Characterization, fate and impact of ISB products from different types of crude oils: Literature review and experimental study for ISB predictive modelling and SIMA process

Philippe Blanc
TOTAL S.A., CSTJF, Avenue Larribau, 64018 Pau, France
Ronan Jezequel, Lucie Blondel, Stéphane Le Floch, Silvère André
CEDRE, 715 rue Alain Colas - 29218 Brest, France
Benjamin Livas and Olivier Zaouak
MODIS, Technopole Hélioparc, 4 rue Jules Ferry, 64 053 Pau, France

ABSTRACT

In situ burning (ISB) is an OSR (Oil Spill Response) technique generally not accepted as a "standard" response by most regulators. Main reluctance generally comes from the occurrence of large and dark smokes plumes as well as possible heavy burn residues likely to sink and reach the seafloor. However, ISB has been widely used during the Macondo oil spill in 2010 and highlighted as a promising operational technique. Additionally, standard OSR modeling tools do not consider ISB, as there is a lack of knowledge in the capacity to predict accurately the physico-chemical characteristics, fate and ecotoxicity, of the burn products from large varieties of crude oils.

In order to provide dispassionate arguments, we have conducted a study to gain knowledge and try to develop predictive capabilities to infer composition and fate of burn products from characteristics of starting crude oils. The study comprises both large literature review and experimental work where six crude oils of different types (along with corresponding weathered oils) were burnt, and all products quantified and analyzed (physico-chemistry), at both laboratory scale (burning bench) and pilot scale (fire platform). Additionally, ecotoxicity testing on *Vibrio fischeri* bacteria and *Phaeodactylum tricornutum* algae were conducted on crude and weathered oils, burn residues, water and soot. The fate of burn residues was also investigated through dispersibility, emulsification and biodegradability testing. The experimental work led to a very large set of data which was subject to multivariate regression statistical treatments to build predictive models. Main data investigated were burn efficiency,

density, viscosity, SARA (Saturates, Aromatics, Resins, Asphaltenes) composition, *n*-alkanes and PAHs (polycyclic aromatic hydrocarbons) distributions in burn residues, gas emissions composition, soot' PAHs distribution in the smokes, and ecotoxicity data of burn residues, soot and water. The paper describes the main results of this study, with promising outcomes to develop predictive ISB modeling and help addressing objectively the relative impact of ISB within the SIMA process in comparison with other cleaning responses.

KEY WORDS: oil spill response, *in situ* burning, burn experiments, oil types, burn products, ecotoxicity, multivariate analysis, predictive modeling.

INTRODUCTION

Oil spills are among the most known feared ecological disasters likely to disrupts ecosystems and to cause mortalities of birds, mammals, fishes and other organisms during the first days (Lamine and Xiong, 2013). Hence, it is important to rapidly react and deploy efficient oil spill responses in order to minimize the environmental impacts of such pollution. Generally, the spill is contained using booms and mechanically recovered by skimmers. However, some alternative methods have been developed such as the use of dispersant agents or the burning of the oil, the latter also known as *in-situ* burning (ISB) (Fingas, 2016).Although known for years, ISB is an OSR technique generally not accepted as a "standard" response by most regulators. Main concern comes from the occurrence of large and dark smoke plumes as well as possible heavy burn residues likely to sink and reach the seafloor. However, ISB has been widely used during the Macondo oil spill in 2010 and highlighted as a promising operational technique. It has also allowed to expand the current datasets with real-scaled field data, leading to several guides and scientific publications (Perring *et al.*, 2011; Reddy *et al.*, 2012; Shigenaka *et al.*, 2015; Gullett *et al.*, 2017) and sharing acquired experience about execution of burning experiments.

In the meantime, standard OSR modeling tools do not consider ISB as an option, as there is a lack of knowledge in the capacity to predict accurately the physico-chemical characteristics, fate and impact, of the burn products from large varieties of crude oils. The same lack of knowledge also leads to incapacity to consider efficiently ISB in the spill impact mitigation assessment (SIMA) process (IPIECA-API-IOGP, 2017), thus limiting the incorporation of ISB in oil spill contingency plans (OSCP). As an example, the buoyancy of the residues of burning experiments remains a major interrogation as for their sinking behaviour. A predictive tool of real-time determination of the residue density was developed in order to determine a sinking threshold according to initial density of crude oil (S.L. Ross Environmental Reasearch Ltd., 2002). However, more complex mathematical tools have to be considered in order to develop predictive models of ISB products fate according to crude oil composition, such as the use of multivariate approach involving chemometrics (Khanmohammadi et al., 2012). Development of multivariate regression models require large volumes of data as they need to be trained by the variability between the different samples. In order to help provide dispassionate arguments for the possible use of ISB for OSR and consideration in modeling tools and SIMA approach, we have conducted an extensive and comprehensive study to gain knowledge and try to develop predictive capabilities to infer composition and fate of burn products from characteristics of starting crude oils. The study comprises both a large tentative “predictive” literature review and experimental work where six crude oils of different types (along with corresponding weathered oils) were burnt, and all products quantified and characterized (physico-chemistry and toxicity), at both laboratory scale (burning bench) and pilot scale (fire platform). A multivariate regression model statistical approach has then been performed on the dataset, in order to develop predictive models. The present paper gives a synthetic overview of the main outcomes of this study within the scope of better integration of ISB in the SIMA process.

MATERIAL AND METHODS

"Predictive" literature study

Principle of the "predictive" literature study is to collect all published and available physico-chemical data of oils submitted to burning (either lab, pilot, or field case) as well as data and information on corresponding burn products (for their nature, physico-chemical characteristics, behaviour, and ecotoxicity), in order to try and make a statistical treatment leading to some trends for possible prediction capacity. In a 1st step, all bibliographical data available on ISB has consequently been collected, resulting in an amount of 20,100 references. Then, only documents focusing on the oils' characteristics, the burning residues and atmospheric emissions, their fate and the environmental and societal impacts, were selected and further analysed (scientific articles, peer reviewed papers, operational guidelines, JIP reports and presentations, etc.). In this work, the air (smokes generated to the atmosphere) and water (air/water interface, water column and seafloor) compartments have been treated separately, because the composition and the fate of the ISB products are specific to each environment. Ideally, references showing results on both compartments were desired.

