WP3 – Application of response tools: in situ training and table top exercises

D3.3 – MANIFESTS sea trial & catalogue of sensors and their HNS detection capacity

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Glossary

ADR: Agreement concerning the International Carriage of Dangerous Goods by Road

CEPPOL: Centre of practical Expertise for anti-pollution

ECHA: European Chemicals Agency (ECHA)

FLIR: Forward Looking Infrated

HDPE: High Density Polyethylene

HNS: Hazardous and Noxious Substance

IMDG: International Maritime Dangerous Goods code

PTFE: polytetrafluoroethene

SEBC: Standard European Behaviour Classification

UAV: Unmanned Aerial Vehicle

Executive summary

Responding to a spill at sea is always challenging, especially when the chemicals involved are liquids with high vapour pressure (i.e. > 3 kPa) or liquefied gases. The slicks formed will rapidly evaporate and potentially form toxic, flammable or even explosive gas clouds. It is therefore essential to characterise the risks issued from the evaporation of such substances in order to adapt the response and guarantee safety of first responders.

To improve understanding of the actual behaviour of chemicals spilled at sea, CEPPOL (French Navy) and Cedre have been jointly organising experiments involving real spills of oil and HNS at sea for over 20 years, in compliance with international regulation. In 2021, CEPPOL (French Navy) provided strong administrative and logistical support to allow the conduct of a preliminary sea trial held at national level, so-called ‘IPOMAC’. This trial involved the response vessel SAPEUR that was used to discharge HNS in seawater and testing available and new sensors.

The overall objectives of the MANIFESTS sea trial were to:

i) test sensors (existing and under development) in order to feed a catalogue of sensors with information from field trial,
ii) validate forecast drifting and atmospheric dispersion models.

Substantial preparation was required to allow the successful discharge of six different HNS. On the one hand the discharge system was tested and, on the second hand, three discharge slots were organised to ensure safe and coordinated aerial flyover of each HNS slick, as several aircraft from military and civil French organisations were involved.

The HNS discharged during the IPOMAC sea trial were butyl acetate, acetone, heptane, methanol, toluene and a mixture of xylene isomers. The sensors tested included a portable FLIR camera from Cedre, an airborne FLIR camera mounted on a UAV (Drone Réponse, France), the FLIR optronic ball on board the French Navy's Caiman helicopter (NH90), optronic systems on board the French Navy's FALCON 50, ATL2 STD5 and ATL2 STD6. Other sensors under development were used and included the HYPERCAM hyperspectral IR camera (TELOPS, Canada, airborne) and the SIMAGAZ multispectral IR camera (ONERA, France, on board vessel).

Considering the success of the IPOMAC preliminary sea trial a second sea trial was organised in 2022 in the framework of the MANIFESTS project, once more with a great support of the French Navy. Using the discharge system, previously tested in 2021, it was possible to i) refine and diversify the HNS discharged at sea, ii) use new airborne sensor (multispectral) and iii) enlarge the number of organisations including from other member states (Belgian). The HNS discharged during the MANIFESTS sea trial were acetone, butyl acetate, N-propyl acetate, Isopropyl acetate, Methyl Ter Butyl Ether (MTBE), toluene, xylenes and soyabean oil. The sensors tested included two portable FLIR cameras from Cedre and Belgian DG Environment, the SIGIS2 camera from the Belgian civil protection and the SIMAGAZ multispectral IR camera from ONERA (France).

Main results from observation made by the different sensors tested are displayed in the following table:

HNS	Detection on board vessel (handled or standoff)		Airborne detection (Aircraft or RPAS)	
	Slick	Vapours	Slick	Vapours
Acetone	IR M+	IR M+ (quantification)	IR, H M+	- M++
Butyl acetate	IR M+	IR M+++	IR, H M+	- M+
Heptane	IR M++	IR M	IR, H /	- /
Isopropyl acetate	IR M++	IR M+++	/ /	/ M+++
Methanol	IR M+	IR M-	IR, H /	- /
MTBE	IR M++	IR M+	/ /	/ M+
N-propyl acetate	IR M++	IR M+	/ M++	/ M+++
Soyabean oil	IR, M -	M- -	/ -	/ M-

Toluene	IR M++	IR M-	IR, H M++	- M-
Xylenes	IR M++	IR M-	IR, H M++	- M-

/ is indicated for absence of experimentation

- is indicated for negative of detection

IR is indicated for positive detection using IR detection based tool

H is indicated for positive detection using hyperspectral detection based tool

Observations made with multispectral camera:

'**M-**': absence of detection or observation

'**M+**' low positive detection, dependent on the observation conditions

'**M++**': positive detection

'**M+++**': detections or observations with automatic detection made with the current processing tool

During the MANIFESTS sea trial, the **SIGIS2** sensor was mounted on the deck of the SAPEUR vessel and provided positive detection for all chemicals released, excepted for soyabean oil, acetone and xylenes. Live positive detection was obtained for MTBE and N-butyl acetate.

