Design of an operational decision aid software to model pollution in the Mediterranean Sea

APRIN L.[a], LEFLOCH S.[b], , GARREAU P.[c], JAMES A.[d], DANIEL P.[e], DAUMAIL V. [f], MOURIES M.[g], BACCOU J.[h] THEBAULT H.[i], ETASSE C.[j], ROURE J.F.[k], MERCANTINI J.M.[l] , OLIER R [m],

[a] LGEI, Ecole des Mines d'Alès, 6 Avenue de Clavières, 30319 Ales Cedex, France, 04 66 78 27 58, 04.66.78.27.01, laurent.aprin@ema.fr

[b] CEDRE (Centre de documentation, de recherche et d'expérimentations sur les pollutions accidentelles des eaux) service intervention, 715 rue Alain Colas - CS 41836 - 29218 Brest Cedex 2, France, 02.98.33.67.02, Stephane.Le.Floch@cedre.fr

[c] IFREMER (Institut français de recherche pour l'exploitation de la mer) service Applications Opérationnelles (DEL/AO), Z.I. Pointe du Diable, B.P. 70 29280 Plouzane, France, 02.98.22.43.59, Pierre.Garreau@ifremer.fr

[d] Cellule mixte Ifremer/INERIS d'Analyse des Risques Chimiques en milieu marin (ARC), Département Biogéochimie et Ecotoxicologie, Centre IFREMER de Nantes B.P. 21105, 44311 Nantes Cedex 3, France, 02.40.37.41.48, Alice.James@ifremer.fr

[e] Météo France, Direction de la prévision, division Marine et Océanographie, 42, avenue Gaspard Coriolis, 31057 Toulouse Cedex 1, France, 05.61.07.82.92, pierre.daniel@meteo.fr

[f] APSYS-EADS Agence Sud Est, CTMA - Bat B, 13127 Vitrolles, France, 04.42.89.80.82, capucine.sanchez@apsys.eads.net

[g] GEOCEAN-MERCLEAN, Quartier du Brégadan, ZA Technoparc, CS 60001, 13711 CASSIS Cedex, France, 04.42.18.02.18, m-mouries@merclean.fr

[h] Institut de Radioprotection et de Sureté Nucléaire, IRSN/DPAM/SEMIC,Bat. 702 – CE, Cadarache, 13108 Saint Paul lez Durance, France, 04.42.19.94.53, chantal.casselman@irsn.fr

[i] Institut de Radioprotection et de Sureté Nucléaire, Laboratoire d'Etudes Radioécologiques des milieux Continental et Marin, IFREMER BP 330, 83507 La Seyne-sur-mer, France, 04.94.30.48.46, Herve.Thebault@ifremer.fr

[j] TOTAL S.A., Trading & Shipping / Transports Maritimes/ Service Environnement et Lutte Anti-Pollution, Tour Coupole, 2 Place de la Coupole, La Défense 6, 92078 Paris La Défense Cedex, France, 01.47.44.82.23, celine.etasse@total.com

[k] Service Départemental Incendie et de Secours du Gard, 982 av Joliot Curie, 30900 Nîmes, France, 04.66.63.36.16, jfroure@sdis30.fr

[l] Laboratoire des Sciences de l'Information et des Systèmes (LSIS), UMR CNRS n° 6168, domaine Universitaire de St Jérôme, Av. Escadrille Normandie-Niemen, 13397 Marseille cedex 20, France, 04.91.05.60.15, jean-marc.mercantini@lsis.org

[m] Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, UMR CNRS 6521, Université de Bretagne Occidentale, 6 avenue Le Gorgeu, CS 93837 - 29238 Brest Cedex 3, France, 02.98.01.60.28, rene.olier@univ-brest.fr

1. Introduction

Within a few decades, the European coasts and seas endured important environmental accidents by chemical pollution. The accident of the "Ievoli-Sun", October 31, 2000, which transported 4000 tons of styrene or the shipwreck of the "Balu", March 20, 2001 in the Bay of Biscay, in charge of 8000 tons of sulphuric acid. All these accidents are due to the development of human activities and its economic environment and involve serious toxicological and ecotoxicological effects on maritime fauna and flora and sometimes on the population

Approximately 30% of the volume of the international sea traffic relates to the Mediterranean ports, or forwards in the Mediterranean, while it is estimated that 50% of the transported goods by sea can present a risk at various degrees. The traffic (tonnage, frequency) and, consecutively, the risks of major accidents will increase in the future.

