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Multicomponent Dispersion of Hydrocarbons at Sea: Source Term Evaluation and Hydrodynamic Simulation of the Spill

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The evaluation of the ecological consequences of spill accidents including factors such as persistence, and long-term exposure became more stringent following some notable events and still represents an up-to-date research issue. This study focuses on the possibility of proper source identification of a multi component sea spill and is motivated by actual findings of small quantities of floating and/or stranded waxy material in some areas of Liguria and Tuscany, in early summer 2017. The paper presents a thorough hydrodynamic simulation, carried out with an oil-spill Lagrangian particle model to study the trajectories of the different released material and determine its probable source. A short-cut mathematical simulation of the step-by-step process of formation by on-board activities and subsequent water interaction is proposed so as to highlight the limitations and the potential applicability of the method, also in light of setting-up early warning systems to prevent stranding of the oil slick in sensitive coast environments.

1. Introduction

The development of risk based approach for oil and hazmat spills in sea environment must consider two different release scenarios, namely: open sea navigation and harbour or port area. In each context, consequence analysis is based on intrinsically different events and different frequencies of occurrence of identified hazardous events are expected. Recalling the process sector approach, risk reduction strategies aiming at reducing frequency, or mitigating the severity of the impact can be categorized as: engineered active and passive; managerial and procedural; inherent (Palazzi et al., 2015). A preferable way to deal with hazardous spill risks is through prevention, which can be mainly based on technical requirements, operational measures for tankers and personnel requirements. Mitigation for the given context is mainly based on preparedness to respond to a spill and should include safety operations, identification of site-specific hazards and risks and protection needs and available resources**.** Considering failure of preventive measures and occurrence of oil spills, an effective contingency plan becomes important to minimize impacts (Vairo et al.,2017). In fact, owing to the large area potentially affected by spill evolution, environmental remediation efforts for such releases can be geographically widespread, long term, complex and extremely expensive. The evaluation of the ecological consequences of spill accidents including factors such as persistence, bioaccumulation and long-term exposure became more frequent following some notable events affecting surface/sea water, such as Sandoz, Exxon Valdez and more recently BP Deepwater Horizon. The last one occurred within the Mexico Gulf and led to the release of 4.9 million barrels oil, thus representing the largest spill event in the U.S. history. In this event, chemical dispersants were directly injected into oil release to improve the dispersion supporting by the buoyancy and hydrodynamics, the solubility and limit the oil slick formation on the sea surface. A drawback of this technique is that the fate of chemically dispersed oil droplets is poorly known. Modelling of oil spill trajectory and fate in sea environment is already a complicated problem, in which the spatial and temporal variability of the environmental conditions need to be addressed. The presence of different phases poses additional complexity to this challenging problem. The fate and behavior of oil spill in marine environment is governed by a series of complex, physical and chemical processes, such as spreading, evaporation, emulsification, dissolution, biodegradation, current transport, sedimentation, highly depending on the properties of the spill, hydrodynamic and environmental conditions. The reader is addressed to the overview of different numerical models of oil spill processes provided by Reed et al. (1999). Mitigation associated with oil spill impacts depends largely on the formulation and implementation of adequate contingency plans, which should incorporate the source identification, the simulation of the respective dispersion patterns and the characterization of areas (sea and shore), that could be affected by a spill. Stochastic modelling including seasonal variability simulating the potential fate and behavior of a crude oil spill into a river proved to be effective for the formulation of refined plans aiming at efficient spill response and mitigation (Kafarov et al., 2017). The most common forensic oil spill identification is based on the expensive and time-consuming GC-MS fingerprinting, according to the well-known Nordtest method for spill identification. The numerical or analytical resolution of the relevant inverse problem starting from field experimental data back to the pollution source requires a proper regularization technique (e.g. Reverberi et al., 2103), and is clearly limited in case of complex geometries. In June 2017, different slicks consisting of either homogeneous materials, or yellow, non-homogeneous materials were observed and sampled in the Ligurian Sea (Italy). Chemical analyses of samples revealed that both types of collected material are traceable to paraffinic, or polyethylene hydrocarbon waxes, probably due to the washing of the tanks of a ship performing hydrocarbons transport. The remainder of the paper presents a thorough hydrodynamic simulation, carried out with an oil-spill Lagrangian particle model to study the trajectories of the different released material and determine its probable source. A hypothesis about the mechanism of formation of the two different types of paraffin wax is also formulated, starting from the materials in the ship tanks and relevant operative conditions.