<u>Drifting of soyabean oil</u>

The MANIFESTS sea trial offered the possibility to follow the drift of slick(s) using commercial and homemade buoys. Results obtained from forecast model demonstrated a good accuracy compared to actual drift obtained with MOTHY (METEO-FRANCE) and OILMAP (RPS ASA). Moreover, buoys followed similar drift compared to soyabean oil, including homemade buoys.

1. Introduction

Responding to a spill at sea is always challenging, especially when the products involved are liquids with high vapour pressure (i.e. > 3 kPa) or liquefied gases. The slicks formed will rapidly evaporate and potentially form toxic, flammable or even explosive gas clouds. It is therefore essential to characterise the risks issued from the evaporation of such substances in order to adapt the response and guarantee safety of first responders.

To this end, CEPPOL (French Navy) and Cedre have been jointly organising experiments involving real spills of oil and HNS at sea for over 20 years. These trials enable pollution response authorities and first-responders to improve their knowledge of both the behaviour of pollutants discharged in the natural conditions and the response means to be deployed to handle any accidental release at sea.

Such sea trials are performed in compliance with international regulations in force, especially the international convention for the prevention of pollution from ships 1973[1]. Indeed article 2 of MARPOL Convention reminds that "**discharge" does not include release of harmful substances for purposes of legitimate scientific research into pollution abatement or control**. Concerning experimental conditions, a specific area, far from the shoreline is chosen by the French Navy to prevent any marine activity or population from being exposed to a toxic or flammable gas cloud. Cedre also selects chemicals excluding those that could present significate damage for the environment (e.g. classified as marine pollutants as per IMDG code). In these legal and experimental frameworks, an operation order is established and granted by the French Navy to lead sea trials.

In the case of HNS, recent sea trials, enabled to successfully assess the detection capacity of various on board and airborne infrared sensors for the remote detection of volatile chemical slicks and the associated gas cloud.

Last observations made during the MANIFESTS sea trials have been achieved thanks to sea trials spaced out during the last two years. In 2021 the IPOMAC sea trial organised with the support of French Navy allowed to perform sea trial involving national resources, with main objectives to validate the discharge system, test sensors and offer proposer coordination and safe conditions for the aerial manoeuvre. In 2022, the framework of the MANIFESTS project offered the opportunity to scale up the sea trial at international level with objectives to

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[1] https://wwwcdn.imo.org/localresources/en/KnowledgeCentre/ConferencesMeetings/Documents/MARPOL%201973%20-%20Final%20Act%20and%20Convention.pdf

discharge new chemicals, test new sensors and collect observation data in the field to validate models.

The report is structured in three main parts. A first chapter presents the IPOMAC sea trial with main results obtained, reminding that this field trial was necessary in order to prepare properly the MANIFESTS sea trial. The second chapter focuses on the MANIFESTS sea trial that involved European partners. In the first chapters, catalogue of sensors is presented, highlighting performances obtained in the field with innovative sensors.

2. The IPOMAC sea trial

2.1. Objectives

Two main objectives of the IPOMAC sea trial were:

1) To check our ability to handle all administrative and logistical aspects inherent to the organisation of any exercise in real conditions involving the discharge of evaporating (flammable) liquids. Different sub task were to be fulfilled i) regulatory to grant authorisation and comply with regulations in force, ii) logistical to deliver chemicals in due time for the trial and iii) technical to prepare a system to release chemicals at sea. The achievement of this objective was a prerequisite to organise the MANIFESTS sea trial while widening to aircrafts from other European member states.

2) To assess the detection capacity of vapours produced by the evaporation of a HNS slick at sea surface, and, if possible, validate or calibrate forecast models (drifting and atmospheric dispersion).