When a disaster occurs, the actions taken to prevent pollution (controls and more severe sanctions), the populations and the authorities aspire to a faster and more effective management of pollution to limit its consequences. So far, the French authorities charged to take medical or economic protection during a chemicals or hydrocarbons pollution haven't aid decision tools adapted to the operational interventions.

It is in this particular and significant context of crisis management that the CLARA II project is being developed (Calculations related To the Accidental Releases in the Mediterranean), and more precisely in an objective of forecast and assistance during an accidental pollution in the Mediterranean. This project is carried out, since November 2006, by Ecole des Mines d'Alès, the Cedre, Ifremer, Météo France, Cellule ARC (Ifremer/INERIS), APSYS-EADS, Géocéan-Merclean, IRSN, Total, SDIS 30, UBO and the LSIS. This project is financing by the National Agency of Research (ANR) for the Program "Ecotechnologies and Développement Durable" (PRECODD).

The objective of CLARA II is to provide an aid decision tool for the risks related to chemical pollution in the Mediterranean. It will propose relevant zones of exclusion in order to alert, protect the populations, the goods and the environment, mobilization of the rescuer to anticipate the situation in the short or medium term.

This paper presents the two preliminary phases, the analysis of the need and the analysis of the products

2. Traffic Analysis

For the last two decades, maritime transportation and harbour storage of chemicals have been considerably developing. Although maritime traffic is still dominated by hydrocarbon exchange, the percentage of other chemicals has been increasing more and more. For example in the English Channel, the transportation of chemicals varied from 30 million tons in 1988 to 150 million tons in 2000, which represents an increase of five hundred percent in twelve years. This growth raises the question of the risk involved by accidents, which is increasing as much as the quantity. To prevent those risks as accurately as possible, it is necessary to have a good knowledge of the sea traffic of chemicals.

It is often said that the Mediterranean east one of the seas most exposed to the risk of accidental pollution by oils and other dangerous substances. That is explained by:

- The very dense sea traffic,
- The importance of the volume of the crude oil and products refined transported in the area,
- The existence of a great number of ports,
- The presence of many islands, especially in certain important zones of traffic,
- The dangerous passage because of the straits of Bonifacio and Messine.

Data-gathering on the accidents causing or likely to cause pollution in the Mediterranean by the substances excepted oils was started by the REMPEC in January 1988.

To take into account uncertainties concerning the type of cargo of the ships implied in the accidents, the diversity of the products included in the "harmful substances others that oils" (gas, liquids, solids) and of the various methods of transport of the products (in bulk, packing), the data available at the REMPEC are less precise than those relating to oils and do not make it possible to draw up clear statistics nor to draw some the reliable conclusions.

It nevertheless is established that at least 79 accidents of navigation raised in the Mediterranean between 1988 and 1997 implied ships transporting of the cargoes being able to be regarded as "harmful". These cargoes include/understand:

- cargo (ores, manure, sulfur, various chemicals),
- liquid (various acids, alcohols, ethers, alumina, glycol),
- bulk transported gas (LPG, propylene, GNL),
- various packed chemicals (pesticides, hydroxide, peroxide, acetylene, oxide of ethylene, mercury).

As for the accidents implying of oils, all the accidents implying of the harmful substances do not involve the discharge of the products in the environment. Indeed, only 21 accidents (27%) raised during period 1988-1997 involved the discharge of the cargo in the marine environment while for 58 accidents (73%) the harmful cargo was not affected by the accident.

Observations made on the data collected on the accidents implying other dangerous substances that oils in the Mediterranean, over the period 1998-2003, are as follows:

- total number of accidents: 94,
- total quantity of other products than petrol: 135.866 Tons.

Accidents are separated in five categories:

- collisions,
- fires/explosions,
- failures,
- shipwrecks (caused per any the preceding reasons)
- other types of accidents.

Since 1988 a clear reduction in "the other" accidents appears, just as for the fires/explosions, strandings and collisions since the period 92-95. The accidents entering the "different" categories, "collisions" and "strandings" even completely disappeared in 2000-2003.

On the contrary, the number of shipwrecks did not cease increasing since 92-95 and constitutes by far (90%) the principal type of accident over the period 2000-2003.