2. Sea spill in sensitive harbour area

Following the request received by the Coast Guard, a modelling study was conducted, to assess the possible causes of a solid waxes beaching in some areas of Liguria from west to east) and in Massa Carrara, in the days from 15.6.2017 to 17.6.2017. The region includes the sensible area represented by Portofino promontory (Italy) with 13 km of rough coastline, steep seabed and high indices of biodiversity, both in its terrestrial and marine ecosystems. The paraffin waxes spillage was hypothesized by the Port Authority as issued by a ship in transit from Genoa to Livorno on the days between 4.6.2017 and 7.6.2017, due to the accordance between the findings along the coast and the material carried by ship and the route travelled. The ship's route, supplied by the Coast Guard, is compatible with the tank washing activities, as evidenced by the come-and-go on the route between Genoa and Livorno, as shown in Fig. 1.

2.1 Materials and methods

The beached material presented slightly different characteristics: on the beaches of Finale Ligure and Sori a paraffinic material of whitish colour and flake waxy consistency has been found. On the northern coast of Tuscany, higher density material of similar appearance but a more yellowish colour has been found and identified as paraffinic, or polyethylene hydrocarbon wax. Thus, in parallel to the hydrodynamic simulation, a study on the possible interactions between the released material and the environment was conducted, in order to narrowly assess the source term.

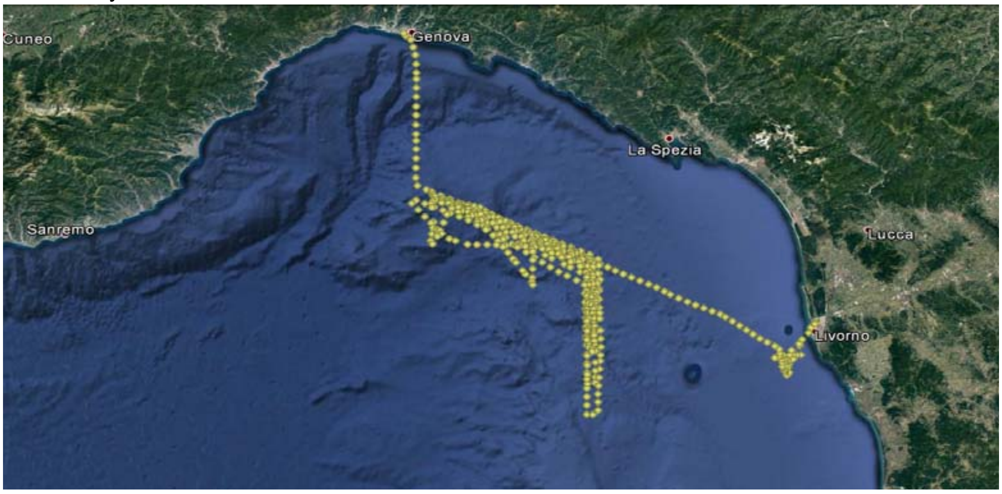

Figure 1: Actual ship route in the Liguria Sea along the way from Livorno to Genova.

Figure 2 a:Sightings of floating/beached materials; b:Representative sample types collected along the shores.

A detailed localization of the mass of released material sightings along the shore is summarized in the following:

- 15.6.2017 – Finale Ligure (SV), beached white, paraffinic material.
- 16.6.2017 – Massa, beached white, paraffinic material.
- 17-18.6.2017 – Marciana Marina e Procchio (Elba island), floating paraffinic solid material (250 Kg).
- 19.6.2017 – Golfo di Baratti (Piombino), floating / beached yellow paraffinic solid material.
- 18-19-20.6.2017 – San Vincenzo, Donoratico, Marina di Castagneto, Carducci (Piombino), floating / beached yellow paraffinic solid material.
- 20.6.2017 – Massa, Montignoso, floating paraffinic material
- 20.6.2017 – Torre del Lago (Viareggio), beached paraffinic material
- 21.6.2017 – Cerboli (Elba island – Piombino), floating / beached yellow paraffinic material (105 Kg)

Preliminary chemical analyses of samples collected on the shores revealed that both types of sampled material are traceable to paraffinic or polyethylene hydrocarbon waxes, probably due to the washing of the tanks of a ship performing hydrocarbons transport. Fig. 2 a and b respectively show the domain of study for the modelling, including a visual representation of the different solid HC findings at sea, and two collected sample types. The MARPOL 73/78 standard for these categories of products foresees that the operation of washing the tanks with release at sea may be lawfully carried out observing the following requirements: distance ≥ 12 nautical miles from the coast; cruising speed ≥ 7 knots; drain underneath the surface of the water. These regulations are enforced to avoid that the products, not sufficiently diluted, may tend to re-aggregate. The re-aggregation of the product may be determined by the particular marine weather conditions, or by non-compliance with the directive.

