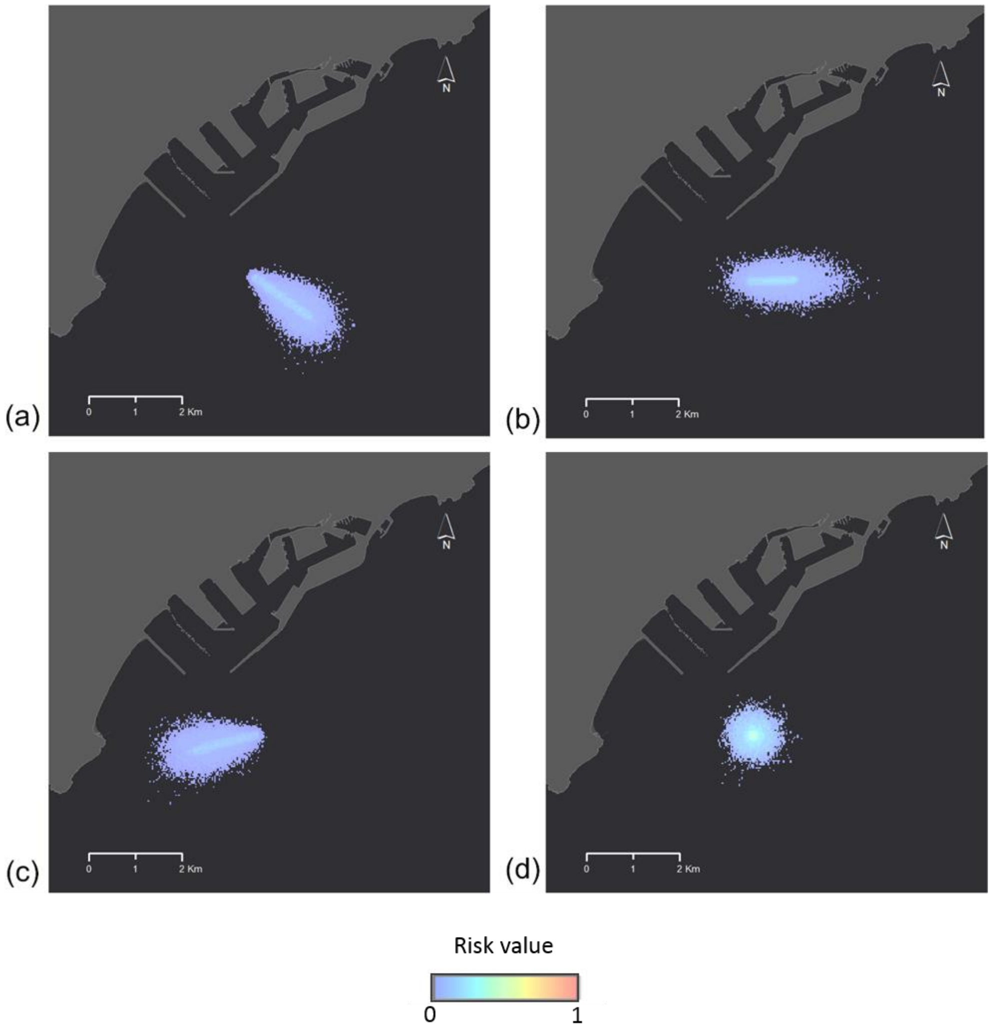


Figure 4.4 Environmental risk values and potentially affected areas near the monobuoy at the Tarragona harbor for (a) met-ocean condition Vc_1, (b) met-ocean condition Vc_2, (c) met-ocean condition Vc_3, and d) met-ocean condition Vc_4.

The total potentially affected area around the monobuoy (Figure 4.5) was calculated to be 5.6 km^2, with a mean risk value of 0.099, a maximum risk value of 1 (located close to the monobuoy) and a minimum risk value of 0.003. Of the total affected area, only 1% displayed risk values between 0.5 and 1 (Figure 4.6), and all these areas were located in the area immediately surrounding the monobuoy (200 m) (Figure 4.5). Risk values between 0.1 and 0.5 represented 28% of the total affected area, while risk values greater than 0.0 and below 0.1 represented 71% of the total affected area (Figure 4.6).

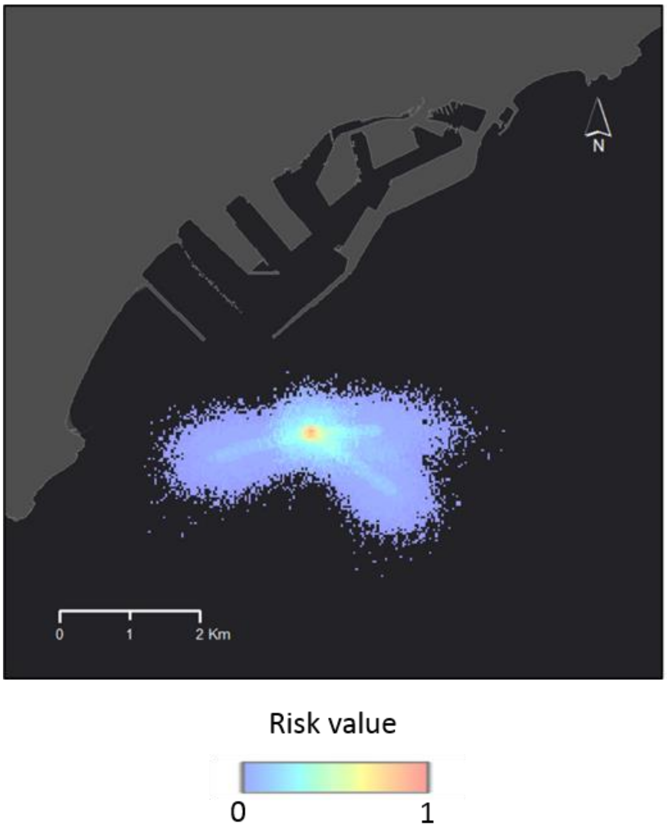


Figure 4.5 Environmental risk values (RL_F) and potentially affected areas near the monobuoy at the Tarragona harbor.

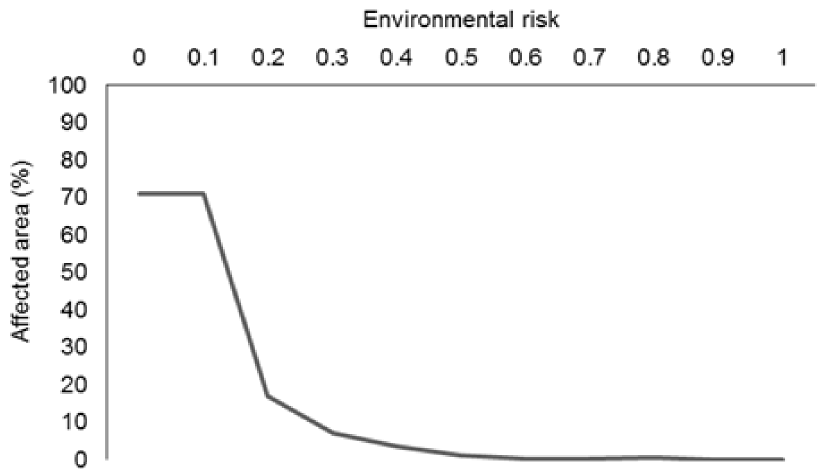


Figure 4.6 Frequency distribution of environmental risk values in the total potentially affected area near the monobuoy at the Tarragona harbor.

4.3 Discussion

In the ERA process, the identification and characterization of the hazard phase is extremely important. The quality of all subsequent stages depends largely on the quality of this initial phase. Characterization (e.g., pollution loads and pollutant diversity) is a challenge in the analysis of environmental risks for facilities where the loading and unloading of liquid bulk occurs. An appropriate method to address this challenge is the application of quantitative tools in the whole ERA process. Currently, most potential effect assessment methods ignore the characteristics of the agent itself and evaluate hazards based on hypothetical scenarios (Gómez, 2010; Lahr and Kooistra, 2010).

The method proposed in this chapter builds on this background by identifying and characterizing hazards from the limited information available in local oil spill databases. It derives quantitative estimates (Q_j, D_k, f_i) from semi-qualitative information (S_i, A_i), addressing the issue of representing the specific cases of pollution for oil spills associated with a specific facility, thus allowing a realistic, quantitative and probabilistic characterization of potential ERA scenarios (Figure 4.3). Quantitative results obtained for the monobuoy at the Tarragona harbor allow us to note that the extent of the affected areas is not directly proportional to the quantity of product discharged in each ERA scenario. It depends on the combination of the quantity and density of the spilled product. Thus, common patterns can be observed for the 4 met-ocean conditions (Figure 4.7).

For light hydrocarbons (d= 0.73), a reduction of the extent of the affected area is observed when the discharged quantity increases. For hydrocarbons of intermediated densities (d= 0.83), a common pattern for all met-ocean conditions is presented: lower extensions for intermediate quantity discharge scenarios (Figure 4.7). Conversely, for higher density hydrocarbons (d= 0.98), the extent of the affected areas increases with the amount spilled. In general terms, the smaller the affected area is, the higher the density of the discharged product. Additionally, the smaller the amount spilled is, the greater the difference between the extent of the affected area for light and medium oil (0.73 to 0.83) and heavy hydrocarbons (0.96 to 0.98) (Figure 4.7). Therefore, spill type density is a key piece of information for light oils and low quantity discharges. Given these trends, generic classifications are established to determine the relative density of the material spilled (IMO, 2005). Owing to the difficulty of knowing the specific type of product and source of crude oils from which a spill is derived, more accurate data about pollution incidents in terms of the physicochemical properties of the product spilled would improve the capacity of our method to discriminate between ERA scenarios associated with different product types (D scenarios). This means that this method has the potential to identify and characterize hazards, selecting representative ERA scenarios based on real world conditions (in terms of environmental variability and cases of oil spills). However, the precision of the results depends directly on the quantity and quality of data recorded in available local databases.

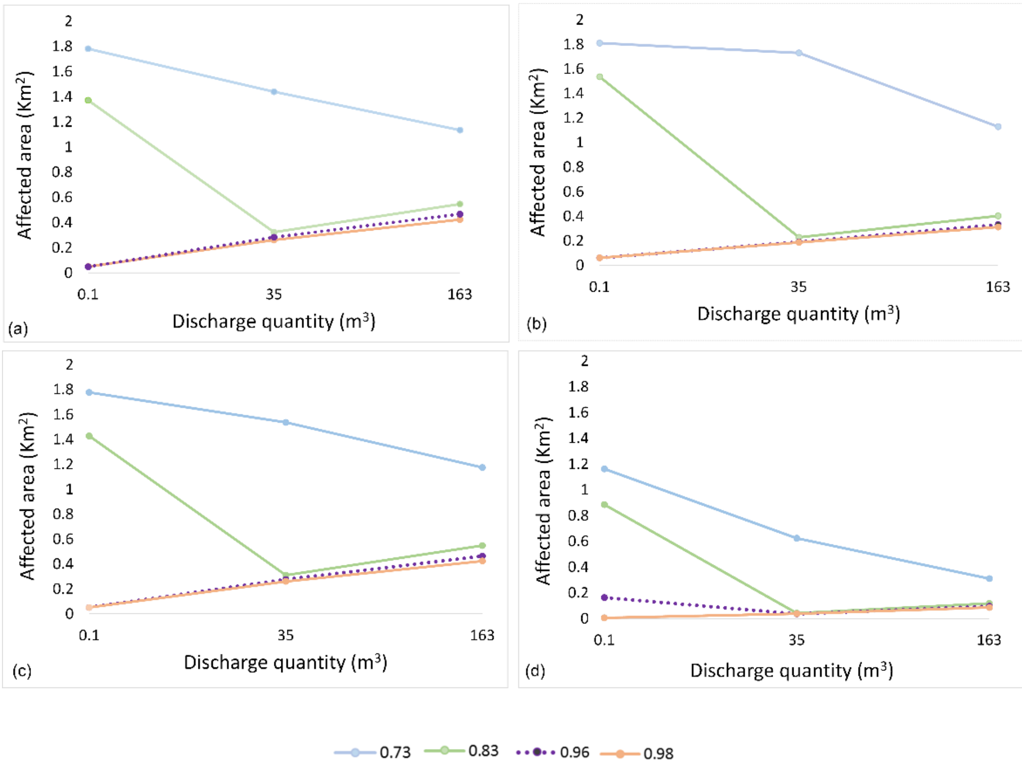


Figure 4.7 Affected area in terms of discharged quantity and density at the monobuoy in the Tarragona harbor for (a) Vc_1 met-ocean condition, (b) Vc_2 met-ocean condition, (c) Vc_3 met-ocean condition, and (d) Vc_4 met-ocean condition.

ERA methods for non-point discharges are primarily based on the concept of distance-agent. This concept considers an exposure directly proportional to the distance between the agent and the receptor. Radial proximity, assuming linear agent dispersion, has been widely used, ignoring environmental and agent characteristics. For calm conditions, as in Vc_4 in Tarragona (Figure 4.4 (d)), the distance-agent method could be used because transport processes generated by currents do not affect oil discharges. However, when other met-ocean conditions are taken into account, pollution is not transported linearly by hydrodynamic currents driven by wind or water elevation. Affected areas form cone shapes (Figure 4.4 (b)) or ellipses (Figure 4.4 (a), (c)) from the discharges.

The consideration of spatial and temporal components has an important role in the realistic description of the potential effects of oil spills at a facility. This information is essential to recognize the complex interactions between these potential impacts and the location of different habitats or receptors. In that sense, environmental risk assessment and environmental monitoring are two linked tools that provide each other feedback. Spatial-temporal probabilistic ERA results are extremely important in the anticipatory system evaluation of environmental quality to design environmental monitoring (for instance, to establish the location of sampling stations for a specific facility). An effective environmental monitoring design can in turn provide evidence of the disturbances caused by harbor activities, establishing the connections between the disturbance and its possible effects (Ondiviela et al., 2012). The ERA results for the monobuoy in Tarragona provided maximum risk values (close to 1) for all met-ocean conditions: i) around the monobuoy; and, ii) close to the center of the trajectory of the oil spill particles (defined by a different axis for each met-ocean condition) (Figure 4.5). In contrast, minimum risk values (close to 0) were located: i) far from the monobuoy; and, ii) distant from the oil particle trajectories (Figure 4.5). These results would allow us to properly design a monitoring program to assess the potential impact of the handling activity at the monobuoy. Sample stations would be located: i) around the monobuoy at a maximum distance of 300 meters (where higher values of environmental risk were found); and, ii) along the three axes defined by the oil particle trajectories for the different met-ocean conditions, where the risk values were above 0.1. The maximum distance to locate a sampling point would be 1500 meters from the monobuoy because no environmental risk is detected beyond that distance (Figure 4.4 (e)).

Additionally, the spatial-temporal distribution of risk allows managers and stakeholders to identify potentially threatened environmental and community resources, infrastructure (e.g., roads) and other economic, societal or environmental goods. For this reason, as mentioned in chapter III, spatial-temporal risk maps are also relevant information for the development of contingency plans (coordination of response elements and response operators) (IMO, 1995; AMSA, 2014). Here, the type and quantity of vessels and material required to remove the product from the water and the number and capacity of containers to store the product removed are decisions that could be made based on the identification of the hazards phase of the ERA method proposed. In Tarragona, ERA maps at handling facility level permit us to assert that neither swimming nor protected areas would be affected by oil handling activity at the monobuoy. Economic damages from damage to infrastructure would not occur as long as the discharge is contained within 2 hours (resolution time considered). However, maritime traffic could be affected because areas located between the entrance channel of the harbor and anchorage zone have risk values above 0. Both the type and quantity of vessels and material required to remove the product from the water and the number and capacity of containers to store the product once removed are decisions that could be made based on the ERA results. The location of all necessary materials is also important for an effective response.