It appears clearly that the number of conveyers LNG and LPG, bulk carriers and chemicals implied in accidents dropped regularly between 1988-1991 and between 2000-2003. Moreover, conveyers LNG and LPG, the bulk carriers and "the other" types of boats contributed to no incident causing or likely to cause a marine pollution the Mediterranean by products other than oils over the period 2000-2003.
On the other hand, the proportion of ships cargo liners implied in these incidents increased significantly to reach 90% for this period 2000-2003.

The general tendency for the future, is an important drop of the rejections of operational and accidental cumulated pollution (- 17,6% per year between 1985 and 2000). But the report is to be moderated on two levels.

On the one hand, two important flows (of which the increase is probable 28) are not known: accidental rejections except oil and losses of containers at sea.

In addition, this general tendency masks the increase of two operational pollutions whose volume becomes important:

- Residues of fuel and oils (water of draining)
- Discharge of waste water of the chemicals.

The basic scenario envisages a total increase in the rejections (5% per year between 2000 and 2025), primarily related to:

- aggravation of the located tendencies (increase in the water discharges of ballast of the chemicals),
- light reorientation with the rise of the accidental rejections and oil release, under the effect of the very strong increase awaited in the sea traffic.

3. Experimental study of the products

Project CLARA II integrates a software of decision-making aid and its own data base physico-chemical and ecotoxicological. In its initial version, the database reference a little less than one hundred of substances, selected among the substances liquide most massively and frequently transported by sea to the Mediterranean. This data base is conceived to be evolutionary. It informs the parameters necessary to the modeling of the physico-chemical behavior of the systems atmosphere/sea water/substance/sea-bed. The model takes into account these parameters for the forecast of the space-time behavior and the ecotoxicological effects of the poured substance.

3.1 Physicochemistry

The knowledge of the physico-chemical properties of the substances is necessary to the forecast of their behavior. This one is considered, in the course term, as governed by these properties. The long-term evolutions are not concerned.
The most important processes in the dissemination of the substance in the environment are primarily:

- behavior according to classification SEBC from which the behavior in the very short term results from the substance [3]. The product floats or sinks.
- For a floating product, the first phenomenon to be taken into account is the spreading out of the spill on the surface. Secondarily, the product can evaporate, dissolve, dispersed and to form, according to the agitation of the medium, the aerosols, the droplets dispersed in the water column, of foams, the water emulsions in the substance.
- For a product sinking, the process of spreading out on the surface of the sea and evaporation could, initially, be ignored. If the substance is not very soluble, to become to it spill will depend on the morphology of sea-bed (flow, stagnation, infiltration,…). The immediate ecotoxicological impact will relate to the species living on the bottom (or nourishing species there alive).
- For a water soluble substance, it is advisable to distinguish the limits of solubility, rather largely referred in the literature (although little is described there with regard to the influence salinity sea water), the speed of solubilization, which strongly depends on the energy deposited in the medium (by the wind, the swell, currents,…). In lower part of a certain threshold of agitation, the dominating phenomenon is the stratification according to the respective densities of sea water and the substance. In this case, although the solubility-limit can be important, the solubilized quantity will only increase very slowly. These speeds of dissolution are referred very little in the literature because same of their dependence of the conditions of agitation.
- For a dissolved substance, the process of volatilization can also be taken into account (to be distinguished from the evaporation of the pure substance)

The physico-chemical parameters selected to appear in the data base are as follows: melting points and evaporation, density, viscosity, saturating steam pressure, surface tension, limits solubility in water, enthalpy of vaporization, specific heat of the liquid, constant of Henry, coefficient of division octanol-water (Kow), coefficient of organic division carbon – water (Koc).

The user informs the environmental data: temperature, salinity, speed of the wind, initial position of the spill as well as the poured quantity.

The software will take into account the evolution of the parameters with the temperature and salinity instead of discharge.

3.2 Selection of the chemical substances

For the chemical substances for which information will be available in the data base, the work of selection mainly consisted of the taking into account of the sea traffic. A setting in priority of the substances was thus carried out on the basis of tonnage transported per annum in the largest Mediterranean ports [3]. The solid, gas substances or in the form of solid melted, are not taken into account in CLARA II.
On the whole, 71substances chemical was identified in order to initially feed the data base of CLARA II.