Selection of crude oils

This initial dataset is composed of six different crude oils selected on the basis of their density and relative composition to cover a wide range of oil types (Table 1): 2 very light oils (LO1 and LO2), 2 medium oils (MO1 and MO2) and 2 heavy crude oils (HO1 and HO2). MO2 and LO2 are paraffinic oils and in solid state at 20°C.

Table 1. Properties of crude oils.

Name	Viscosity (mPa.s) (20°C)	Density (20°C)	SARA distribution (%wt)	*n*-alkanes (µg/g)	PAHs (µg/g)
HO1	2480	0,957	42 / 22 / 30 / 6	882	6 101
HO2	137	0,921	57 / 16 / 23 / 4	1 133	11 936
MO1	92	0,890	54 / 12 / 27 / 7	80 106	7 944
MO2	nm	0,858	82 / 4 / 13 / 1	183 181	19 370
LO1	2,9	0,827	62 / 6 / 30 / 1	123 112	15 335
LO2	nm	0,815	75 / 4 / 19 / 2	336 963	10 949

nm: not measured (paraffinic oils solid at 20°C).

Burn experiments were conducted on the fresh crude oils and corresponding artificially weathered oil samples (evaporated, oxidised, and emulsified), in order to consider the influence of weathering on burning process and outcomes.

Protocols for oil weathering simulation

To simulate the main weathering processes at sea, the 6 crude oils were exposed in laboratory to a systematic, stepwise procedure including distillation at 3 different temperatures (vapor temperatures of 150, 200 and 250°C) and emulsification (50% water, 75% and maximum uptake) and photoxidation processes (4 days exposition to UV). The protocols are detailed respectively in Stiver and Mackay (1984) and Hokstad *et al*. (1993). In the end, for a given starting crude oil, this protocol leads to a maximum of 16 weathered oil samples, so potentially a total of 102 oil samples (crude and weathered) to be tested. In fact, due the nature of the crude oils, some weathered samples were not obtained as some of the weathered oils could not be burnt, thus limiting the number of tested conditions.

Lab-scale burning experiment: the "burning bench"

The lab-scaled experiments were performed on an in-house equipment (Jézéquel *et al.*, 2014) presented in Fig.1. The oil slick (100 mL, 10 mm thickness) was maintained in a 10-cm diameter ring (h = 3 cm, ø = 10 cm) placed in a 5-L beaker of sea water (h = 30 cm, ø = 20 cm). The thickness of the slick was settled at 10 mm because it is the minimum level from which the burning efficiency does not evolve (Garo *et al.*, 1994; Cedre, 2013). A propane torch was used for ignition (Fig.1B) and, in order to avoid the boil over phenomenon, a magnetic stirrer ensures a continuous temperature homogenization in the water column. The experiments were conducted in a glass-secured enclosure (Fig.1A) where soot was recovered by cyclonic effect using an extractor hood (Fig.1B). After burning, oil residues were recovered for laboratory analyses.

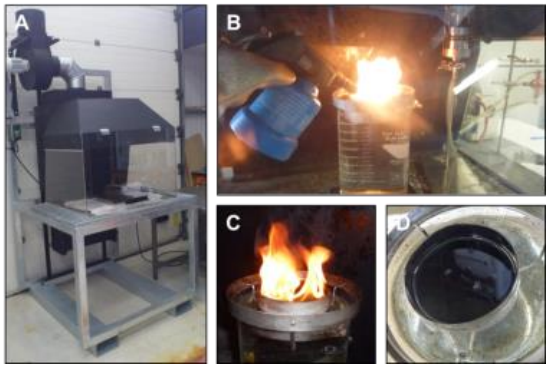

Figure 1. Lab-scaled burning experiment; A) in-house experimental set-up; B) ignition of the slick; C) burning phase; D) residue obtained after burning experiment.

Pilot scale burning experiment: INERIS facility

The pilot-scale experiments were conducted at INERIS institute (France) in a dedicated "1000m^3 burning room" (Fig.2A). The oil slick (20 L, 10 mm thickness) was disposed on a 2-m^2 sleeve full of salted water (35 g/L), in a confinement ring of 160 cm diameter. Water-circulation with a pump allows keeping the water at a constant temperature. Ignition was performed manually by using a propane torch (Fig.2B). After burning, residues were recovered manually for in-site quantification (Fig.2D). Further analyses were then performed at Cedre laboratory. Parameters such as atmospheric pressure, temperatures or sleeve weight were measured in real time thanks to various captors. In addition, an exhaust fan was used to extract and canalize the smoke plume to a control unit where a Fourier-transform infrared (FTIR) spectrometer measures gaseous compounds concentrations.

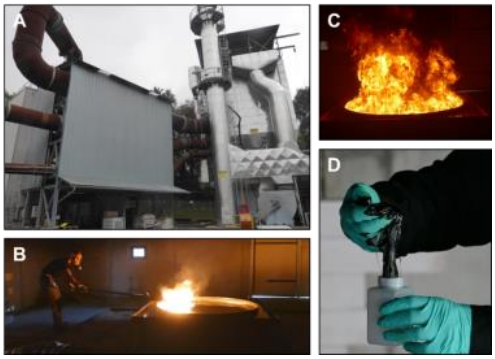

Figure 2. Pilot-scaled experiments conducted at INERIS institute; A) INERIS facilities: 1000 m^3 burning room on the left, smoke plume collection device on the right; B) ignition of the oil slick; C) burning phase; D) residue recovery.

Four out of the 6 fresh crude oils studied at lab scale have been selected to be tested at pilot scale on the basis of the results of burning efficiencies obtained at lab scale. Thus, only HO2, MO1, LO1 and LO2 oils have been selected. In addition, burning operations on LO1 and HO2 have been repeated, resulting in a pilot-scaled dataset of 6 experiments.

Characterization of oils and burn residues

In order to compile a complete dataset enabling to apply multivariate statistical tools, the following characterizations were carried out on crude and weathered oils as well as burn residues: density, SARA distributions, *n*-alkanes and PAHs concentrations, biodegradability, and ecotoxicity. On the atmospheric emissions, those obtained during the lab-scale experiments were characterized for the soot amount while for those obtained during pilot-scale experiments, the following measurements were made: gas composition (CO, CO_2, O_2, NOx, SO_2, HCt, CH_4, C_2H_2, C_2H_4), soot amount, black carbon, heat flow.