2.2 Source term evaluation

As previously reported the development of an effective contingency plan to mitigate spill risk should incorporate the source term identification, the modelling of the dispersion patterns and the characterization of sensitive areas potentially affected by the spill. Generally speaking, the quantification of uncertainty of modelling results and the optimal selection of the model is based on an accurate evaluation on how model uncertainty in model inputs affects the outputs (Vairo et al. 2014). For example, uncertainty resulting from variation in source term and weather conditions is the main factor to be considered when dealing with atmospheric dispersion modelling (Pandya et al., 2013). Following sample characterization, the released substance in form of mixture were obtained from the register of the products of the ship performing the activities in the area, as follows.

- Microwax SR2030, CAS nr. 63231-60-7. A complex combination of saturated straight and branched chain hydrocarbons predominantly greater than C35, obtained from residual oils by solvent crystallization. Colour: brown; Melting / pour point: 70-73°C; Boiling point: >380°C; Vapour density: >1.
- Interwax 100, 150, 330, CAS nr. 64742-61-6. A complex combination of saturated straight and branched chain hydrocarbons predominantly greater than C20 hydrocarbons obtained from a petroleum fraction by solvent crystallization or as a distillation fraction from a very waxy crude. Colour: yellow; Melting / pour point: 52-56°C; Boiling point: >380°C; Vapour density: >1.

- Interwax 600, CAS nr. 8009-03-8. A complex combination of saturated crystalline and liquid hydrocarbons predominantly greater than C25, obtained as a semi-solid from dewaxing paraffinic residual oil. Colour: white / light yellow; Melting / pour point: 66-70°C; Boiling point:>380°C; Vapour density: >1.

Assuming that the cleaning of the ship tanks was carried out in accordance with the regulations at T ≥ 80°C, a working hypothesis about the phenomenon of subsequent re-solidification was established. As amply known, the paraffin crystallization process can be influenced by many factors, such as paraffin composition, solvent nature, polydispersity, cooling rate, P, T, kinetics and presence of impurities. The above-mentioned waxes are non-polar hydrophobic hydrocarbon and are insoluble in water. In contact with water at high temperature, two immiscible liquid phases are formed. If thermal energy is supplied (or if there is agitation), an emulsion may form with droplet diameter between 0.5 and 100 μm. The unstable conditions, due to the free energy excess associated with the interfacial tension of the dispersed phase, cause droplet aggregation in the absence of surfactants. The chemical and visual difference between the beached materials may be explained by the fact that the slack waxes started to melt first, followed by the petrolatum and at last by the microcrystalline wax. It is hypothesized that the contact with the colder sea water (16-18 °C) and the lack of agitation due to calms sea conditions have hindered the emulsion process and coalescence phenomena. On these basis, in modelling the spill fate, the source term was characterized by solving the mass balance and dividing the ship's route into the three time intervals connected to the different release times of the identified compounds.

2.3 Modelling

A combined forecast modelling approach was selected in order to simulate a release scenario of supernatant material along the ship route and to evaluate the fate and time of beaching of this substance on the coasts of the Ligurian Sea and Northern Tyrrhenian Sea. The three-dimensional hydrodynamic circulation model is achieved utilizing MIKE 3 HD approach (Hørsholm, Denmark), which simulates level and stream variations as a function of all the relevant phenomena affecting coastal hydrodynamics. The hydrodynamic circulation model relies on data from the Mediterranean-scale circulation (Model MFS Copernicus) which were combined with weather data from the meteorological model MOLOCH developed at the CFMI-PC (ARPAL). According to a previous study (Vairo et al., 2017), it was adopted a numerical finite volume discretization method, on the flow and transport equations in the horizontal dimension, with a non-structured triangular mesh having a variable resolution from offshore and towards the coast. A Lagrangian modelling approach is used both for oil spills and non-reactive floating material, allowing to simulate the trajectories of dragged and dispersed particles under the combined action of current and wind. The applicative phase includes continuous hydrodynamic simulation runs carried out over the time span from 1.6.2017 to 20.6.2017.

3. Results and discussion

Based on mass balance, a continuous release of inert and non-degradable floating particles on the ship route has been set as a source, focusing on the time span corresponding to 15 nautical miles distance from the coast until the moment when the ship heads towards Livorno port. The pollutant multi source considers 30-minute time bands, starting from 4.6.2017 at 17:30, until 7.6.2017 at 6:00, while the model outputs are considered at 1 h intervals. Fig. 3 shows the modelled position of the particles heading towards NNW on 4.6.2017, after nearly 2 hours from the starting of the release; the particles, according to the currents regime.