The method proposed in this chapter is versatile enough to be applied to other fields or disciplines. For instance, offshore petroleum activities also require relevant information on the possible drift and fate of oil spills for an adequate environmental risk assessment. Although our method has been designed for application to harbor areas, it would be readily applicable to offshore oil handling installations. In that case, 3D hydrodynamic and transport models should be used to calculate the trajectory of spills originating under the surface. In addition, environmental managers and the scientific community are currently concerned about Hazardous Noxious Substances (HNS) spill preparedness and response (Neuparth et al., 2011). The probability of a HNS spill has traditionally been considered small, most likely because of high safety standards. However, maritime transportation of HNS has grown, and an effective response regime is needed for HNS spills. In this context, ERA has been applied to estimate the potential risk of chemical spills. HNS are very well characterized substances, and specific numerical models have been developed, including chemical kinetics (Wania and Mackay, 1999; Horiguchi et al., 2006; Yamamoto et al., 2009; Gómez, 2010). Although the method presented here has been designed for application to oil handling facilities, it could be applicable to HNS handling with adequate numerical models.

Finally, methods of risk analysis are predictive tools. Thus, future investigation should evaluate whether estimated risk corresponds to actual environmental impact. Such future studies must analyze the actual environmental impacts when spills occur. Analyzing the concentration of pollutants in the water and/or sediments samples and the response and status of biological communities potentially affected could give us an answer to the following question: does the risk estimated by the ERA process reflect the actual environmental impact? In this sense, the definition of environmental risk could be refined, basing it not only on the presence or absence of spills but also on the pollution's concentrations in the water and sediment and its bioaccumulation in biota. In addition, methods for quality standards established by different authors and/or organizations (US EPA, 1992; 2014; Thatcher et al., 2005; European Commission, 2003; 2013a) could be applicable. This would permit the inclusion of critical concentrations that can cause adverse environmental effects with a certain probability in the environmental risk definition. This question is addressed in Chapter VI of this thesis.

4.4 Conclusions

At this chapter a method to assess the spatial and temporal environmental risk of oil handling facilities in harbor areas is proposed. ERA scenarios for a specific facility are defined by the combination of spill types and met-ocean conditions. The end products are risk maps of potentially affected areas considering the spatial components in probabilistic terms. The method was tested by its application to the monobuoy of Repsol Petróleo, S.A. at the Tarragona harbor.

From the application, we can conclude that this method allows the identification and characterization of environmental hazards when hardly any information is available about a specific incident. Quantitative results obtained for the monobuoy allow us to note that the extent of the affected areas is not directly proportional to the quantity of product discharged in each ERA scenario. It depends on the combination of the quantity and density of the spilled product. In general terms, the smaller the affected area is, the higher the density of the discharged product. Additionally, the smaller the amount spilled is, the greater the difference between the extent of the affected area for light and medium oil and heavy hydrocarbons. Therefore, spill type density is a key piece of information for light oils and low quantity discharges. On the other hand, pollution is not transported linearly by hydrodynamic currents driven by wind or water elevation. Affected areas form cone shapes or ellipses from the discharge points. Thus, the consideration of spatial and temporal components has an important role in the realistic description of the potential effects of oil spills at a facility or discharge point.

The results obtained through this method would allow to properly design a monitoring program to assess the potential impact of the handling activity. Additionally, the spatial-temporal distribution of risk would allow managers and stakeholders to identify potentially threatened environmental and community resources, infrastructure (e.g., roads) and other economic, societal or environmental goods. Accordingly, the method presented in this chapter provides decision-making support for the development of contingency plans. Moreover, the method proposed is versatile enough to be applied to other fields or disciplines. For instance, with adequate numerical models, it would be applicable to offshore petroleum activities or Hazardous Noxious Substances (HNS) spill preparedness and response. Finally, in order to evaluate whether estimated risk corresponds to actual environmental impact, the following question: does the risk estimated by the ERA process reflect the actual environmental impact? Is addressed in Chapter VI.

Chapter V

SPILL Tool

CHAPTER V. A GIS TOOLBOX TO ASSESS THE ENVIRONMENTAL RISK OF OIL SPILLS IN HARBORS

This chapter is an edited version of the research article published in Journal of Environmental Management, 170: 105 - 115 by Valdor, P. F., Gómez, A. G., Velarde, V. Puente, A. with the title 'Can a GIS toolbox assess the environmental risk of oil spills? Implementation to oil facilities in harbors'.

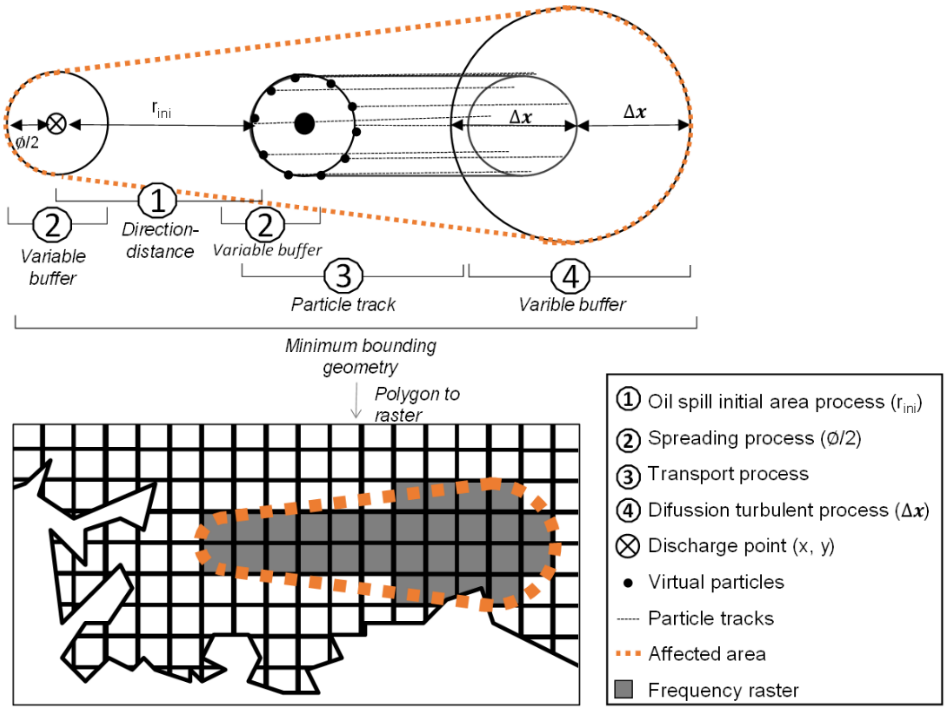


Figure 5.1 Graphical abstract.

Abstract

Oil spills are one of the most widespread problems in port areas (loading/unloading of bulk liquid, fuel supply). Specific environmental risk analysis procedures for non-point oil sources that are based on the evolution of oil in the marine environment are needed. Non-point sources such as oil spills usually present a lack of information, which makes the use of numerical models an arduous and occasionally impossible task. Furthermore, numerical models are limited to expert users and still require very complex input information. For that reasons, a tool that can assess the risk of oil spills in near-shore areas by using Geographical Information System (GIS)

is presented. The SPILL Tool provides immediate results by automating the process without miscalculation errors. The tool was developed using the Python and ArcGIS scripting library to build a non-ambiguous geoprocessing workflow. The SPILL Tool was implemented for oil facilities at Tarragona harbor (NE Spain) and validated showing a satisfactory correspondence (around 0.60 RSR error index) with the results obtained using a 2D calibrated oil transport numerical model.

5.1 Introduction

Environmental risk assessment (ERA) on aquatic systems has traditionally focused on point contaminant sources, but in coastal areas, diffuse sources are also an important introduction of pollution (Preston, 2002; Gómez, 2010). This fact is highly noted in port areas, where the water quality is a consequence of the uses and activities conducted in these environments (Darbra and Casal, 2004). Previous studies and records of contaminating events in port areas have noted that accidental spills are the main cause of water pollution, with a great proportion of oil spills in these areas occurring due to the loading and unloading of bulk liquid (Darbra and Casal, 2004; Peris – Mora et al., 2005).

Many of the critical problems that arise in dealing with the pollution of aquatic systems by diffuse contaminant sources in port areas are inherently spatial issues. On many occasions, the interaction of possible influences complicates the precise identification of surrounding hazards (stressors), their multiple effects, and consequently, the pathways to resolution (Gómez et al., 2015). These interactions are more pronounced in port areas, where there is a heavy industrialization and, therefore, a high number of sources of non-point pollutants. Several authors (Su et al., 2009; Sieber et al., 2010; Rioux et al., 2010) have implemented the response-distance method to establish the impact of air or soil pollution (Gómez, 2010). Radial proximity, assuming linear agent dispersion, has been widely applied while ignoring environmental variability and agent characteristics. This concept has been used primarily in the determination of the impact of diffuse contaminant sources on air pollution (Su et al., 2009; Rioux et al., 2010) or soil pollution (Sieber et al., 2010). However, a spatial description of environmental risk is essential to answer the following questions: i) is it possible to localize contaminant sources (both point and non-point)?; ii) is it possible to know these sources' contribution to the global environmental pollution for a specific area?; iii) what is the true impact on the environment, and where this impact is located?; and, iv) where should the monitoring strategy be focused if an environmental monitoring program is conducted? Therefore, as mentioned before, 'inventories and maps' are essential aspects of the ERA process in risk management context because they can be used to support contingency planning, environmental monitoring program design and decision-making.

As previously mentioned in Chapter IV, an ERA process for any non-point oil source requires the study of the evolution of the oil in the marine environment to calculate the trajectory of the spill and the final potential affected areas (Valdor et al., 2015). Currently, calibrated numerical models are used extensively to simulate the movement of oil via wind, surface currents and turbulent diffusion. As Otero et al. (2015) recognized, most of the available tools that permit drift trajectories to be visualized are Lagrangian models that must be run by a qualified technician (e.g., GNOME; ROFF, Carr et al., 2008; MEDSLINK-II, De Dominicis et al., 2013) and provide outputs that are difficult for a non-expert to understand (Roberts et al., 2010). In addition, these models involve, in most cases, a huge computational cost (Roberts et al., 2010) and require a detailed characterization of contaminant sources and environmental conditions. For these reasons, there is an increasing tendency to design tools with low computational costs to predict responses of products released on aquatic systems.

Geographic Information System (GIS) is becoming an increasingly common tool for analyzing spatial distributions and supporting decision makers via environmental risk assessment. In this context, Lu et al. (2014) divided the existing GIS-based environmental models into two groups: i) models that primarily use GIS to visualize model results over a geographical area (Dixon, 2005; Reshmidevi et al., 2009; Pathak and Hiratsuka, 2011; Vafai et al., 2013); and, ii) models that are encapsulated into GIS with a shared GIS interface or GIS components embedded into the developed system (Vairavamoorthy et al., 2007; Akbar et al., 2011; Giordano and Liersch, 2012). However, GIS-based environmental models are limited to expert users and still require very complex input information (Otero et al., 2015), which is generally unavailable for non-point contaminant sources.

To overcome these gaps, Gómez (2010) proposed a general methodology to assess the impact of diffuse contaminant sources based on GIS techniques (Juanes et al., 2013). This method, used in Chapter III, obtains the contaminant source extension as a function of three categorized factors: product aggregation state (liquid/solid), released product density, and magnitude of release (Eq. 3.3). The same transport processes were considered for all types of products while ignoring specific physical and chemical processes.

In summary, the main gaps of the previous works are that methodologies developed ignore the environmental variability as well as the physical and chemical characteristics of products spilled. At the same time, numerical models that do not ignore them are limited to expert users.

The main novelty of this work is the advancement of knowledge in the developing of a GIS tool that can provide the spatial and temporal environmental risks of potential oil spills in port areas based on different spilled volumes, discharge source locations, product released and environmental conditions. All this developed through a simple and quick procedure. The GIS Tool was used to assess the environmental risks of an oil handing facility at Tarragona harbor.

Following, SPILL Tool is described and results of its application to oil facilities at Tarragona harbor are presented.

5.2. Material and methods

5.2.1 SPILL Tool description

A user-friendly toolbox was developed in ArcGIS (10.1) (SPILL Tool) by using the Python and ArcGIS scripting library. The tool is easy to load through the ArcToolbox of Geographical Information System (GIS) software (ArcGIS 10.1 by ESRI^{TM}) and is easy to operate through the auto generated Graphical User Interface (GUI). It is a custom script tool that has been fully integrated under the ArcGIS Geoprocessing Framework; therefore, it can easily be reused and combined inside new workflows and models with ArcGIS ModelBuilder. The Tool provides a raster output of probabilistic potential affected areas for a specific scenario (spill type and met-ocean conditions).

The results obtained through the SPILL tool are calculated considering four main processes (Figures 5.2 and 5.3):

1. *Oil spill initial area process*: SPILL Tool uses the Direction-Distance tool (Editor Tool from ESRI ArcGIS 10.1) for a first oil spill displacement, considering the direction and intensity of currents at the discharge point location (Figure 5.2 (1), Figure 5.3 (1)). The oil spill initial area process considers a circumference as the initial shape, with the radius a function of the spilled product volume and density (Lehr, 2001) (Eq. 5.1).

$$r_{ini} = 1.84\left(\frac{\Delta w \times Q^5}{\nu^2}\right)^{1/8} \qquad \text{Eq. (5.1)}$$

where r_{ini} is the oil spill initial radius (m), Δw is the reduced gravity, calculated as $\Delta w = (\rho_w - \rho_{oil}) / \rho_w$, where ρ_w is the water density (kg/m^3) and ρ_{oil} is the spilled product density (kg/m^3), Q is the spilled product volume (m^3), and ν is the kinematic viscosity of water ($1 \cdot 10^{-6}$ m^2/s).

2. *Spreading process*: The SPILL Tool calculates the spreading of the slick as a Variable Buffer (Buffer tool of Analysis Tool ESRI ArcGIS 10.1) (Fig. 5.2 (2), Figure 5.3 (2)), considering a diameter of the circumference that depends on the spilled product volume and density and the resolution (simulation) time (Fay, 1969) (Eq. 5.2).

$$\emptyset = 1.45\left(\frac{g \times \Delta w \times Q^2 \times T^{3/2}}{\nu^{1/2}}\right)^{1/6} \qquad \text{Eq. (5.2)}$$

where $\emptyset$ is the diameter of a spill circumference due to the spreading process, g is the constant gravity (9.81 m/s^2), Δw is the reduced gravity, Q is the spilled product volume (m^3), T is the simulation time (s), and ν is the kinematic viscosity of water ($1 \cdot 10^{-6}$ m^2/s).

3. *Transport process:* Depending on the simulation time and the intensity of the currents, the transport process is determined in two different ways (Figure 5.2. (A) and (B)). The transport of virtual particles is performed by means of the Particle Track Package (Spatial Analyst Tool ESRI ArcGIS 10.1) (Figure 5.3 (B)). The tool uses a predictor-corrector scheme to predict the future location of virtual particles that are located equidistantly around the spill slick perimeter due to the spreading process. The particle

displacement to a certain distance (step length) depends on the local intensity and direction currents (raster datasets) (Konikow and Bredehoeft, 1978; Gómez, 2010). A unified polygon from buffers of all virtual particle tracks is finally obtained as the transport area (Figure 5.3. (B.1) and (B.2)).

4. *Turbulent diffusion process:* The SPILL tool calculates a circumference using the Variable Buffer (Buffer tool of Analysis Tool ESRI ArcGIS 10.1) (Figure 5.2 (4), Figure 5.3. (4)), depending on the diffusion coefficient and the remaining simulation time (Fay, 1969) (Eq. 5.3).

$$\Delta \mathrm{x}^2 = 2 \times C_D \times \Delta \mathrm{T} \qquad \text{Eq. (5.3)}$$

where $\Delta \mathrm{x}^2$ is the quadratic displacement due to turbulent diffusion (m), C_D is the diffusion coefficient ($m^2 \cdot s^{-1}$), and ΔT is the remaining simulation time (s).

The polygons created at sequential stages are unified using the Union tool, the Dissolve tool and the Minimum Bounding tool (Analysis Tools, Data management Tools ESRI ArcGIS 10.1) (Figure 5.2). The result obtained is the affected area for a specific scenario (spill type and met-ocean condition). Finally, the polygon is converted to a raster dataset, in which all cells of the affected area have the value of the scenario frequency [0-1].