Physico-chemical characterization

Density, Viscosity, and SARA fractionation

The density of the samples of surface oil was determined according to the ASTM method ASTM D5002: 2013 (ASTM, 2013). The viscosity of the oil samples was measured by establishing the rheological curve using a Haake VT 550 viscosimeter at 20°C.

The evolution of the oil composition was assessed by fractionation into 4 chemical families. Asphaltenes were precipitated in *n*-pentane and were filtered on a glass fibre filter. The maltene fraction was then separated on a silica-alumina column (30 cm x 1 cm). Saturates were eluted with *n*-pentane, aromatics with a *n*-pentane/dichloromethane 80/20 mixture, and resins with a mixture methanol/ dichloromethane 50/50. The various fractions were weighed after evaporation of the solvent and stabilization of the masses.

Quantification of n-alkanes and PAHs

The internal standard method was used for *n*-alkanes and PAHs quantification. More details are presented in Jézéquel *et al.* (2019).

Biodegradability testing

A protocol adapted from De Mello *et al.* (2007) was used to simulate the biodegradation process. Nutrients were added to the water, in accordance with the French standard NFT 90-347 (AFNOR, 1990). The protocol is fully described in Jézéquel *et al.* (2019).

Dispersion and Emulsification testing

The chemical dispersibility of the residue were measured by using the IFP test method (NF T 90-345 French Standard) at 20°C with a reference dispersant (Finasol OSR 52).

The emulsification of burn residues was assessed according to the protocol described previously. Briefly, emulsions were formed by rotating cylindrical separatory funnels containing equal amount of water and burn residue. After 24 hours of agitation, the emulsion was recovered, and its water content was measured according to the ASTM D95-05 (2010).

Ecotoxicity testing

The ecotoxicity tests were conducted on a marine bacteria *Vibrio Fischeri* and a marine algae *Phaeodactylum tricornutum*. For each organism, standardized protocols were followed: NF EN ISO 11348-3 (2009) for the marine bacteria and NF EN ISO 10253 (2016) for the algae.

To assess the ecotoxicity of burn residue or soot, WAF (water accommodated fraction) were prepared following the CROSERF protocol (Chemical Response to Oil Spills Ecological Effects Research Forum) (Aurand et Coelho, 1996).

Statistical analyses

The statistical developments are performed by using MATLAB® environment, version 9.6, and the Eigenvector PLS_toolbox, version 8.7. Principal component Analysis (PCA) and Partial Least Squares (PLS) regression method are used as multivariate statistical methods.

RESULTS AND DISCUSSION

"Predictive" literature study

The initial aim of the "predictive" literature study was to infer general modeling trends from statistical treatment of the composition, fate, and impact data of burn products (on both solid residues and smokes), and the physico-chemical characteristics of the starting oils. Although the study revealed a large amount of publications dealing with ISB, it soon appeared that this statistical approach was not possible in practice because (i) very few papers are exploitable: from the 60 peer reviewed papers, reports and technical documents selected and analyzed, only 26 reference documents appeared to contain relevant information and data for the study, (ii) most of the reference papers either deal with the water compartment (burn residues) or air compartment (soot, particles, gases…) but very few with both, (iii) there is a lack in the physico-chemical data of the starting oil as well as of the burn products: most papers mainly focus on density and PAH issues, and (iv) for the data recovered, there is a lack of well documented and standardized protocols, which prevents from validated direct comparison between studies; additionally, burn conditions and efficiencies addressed can be different from one paper to the other as well.

In the end, only 12 different oils can be considered (6 light oils, 5 medium oils, and 1 heavy oil), with very few data directly taken from the papers. They have thus been completed with proxy data found in the literature or calculated. From this analysis and from selected reference studies (Allen and Ferek, 1993; Ross et al., 1996; Faksness et al., 2012; Shigenaka et al., 2015; Stout and Payne, 2016; Gullett et al., 2017), some general trends have however been inferred, and we will limit here to the following: (i) Except for the DWH case, the fate of residues after burning (float or sink) is not well known and can vary on "external" conditions. The density of burn residue depends on the density of the starting oil, but also on the SARA composition of the latter; (ii) CO2 and CO are the main atmospheric compounds and their

contents are less dependent on oil composition than the other compounds; (iii) Ecotoxicity of products after ISB seems to be lower but is still poorly documented.

Experimental study: Physico-chemical analysis

Burning efficiency

Burning efficiency (BE) can be defined as : $\mathrm{BE}\,(\%) = (1 - \frac{residue\ quantity}{initial\ quantity}) \times 100.$

In our study, BEs obtained for the lab-scale experiments (10 cm pool) range between 15% for the paraffinic MO2 oil and 58% for the LO2 light oil. Additionally, BEs tend to decrease with increasing weathering levels (Fig.3).

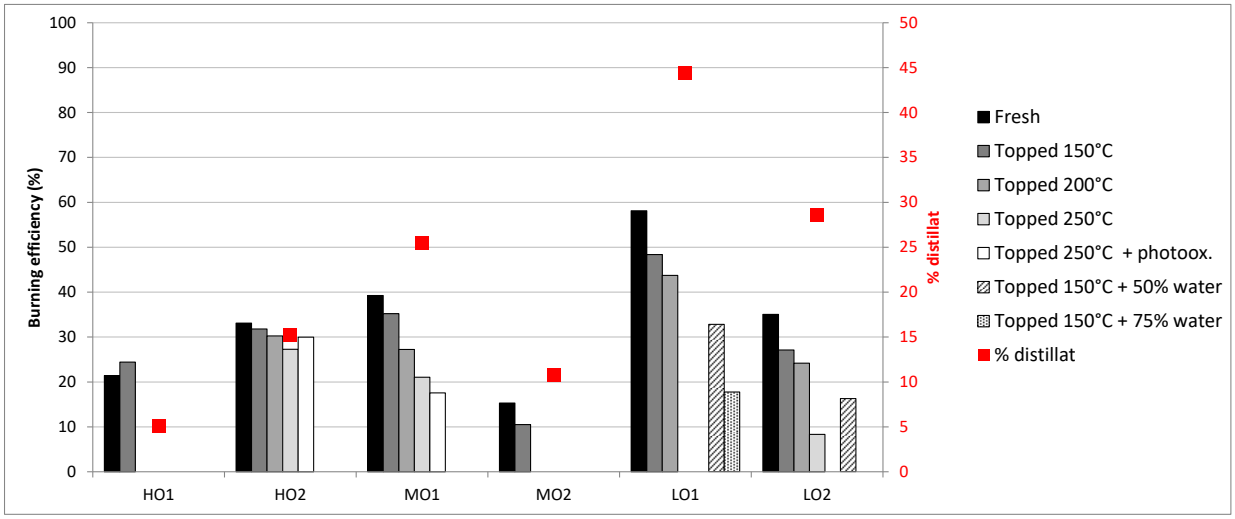

Figure 3. Evolution of burning efficiencies for the 6 crude oils (non-ignitable weathered oils are not presented).