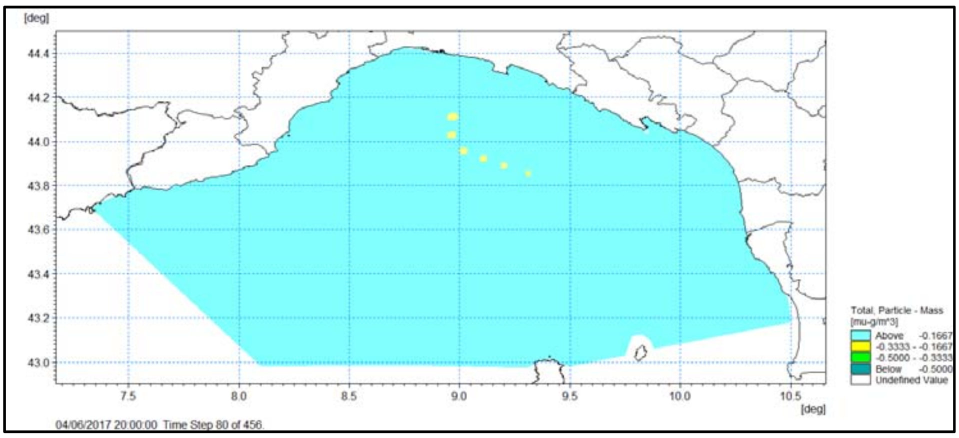

Figure 3: Multi source term simulation, based on actual ship route, at local time 20:00 4th June 2017.

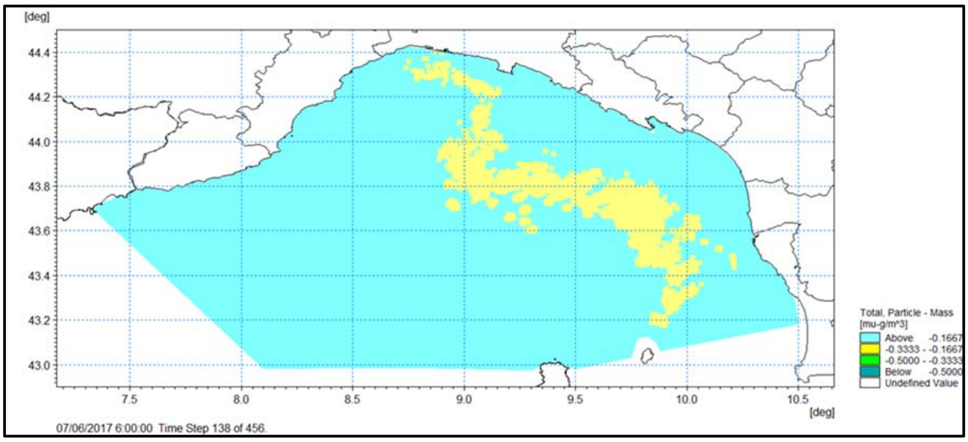

Figure 4: Localization of the particles at local time 06:00 7th June 2017 corresponding to release end.

In Fig. 4 releases along the entire ship's route are simulated with the Lagrangian model, until 7.6.2017 at 6:00, when the ship finally heads towards the port of Livorno. The first material beachings are observed on the shores of Savona (West) on 9.6.2017 at 15:00, while the particles begin to spread also towards the East Ligurian and Tuscany coasts (see Fig. 5). As clearly evidenced in Fig. 6, on 16.6.2017, the material reaches the beaches of Tuscany and East Liguria, on the beaches of Sori, Recco, Chiavari, Moneglia and Marina di Pisa. Fig.7 depicts the final time of the simulation, with all the trajectories of the released floating particles coloured in white, evidencing the overall extent of the coastline affected by the particle beaching.