2.2. Course of the trial

The IPOMAC sea trial was authorised by the French Navy that granted an operation order to perform experimentations. The discharge location was in the Atlantic Ocean, off the island of Sein from the 17th to the 19th of May 2021. The discharge of chemicals was performed in an area of less than 3 nautical miles around the geographical point 47°20’30’’N ; 005°05W.

2.3. Preparation of experimentation

2.3.1. System to release chemicals at sea

The overall system to release chemicals is described in Figure 1 below:

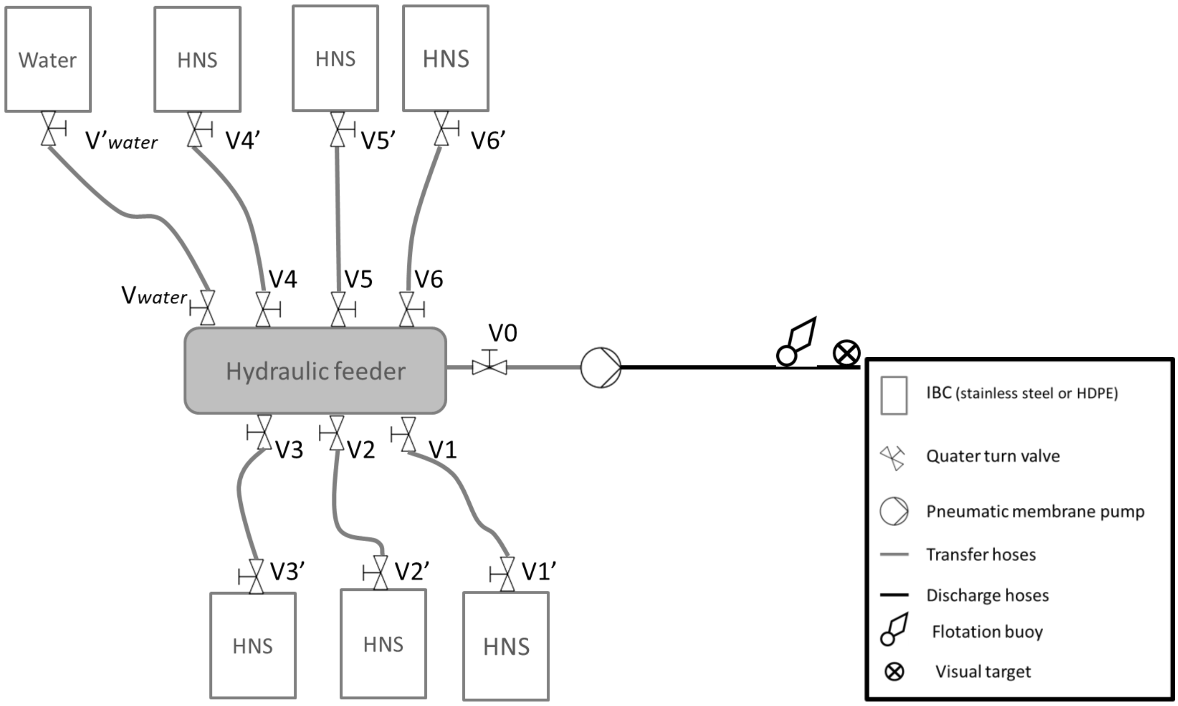
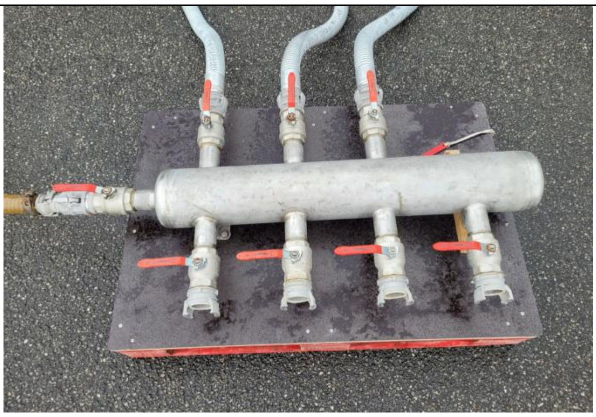


Figure 1: descriptive diagram of the main components of the discharge system.

Each IBC is equipped with a valve at the bottom of the tank: a DN50 type for stainless steel IBCs and a male threaded outlet for HDPE IBCs. For the latter, the connexion of the aluminium pipes to the feeder is allowed thanks to symmetrical half-couplings with a female threaded lock (PP) / DN50 (aluminium).