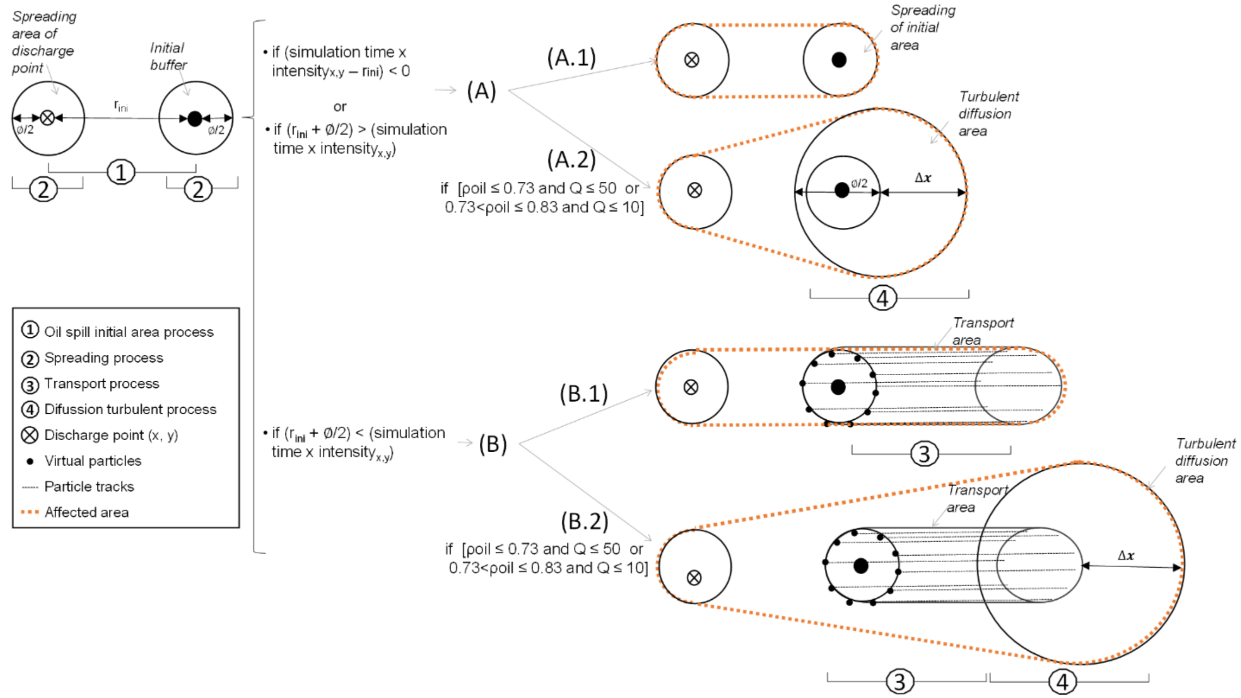


Figure 5.2 Graphic representation of main processes used to obtain the affected area of a scenario, considering hydrodynamic currents with a constant intensity and a 90º direction.

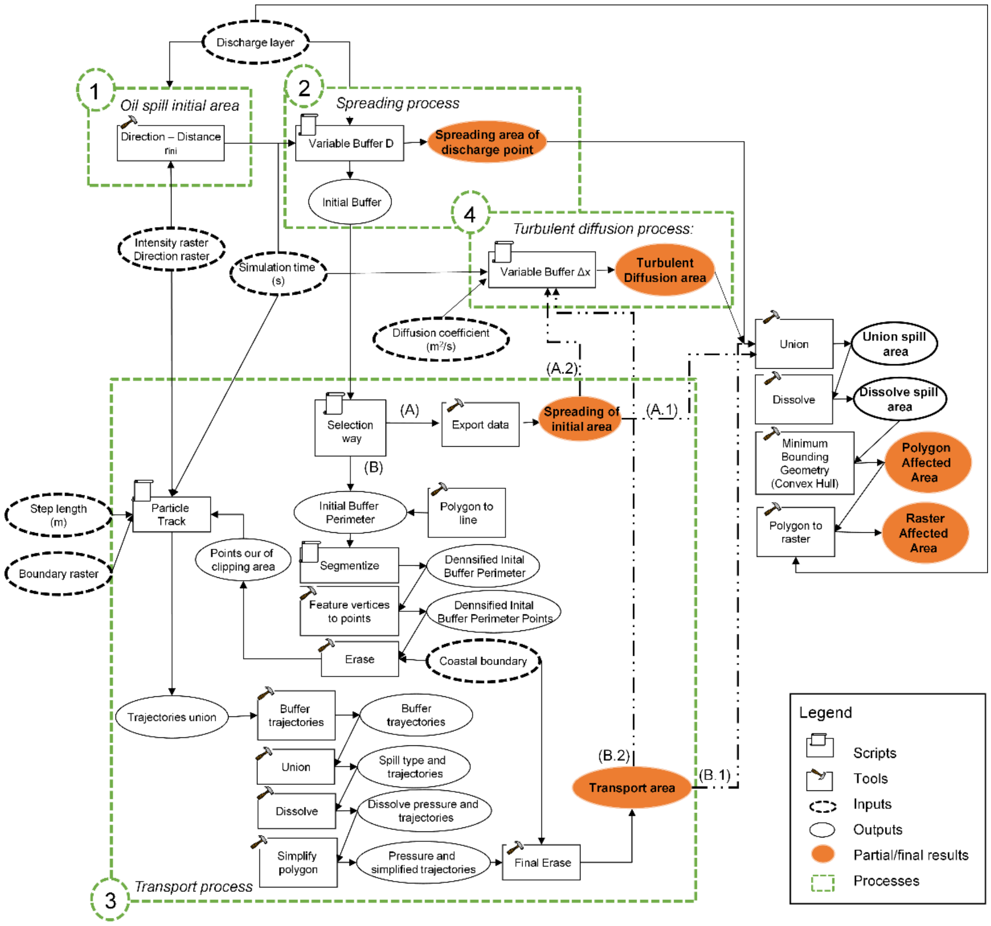


Figure 5.3 Graphic workflow representation of the SPILL Tool (1) Oil spill initial area process, (2) Spreading process, (3) Transport process, and (4) Turbulent diffusion process.

5.2.2 SPILL Tool application

To apply the SPILL Tool, the following inputs are required: i) discharge layer with discharge point location (x, y), scenario code, spilled product volume (m^3), spilled product density (kg/m^3), water density (kg/m^3), water kinematic viscosity ($m^2 \cdot s^{-1}$), and scenario frequency ([0-1]); ii) coastal polygon boundary; iii) intensity of currents in the study area (raster grid dataset, $m \cdot s^{-1}$); iv) direction of currents in the study area (raster grid dataset, °); v) boundary raster dataset delimiting the study area; vi) simulation time (s); vii) step length (m); and, viii) diffusion coefficient ($m^2 \cdot s^{-1}$).

The discharge layer provides the scenario characterization. A statistical classification of the most-representative met-ocean conditions at the local scale and the database spill types from local databases should be performed (*See section 4.2.2 for more details)*. Hydrodynamic currents related to met-ocean conditions should be calculated by using numerical models or by considering a constant intensity and direction for the entire study area. If numerical models are used, the bathymetry of the study area is required. Hydrodynamic conditions must be presented in two separate raster that contain the intensity (raster grid dataset, $m \cdot s^{-1}$) and direction (raster grid dataset, °) information for the currents in the study area. Simulation time, as previously mentioned in Chapter III, is defined as the period between the detection and the response to an oil spill with equipment that has been designed specifically to remove the product (Valdor et al., 2015). Simulation time should be established based on registered spill information. Finally, the diffusion coefficient depends on the environmental and product characteristics (1-100 $m^2 \cdot s^{-1}$).

The SPILL tool was applied to the Repsol Petróleo, S.A. oil handling facility (*see Chapter II for more information*) by considering 48 scenarios at each discharge point at Tarragona harbor, which represents a total of 192 cases (48 scenarios x 4 discharge points). The combination of the most probable met-ocean conditions (4) and spill types (12) determines the so-called environmental risk assessment (ERA) scenarios (48) of each discharge point in Tarragona (*See* section *4.2.3 for more details*). Each ERA scenario has a specific product density, volume released and frequency of occurrence (Figure 4.3). The spatial environmental risk assessment at the discharge point level was obtained as a result of summing the frequencies of the 48 ERA scenarios to obtain a spatial variation of the risk with values between 0 and 1.

5.2.3 SPILL Tool validation

To validate the confidence in the performance of the developed SPILL Tool, the results provided by the tool were compared with those obtained using a calibrated oil transport model: TESEO 2D-model (Abascal et al., 2007; 2016). The validation is conducted comparing affected areas at the case level (192) and comparing environmental risk assessments at the discharge point level (4).

The affected areas obtained from both tools for each of the 192 cases were compared by computing the coincident affected area. Coincidence percentages values over 70% were considered satisfactory.

Statistical cell-by-cell evaluation of environmental risk assessment obtained from both tools for each discharge point was performed by using the RMSE-observation standard deviation ratio (RSR) (Bennett et al., 2013). The method considers the pairs of values for the same point in time or space. The TESEO 2D-model results were the observed values, and the SPILL Tool results were the modeled values. Based on the recommendation by Singh et al. (2004) and Moriasi et al. (2007), RSR values close to zero were considered to indicate a perfect fit between observed and simulated data, and RSR values ≤ 0.70 indicated a satisfactory model simulation.

5.3 Results

5.3.1 SPILL Tool application

A discharge layer by each discharge point at Tarragona harbor with all of the information required for each scenario was obtained. Hydrodynamic currents for each met-ocean condition were calculated by considering the advective velocity to be a result of the linear addition of superficial velocity currents (Uc) and currents of superficial layers of water column generated by wind (Uv) (Eq. 5.4).

$$U_a = U_c + U_v = U_c + 0.03 \times W_{10} \qquad \text{Eq. (5.4)}$$

To obtain the superficial velocity of currents (Uc), a quasi-three-dimensional model (H2DZ model) (García et al., 2010) was used, considering a Friction Chezy coefficient of 55 $m^2 \cdot s^{-1}$, an eddy viscosity coefficient of 1 $m^2 \cdot s^{-1}$, and a wind drag coefficient of 0.0026 (Gómez at al., 2014a). Bathymetry data were used to obtain a finite element grid of regular squared cells (452x371, with a cell dimension of 30 m) (see Chapter II for more details). The currents of superficial layers of water column generated by wind (U_v) were calculated by considering a 3% wind velocity at 10 meters above the surface (W_{10}, $m \cdot s^{-1}$) (Eq. 5.4) (Overstreet and Galt, 1995; Sobey and Barkey, 1997).

Finally, the advective velocity (U_a) of the 4 met-ocean conditions was transformed into two separate raster of regular squared cells (452x371, with a cell dimension of 30 m) containing the intensity ($m \cdot s^{-1}$) and direction (°) information for the currents.

The affected areas for the 192 cases were computed using the SPILL Tool. The SPILL tool was run with a diffusion coefficient of 25 $m \cdot s^{-2}$ for the monobuoy (discharge point at the exposed port area) and a diffusion coefficient of 1 $m \cdot s^{-2}$ for P11, P35 and P80-100 (sheltered port area discharged points) (Figure 2.1). A simulation time of 2 hours (Valdor et al., 2015) and a step length of 15 m (one-half of the cell dimension) were considered. For each discharge point, the frequencies of 48 ERA scenarios were summed to obtain the spatial environmental risk (Figure 5.4).

The extension of the total potentially affected areas was very similar at the P11, P35 and P80-100 discharge points, whereas it was larger for the monobuoy (Table 5.1). These potentially affected areas stretched along the three axes defined by the representative wind directions: calm (circular form around discharge point); south-east; east; and west south-west (cone shapes or elliptical forms from discharge point) (Figure 5.4). The mean risk values in the total potentially affected areas were proven to be very similar, with each area having a value of approximately 0.1 (Table 5.1). The minimum risk values detected were slightly higher (0.038) for the monobuoy compared with the other discharge points (0.003), whereas maximum risk values were very similar, with values of approximately 0.9 (Table 5.1).

With regard to frequency distribution of environmental risk values, only 0.35% of the total affected area of the monobuoy displayed risk values between 0.5 and 1.0 (Figure 5.5), and all of these values were presented in the area immediately surrounding the monobuoy (115 m was the maximum distance). At the long dock discharge points (P11, P35, P80-100), approximately 2% of the total affected area presented risk values between 0.5 and 1.0, and these values were all presented in the area nearest the discharge point (83 m, 92 m and 65 m was the maximum distance, respectively). Risk values between 0.1 and 0.5 represented 39% (monobuoy), 44% (P11), 42% (P35) and 41% (P80-100) of the total affected area, whereas risk values below 0.1 represented 61% (monobuoy), 56% (P11 and P35) and 59% (P80-100) of the total affected area (Figure 5.5).

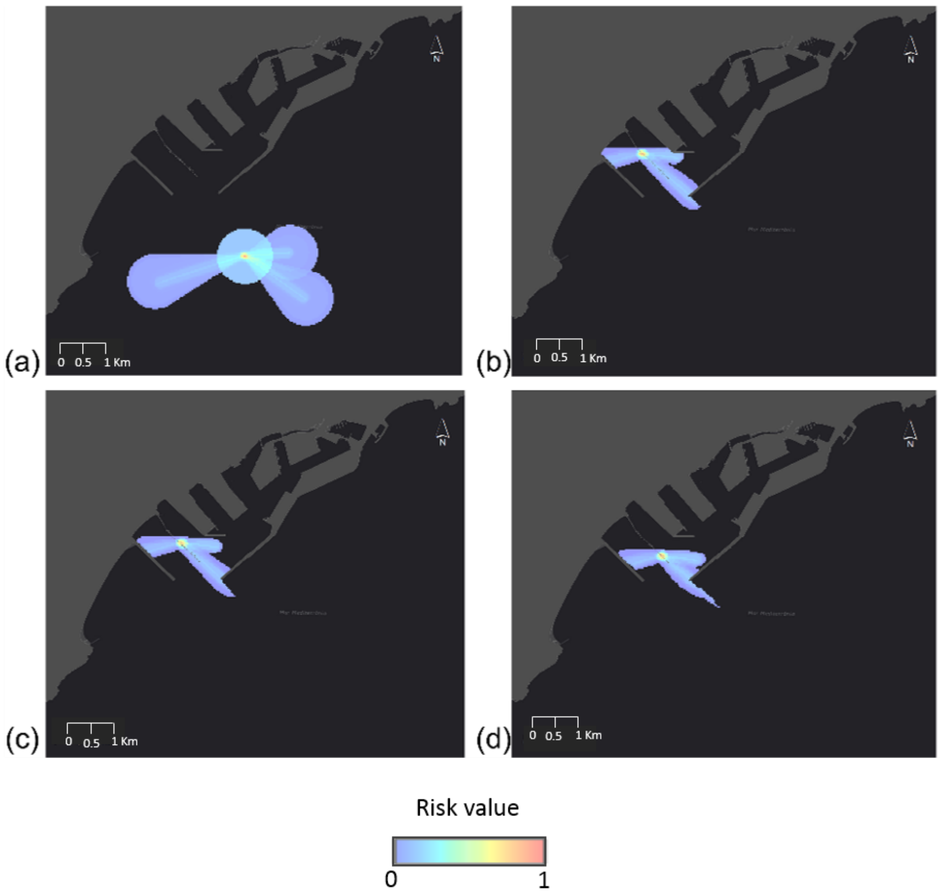


Figure 5.4 Environmental risk assessment and potentially affected areas for (a) monobuoy, (b) P11, (c) P35 and, (d) P80-100 at Tarragona harbor.