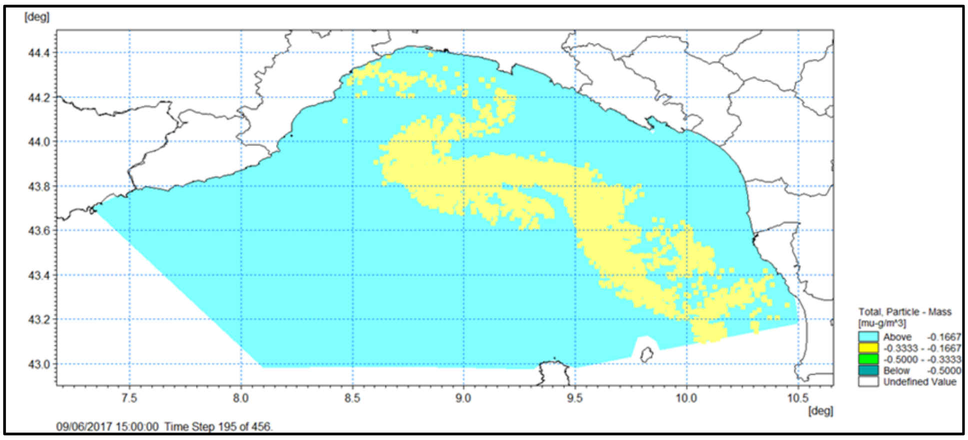

Figure 5: Localization of the particles at local time 15:00 9th June 2017

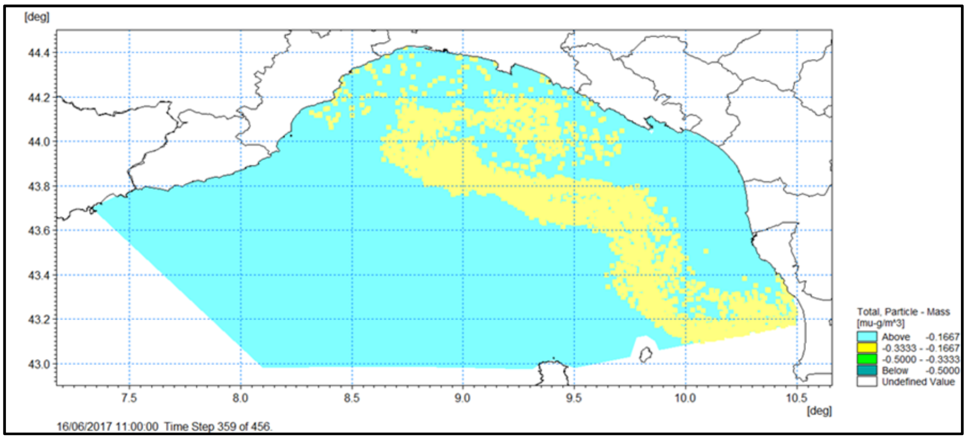

Figure 6: Localization of the particles at local time 11:00 16th June 2017

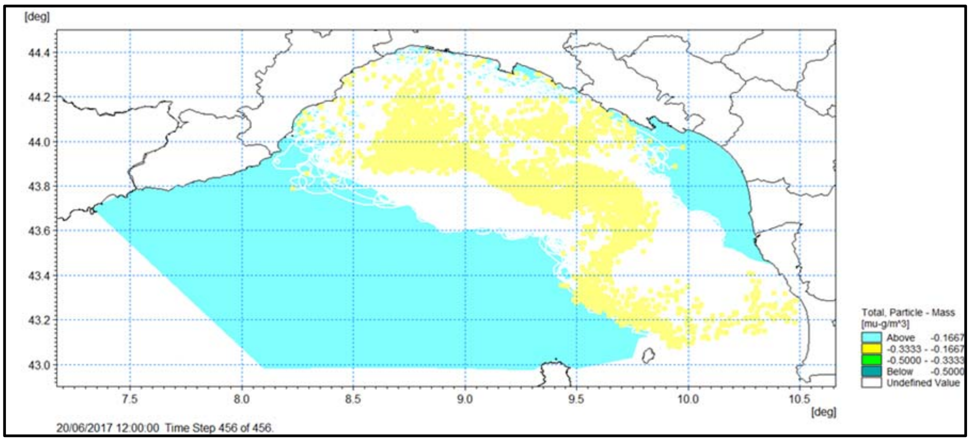

Figure 7: Localization of the fate of the particles at local time 12:00 20th June 2017

Comparing the simulation results with the locations of material along the coast, a remarkable agreement was found, thus providing a validation of the proposed mechanism. It can be concluded that the hypothesis that the beached material comes from tank washing of the ship on the trajectory was found to be convincing.

4. Conclusions

The use of numerical modelling can provide important information to predict or reconstruct possible accident scenarios either in the operational emergency phase, or in forensic investigation, thus representing an effective tool to support Public Authorities. This paper presents a thorough reconstruction of the multi-source release and the hydrodynamic simulation by an oil-spill Lagrangian model The agreement between sightings of material and particle tracking simulation supports the coherence of the pollution hypothesis. The proposed approach is simple as it considers the transport of passive components, but has the potential to be further developed to include weathering processes and consider the ageing of the particles released, so as to become a robust simulation model for better understanding hydrocarbons fate and its environmental effects.

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