Individual elements of the release system are presented in Tableau 1.

Tableau 1: individual elements of the release system are presented in the following table

Hydraulic feeder The feeder is surrounded by 7 quarter-turn valves equipped with symmetric DN50 connectors, and fixed to a wooden pallet to facilitate handling.	
Pneumatic membrane pump The reference of the pump is a Husky 2150 pneumatically operated and made up with aluminium, stainless steel and ductile iron. The membrane material is made up with PTFE to ensure the best compromise in terms of compatibility with the chemicals pumped. Male Camlock connectors are used at the inlet and outlet of the pump (2'' diameter). The actual flow rate is 13 $m^3.h^{-1}$ and the pump is certified ATEX Zone 2 (II 2 GD c IIC T4), i.e. location where an explosive atmosphere is not likely to occur during normal operation or, if it does occur, it is of short duration. The pump is equipped with ISO connectors for compressed air supply. Adaptors from ISO to ASIA connectors were required to connect the compressed air circuit of SAPEUR vessel.	

Transfer hoses All hoses connected to the feeder are chemical resistant (composite material) and have symmetric connectors, excepted the 1 m hose connected to the inlet of the pump that has female Camlock connector.	 
Discharge hoses 2x25m lengths black chemical resistant hoses are connected behind the pump to allow the release of chemicals (one by one) at sea.	
Flotation buoy The use of a membrane pump creates pressure surges and leads to the formation of a geyser above the water surface rather than a continuous release. To counteract this effect, which could lead to a rapid evaporation of the chemical discharged, the use of a floating anchor allows simulating a spill slightly in subsurface. The device was also considered compatible with the reduced speed of the SAPEUR vessel during each release. The discharge pipe was towed and positioned on the SAPEUR's deck during movements at higher speeds to avoid any risk of excessive traction on it.	

Visual target To facilitate the location of the slick by the crew of the aircrafts, a high visibility buoy was used to create a sight.	

2.3.2. Safety

A prevention plan was drawn up jointly by the SAPEUR’s crew and Cedre to cover the risks associated with navigation and all issues related to the handling of chemicals. Only personnel identified to handle chemicals related to discharge operations were authorised to approach the IBCs and the spill system. An exclusion zone was also marked on the deck with warning tape.

The following PPE were provided by Cedre (Figure 2):

- Helmet with visor (when using the crane to load IBCs on board SAPEUR vessel);
- Safety shoes;
- Type 3 "organic solvent" protection suits;
- Long nitrile gloves to ensure good forearm coverage in addition to the suit;
- Boot cover or overshoes;
- Full face mask with filter cartridge type AX (for solvents with a boiling temperature below 65°C);
- SOLAS certified lifejacket, standard EN ISO 12402.

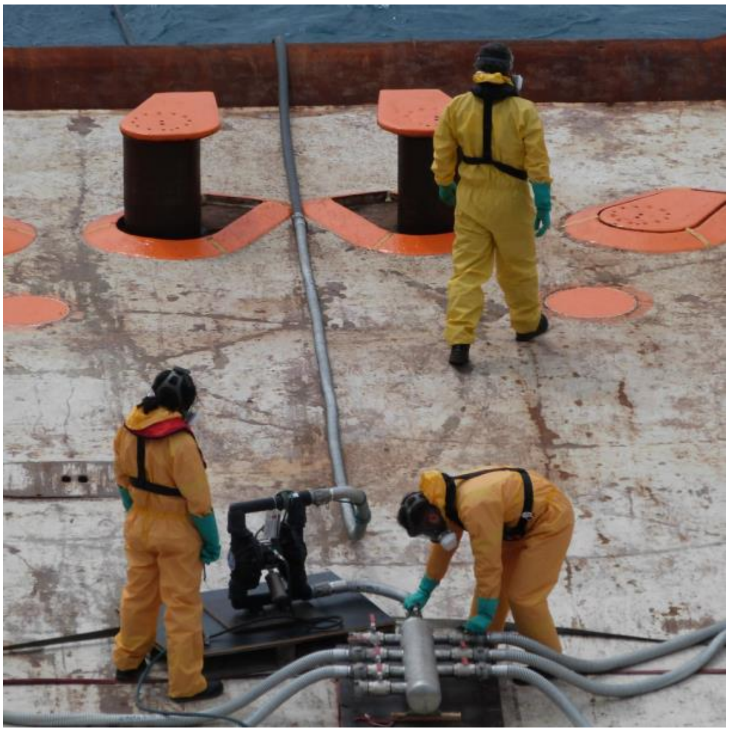


Figure 2: operators on board SAPEUR vessel during discharge of chemicals.