Discharge point	Affected area (Km^2)	Mean ERA	Min ERA	Max ERA	RSR
Monobuoy	5.1	0.109	0.038	0.942	0.60
P11	1.1	0.100	0.003	0.923	0.51
P35	1.0	0.099	0.003	0.923	0.54
P80-100	0.9	0.102	0.003	0.923	0.54

Table 5.1 Extension of the global affected areas, mean, minimum and maximum risk and RSR index values by discharge point at Tarragona harbor

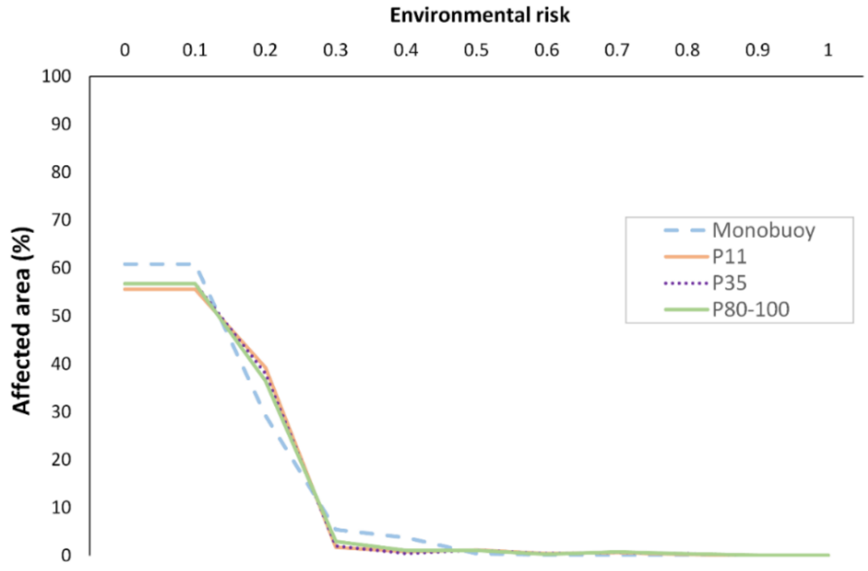


Figure 5.5 Frequency distribution of environmental risk values in the total potentially affected areas at the monobuoy, P11, P35 and P80-100 at Tarragona harbor.

5.3.2 SPILL Tool validation

The extension of the affected area obtained by both tools, i.e., the TESEO 2D model and the SPILL Tool, and the extension of the coincident area between the results obtained using both tools (Coincident) are represented for the 192 cases at Tarragona harbor (Figure 5.6). Similar patterns were observed for the results obtained at P11 (Figure 5.6 (b)), P35 (Figure 5.6 (c)) and, P80-100 (Figure 5.6 (d)) for the same cases (E01 to E48), whereas the results obtained for the monobuoy were markedly different (Figure 5.6 (a)). Moreover, the extension of the affected area was greater at the monobuoy than at the long dock discharge points (P11, P35 and P80-100), except for two specific scenarios (E03 and E39).

Of the cases, 89.1% obtained coincidence percentages greater than 70%. Most of the cases with a coincidence percentage less than 70% were spill types of higher densities (0.96 and 0.98) and corresponded to the E03, E04, E27, E28, E31, E36 and E39 scenarios, ultimately obtaining a minimum coincidence of 3.1% for E28 at the monobuoy and a maximum of 51.1% for E04 at P35. There were only two cases of lower densities (0.73 and 0.83) that presented a coincidence percentage below 70%: E30 (55.7%) and E41 (53.4%) at the monobuoy.

For the statistical evaluation, the RSR obtained at the monobuoy was 0.60 (Table 5.1). At P35 and P80-100, the results for the RSR error index were 0.54. Finally, at P11, the result of the statistical metric was 0.51. Consequently, the results of affected area simulated by the SPILL Tool can be judged as satisfactory because they demonstrated a good correspondence to the results obtained using a calibrated TESEO 2D transport numerical model.

5.4. Discussion

5.4.1. Implementation in Tarragona harbor

The TESEO 2D model, as applied in different operational exercises (Sotillo et al., 2008), was used in Tarragona harbor to calibrate and validate the SPILL Tool. The TESEO 2D model was considered to be the observed result that the proposed SPILL Tool should approach to show a good correspondence.

At Tarragona harbor, the diffusion coefficient selection is related to the location of the discharge points. The discharge points at the dock facility are located very close to the non-exposed area, which is sheltered by the main breakwater of the harbor. The monobuoy is located outside the breakwater sheltered area and is thus exposed to stronger currents. Accordingly, a diffusion coefficient value of 1 $m^2 \cdot s^{-1}$ was considered at the dock discharge points, with a 25 $m^2 \cdot s^{-1}$ value for the monobuoy. Thus, similar patterns were observed for the results obtained for the same cases (E01 to E48) at the dock discharge points, whereas the results obtained at the monobuoy were markedly different. Moreover, the trajectory of spills occurring at the dock discharge points was interrupted by the same physical barriers (e.g., dams), and no barrier interrupted the trajectory of spills simulated at the monobuoy.

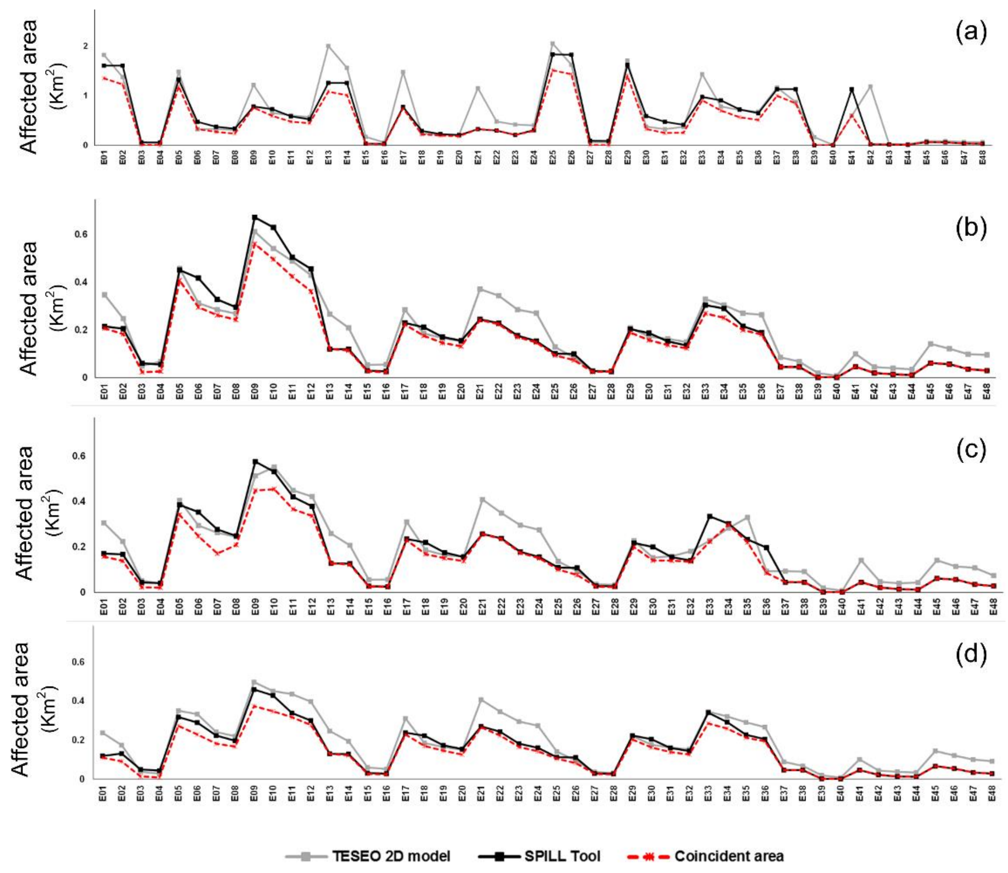


Figure 5.6 Extension (km^2) of the total affected area at case level for (a) the monobuoy, (b) P11, (c) P35 and (d) P80-100 at Tarragona harbor.

From 192 cases simulated at Tarragona harbor, the scenarios that had a smaller percentage of spatial coincidence between the SPILL Tool and the TESEO 2D model results were those with higher density products (0.96 and 0.98). Most of these cases had a coincidence percentage less than 70%. In Figure 5.7, the results obtained for a high-density scenario (E03) and a low-density scenario (E26) at the monobuoy and P11 are shown. Due to the differences in particle transport, a small displacement in the direction between the results obtained using both tools was obtained. The greater diffusion of lower density product released (E26) allowed the SPILL Tool to ignore possible differences in direction and extent of trajectories of particles (Figure 5.7). The differences were more pronounced when the product spilled had a density above 0.96 (as in the E03 scenario). Displacements of a few meters in the direction of the trajectory can lead to interruption of the trajectory of the particles by different physical barriers (Figure 5.7). Despite this interruption, the statistical analysis of spatial and temporal risk components of the SPILL Tool was satisfactory and obtained better results at the sheltered discharge points than at the discharge point that was exposed to a higher current intensity.

On the other hand, from cases simulated at Tarragona harbor, the scenarios that showed the highest difference between the total extension (km^2) of affected area calculated by TESEO 2D model and by SPILL Tool are those of higher quantities (163 m^3) of oil spilled (E9 to E12, E21 to E24 and, E45 to E48). This could be related to the function used to calculate turbulent diffusion. During the SPILL Tool validation process, the function used to calculate the displacement of oil spilled due to turbulent diffusion was limited to the following conditions, $\rho_{oil} \leq 0.73$ and $Q \leq 50\ m^3$ or $0.73 < \rho_{oil} \leq 0.83$ and $Q \leq 10\ m^3$, to obtain the best correspondence between the TESEO 2D model and the SPILL Tool results. However, detailed information on scale of oil spills occurring in harbor areas and the detailed spatial evolution would allow us to perform a real data calibration and validation process of the designed tool.

Finally, regarding the environmental conditions at Tarragona harbor, the cases that were simulated under higher wind intensity (E01 to E12 and E25 to E36) obtained results closer to the TESEO 2D model.

In any case, as mentioned before, the results of the affected areas simulated by the SPILL Tool can be judged as satisfactory because they showed a good correspondence to the results obtained using a calibrated numerical model.

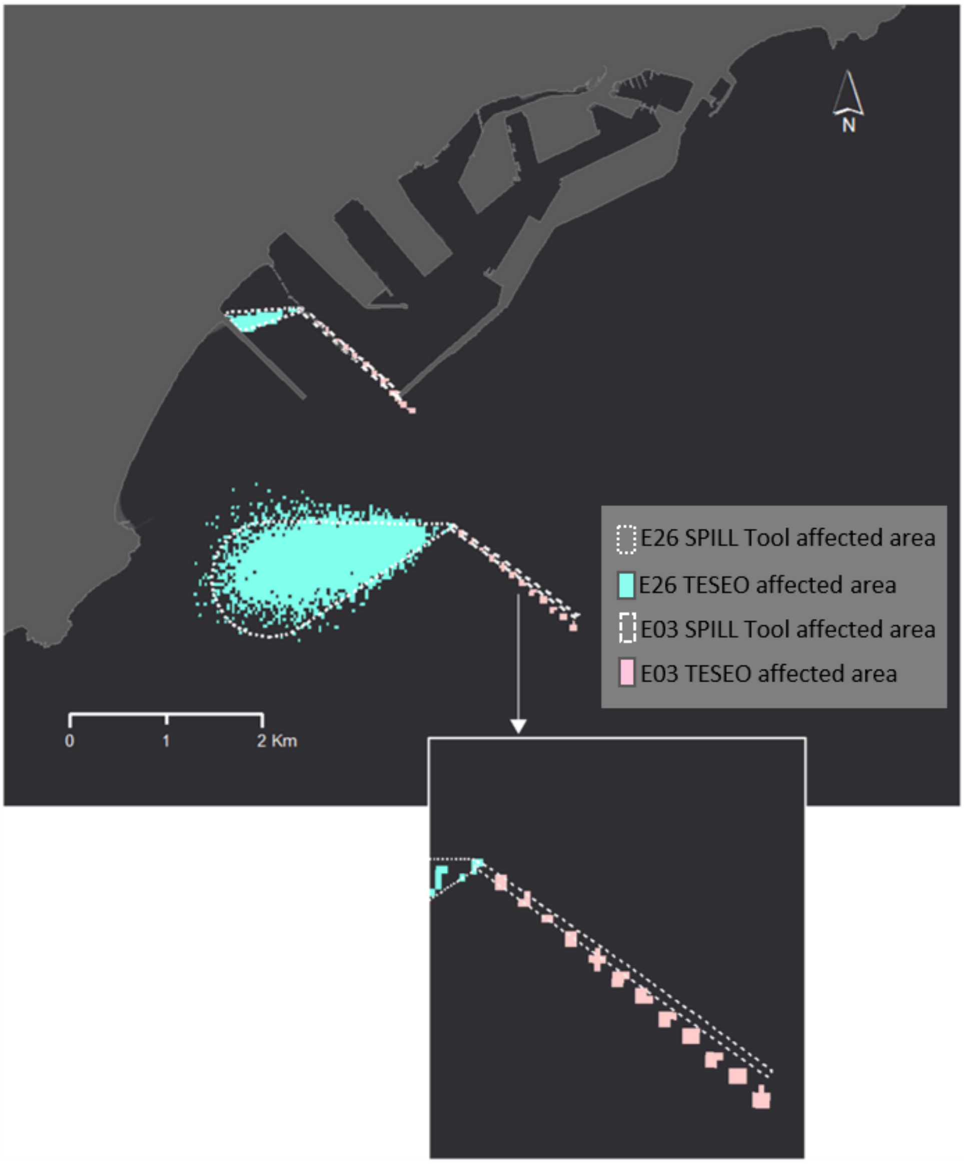


Figure 5.7. Total affected area at E26 and E03 scenarios for the monobuoy and P11 at Tarragona harbor.

5.4.2. SPILL Tool to assess the environmental risk

One of the great current difficulties in the ERA process for non-point contaminant sources is the complexity of their characterization. However, without the exact information about quantity and quality of pollution sources, reduce pollution is not possible (Valipour et al., 2012). Those sources usually present a lack of information, which makes the use of numerical models an arduous and occasionally impossible task.

To quantify the real environmental impact, an environmental risk assessment in probabilistic terms should be performed. For this reason, real data concerning the quantities and densities of the product spilled (spill types) as well as the frequencies of spill types and most probable environmental conditions are indispensable. The environmental data required by the SPILL Tool (water characteristics, coastal line, boundary and current raster grid dataset) are easy to obtain from specific databases or tools. As mentioned in Chapter IV, local databases usually provide basic information (e.g., a description of the appearance of the discharge in the water) that can be very useful to characterize pollution incidents in terms of quantity and density (Valdor et al., 2015). The spill data required by the SPILL tool can be obtained by applying scenario selection methodologies to the data obtained from local databases.

Depending on the characteristics of the substance or material that is released on the aquatic environment, many complex and diverse physical and chemical processes affect their fate and transport. Thus, specific tools that consolidate particular product formulations are needed. The SPILL Tool is an oil-specific GIS tool that is based on simplifications of the most extended formulations used in oil spill numerical models (Fay, 1969; Lehr, 2001). Accordingly, the use of the SPILL Tool allows a wide range of users (e.g., environmental technicians, managers, port authorities, stakeholders) to obtain results similar to those obtained using a calibrated numerical model with a simple and quick procedure. Maps of environmental risk obtained by the SPILL Tool will allow managers and stakeholders to define the area that is potentially affected by a specific oil handling facility. However, as mentioned in Chapter III, an area may be affected by more than one activity. In that case, the environmental risk for different hazards affecting the same area must be integrated. The method developed in Chapter III overlays the potentially affected areas in a subsequent normalization considering different contaminant sources. The integration procedure provides ERA maps (prioritization maps) that permit stakeholders to know the contribution that a specific discharge point has made to the global environmental pollution for a specific zone. Moreover, as mentioned before, prioritization maps would allow for the proper design of a monitoring program by locating sample stations where higher values of environmental risk can be found and defining a maximum sampling distance where no environmental risk would be detected. In this way, detailed studies of the real environmental impact would be conducted in the potentially affected areas.