Additionally, there is also an excellent correlation between BE of crude oils and % distillate of oils obtained during topping operation. Comparison with the pilot-scale experiments (160 cm pool) shows that BEs are higher with larger fire pools (Fig.4), with values lying in the 80-90% range. These results are in concordance with the results from literature which usually exceed 80% for fresh crude oils (SL Ross, 1999).

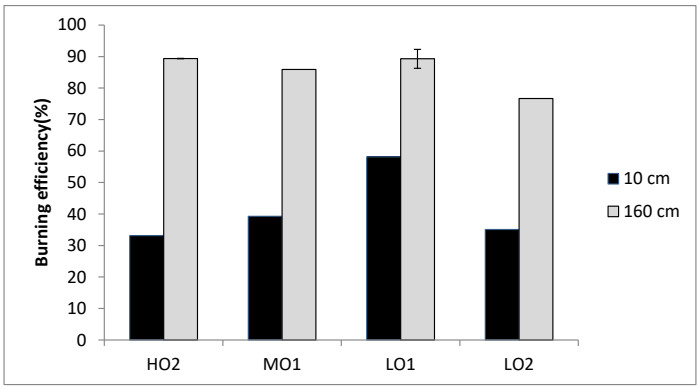

Figure 4. Evolution of burning efficiencies for 4 crude oils according to oil slick diameter (cm).

Integration of data obtained from previous burn experiments conducted at Cedre (not shown here) tend to indicate that a maximum of BE is reached from ca. 70cm-1m pool diameter.

Physico-chemical characterization of burn residues

Evolution of densities and viscosities obtained on raw samples before burning (fresh crudes and weathered oils) and on residues after burning, show very interesting features that can be summarized as follows (cf. Fig.5): (i) density and viscosity of burning residues significantly increase compared with starting crude or weathered oils, (ii) while density and viscosity both increase with weathering level, the latter has almost no influence on the density of corresponding burning residues, which tend to reach a maximum level for a given starting oil, (iii) density and viscosity of residues are higher in pilot scale experiments, with highest density values close to density of sea water and (iv) paraffinic oils follow a specific lower density trend.

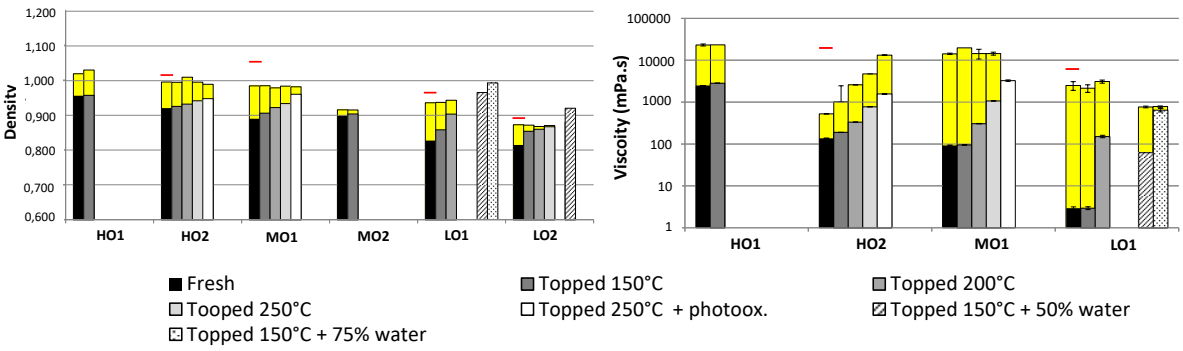

Figure 5. Evolution of density (left) and viscosity (right) of crude and weathered oils, and their corresponding burn residues (yellow bars addition) for the 6 oils tested at lab scale, and for the 4 oils tested at pilot scale (red lines).

The geochemical analyses highlight the following features (Fig.6): (i) the SARA composition of the burn residues closely depends on SARA composition of the starting crude oils, (ii) there is a tendency to have an increase in asphaltenes and aromatics contents for heaviest oils (all the more if BE is high), and (iii) there is a tendency to have an increase in asphaltenes and decrease in resins for lighter oils.

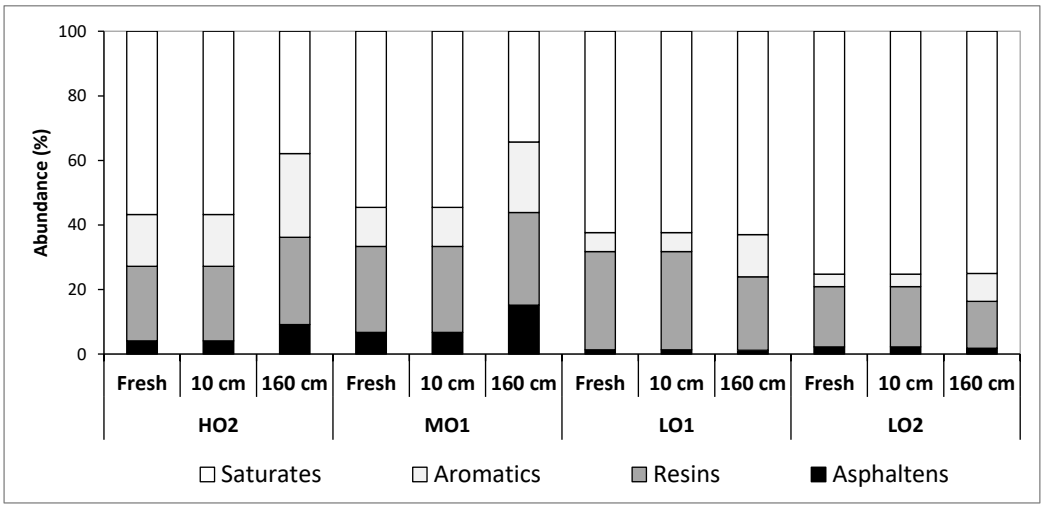

Figure 6. Evolution of SARA distribution between the 4 fresh oils and their burn residues collected after lab-scale burns (10 cm) and pilot-scale burns (160 cm).