A set of priorities was established for the study of these substances. The substances to be treated in priority are those for which part of the data were already collected in CLARA. Then, the criterion of priority which it was selected to apply is that of the Mediterranean traffic

Project CLARA II also includes an experimental phase in laboratory aiming at characterizing on the physicochemical level some substances in order to evaluate their properties in sea water and to apprehend the principal environmental parameters being able to influence their behavior once poured in the marine environment. For the selection of these chemical substances tested in laboratory, it seemed relevant that each dominating physicochemical behavior in the short run is represented, as well as a substance in solution. Among the substances selected for the data base, 9 substances were thus selected, each one representing of the combinations different from the behaviors described in classification SEBC, classification of the groups of behaviors of the chemical substances in the marine environment [1]: Floating (F), Evaporating (E), which dissolves (D) and/or which sinks (S) (Table 1). These tests will take place at the same time on a laboratory scale and sea water column of 5m of the *Cedre*.
Lastly, project CLARA II at sea performed an experimental phase, which would consist of a discharge of chemical substances in order to follow *in situ* their evolution and in particular their kinetics of evaporation and solubilization. On the whole, 3 substances were preselected because of their behavior according to code SEBC: xylenes, the n-butanol and the Radiagreen oil. The follow-up of the substance F ((a) (Radiagreen) will make it possible to validate the module of drift, and the follow-up of the substances FE (xylenes) and ED (n-butanol) will make it possible to validate the equations defining the kinetics of evaporation and solubilization. These tests at sea were carried out in agreement with the maritime authorities.

Priority laboratory	Priority data base	Priority HASREP	Name CASE	Number CASE	Behavior SEBC	Exp. in laboratory	Exp. at sea
1	9	24	methyl metacrylate	80-62-4	ED	X	
2	1	2	xylenes	1330-20-7	FE	X	X
3	36	57	Radiagreen	103-21-3	F	X	X
4	1	(23)	1,2-dichloroethane	107-06-2	SD	X	
5	1	5	MTBE	1634-04-4	ED	X	
6	1	15	ethylene glycol	107-21-7	D	X	
7	32	53	N-butanol	71-36-3	D	X	X
8	1	6	styrene	100-42-5	FE	X	
9	1	1	Sodium hydroxide in solution	1310-73-2	D	X	

Table 1: Chemical substances selected for the experimental tests in laboratory and at sea

4. Conclusion

In addition to the actions carried out with an aim of preventing all other pollution the such reinforcement of the regulation, of controls and the more severe sanctions, when a disaster occur, the populations and the authorities wish a faster and more effective management of pollution to limit the consequences of them. The objective of CLARA II is to propose, with the managers of the crisis, a management tool of the risks related to chemical and oil marine pollution in the Mediterranean, enabling them to quickly set up relevant zones of exclusion with an aim of alerting, but also to protect the populations, the goods and the environment, to mobilize the adapted means of fight and of anticipating the situation in the short or medium term. CLARA II will have to be of a great ease of use because the tool will be implemented on the ground by organizations non-specialists of the models of simulation.
Project CLARA II has as an ambition to fill partly the existing vacuums in particular through the modeling of the Mediterranean hydrodynamics, of the comprehension of the physicochemistry of the products studied and their mixture with sea water, of methodologies on the conduits to be held, of the improvement of the techniques of fight and the development of new solutions of recovery. This best

knowledge will be able at sea to allow a technological approach improved of the containment of the poured products and, more generally, treatment of pollution.
The objectives of the project Clara 2 are multiple, and consist to prevent or limit the consequences of a discharge of chemical for the environment:

- from the ecological point of view, by the protection of the significant natural zones,
- the from an economic standpoint, by the protection of the uses and other economic activities in the vicinity,
- from the point of view of the protection of the health of the speakers.

Acknowledgments

The members of consortium CLARA II thank the National Agency for Research (ANR), the Program Ecotechnologies and Durable Développement (PRECODD) and the Maritime Authorities (CEPPOL and Prefecture Maritime)for their support in the realization of this project

References

[1] AMRIE (2005). Carryforward one task 1 “Monitoring off the flow off chemicals transported by sea in bulk and in package form”. Carryforward off the European Union Project HASREP: Response to harmful substances spilled At sea. 38 p.

[2] E.C. (2003). Technical guidance document in support off Commission Directive 93/67/EEC one risk assessment for new notified substances and Commission Regulation (EC.) No1488/94 one risk assessment for existing substances and Directive Commission (EC.) 98/8 one biocides, European Commission.

[3] GESAMP (2002). Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships. London, GESAMP (IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/ONE/UNEP Group Joint off Expert one the Scientific Aspects off Marine Environmental Protection): 126.