A great number of environmental hazards to water quality have been identified in harbor areas as a consequences of the great range of activities developed (Gómez et al., 2015). Hazardous Noxious Substances (HNSs) are very well characterized substances whose handling is liable to cause discharges into the water. Considering HNS handling points to be non-point source discharges, ArcGIS tools could be developed to estimate the potential risk of chemical spills. To create integrated maps of environmental risk from diffuse sources in nearshore areas, specific tools should be developed for different types of products and activities. Based on the SPILL Tool code, transport processes for different products could be included by adapting formulations from specific HNS numerical models (Wania and Mackay, 1999; Horiguchi et al., 2006; Yamamoto et al., 2009; Gómez, 2010). In this way, simple and quick GIS procedures could be developed to support contingency planning, environmental monitoring design and decision-making for a great range of products.

Furthermore, the SPILL Tool could be used to manage a contaminant event by rapidly providing information about the spatial-temporal distribution of environmental risk at the location where a specific spill occurred. This information is essential because it allows managers and stakeholders to identify potentially threatened environment and community resources, infrastructure and other economic, societal or environmental goods.

5.5 Conclusions

This chapter shows a tool that was developed to assess the spatial and temporal environmental risk of oil-handling facilities in nearshore areas. The tool (SPILL Tool) was developed in ArcGIS (10.1) using the Python and ArcGIS scripting library. The SPILL tool is easy to load through the ArcToolbox of Geographical Information System software (ArcGIS 10.1 by ESRI™) and is easy to operate through the auto generated Graphical User Interface (GUI). The affected areas that are calculated using the SPILL Tool show a good correspondence to the results obtained using a calibrated 2D transport numerical model. Thus, the SPILL Tool constitutes an advanced, precise and detailed procedure that is suitable for managing this type of activity. Nevertheless, further investigation should be focused on obtaining and analysing detailed information of oil spills at harbor areas in order to: i) calibrate turbulent diffusion coefficient; and, ii) calibrate parameters in the conditions which establishes a differentiation in the calculations for estimating the turbulent diffusion process depending on the type of product spilled.

The SPILL Tool is a simple and quick procedure that can be used by a wide range of users, including managers, port authorities, and stakeholders.

Chapter VI

ERA of oil handling facilities

CHAPTER VI. A METHOD TO ASSESS THE ENVIRONMENTAL RISK OF OIL HANDLING FACILITIES

This chapter is an edited version of the research article accepted in the journal Marine Pollution Bulletin by Valdor, P.F., Puente, A., Gómez, A.G., Ondiviela, B. and Juanes J. with the title 'Are environmental risk estimations linked to the actual environmental impact? Application to an oil handling facility (NE Spain)'.

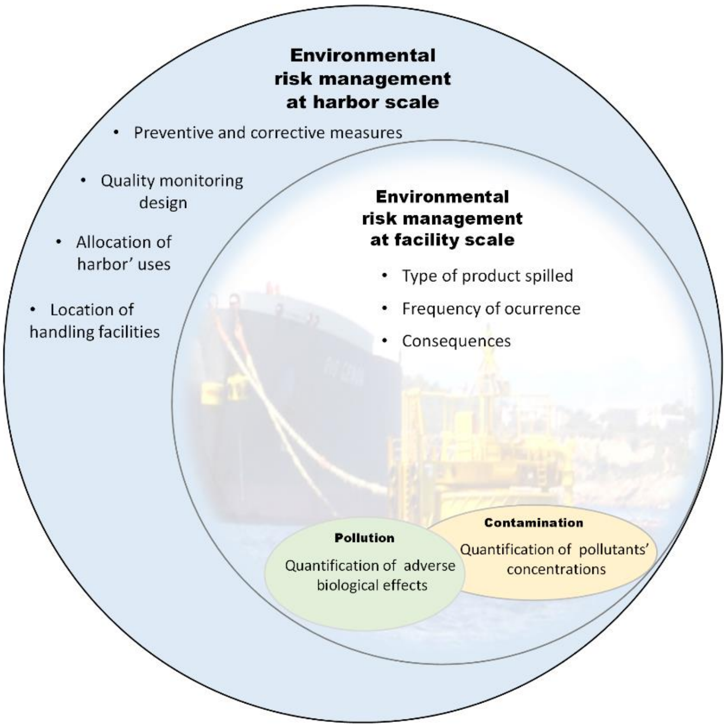


Figure 6.1. Graphical abstract.

Abstract

In this chapter, a method to assess the environmental risk of oil handling facilities is presented. A study of the relationship between the environmental impact and the environmental risk assessment at a specific isolated oil handling facility was undertaken. The environmental risk of the monobuoy of Tarragona, considering the consequences of specific pollutants, was estimated and the associated environmental impact was quantified based on a 'weights of evidence' approach.

The contamination quantified at the potentially affected area around the monobuoy of Tarragona proved to be related with environmental risk estimations. In spite of the above the lines of evidence obtained do not allow us to assert that the activity developed at this facility has an associated environmental impact.

6.1 Introduction

The effects of anthropogenic stressors on ecological systems are faced by environmental scientists and decision-makers. The evaluation of the likelihood that adverse ecological effects may occur as a result of exposure to one or more stressors is so-called the environmental risk analysis (ERA). The disturbance caused by harbor activities on the water column has a direct effect which can be detected immediately but for a short period of time. On the contrary, sediment compartment constitute a depository that can absorb and release contaminants and have an influence on the overlaying water and its quality (Gonçalves et al., 2013), being a source of in-place contaminants through its potential remobilization and resuspension (Evans et al., 1997). In fact, the most toxic and persistent contaminants (PCBs, PAHs, heavy metals, etc.) and organic compounds (organic matter, nutrients) are accumulated or retained in this compartment (Ondiviela et al., 2012). Therefore, sediments are an essential and dynamic part of the harbor and their quality and quantity are constituent parts of the ecosystem health (Mali et al., 2016).

Pollution deriving from liquid petroleum may cause serious environmental impacts when released into the marine environment, whether as catastrophic spills or chronic discharges (Martínez-Gómez et al., 2010). Oil spills are frequent amongst accidents occurred in harbor areas (59% of harbor releases) (Darbra and Casal, 2004). The consequences (effects derived from stressors introduced by environmental hazards) of oil spills have traditionally been estimated in economic and environmental terms. Environmental terms usually considered the arrival of the product into environmental resources (recreational areas, areas designated for the abstraction of water, fisheries and aquaculture areas or protected areas for flora and fauna conservation). The type of product also plays an important role in the fate and effects of spills. The acute toxicity of heavy oils is much lower than that light ones. Heavy oils disperse in the shape of droplets, whereas the remaining crude oil partly dissolves in the water and partly forms tar. Light oils spread rapidly and do not tend to adhere to surfaces, but penetrate porous materials, including muddy or sandy sediment, and may persist in such matrices. So, there are situations in which oil spills do not reach economic or environmental resources, but still have an impact on the environment. The analysis of sediment seems appropriate for the study of pollutant sources which have *a priori* a moderate but sustained level of pollution over time. This is especially suitable for diffuse oil sources with low to moderate impact that is sustained over time. So, new methodologies that can estimate the consequences of oil spills by consideration of the contamination on sediments are required, especially when chronic effects are under study.

Some of the challenges of the environmental risk analysis of aquatic systems are the following: i) pollution is usually provided by a complex mixture of substances with different levels of toxicity, persistence and bioaccumulation; ii) synergic or additive effects can be caused; iii) the effects differ for each species, functional group and development stage level; and, iv) sub-lethal effects are difficult to identify and quantify, at least at population or community level. In spite of this, a great number of methodologies which aim to identify environmental hazards (Darbra et al., 2004; Petrosillo et al., 2010), estimate the potentially affected areas (Castanedo et al., 2009; Abascal et al., 2010; Valdor et al., 2015; 2016) and calculate the environmental risk of hazards in general terms (Ondiviela et al., 2012; Juanes et al., 2013; Gómez et al., 2015) have been developed specifically for harbor areas. However, not many studies aimed at estimating the consequences of a specific diffuse source of pollutants have been developed. Studies focusing on isolated facilities will be useful to develop new methodologies and estimate the consequences of diffuse pollution in harbor areas. These methods should consider contamination factors, but also the pollution on sediments, especially when chronic effects are under study.

From a management point of view, a description of the relationship between predicted environmental risk and measured actual impact is essential to answer relevant issues relating to harbor aquatic systems: Is it possible to know the contribution of the pollutant sources to the global environmental pollution of a specific area?; What is the real impact on the environment?; Where is this impact located?; Where should the monitoring strategy be focused?; and, What are the ecological risks associated to a particular management option (e.g., for a specific facility)?. To answer these questions accurately the following matters should be dealt: i) integration of both temporal and spatial variability of the consequences of specific stressors in ERA; and ii) validation of ERA predictions (e.g., field work to assess the validity of predictions) (Chapman, 2002).

With regards to field validation of ERA predictions, uncertainties should not be obviated. Several studies showed that the effects of pollution are in many cases lower than expected (Juanes et al., 2007; Puente et al., 2009; Albaigés et al, 2015; Puente and Diaz, 2015). In that sense, lower level of impacts could be explained by the resilience of some species (Puente and Diaz, 2008; Ondivela et al., 2013) , the system's high energy (Echavarri-Erasun et al., 2007; Puente and Diaz, 2015) or the bioavailability of toxic substances (De los Ríos et al., 2016). On the other hand, synergic or additive effects could derive on a higher pollution effects than expected. Thus, quantifying the environmental impact associated to each environmental hazard is a real challenge. To reduce the uncertainties, nowadays, a battery of indicators or 'weight of evidence' is commonly used by considering the different levels of biological organization. This approach usually integrates analysis of water and sediment concentrations of pollutants, bioaccumulation analysis, and studies of the effects on different levels of biological organization: i) biomarkers (cell level effects); ii) toxicity test (individual level effects); and, iii) community structure and composition (community level effects) (Chapman and Anderson, 2005; Benedetti et al., 2012; Bebianno et al., 2015).

An increasingly extended and standardized set of techniques used to measure the effects at individual or population level under controlled laboratory conditions are the bioassays or toxicity tests. The use of *proteobacteriae*, crustaceans and echinoderms in eco-toxicological tests is widely standardized. These are included in several national regulations, e.g., regulations for the management of dredged material (ASTM, 2004; Environment Canada, 2011; CIEM, 2015) and have been submitted satisfactorily to intercalibration processes (Arizzi Novelli et al., 2007). *Vibro fischeri* inhibition of luminescence tests as well as embryological development of sea urchin tests (*Paracentrotus lividus*) allow to quantify the toxicity of complex samples, such as contaminated sediments by measuring sub-lethal ecotoxicologic effects (Volpi Ghirardini et al., 2003; Lera et al., 2006). The main disadvantage of bioassays is that they do not reflect the complexity of environmental conditions on the natural environment. The changes caused by stressors in the composition and structure of biological communities should be complementary to bioassays. In these regards, benthic invertebrates constitute one of the biological groups that are most widely used to measure the health of aquatic ecosystems, and are one of the biological quality elements required by the Water

Framework Directive (WFD) for assessing the ecological status of water bodies (Pinto et al., 2009). Moreover, they have been proposed by some authors for the evaluation of the ecological potential of heavily modified water bodies in harbor areas (Ondiviela et al., 2013). Their sedentary nature, their relatively long life cycle, and their taxonomic, functional and response diversity against environmental changes make these organisms good indicators of acute and chronic effects and therefore of the quality of aquatic systems (Diaz and Rosenberg, 2008). On the other hand, biomarkers showed a strong relationship with several parameters of macroinvertebrate benthic communities. So, the measurement of biological effects at suborganismic levels could serve to anticipate damage of higher ecological relevance (Cajaraville et al., 2000; De los Ríos et al., 2016). Although the relationship between the presence of the contaminant and its effect at organism level is very selective, there are several standardized tests that could serve to anticipate damage and to reduce, in terms of time and resources, the effort required to detect the effects of contaminants (De los Ríos et al., 2016).

Chronic exposure to hydrocarbons is expected in areas where oil handling activity is developed. Thus, the incorporation of contaminants from product spilled into sediments is expected around oil handling facilities where refine products are handled and small -but sustained over time- spills occur. Under this hypothesis, the main goal of the this chapter is to develop a method to estimate the consequences of oil handling activities and studying the relationships between the estimated risk and the impact measured at an isolated oil handling facility at the Tarragona harbor.

6.2 Materials and methods

In order to obtain the environmental risk of the monobuoy of the Tarragona harbor (*see Chapter II for more information*), the consequences of specific pollutants are estimated. With the aim of quantifying the contamination and the associated environmental impact, the level of contamination in sediment, the responses at individual level (toxicity) and the effects at biological community level (macrobenthic community) are measured at sampling sites located along the preferred trajectories of potential spills. Finally, in order to validate the ERA predictions, the relationship between the environmental impact and the environmental risk assessment is studied based on a ‘weight of evidence’ approach.

6.2.1 Estimation of environmental risk

Environmental risk (RL_F) is estimated considering the presence of product spilled in each grid cell, the probability associated to each scenario (*see Chapter VI for more information*) and the consequences Eq. (6.1):

$$RL_F = \sum_{w=1}^{b} Rw = \left((PR_{gh_1} x f_{gh_1} x Co_{gh_1}) + (PR_{gh_2} x f_{gh_2} x Co_{gh_2}) \ldots \right) \quad (w = 1,\ldots b) \qquad \text{Eq. (6.1)}$$

Where RL_F is the environmental risk for a discharge point, b is the number of ERA scenarios, R_W is the risk associated to each scenario, $_{gh}$ is a specific grid cell, PR_{gh} is the presence (PR_{gh}=1) or absence (PR_{gh}=0) of product spilled in each grid cell, f_{gh} is the probability associated to each scenario and Co_{gh} are the consequences at cell level.

Presence of spilled product is estimated by means of numerical models or GIS tools. Consequences (Co_{gh}) are expressed in terms of persistence of hazards on the aquatic environment and their potential affection Eq. (6.2):

$$Co_{gh} = \frac{P_{gh} - Evp_{gh}}{100} \qquad \text{Eq. (6.2)}$$

Where P_{gh} is the percentage of specific pollutants liable to cause impact on the environment from the products spilled and Evp_{gh} is the percentage of the specific pollutants liable to be evaporated at cell level (gh).

The spatial environmental risk assessment in probabilistic terms (PR_{gh} x f_{gh}) at the specific case of the monobuoy of the Tarragona harbor was obtained from a previous study developed at Chapter V. 48 ERA scenarios were considered for the oil handling facility at the Tarragona harbor, which were obtained by combining the most probable met-ocean conditions (4) and spill types (12). Each ERA scenario had a specific product density, volume released and frequency of occurrence (Figure 4.3). The environmental risk was estimated at a 452x371 mesh grid with a 30 m of cell dimension by means of using the SPILL Tool (*see Chapter V for more information*).

The consequences are related to oil spills and estimated accordingly to the specific pollutants quantified from sediment samples. From cells affected (presence), the consequences are estimated considering the percentage of PAHs liable to impact the environment (P_{gh}) null for gasolines, 5% for diesel, 40% for heavy crudes and 50% for fuel oils (Hollebone, 2015). The percentage of evaporation (Evp_{gh}) is calculated for each specific ERA scenario by means of the equation defined by Fingas (2015) Eq. (6.3) for each product type identified at the specific facility (Valdor et al., 2015).

$$Evp_{gh} = [\ 0.0254\ (Dk) + 0.01\ (T - 15)]\ \sqrt{\tau} \qquad \text{Eq. (6.3)}$$

Where Dk is the percentage of the product distilled at 180 °C, T is the temperature in Celsius degrees and τ is the time in minutes. At the monobuoy study case, D took the value of 100 for gasoline, 30 for diesel fuel and 5 for fuel and crude oil (Fingas, 2015), temperature was considered 15°C and time was equal to 120 minutes.

The environmental risk at facility level is estimated by combining the risk of the local scenarios (Eq.6.1).

Finally, the risk values estimated without considering the term of consequences (RL_F^1) on previous work (Valdor et al., 2016) are compared with the risk values estimated with considering the term of consequences (RL_F^2).