At the molecular level, the following trends are observed: (i) *n*-alkanes and PAHs contents strongly decrease in burning residues, (ii) whatever the weathering levels, *n*-alkanes and PAHs contents in residues remain at similar levels, (iii) weathering induce loss of lighter *n*-alkanes and there is also a significant loss of *n*-alkanes in burning residues (up to *n*-C26), (iv) burning has a bigger impact on loss of *n*-alkanes than the maximum weathering effect (250°C evaporation & photo oxidation), (v) for PAHs in burn residues, there is a complete loss of benzothiophene's, a very pronounced loss of naphthalene's, a partial combustion of compounds up to dibenzothiophene, and preservation of heavier compounds, and (vi) the loss of lighter *n*-alkanes and PAHs is much more pronounced for pilot-scale experiments than on burning bench (influence of BE).

Behavior of burn residues

Whatever the oil type, the burn residues appear to be non-dispersible and non-emulsifiable. Additionally, they are very poorly biodegradable compared to crude oil, all the more for residues obtained during pilot-scale experiment, hence demonstrating an influence of burning efficiency (Fig.7).

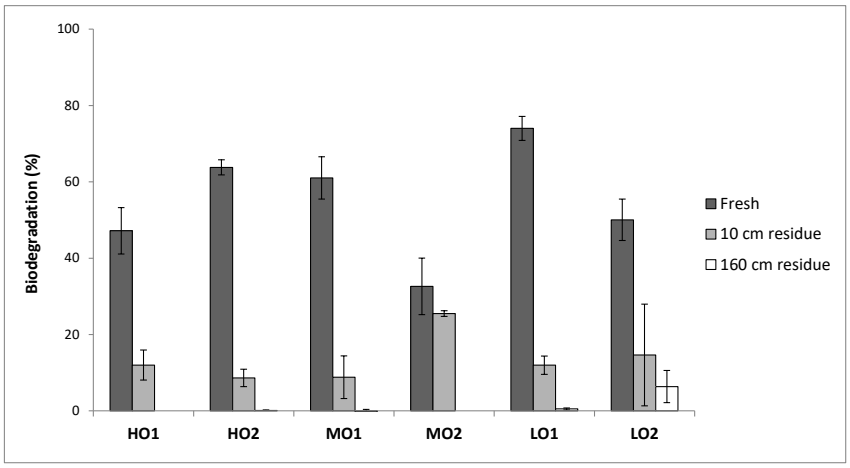

Figure 7. Comparison of biodegradability (n=3) of fresh oils and their burn residue collected after lab-scale burn (10 cm) and pilot-scale burns (160 cm).

Physico-chemical characterization of atmospheric compounds

As already shown in previous studies, atmospheric emissions are mainly composed of gases (CO_2, CO, NOx, PAHs, VOCs,…), and particulate matter under the form of soot. Additionally, the following observations were made in our study for the soot part: (i) the quantity of soot emitted is clearly proportional to the burning efficiency and tends to decrease with oil weathering (cf. Fig.8), (ii) there no clear tendency of decrease or increase in total PAHs contents in soot from large scale testing compared to lab-scale bench burns, but at molecular level the heavier PAHs are only present in soot from large-scale experiments, which is probably due to higher BEs.

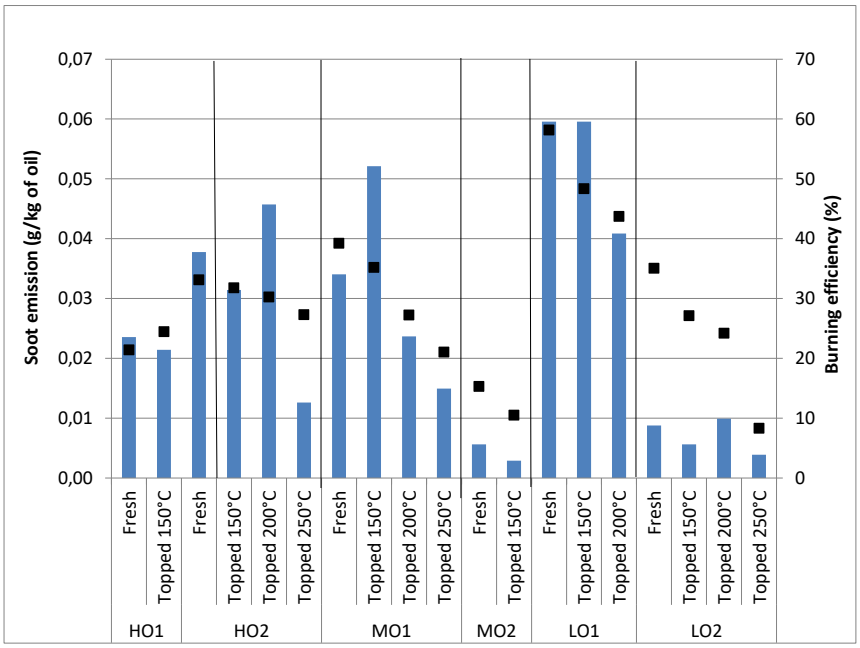

Figure 8. Evolution of the quantity of soot emitted during lab-scale burning (blue bars), compared to burning efficiencies (black dots).

For the gas part, similar concentrations in gaseous compounds for the different crude oils burnt, with predominance of CO_2 and CO, are observed. However, it can be noted that there is a significative presence of SO_2 in gas emissions for the sulphur-containing oils (MO1 and HO2, containing 0.5 to 1% S) (cf. Fig.9).