After loading and positioning of the IBCs on board SAPEUR vessel, insulated electrical wires were used to connect all tanks to the SAPEUR's hull which played the role of electric ground.

2.3.3. Storage and transportation of chemicals

The 18 IBCs were directly transported to the facilities of SARP OUEST close to Brest. This company was chosen to ensure safe storage as it is Classified for the Protection of the Environment, in compliance with French regulations. Moreover the site of SARP has the advantage to be close to the naval base of the French Navy which allows to transport and load chemicals on the ship the same day. Following the establishment of a prevention plan, a special authorization was granted to allow the entrance of chemicals in the naval base. Two rounds were then necessary to deliver the chemicals with a flatbed truck. Cedre was responsible for the transport and the ADR transport declaration documents were completed. Once completed the ADR transport declaration documents were sent to the driver from SARP OUEST.

2.3.4. Loading chemicals on board SAPEUR vessel

The SAPEUR vessel (IMO: 9270397) is a Fire Fighting Vessel built in 2003 and sailing under the French flag. She is chartered by the French Navy and its role is to support and provide assistance to other vessels. Its overall length is 74.2 meters and its width is 16.92 meters (Figure 3).

Figure 3: SAPEUR vessel (IMO: 9270397).

The positioning of each IBC on the SAPEUR deck was organised according to the order of discharge and the different sequences to release chemicals at sea, that are specified in section 3.2 Moreover the operation of unloading the truck and loading the ship was defined so that at no time an IBC lifted by the crane passed over another IBC filled with a chemical.

Due to the presence of a fixed roof on the truck's platform, the naval base's safety department granted a waiver for the transporter to take the IBCs out with a forklift and put them down for a short time so that they could be picked up by the SAPEUR's crane with the help of a pallet lifter, lent by the national stockpile centre POLMAR in Brest, and loaded onto the ship's deck (Figure 4). During this same operation, a box of equipment was loaded. The loading, positioning and stowage on the deck of the SAPEUR vessel lasted for half a day.