6.2.2 Impact indicators

A specific sampling task was conducted in July 2014. Seven sampling sites were located along the preferred trajectories of potential spills and distributed in two radii r1, covering the first 500 to 600 m away from the monobuoy (E1, E2 and, E3) and r2, between 900 to 1500 m away from the monobuoy (E4, E5 and, E6) with a depth from 35.5 m (E6) to 48 m (E4) (Figure 2.11). Five sediment samples were collected at each site using a 0.04 m^2 Van Veen grab sampler.

One sample was intended to analyze physicochemical variables (grain size, organic matter) and specific pollutants were analyzed: metals (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, V and Zn) and organic compounds (acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene).

Two samples were collected and sieved *in situ* to study the macrobenthic community composition. The retained material was combined and stored with a mixture of seawater and 4% formaldehyde. 24 hours later the formaldehyde was replaced by a mixture of salt water and 70% ethanol for preservation until the identification process was carried out.

Finally, two sediment samples were designated to perform two different toxicity tests: *Vibrio fischeri* bacteria luminescence inhibition and *Paracentrotus lividus* embryology test.

Granulometry was determined using the dry sieving technique, following the Wentworth scale. The organic matter was estimated from dried sediments (65 ºC, 48 h) as loss on ignition in a muffle furnace up to 550 °C for 6 h. The heavy metals analytical methods used followed the normalized U.S. Standard method (US EPA, 2007b). A certified reference pattern was used for quality control (Loamy Clay, CRM 052, Resource Technology Corporation, US). Polycyclic aromatic hydrocarbons were determined by high-resolution gas chromatography (HRGC-HRMS).

Benthic macrofauna was identified at the lower taxonomical level possible. Specific abundance (number of individuals/m^2), species richness (number of species/m^2) and diversity (Shannon Index) were calculated for each sample. The Mediterranean Occidental index (MEDOCC) (Pinedo et al., 2015) was calculated to assess the ecological status (ES) according to WFD requirements and the relative abundance of ecological groups described by Pinedo et al. (2015) was considered. The MEDOCC index value is 0 when sensitive species are the dominant group and 6 when opportunistic species are prevalent being 1.6, 3.2, 4.77 and 5.5 the threshold values amongst high, good, moderate, poor and bad ecological status.

Pore water was extracted from sediment samples for *V. fischeri* toxicity analysis by the use of a 0.47 µm filter coupled to vacuum. The organic extract was obtained following the EPA 3546 method (US EPA, 2007a) and filtered by a 0.47 µm filter paper. The filtrate was concentrated by rotary evaporation in order to eliminate the organic solvent. The remaining content was collected by 4 ml of dimethylsulfoxide. Finally, a *Basic test* for organic extract and a 90*% Basic test* for aqueous extract were performed using a Microtox 500 Analyser (SDI, USA). Results of *Vibrio fischeri* toxicity tests were expressed as EC_{50} (the effective concentration of toxicant that causes a 50% decreased in the bacteria light output) (Coz et al., 2008). Pore water results were expressed as a percentage of the effect, while organic extract results were expressed as sediment units (mg) per volume of reaction mixture.

Sea urchin toxicity tests were analyzed following a normalized Spanish standard method (CIEM, 2015). A portion of sediment of 250 g was added to 1L of filtered seawater. Water and sediments were mixed in a rotatory shaker at 50 rpm during 30 minutes and the mixture was decanted for 12 hours at 4ºC in darkness. The supernatant (at least 500 ml) was extracted by suction and the assay was performed within one week after. Fold serial dilutions were prepared from the elutriate and 5 replicates of 20 ml were extracted from each dilution. Additionally, 5 replicates of 20 ml filtered seawater were used for control purposes. Fertilized eggs were added to each replicate (600 to 800 eggs) and incubated at 20ºC during 48 hours. After incubation, embryogenesis and development were estimated by scoring the percentage of normal pluteus larvae at each replicate.

Statistical analyses were carried out to identify redundant variables between physicochemical and specific pollutants. The variables presenting a $|r|>0.8$ at $p<0.001$ correlation from a Spearman's rank correlation analysis were grouped. One variable of the group were selected for subsequent analysis. To identify spatial patterns in terms of sediment contamination, a Principal Component Analysis (PCA) including non-redundant physicochemical and specific pollutants variables was performed.

6.2.3 Correspondence between the estimated risk and indicators of impact

Each sampling site was geographically related to a cell in the finite element grid and the average value of the environmental risk value at sampling site and at the eight adjacent grid-cells was considered as a representative risk value for each sampling site. Calculated RL_{Fgh}^1 and RL_{Fghj}^2 were obtained for each sampling site. Finally, a Spearman's rank correlation analysis between risk values and environmental variables was performed at sampling site level. Specific pollutants, macrobenthic metrics (Figure 6.4), EC_{50} values (*Vibrio fischeri* toxicity test) and % normal embryos (sea urchin test) (Table 6.6) were considered.

6.3 Results

6.3.1 Estimation of environmental risk

The ArcMap (ArcGIS 10.1 by ESRI™) was used to calculate consequences (Eq. (6.2)) and combine the risk of the monobuoy' local scenarios (Eq. (6.1)) (*see Chapter IV form more information*) in order to obtain the environmental risk at the Tarragona oil facility.

A representation of the risk values estimated without (RL_{Fgh}^1) and with (RL_{Fgh}^2) considering the term of consequences is shown in Figure 6.2.

Differences in the total affected areas were showed between the environmental risk results estimated by considering the presence (PR_{gh}=1) or the absence (PR_{gh}=0) of product spilled ($RL_{Fgh}^1 = PR_{gh} x\ f_{gh}$) and results estimated by considering presence (PR_{gh}) and consequences (Co_{gh}) of product spilled ($RL_{Fghj}^2 = PR_{ghj}$ x f_{gh} x Co_{gh}) (Table 6.1).

The total affected area was lower on considering the estimation of consequences (3.2 Km^2 lower) and the risk values showed lower mean, minimum and maximum values (Table 6.1).

Monobuoy	Affected area (Km^2)	Mean ERA	Min ERA	Max ERA
$RL_{Fgh}^1 = PR_{gh}$ x f_{gh}	4.7	0.109	0.038	0.942
$RL_{Fgh}^2 = PR_{gh}$ x f_{gh} x Co_{gh}	1.5	0.017	0.001	0.206

Table 6.1 Extension of the global affected areas, mean, minimum and maximum environmental risk values estimated at the monobuoy of the Tarragona harbor.

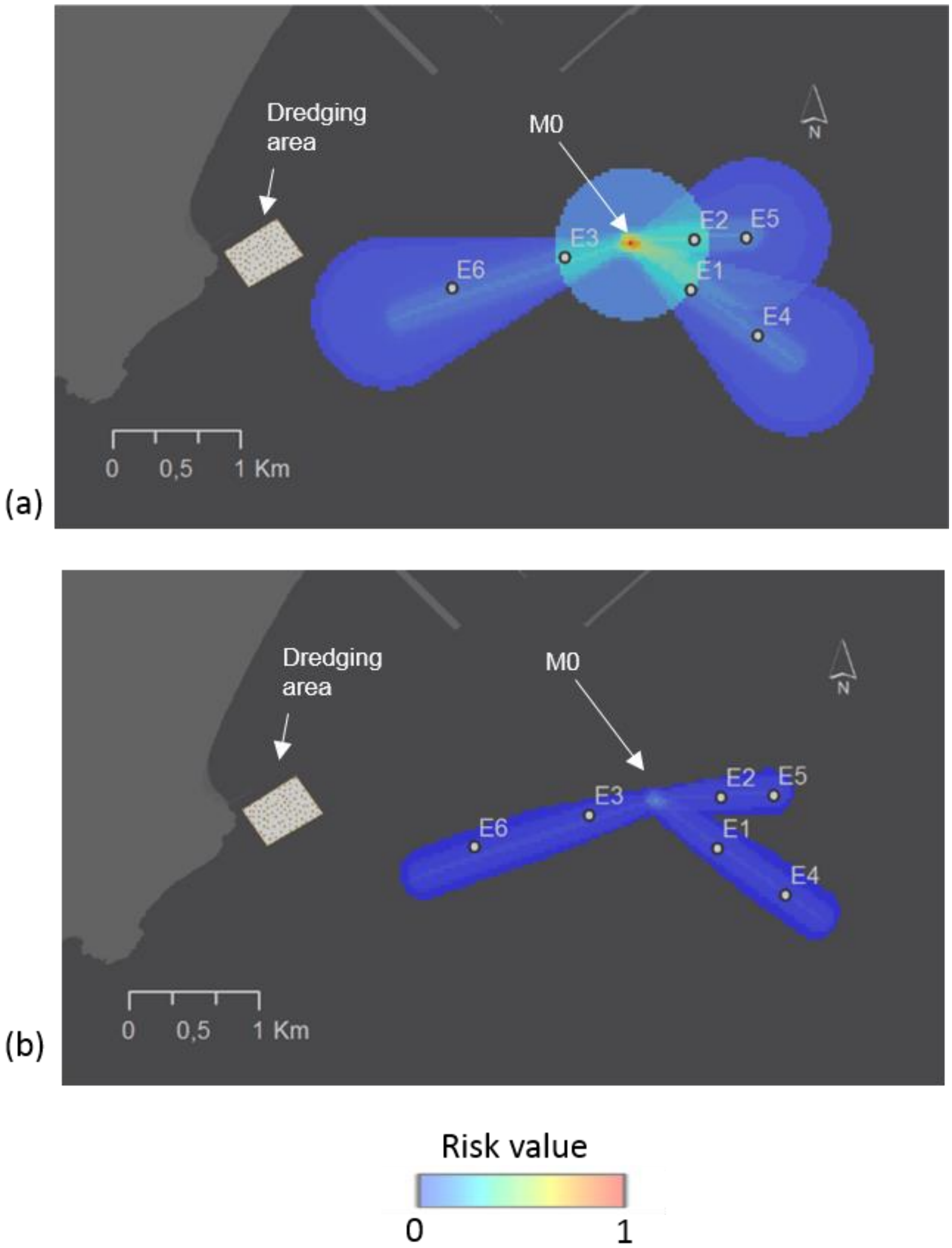


Figure 6.2 Environmental risk values of the monobuoy (RL_{Fgh}) estimated without (a) and with (b) consideration of the term of consequences.

6.3.2 Impact indicators

The granulometric and organic matter analysis revealed slight differences among the sites under study. Samples collected around the monobuoy of Tarragona contained high percentages of clay (73% to 94%) and moderate levels of organic matter (6% to 10%) (Table 6.2).

	M0	E1	E2	E3	E4	E5	E6
Clay (%)	88.15	89.85	73.47	90.37	93.81	77.82	86.93
Sands (%)	11.77	10.15	22.27	9.63	6.18	22.04	13.06
Gravel (%)	0.08	0.00	4.27	0.00	0.01	0.13	0.01
Organic matter (%)	7.51	9.09	6.83	6.76	8.22	6.54	7.85

Table 6.2 Organic matter content (%), and grain size classes (%) of sediment samples collected at the monobuoy of the Tarragona harbor.

Only nickel showed concentrations bellow the detection limit (0.10 µg/g), presenting a great difference between site E4 (9.12 µg/g) and the remaining sites (<0.10 µg/g). Scarce differences for the concentrations of the rest of metals were observed between sites (Table 6.3). E4 showed the higher concentrations of metals analyzed with the exception of cadmium, mercury and copper which presented the higher concentrations on M0 and E1, E6 and E3, respectively.

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	V	Zn
M0	5.39	0.10*	3.17	15.1	9.61	0.29	<0.10	20.5	13.8	33.6
E1	5.09	0.10*	3.39	17.8	10.1	0.29	<0.10	22.3	14.1	35.6
E2	4.49	0.09	3.28	16.4	9.17	0.29	<0.10	20.9	14.3	33.1
E3	5.12	0.09	3.34	17.1	10.3*	0.37	<0.10	22.1	15.1	34.9
E4	5.69*	0.09	3.67*	19.1*	10.2	0.28	9.12*	23.1*	15.2*	36.2*
E5	4.69	0.09	3.12	15.4	8.47	0.23	<0.10	19.7	14	31.1
E6	4.81	0.09	3.15	15.9	9.94	0.68*	<0.10	21.5	14.7	35.1
T_{20}	7.40	0.38	-	49.00	32.00	0.14	15.00	30.00	-	94.00
TEL	7.24	0.68	-	52.30	18.70	0.13	15.90	30.24	-	124.00
ERL	8.20	1.20	-	81.00	34.00	0.15	20.90	46.70	-	150.00

*maximum values
T_{20}: concentration of pollutant that corresponds to the 20 proportion of toxic samples for amphipod survival; TEL: geometric mean of the lower 15th percentile of effects data and the 50th percentile of no-effect data; ERL: concentrations below which adverse effects are expected to rarely occur

Table 6.3 Metal concentrations (µg/g) in sediment samples collected at the monobuoy of the Tarragona harbor and NOAAs' thresholds of potential toxicity for marine sediments (T_{20}; TEL; ERL).

From the 16 analyzed, 3 PAHs (acenaphthene, acenaphthylene and dibenzo(a,h)anthracene) showed concentrations below the detection limit at all sites (<10 µg/Kg). Only indeno(1,2,3-cd)pyrene, fluorene and phenantrene showed the highest concentrations within the area comprised in radius r2 (900 to 1500 m away from the monobuoy) at E5 and E6 sites. For the remaining PAHs analyzed, the highest concentrations were detected at site M0 (Table 6.4).

	Ace	Acy	Ant	BaA	BaP	BbF	BghiPer	BkF	Chr	DahA	Fl	F	I123cdPyr	N	Phe	Pyr
M0	<10	<10	**46***	49*	48*	51*	35*	29*	41*	<10	110*	<10	31	19*	**74**	89*
E1	<10	<10	<10	12	<10	27	<10	<10	<10	<10	33	<10	<10	15	<10	27
E2	<10	<10	<10	11	11	17	<10	<10	<10	<10	28	<10	<10	<10	9.7	24
E3	<10	<10	<10	<10	<10	<10	12	<10	<10	<10	19	<10	22	12	19	19
E4	<10	<10	<10	<10	<10	9.8	<10	<10	<10	<10	19	<10	<10	12	<10	17
E5	<10	<10	<10	38	35	50	25	17	34	<10	52	<10	35*	<10	<10	46
E6	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	42	**24***	13	<10	**160***	20
T_{20}	19.0	14.0	34.0	61.0	69.0	130.0	67.0	70.0	82.0	19.0	119.0	19.0	68.0	30.0	68.0	125.0
TEL	6.7	5.9	46.9	74.8	88.8	-	-	-	108.0	6.2	113.0	21.2	-	34.6	86.7	153.0
ERL	16.0	44.0	85.3	261.0	430.0	-	-	-	384.0	63.4	600.0	19.0	-	160.0	240.0	665.0

Ace: Acenaphthene; Acy: Acenaphthylene; Ant: Anthracene; BaA: Benzo(a)anthracene, BaP: Benzo(a)pyrene; BbF: Benzo(b)fluoranthene; BghiPer: Benzo(g,h,i)perylene; BkF: Benzo(k)fluoranthene; Chr: Chrysene; DahA: Dibenzo(a,h)anthracene; Fl: Fluoranthene; F:Fluorene; I123cdPyr: Indeno(1,2,3-cd)pyrene; N: Naphthalene; Phe: Phenanthrene; Pyr: Pyrene.

*maximum values
In bold, values exceeding at least one of the NOAAs' thresholds of potential toxicity for marine sediments (T_{20}; TEL; ERL).

Table 6.4 Polycyclic aromatic hydrocarbon concentrations (µg/Kg) in sediment samples collected at the monobuoy of the Tarragona harbor.

The Spearman's rank correlation analysis between all specific pollutants was performed showing significant $|r|>0.8$ at $p<0.001$ correlations between benzo(b)fluoranthene, benzo(a)anthracene and pyrene. Benzo(a)anthracene was selected as the representative of the variability of this group.