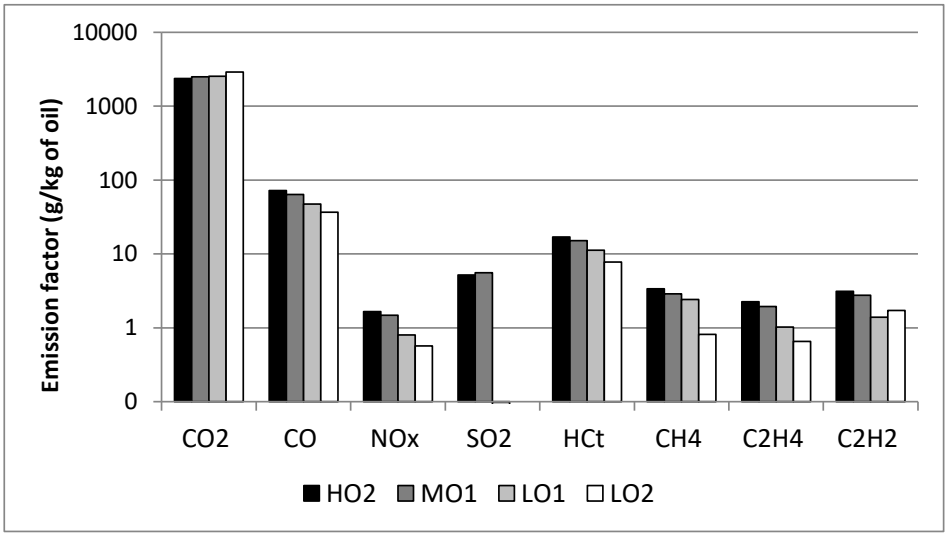

Figure 9. Distribution of gaseous products from pilot-scale burns.

Experimental study: Ecotoxicological analysis

Ecotoxicity testing on marine bacteria of the burn residues of the different crude oils shows that (i) % inhibition for burn residues strongly decreases compared to starting crude oils, even

more with increasing burning efficiency, and (ii) this decrease in ecotoxicity with burn efficiency comes along with a decrease in total PAH content of corresponding WAFs. However, there is no clear correlation between total PAH contents and % inhibitions (Fig.10).

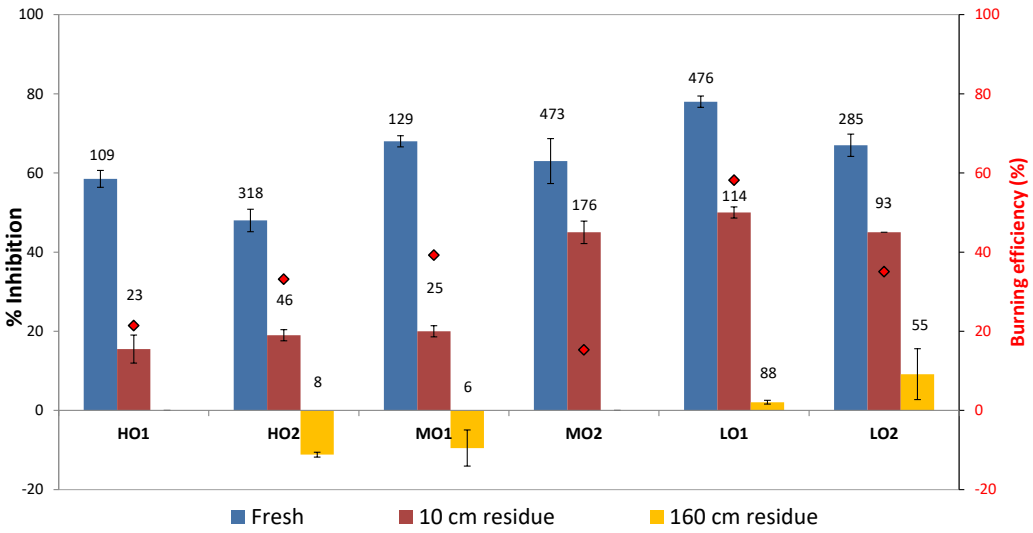

Figure 10. : Inhibition of marine bacteria bioluminescence (Microtox® test) after exposition to WAF from fresh oils and burn residues (lab- and pilot scale burns). Black numbers correspond to PAHs concentrations (µg/L). Red squares refer to burning efficiency (%).

Whereas the 6 starting crude oils can be considered as toxic to extremely toxic to *Vibrio fisheri* bacteria, the resulting burn residues appear to be non-toxic to slightly toxic according to scales in Microtox FX handbook (ModernWater, 2017) and Santiago *et al*. (2002). It is also observed that the % inhibitions of oils tend to decrease with increasing oil weathering levels, revealing a decrease in ecotoxicity. In the same time, the % inhibitions of burn residues of weathered oils also strongly decrease compared with corresponding starting weathered oils. However, the weathering level seems not to play a major role in the variation of the % inhibitions of the corresponding burn residues: for a given starting oil, % inhibitions values appear to be comparable whatever the weathering level (not shown here).

For the soot and water samples, the % inhibitions values recovered show that these fractions exhibit no ecotoxicity in the tested conditions (results not shown here).

Statistical study: Development of predictive models

The aim here is to highlight the most important correlations and estimate the feasibility of predicting parameters of ISB products from crude oil characteristics. Multivariate regression models have been performed to evaluate the feasibility of predicting burning efficiency and residue density from the physicochemical characteristics of the crude oils. First, the developments focused on lab-scaled samples representing the major part of the burns conducted. As an example, the predictive performances of the regression model of residue density are presented on Fig.11A.