The PCA analysis of non-redundant specific pollutants of sediments revealed that the first two principal components explained the 76% of the total variance of sediments around the monobuoy. The distribution of sites along Factor 1 is clearly dominated by the contamination by PAHs. M0 and E5 sites are separated from the other sites being arranged on the positive sector of the first axis (Factor 1) (Figure 6.3). The contaminants that contributed mostly to the differences among M0 and the rest of the sites are benzo(a)antracene, benzo(a)pyrene, chrysene, benzo(g,h,i)perylene, benzo(k)fluoranthene, fluoranthene, indene(1,2,3-cd)pyrene, anthracene, and cadmium (Cd) (Table 6.5). Sites E1, E3 and E4 were arranged on the negative sector of Factor 1, more influenced by metals (Pb, Cr, V, Zn and Co) (Table 6.5). M0, E1, E3 and E4 are arranged on the negative sector of Factor 2, mainly influenced by arsenic (As) and naphthalene. Sites E2 and E6 are on the positive sector of Factor 2, related to mercury (Hg) and fluorene (Table 6.5).

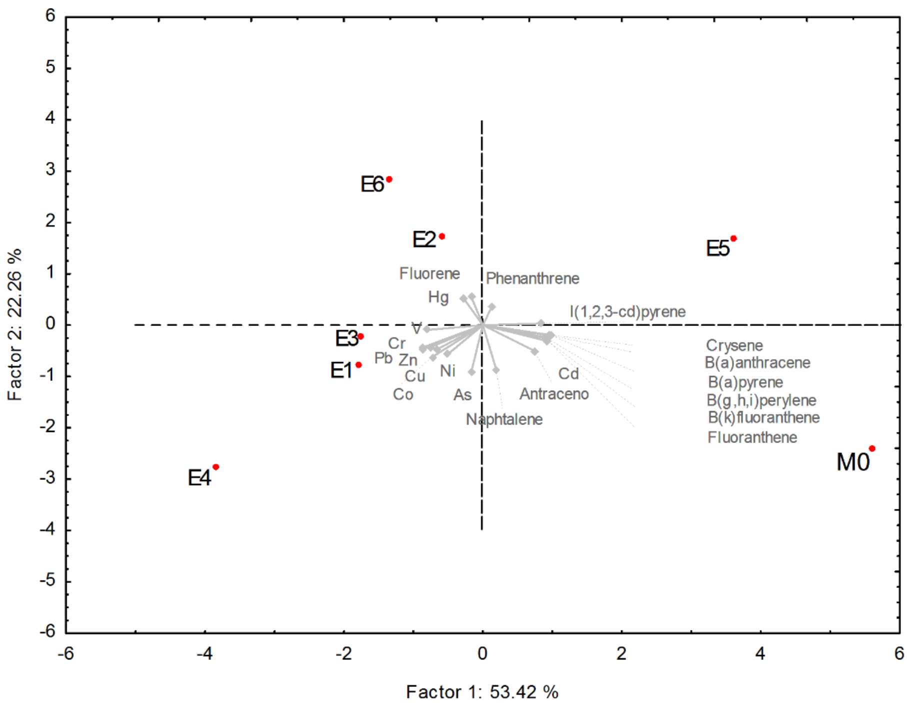


Figure 6.3 Location of sampling sites and specific pollutants with respect to the two-dimensional space defined by the two first two principal components related to sediment variables.

Sediment variables	Factor 1	Factor 2
Anthracene	0.74	-0.50
As	-0.17	-0.91
Benzo(a)anthracene	0.97	-0.20
Benzo(a)pyrene	0.97	-0.19
Benzo(g,h,i)perylene	0.94	-0.26
Benzo(k)fluoranthene	0.94	-0.31
Cd	0.74	-0.50
Co	-0.73	-0.62
Cu	-0.66	-0.47
Chrysene	0.95	-0.19
Cr	-0.85	-0.47
Phenanthrene	0.13	0.36
Fluoranthene	0.89	-0.23
Fluorene	-0.17	0.58
Indene(1,2,3-cd)pyrene	0.83	0.03
Hg	-0.27	0.51
Naphthalene	0.19	-0.87
Ni	-0.50	-0.56
Pb	-0.87	-0.44
Zn	-0.75	-0.43
V	-0.80	-0.09

Table 6.5 Factor coordinates of the specific pollutants, based on correlations with the two dimensional space.

Total richness from samples collected was 80 species. The results of the univariate indices of benthic assemblages and the percentage of species belonging to each ecological group are shown in Figure 6.4. The abundance showed values between 662 and 1500 individuals/m^2 with E1, E2 and E4 being the sites with the lowest values. Biomass presented values between 158.4 and 414.7 mg/m^2 showing the lowest values at sites E4 and M0. Specific richness ranged from 12 to 25, with the lowest value at site E4 and the highest value at site E5. The Shannon-Wiener index (H') presented values between 2.0 (site E4) and 3.0 (site E5). According to the ecological groups defined in the MEDOCC index, species that are tolerant to organic matter are predominant in all sites (from 44.1% at site E5 to the 74.4% at site E4). Indifferent species to enrichment presented a range between 9 of site E4 and 26.4 of site E1. Opportunistic species showed a percentage between 8.9 of sites E3 and E4 and 17.5 of site E5. With the exception of site E3, sensitive species presented the lowest percentage in all sites (Figure 6.4). This is reflected in the values of MEDOCC index for which site E3 presented a good quality status, while the rest of sites showed a moderate status. Nonetheless, the MEDOCC values were very similar for all sites (values from 3 at site E3 to 3.8 at site E6) (Figure 6.4).

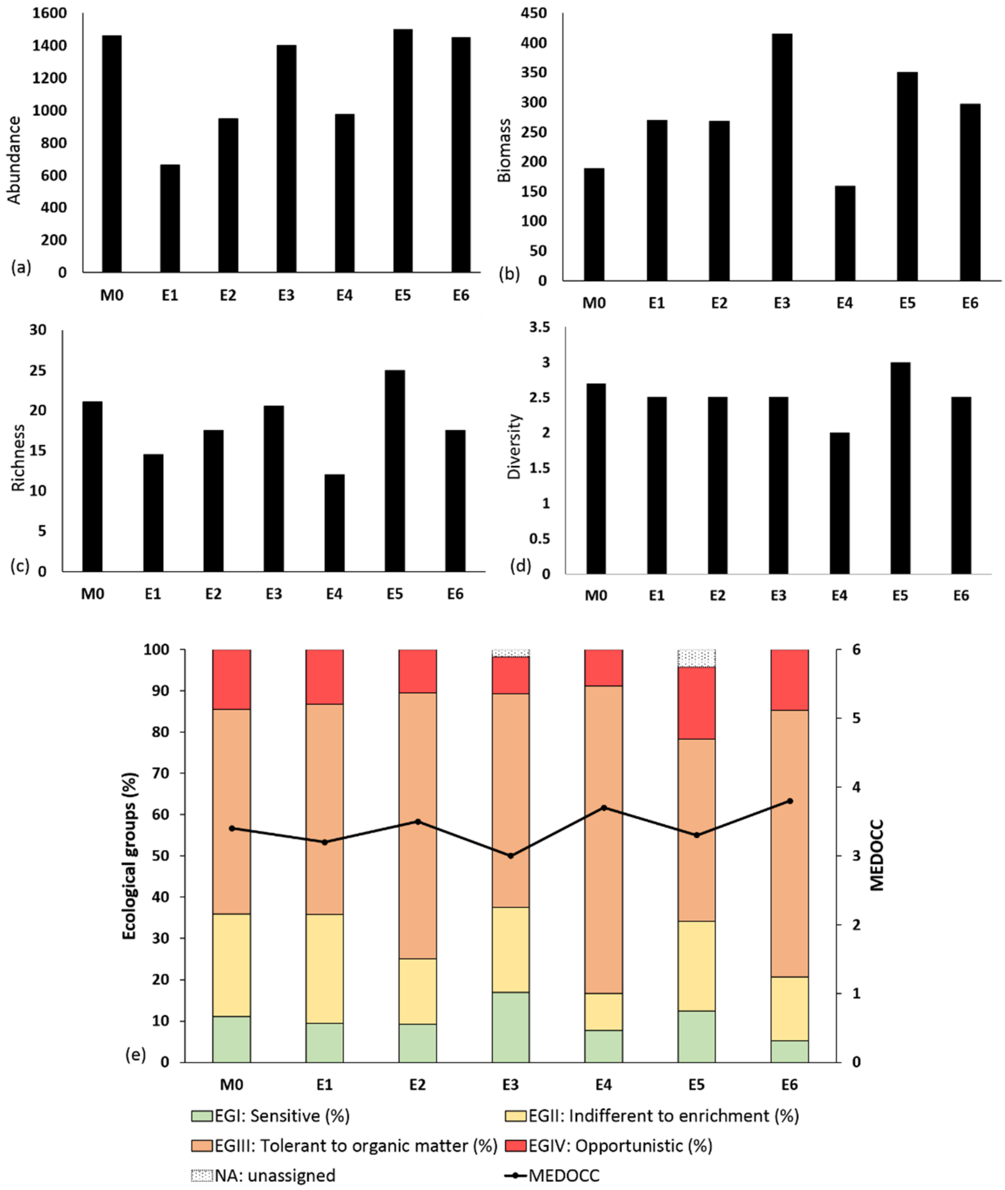


Figure 6.4 Graphical representation of (a) abundance (individuals/m^2), (b) biomass (mg/m^2), (c) richness (S), (d) diversity (H'), and (e) percentages of the ecological groups (EG) of soft-bottom macrofauna and MEDOCC index of samples sediments collected at the monobuoy of the Tarragona harbor.

The taxonomic composition showed a structural pattern that was very similar for all sites. Polychaetes were the predominant group, with values close to 80% of all individuals in all sites. Bivalves and crustaceans reached percentages between 10 and almost 20%.The presence of other groups was marginal. At lower taxonomic level, a total of 80 taxa were identified in sediment samples collected around the monobuoy. Figure 6.5 shows the representation of the 10 most abundant taxa. The composition is very similar in all sites with the tolerant-to-organic-matter taxa *Montichellina heterochaeta* and *Lumbrineris latreilli* representing between 30 and 50% of the total abundance.

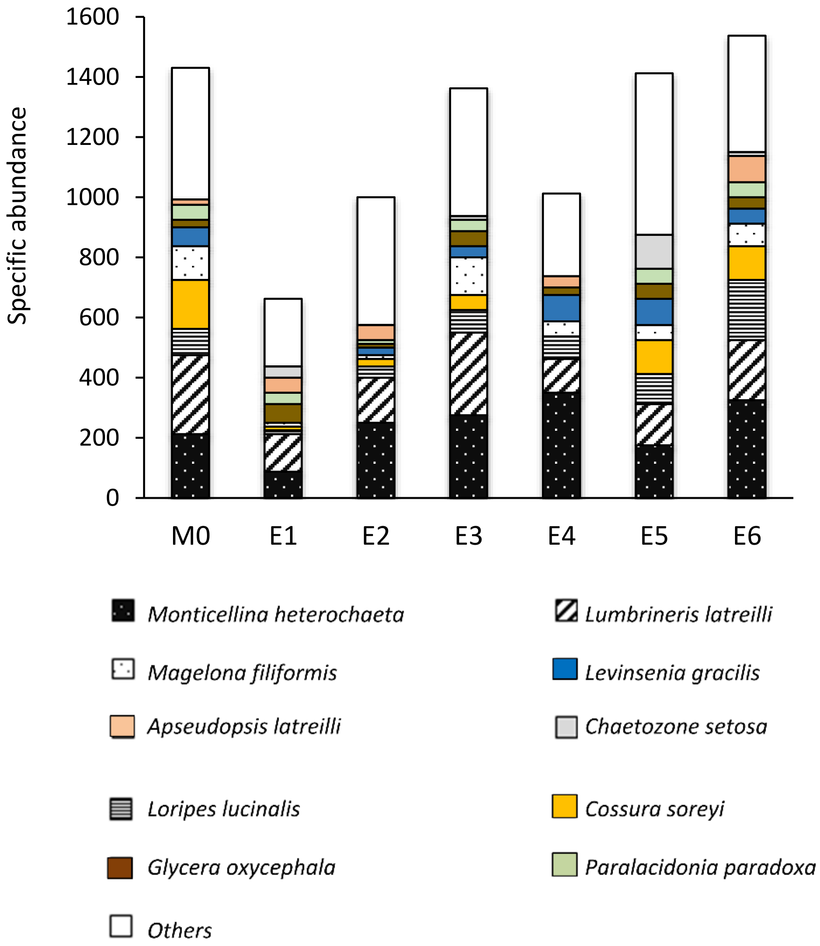


Figure 6.5 Graphical representation of the 10 most abundant species in sample sediments collected at the monobuoy of the Tarragona harbor.

None of the sites showed toxicity to pore water sediment extracts. The organic extract of the sediments collected at site E1 presented the highest EC_{50} value while E6 and M0 showed the lowest values (Table 6.6). The lower the value of the organic extract EC_{50}, the higher the toxicity. On the other hand, sea urchin embryos exposed to sediments from sites M0, E1, E2, E3, E4 and E5 showed a survival percentage between 92 (M0) and 99 (E2) and closed to the percentage showed in the control sample (94.5). Sea urchin embryos exposed to elutriate from E6 registered a 42% of normal embryos.

	Pore water	Organic extract	
	EC_{50} (% vol:vol)	EC_{50} (mg/ml) [min - max]	Normal embryos (%)
M0	>100%	0.440 [0.346 - 0.559]	92.0
E1	>100%	1.322 [0.391 - 0.474]	94.2
E2	>100%	0.945 [0.565 - 1.587]	99.0
E3	>100%	0.775 [0.411 - 1.461]	94.6
E4	>100%	1.227 [1.076 - 1.400]	94.0
E5	>100%	0.900 [0.569 - 1.423]	94.5
E6	>100%	0.407 [0.245 - 0.677] **	42.0**
Control sample	-	-	94.5

** minimum values

Table 6.6 Results from pore water and organic extract *Vibrio fischeri* toxicity tests and mean percentage (%) of normal embryo sea urchin toxicity tests developed with sediments collected around the monobuoy of the Tarragona harbor.

6.3.3 Correspondence between the estimated risk and the indicators of impact

Site M0 presented the highest value of risk for both $RLFij^1$ and RL_{Fij}^2. When consequences were considered (RL_{Fij}^2) sites E6 and E3 showed the lowest values of risk (Table 6.7).

Site	$RL_{Fgh}^1 = PR_{gh} \times f_{gh}$	$RL_{Fgh}^2 = PR_{gh} \times f_{gh} \times Co_{gh}$
M0	0.717	0.119
E1	0.193	0.030
E2	0.332	0.032
E3	0.304	0.026
E4	0.158	0.031
E5	0.176	0.034
E6	0.145	0.029

Table 6.7 Risk values estimated with (RL_{Fgh}^2) and without (RL_{Fgh}^1) considering the consequences at each sampling site located around the monobuoy of the Tarragona harbor.

Spearman's correlations |r|>0.7 are shown in Table 6.8. The analysis of specific pollutant concentrations and RL_{Fgh}^2 (with consequences) risk values showed a significant correlation between the estimations of risk and benzo(a)anthracene and benzo(a)pyrene. Correlation between the macrobenthic metrics (abundance, biomass, richness, biodiversity and MEDOCC) and RL_{Fgh}^2 obtained |r|<0.7 values were not significant for any metrics analyzed. In the same way, the correlation values between EC_{50} of organic extract, percentage of normal embryos of sea urchin and RL_{Fgh}^2 risk values were not significant and were below 0.7. No significant correlation was shown between the RL_{Fgh}^1 (without consequences) risk values and the indicators of impact quantified.

Specific pollutant	r ≥ 0.7
Benzo(a)anthracene	0.82*
Benzo(a)pyrene	0.90**
Benzo(k)fluoranthene	0.74
Chrysene	0.74
Copper	-0.73

*significant correlation at p<0.05
**significant correlation at p<0.01

Table 6.8 Spearman's correlation coefficients (|r|>0.7) between indicators of impact (specific pollutants concentrations, macrobenthic indexes and EC_{50} of sediment organic extract on *Vibrio fischeri* and % normal embryos of sea urchin) and the RL_{Fgh}^2 (with consequences) risk values estimated around the monobuoy of the Tarragona harbor.

6.4 Discussion

The environmental risk calculated at the monobuoy of Tarragona, introducing the term of consequences ($RL_{Fgh}^2 = PR_{gh} \times f_{gh} \times Co_{gh}$), allowed us to identify the area which is liable to be affected by hazards deriving from an oil handling activity (Figure 6.2). Pollution (adverse biological effects) were just expected in 30% of the total area, where the presence of product spilled was detected ($RL_{Fgh}^1 = PR_{gh} \times f_{gh}$). Regarding specific pollutants in sediments, the proposed methodology reflected the spatial gradient of contaminant concentrations of benzo(a)pyrene and, benzo(a)anthracene (as representative of a group of PAHs formed by benzo(b) fluoranthene, benzo(a)anthracene and pyrene) (Table 6.8). However, although a significant correlation between those variables and the risk values calculated considering the consequences (RL_{Fgh}^2) was detected, lower than expected pollutants' concentrations were quantified. It should be noted that there are no sheltered structures in the area where the monobuoy is situated and the system's energy is higher than that at areas located in harbor sheltered waters. A high energy system could imply the low deposition of organic matter, which could be a factor in minimizing the contaminant concentrations.

From the management point of view, the significant correlation detected between the PAHs and $RL_{Fgh}{}^2$ risk values allow us to assume that the 1.5 Km^2 delimitated area represents the monobuoy's contribution to the global contamination from the harbor's activity. But, in terms of impact, when concentrations of pollutants and NOAAs' thresholds of potential toxicity (Buchman, 2008) were compared to screen for substances which may threaten the biological resources (Table 6. 3 and Table 6.4), only 3 of the 16 HAPs analyzed were detected in concentrations that exceeded some of the potential toxicity thresholds. Concentration of anthracene and phenanthrene on sediments of site M0 exceeded T_{20} threshold, while sediments of site E6 showed phenanthrene concentrations above T_{20} and threshold effects level (TEL). Fluorene was detected in concentrations above T_{20}, TEL and probable effects level (ERL) only at site E6. With regards to metals, mercury concentrations exceed the T_{20}, TEL and ERL thresholds at all sampling sites.

At the area where consequences are expected, the MEDOCC index, based on ratios between opportunistic, tolerant and sensitive species, assigns a moderate ecological status to all sites except E3. E3 showed a good quality status, but very closed to the good/moderate boundary. Although opportunistic species appear in sediments collected around the monobuoy, their percentage is below 18% at all sites. This is in agreement with the potential impact arising from the comparison between the mercury concentrations detected and the thresholds of potential toxicity summary by Buchman (2008). However, when the relationship between the indicators of potential impacts at community level and the environmental risk was studied, no correlations were found. So, it is not possible to establish a relationship between hazards and responses at macrobenthic community level. In this respect, the structure and functioning of communities may be altered for many reasons, other than contaminant exposure (Borja et al., 2015). The huge size of the vessels which operate at the monobuoy (around 30,000 DWT (Deadweight tonnage)) combined with the increasingly new propulsion types with larger propellers and greater power could be a disturbing factor. Scour action can be caused by the highly turbulent flows generated by propeller blades, effects of the presence of the rudder

and its deployment, plus propeller reversal effects (Hawkswood et al., 2014).
On the other hand, results of ecotoxicological bioassays developed with sample sediments collected at the monobuoy revealed sites E6 and M0 as the most toxic amongst the sediment collected (Table 6.6). This is in agreement with the potential impact arising from the comparison between the HAPs concentrations detected and the thresholds of potential toxicity summary by Buchman (2008). However, microtox bioassays showed E6 as the highest toxicity site compared to the rest of sites, while the results of sea urchin toxicity tests revealed a normal development above 94% for embryos exposed to sediments of all sites, except E6. Additionally, the correlation values between EC_{50} of organic extract, the percentage of normal embryos of sea urchin and the risk values were not significant. Accordingly, it was not possible to establish a relationship between the hazards and toxicity levels detected at these sites. In this regard, it should be noted that the highest concentrations of fluorene, phenantrene and mercury were quantified at site E6. E3 and E6 sites showed lower estimated risk values ($RL_{Fgh}{}^2$) (0.029 - 0.026) so the pollution and the impacts detected at this site would not be directly related to the monobuoy's loading and unloading activity. Uncertainties relating to the activities developed in this highly industrialized area come into play at this point. High concentrations of phenanthrene in the air have been reported by several studies (Nadal et al., 2009; 2011; Domínguez-Morueco et al., 2015). Thus atmospheric deposition cannot be ruled out as a source of PAHs in contaminated sediment sites situated in harbor areas that are very close to highly industrial and urban areas (Antizar-Ladislao, 2009). On the other hand, dredging takes place annually in an area situated between Cap de Salou and the monobuoy (Figure 6.2). Around 100,000 m^3 of sand is extracted with a suction dredge during one month with the process finishing approximately in April. The consequences for the aquatic systems generated by the dredging operations include physical changes such as burial/covering (sedimentation) or chemical pollution (increased concentration of chemicals) (PIANC, 1997; Gómez et al., 2014b). Considering that site E6 is just 1,200 m away from the dredging area, the fact that it could be affected by the dredging activity should not be overlooked.

Definitively, the lines of evidence obtained from the analysis of the sediments collected around the monobuoy of the Tarragona harbor do not allow us to assert that the activity developed at this facility has an associated environmental impact. In order to reduce the uncertainties mentioned above, a monitoring program including periodic campaigns to allow describing the temporal and spatial variability of concentrations of contaminants should be implemented. This monitoring program should include a proper reference site to compare contamination and pollution detected inside and out of the estimated potentially affected area in order to be able to detect spatial patterns. At the monobuoy, this would allow to know, for instance, if the high concentration of mercury is a contamination problem of the entire harbor area or it is a problem associated with the activity developed at the monobuoy. Furthermore, biomarker analyses could be included in order to know the bioavailability of the detected contaminants. These could provide information about contaminant exposure inside the estimated affected area and the magnitude of the response of the organisms (Cajaraville et al., 2000). Various standardized tests (e.g. AOX, for the specific case of oil pollution) could be applied.

Environmental risk assessment has traditionally focused on: i) a problem formulation phase usually developed by evaluating goals, selecting endpoints and building a conceptual model; and, ii) an analysis phase addressed by evaluating exposure to stressors by describing their spatial and temporal distribution on the environment and co-occurrence of stressors and ecological receptor. Beyond this, the Environmental Impact Assessment (EIA) approach has typically addressed the integration of hazards exposure and stressor-response profiles, discussing lines of evidence and determining ecological adversity caused by the environmental hazards. In this study, the lines of evidence provided by the quantification of impacts serve to address the definition of the consequences term (Co_{gh}) involved in the whole risk assessment process. In this way, risk assessment can address the study of the relationship among risk estimations and the actual environmental impact and provide more realistic estimations of risk (Figure 6.2(a) against Figure 6.2(b)). Otherwise, probabilistic risk estimations based on release and exposure assessment, but not consequence assessment, will overestimate the final risk. Thus, the EIA should be considered as an essential tool to be embedded into the ERA process in order to provide a more realistic risk estimation of environmental hazards.

The methodology applied in this work allows estimating the potentially affected areas in terms of level of contamination, but not pollution. In this way, the specific contribution of the sources to the global environmental contamination deriving from harbor activity could be known. This information is relevant in order to properly manage the quality of harbor water systems, e.g., for an environmental quality monitoring design, allocation of uses to specific areas (as recreational areas) or even location or relocation of handling facilities.

6.5 Conclusions

From the environmental risk assessment results and the actual impact analysis performed based on the 'weights of evidence' approach at an oil handling facility level, we can conclude that:

I. The results of the environmental risk that consider the presence/absence of pollutants in the environment overestimate the actual impact of a contaminant source.
II. The consequences estimated for specific pollutants should be considered in the environmental risk analysis of contaminant sources.
III. The actual (quantified) environmental impact should be considered in the consequences factor definition.
IV. The results of environmental risk that consider the persistence of specific pollutants in marine environments are significantly correlated to environmental contamination, but not to biological adverse effects (pollution).

The ERA methodology is a useful tool to provide the contribution of specific sources to the global environmental contamination in a harbor area. Thus, this method will allow improving the management of harbors' water systems. This way corrective and preventive measures, environmental quality monitoring designs, allocation of uses to specific areas (such as recreational areas) or even location or relocation of handling facilities can be well-founded. Nevertheless, further studies should be developed in order to define methods that estimate the consequences considering not only the persistence and presence of specific pollutants, but also the bioavailability and toxicity associated to specific pollutants and mixtures.

Chapter VII

General conclusions and future research

CHAPTER VII. GENERAL CONCLUSIONS AND FUTURE RESEARCH

The overall aim of this thesis was to develop and validate methodologies and tools for an integrated management of harbor aquatic systems. Quantitative approaches based on stochastic and probabilistic analysis were developed to assess the risk of environmental hazards in harbor areas. To carry out this aim, a specific study at harbor scale was conducted and three works at oil handling facility scale were developed.

7.1. Conclusions

The results obtained allow the extraction of specific conclusions derived from each developed method and tool.

- **Prioritization maps:**

Prioritization maps developed through the methodology presented in Chapter III integrates the estimation of spatial and temporal variability of the contaminants and their effects. Acute and chronic effects of point sources by considering chemical pollution, eutrophication, and bacteriological contamination are combined with the potential effects of the hazardous materials released from diffuse sources and pollutant incidents. Risk maps easily interpretable were obtained.

- Risk values obtained at Tarragona harbor, considering three different integration methods: average-value, worst-case and weighted methods, were significantly correlated with water (chlorophyll a and nitrates) and sediment (lead) quality indicators. The average value and weighted methods were significantly related with total organic carbon in sediments.

- The integration methods (average-value, worst-case and weighted methods) provided different risk values. Low to moderate agreement was computed among them. So, each integration method can be used in function of the peculiarities of the study area and the purpose of risk management at harbor level.

- Prioritization maps allow to define individual, due to one contaminant, and integrated risk, due to multiple contaminants, caused by point and diffuse sources -ordinary operations- as well as by pollutant incidents. So, it is a useful tool which can provide spatial-temporal information at different levels.

- Prioritization maps allow managers to identify the contaminants that are affecting the quality of aquatic systems, the hazards which are altering the different areas of these systems and the hazards' contribution to the total integrated effect from harbor activities.

■ **Scenarios of non-point oil sources:**

The methodology presented in Chapter IV allows the definition of scenarios to assess the environmental risk of oil handling facilities in harbor areas. The scenarios are based on the combination of specific facility spill types (quantity, density) and most probable meteorological and oceanographic local conditions (surface sea level, wind direction and wind velocity).

- The methodology implemented to the oil handling facility of Tarragona harbor allowed to characterize the 4 most probable met-ocean conditions and the 12 spill types linked to the facility, based on quantitative methods.

- The method allows to define and select a small set of real based scenarios of non-point oil sources even when hardly any information is available for specific incidents.

- The proposed method is versatile enough to be applied to other fields or disciplines as offshore petroleum activities or Hazardous and Noxious Substances (HNS) sources characterization.

■ **SPILL Tool:**

SPILL tool, presented in Chapter V, is a custom script tool that is fully integrated under the ArcGIS Geoprocessing Framework. The process of spreading, transport and turbulent diffusion are taken into account. The numerical tool is easily loaded through the ArcToolbox of Geographical Information System software (ArcGIS 10.1 by ESRI^{TM}) and is operated through the autogenerated Graphical User Interface (GUI). SPILL tool can be reused and combined inside new workflows and models with ArcGIS ModelBuilder.

- For a real oil handling facility at Tarragona harbor, most of the calculated affected areas using the SPILL Tool showed a good correspondence to the results obtained using a calibrated 2D transport numerical model (TESEO).

- The SPILL Tool is able to study the evolution of oil spills during the first 2-4 hours, being a useful tool for environmental risk assessment at oil handling facility level and managing contaminant events from oil handling facilities.

- SPILL Tool obtains more accurate results to low density and low current velocity scenarios.

- The SPILL Tool constitutes a simple and quick procedure that is suitable for the environmental management of this type of activity by a wide range of users, including managers, technicians from port authorities, and stakeholders.

- **ERA of oil handling facility:**

The methodology presented in Chapter VI allows the estimation of environmental risk of oil handling facilities considering the consequences of specific handled pollutants. The method express consequences in terms of persistence of hazards on the aquatic environment and its potential affection.

- At the monobuoy of Repsol S.A. in Tarragona, risk values obtained from the developed method were significantly correlated with sediment quality indicators: benzo(a)anthracene, benzo(b)fluoranthene, benzo(a)pyrene and pyrene.

- Results of environmental risk considering the persistence of specific pollutants were significantly correlated to the environment's contamination, but not to biological adverse effects (pollution). So, the methodology presented in chapter VI do not predict the pollution due to oil handling activity.

- The developed ERA methodology is a powerful tool to provide the specific oil spill sources' contribution to the global environmental contamination in a harbor area.

- Corrective and preventive measures, environmental quality monitoring design, allocation of uses to specific areas (as recreational areas) or even location or relocation of handling facilities will be well-founded using this method.

7.2. Future research

Bearing in mind questions raised in Chapter I, related to water quality management in harbor areas, the studies carried out in this thesis have revealed the existence of certain aspects that could be improved in the described procedures.

Although these issues have been analyzed in the discussion section of each chapter, the most relevant aspects that should be addressed by future researches are summarized here.

1. Regarding the definition of effects associated to each hazard to be integrated through **prioritization maps**, further research should be conducted to include the intensity-duration-frequency (IDF) approach to the estimation of effects. Regarding the acute effects, the number of times (frequency) that an area has been affected by pollutant incidents of a specific hazardousness (intensity) could provide a more real effect estimation. In the same way, contaminants introduced by point contaminant sources could be estimated considering the number of times (frequency), how much (intensity) and for how long (duration) the threshold (Maximum Allowable Concentration, MAC) is exceeded.

2. Regarding the vulnerability term considered in the **prioritization maps**,

parameters to estimate the affection on ecosystem services could be included on its definition. The assessment criteria could take into account the affection of waters designated as recreational waters (Directive 2006/7/EC), shellfish waters (Directive 2006/113/EC), areas designated for the abstraction of water intended for human consumption or water bodies designated for coastal protection.

3. Calibrating turbulent diffusion coefficient and the parameters considered in the conditions which establishes a differentiation in the calculations for estimating the turbulent diffusion process will improve the results obtained from **SPILL Tool**. To do this, studies aimed to obtain and analyze detailed information of oil spills at port areas should be developed.

4. ERA tools and methodologies should be developed in order to define methods to estimate consequences of diffuse and pollutant incident sources by considering other types of handled pollutants. Developed methodologies and SPILL Tool could be adapted for the environmental risk analysis of **hazardous and noxious substances** (HNS) in order to be able to assess the environmental risk of HNS handling facilities in harbor areas.

Finally, the implementation to a real case of the methodologies and tools developed in this thesis confirms its usefulness as a decision-making tools to support water quality management in harbors. However, methodologies and tools should be validated also, in a set of representative harbor areas. These study areas should be characterized by different conditions and peculiarities representative of the variability of potential scenarios on harbor areas. At these areas, future studies on the relationship between the actual environmental impact and the environmental risk assessment should be developed. Data obtained at these studies should be enough to carry out robust statistical tests. Besides, data from reference sites should be collected to be able to compare with the data collected at the potential affected areas estimated by the new methodologies and tools developed in this thesis. The selection of indicators should be based not only on the persistence and presence of specific pollutants but on the toxicity, bioavailability and potential biological effects of the contaminants associated with the hazard subjected to the environmental risk analysis.

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