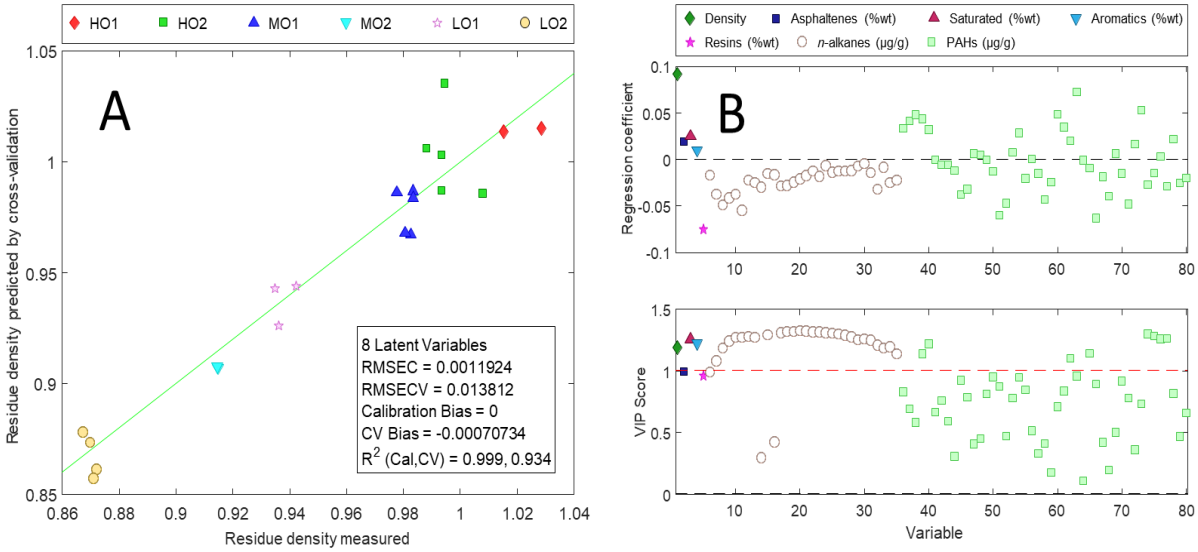

Figure 11. A - Predictions (cross-validation) vs. measured residue densities for the 21 lab-scale burns. B - Corresponding regression coefficients (top) and VIP scores (bottom) obtained for the 80 variables (density, SARA distribution, 30 *n*-alkanes and 45 PAHs concentrations).

Comparing experimental residue densities to predictions, the regression model is satisfactory: (i) RMSECV (Root Mean Square Error of Cross-Validation) is low compared to the range of residue density, (ii) determination coefficient (R^2) is 0.934. The correlations are then determined via the regression coefficients of the model and the most important variables (VIP) associated: plots over the red dotted line in Fig.11B bottom. It appears that there is a correlation between the residue density and the crude oil density, its SARA composition, *n*-alkane concentrations and some of PAHs concentrations (alkylated benzothiophenes and heaviest PAHs). The same work is performed for burning efficiency, which exposes

correlations with the crude oil density, its concentrations in lightest *n*-alkanes (*n*-C_{10} to *n*-C_{12}) and its PAHs concentrations. Then, an extension to pilot-scaled samples was performed and, as observed previously for burning efficiency and residue composition, the model highlighted an important scale dependency. Nevertheless, by introducing a variable expressing the size of experiment, we merged lab- and pilot-scale burns and developed acceptable and satisfactory regression models. The gas emissions of burn experiments were monitored during pilot-scale burns, and regression models were thus developed in order to predict the emissions according to crude oil characteristics. The models exposed correlations between the different weights of gas emitted and physicochemical properties of the crude oils (density, SARA composition, total *n*-alkane concentration). Even if the models were acceptable, univariate developments demonstrated the potential of developing more simple models. As exposed previously (Fig.9), SO_2 emission appeared to be highly correlated to the sulphur part of crude oil composition. Regression models were also developed to evaluate ISB ecotoxicological impacts based on predictions of bioluminescence inhibitions (Microtox® tests) of different WAFs samples (oils, residues, soot) and samples of water collected after burn experiments. The models were acceptable for WAFs of crude oils and WAFs of residues, demonstrating the feasibility of predicting ecotoxicity from crude oil PAH compositions (results not shown here). Regression models for WAFs of soot and samples of water collected after burning experiments were not consistent as the ecotoxicity of these samples was negligible.

CONCLUSION

This 3-phase study (bibliography, burn experiments, statistical treatment) has generated an unprecedented amount of ISB data (ca. 25,000) which brings a noticeable increase of knowledge in our prediction capabilities for the composition, fate and impact of burn products from various oil types generated during ISB OSR operation. This study shows that: **(i)** Once ignition is successfully started (not the purpose of this study), maximum burn efficiency (ca.

80-90%) should be reached with a burning oil pool diameter exceeding 1m. However, special attention is to be paid to paraffinic oils which appear to be poorly ignitable, **(ii)** The physico-chemical properties of a crude oil have a direct influence on the nature and fate of the products generated during ISB operation, especially for the solid residues. While the heavier oils tend to produce the heavier burn residues (but not the only driver), density of the latter should not exceed values close to sea water in most real cases. However, sinking of heavier residues in time will mostly happen under adverse climatic conditions and mixing with mineral and biological matter in the water column. Since residues appear to be non-dispersible and very poorly biodegradable, they should be collected during OSR operations to avoid any risk of sinking or stranding; (**iii**) For the air compartment, special attention should be paid to sulphur-containing oils, which can produce SO_2 during burning, and which associated risks should be specifically addressed; and (**iv**) toxic to very toxic oils will generate non-toxic to very poorly toxic products after ISB operation; in particular, soot and water after burning are non-toxic to *Vibrio fisheri* bacteria.

Acceptable preliminary regression models have been established to predict burn efficiency, residue density, weight of individual emitted gas, and ecotoxicity of burn products, from physico-chemical key features of starting oils, with good perspectives for improvements and additional regression models. All the information and data collected during this study should help further developing full predictive ISB models and addressing objectively the relative impact of ISB within the SIMA process in comparison with other OSR techniques.

REFERENCES

AFNOR NFT 90-347. 1990. Essais des eaux – Produits dispersants – Évaluation en milieu aqueux de l'action inhibitrice sur la biodégradabilité du pétrole.

AFNOR NFT 90-345. 1990. Essais des eaux – Produits dispersants – Évaluation en milieu marin de l'efficacité vis-à-vis de la dispersion du pétrole.

Allen, A.A., and Ferek, R.J., 1993. Advantages and disadvantages of burning spilled oil, in: International Oil Spill Conference. American Petroleum Institute, pp. 765–772.

ASTM D95-05, 2010. Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation. American Society for Testing and Materials International, West Conshohocken, PA.

ASTM D5002 - 13, 2013. Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer. ASTM. American Society for Testing and Materials International, West Conshohocken, PA.

Aurand, D., Coelho, G., 1996. Proceedings of the Fourth Meeting of the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF). Ecosystem Management & Associates, Purdellville, VA. Report 96-01, 50 p.

Cedre, 2013. Étude expérimentale sur le brûlage de nappe. R.13.05.C/3232. Cedre, p. 24.

Daling, P. S. and Strøm, T., 1999. Weathering of Oils at Sea: Model/Field Data Comparisons, in Spill Science and Technology Bulletin., 5 (1), pp. 63-74.

De Mello, J.A., C.A. Carmichael, E.E. Peacock, R.K. Nelson, J. Samuel Arey, and C.M. Reddy. 2007. Biodegradation and environmental behavior of biodiesel mixtures in the sea: An initial study, Marine Pollution Bulletin, 54: 894–904, 2007.

Faksness, L.G., Hansen, B.H., Altin, D., and Brandvik, P.J.2012. Chemical composition and acute toxicity in the water after in situ burning – A laboratory experiment, Marine Pollution Bulletin, 64: 49-55. doi: 10.1016/j.marpolbul.2011.10.024 2012, pp 49-55.

Fingas, M. 2016. In-situ Burning: An Update, in Oil Spill Science and Technology. 2nd Edition. Edmonton, AB, Canada: Gulf Professional Publishing, pp. 483–676.

Garo, J. P., Vantelon, J. P. and Fernandez-Pello, A. C. 1994. Boilover burning of oil spilled on water, Symposium (International) on Combustion. (Twenty-Fifth Symposium (International) on Combustion), 25(1), pp. 1481–1488.

Gullett, B. K., Aurell, J., Holder, A., Mitchell, W., Greenwell, D., Hays, M., Conmy, R., Tabor, D., Preston, W., George, I., Abrahamson, J.P., Vander Wal, R. and Holder, E. 2017. Characterization of emissions and residues from simulations of the Deepwater Horizon surface oil burns, Marine Pollution Bulletin, 117(1), pp. 392–405. doi: https://doi.org/10.1016/j.marpolbul.2017.01.083.

Hokstad, J.N., P.S. Daling, A. Lewis and T. Strom-Kristiansen, 1993. Methodology for Testing Water-in-Oil Emulsions and Demulsifiers – Description of Laboratory Procdures, Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings, MSRC Technical Report Series 93-018, Marine Spill Response Corporation, Washington, D.C., pp. 239-254.

IPIECA-API-IOGP, 2017. Guidelines on implementing spill impact mitigation assessment (SIMA), IOGP Report 593.

Jézéquel, R, Duboscq, K., Valladeaud, F. and Le Floch, S. “Fate, Behavior and Impact Assessment of Biodiesels in Case of an Accidental Spill”. Proceedings of the 42nd AMOP technical seminar, Environment and Climate change Canada, Ottawa, Canada, pp. 919-939. 2019.

Jézéquel, R., Simon, R. and Pirot, V. 2014. Development of a burning bench dedicated to in situ burning study: assessment of oil nature and weathering effect, Proceedings of the Thirty-seventh AMOP Technical Seminar on Environmental Contamination and Response, 2014, pp. 555–566.

Khanmohammadi, M., Garmarudi, A.B., Garmarudi, A.B., de la Guardia, M., 2012. Characterization of petroleum-based products by infrared spectroscopy and chemometrics. TrAC Trends in Analytical Chemistry 35, 135–149. https://doi.org/10.1016/j.trac.2011.12.006

Lamine, S. and Xiong, D. 2013. Guinean environmental impact potential risks assessment of oil spills simulation., Ocean Engineering, 66, pp. 44–57. doi: https://doi.org/10.1016/j.oceaneng.2013.04.003.

ModernWater, 2017. Microtox® FX Analyser - User Manual. 34 pp.

NF EN ISO 10253:2016. Qualité de l'eau -- Essai d'inhibition de la croissance des algues marines avec *Skeletonema sp*. et *Phaeodactylum tricornutum*. 20 p.

NF EN ISO 11348-3 : 2009. Qualité de l'eau - Détermination de l'effet inhibiteur d'échantillons d'eau sur la luminescence de *Vibrio fischeri* (Essai de bactéries luminescentes) - Partie 3 : méthode utilisant des bactéries lyophilisées.

Perring, A.E., Schwarz, J.P., Spackman, J.R., Bahreini, R., de Gouw, J.A., Gao, R.S., Holloway, J.S., Lack, D.A., Langridge, J.M., Peischl, J., Middlebrook, A.M., Ryerson, T.B., Warneke, C., Watts, L.A., Fahey, D.W., 2011. Characteristics of black carbon aerosol from a surface oil burn during the Deepwater Horizon oil spill. Geophysical Research Letters 38. https://doi.org/10.1029/2011GL048356

Reddy, C.M., Arey, J.S., Seewald, J.S., Sylva, S.P., Lemkau, K.L., Nelson, R.K., Carmichael, C.A., McIntyre, C.P., Fenwick, J., Ventura, G.T., Van Mooy, B.A.S., Camilli, R., 2012. Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. Proceedings of the National Academy of Sciences 109, 20229–20234. https://doi.org/10.1073/pnas.1101242108

S.L. Ross Environmental Research Ltd. 1999. Laboratory testing to determine in situ burning parameters for six additional U.S. OCS crude oils. Final Project Report, U.S. Minerals Management Service, Herndon, VA, 41 p.

S.L. Ross Environmental Research Ltd. 2002. Identification of Oils that Produce non-Buoyant In Situ Burning Residues and Methods for their Recovery. API DR145. Ottawa, ON: S.L. Ross Environmental Research Ltd.

Ross, J.L., Ferek, R.J., and Hobbs, P.V., 1996. Particle and gas emissions from an In Situ Burn of crude oil on the ocean. ISSN 1017-3289 J. Air & Waste Manage. Assoc. 46: 251-259.

Santiago, S., Becker van Slooten, K., Chèvre, N., Pardos, M., Benninghoff, C., Dumas, M., Thybaud, E., Garrivier, F., 2002. Guide pour l'utilisation des tests écotoxicologiques avec les daphnies, les bactéries luminescentes et les algues vertes, appliqués aux échantillons de l'environnement 55 p.; 30 cm.

Shigenaka G., Overton E., Meyer B., Gao H., and Miles S., 2015. Physical and chemical characteristics of in situ burn residue and other environmental oil samples collected during the Deepwater Horizon spill response, Conference paper, Interspill 2015, Amsterdam, Netherlands, https://www.researchgate.net/publication/274897699.

Stiver, W., Mackay, D., 1984. Evaporation rate of spills of hydrocarbons and petroleum mixtures. Environmental Science & Technology 18, 834–840. https://doi.org/10.1021/es00129a006

Stout, S. A. and Payne, J. R. 2016. Chemical composition of floating and sunken in-situ burn residues from the Deepwater Horizon oil spill, Marine Pollution Bulletin, 108(1), pp. 186–202.