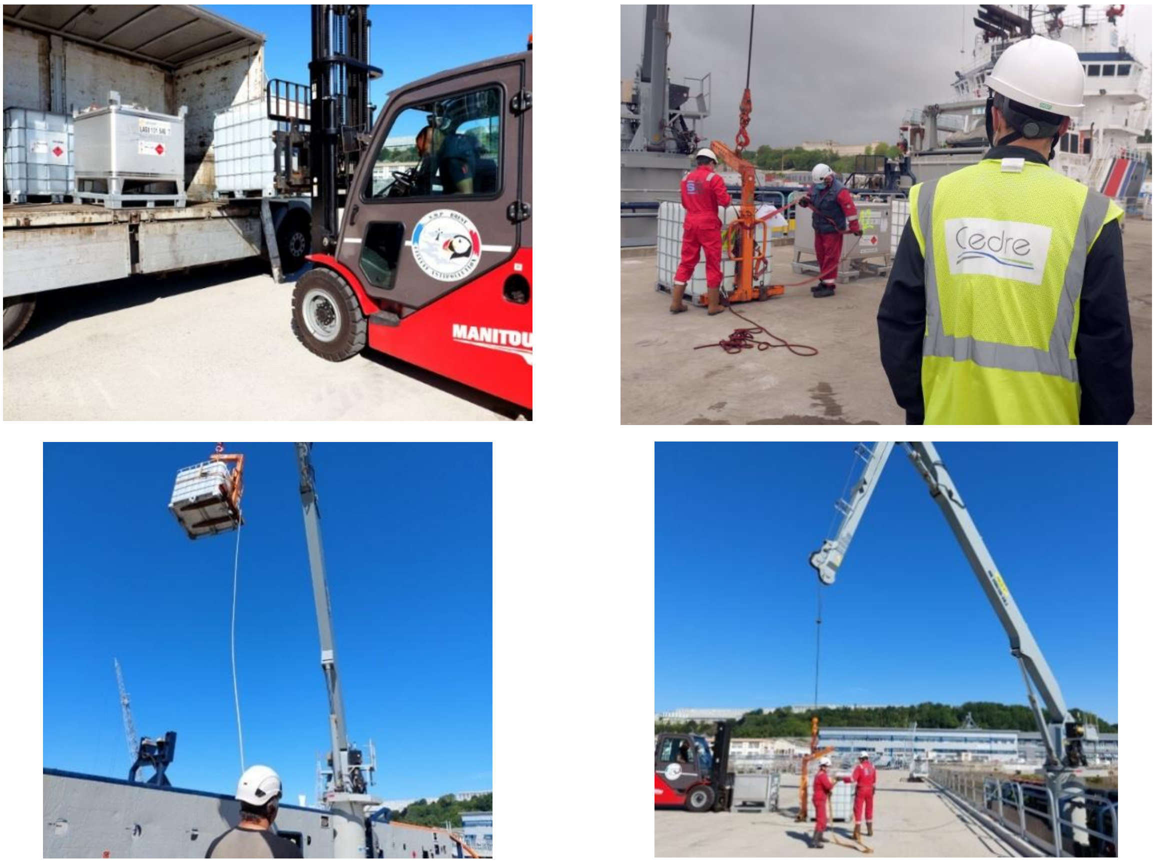


Figure 4: loading operations of chemicals on board SAPEUR on the naval base in Brest.

2.4. Main results

The chemicals discharged during IPOMAC sea trial were butyl acetate, acetone, heptane, methanol, toluene and a mixture of xylene isomers. Soyabean oil was also discharged. Properties of chemicals, including SEBC, are presented in ANNEX I. The sensors tested included a portable FLIR camera from Cedre, an airborne FLIR camera mounted on a UAV (Drone Reponse), the FLIR optronic ball on board the French Navy's Caiman helicopter (NH90), optronic systems for the French Navy, the optronic systems of the FL50, the ATL2 STD5 and the ATL2 STD6, the HYPERCAM hyperspectral IR camera (TELOPS, Canada) and the SIMAGAZ multispectral IR camera (ONERA, France).

During the IPOMAC sea trial, all the infrared sensors deployed were able to detect the chemical slicks. However, the process of evaporation of the products into the atmosphere was only detected by the FLIR portable E75 42° (Cedre) and SIMAGAZ (ONERA, France) cameras.

The SIMAGAZ camera was able to observe three gaseous products in the atmosphere: butyl acetate, acetone and heptane. For the other gases, the SIMAGAZ filters were not suitable and only the surface slicks could be detected.

Hyperspectral camera only demonstrated a capacity to detect spilled chemical slicks but not the associated gas cloud.

Cedre's portable FLIR camera deployed on the deck of the SAPEUR proved effective in detecting two gaseous products: butyl acetate and heptane, in agreement with the observations made by the SIMAGAZ camera.

3. The MANIFESTS sea trial

3.1. Objective

The main objective of the MANIFESTS sea trial was to allow the testing and the calibration of sensors currently used for maritime survey and of sensors under development that may offer an added-value for the detection of gaseous or volatile HNS. Thanks to the experience of the IPOMAC sea trial, different surveillance aircrafts with sensors used in routine (French customs and Belgian coastguard – RBINS) were involved. Due to the relevant results obtained by the multispectral camera during the IPOMAC sea trial, it has been deemed promising to implement such camera both on board vessel and airborne in a plane. This way, this would ensure a combined detection of both the slick and the gas cloud. To this end, an open-sea trial under the responsibility of the French Navy (Maritime Prefecture of Atlantic, Brest) and in conjunction with the CEPPOL and CEDRE was carried out. This trial consisted of the release of 8 HNS (MARPOL Annex II) that were selected according to the results collected through i) the desktop study (task 3.1) performed in the MANIFESTS project, ii) their theoretical behaviour based on the SEBC, iii) their volumes transported at sea and iv) their hazards. Second objective of the MANIFESTS sea trial was to validate forecast drifting models thanks to the discharge of a persistent floater product.

3.2. Course of sea trial

3.2.1. Area of release at sea and meteo-oceanic conditions

The MANIFESTS sea trial was authorised by the French Navy that granted an operation order to perform experimentations. The discharge location was in the Atlantic Ocean, off the island of Sein from the 30th of May to the 1st of June 2022. The discharge of chemicals was performed in an area of less than 3 nautical miles around the geographical point 47°20’30’’N, 005°05W (Figure 1Figure 5).

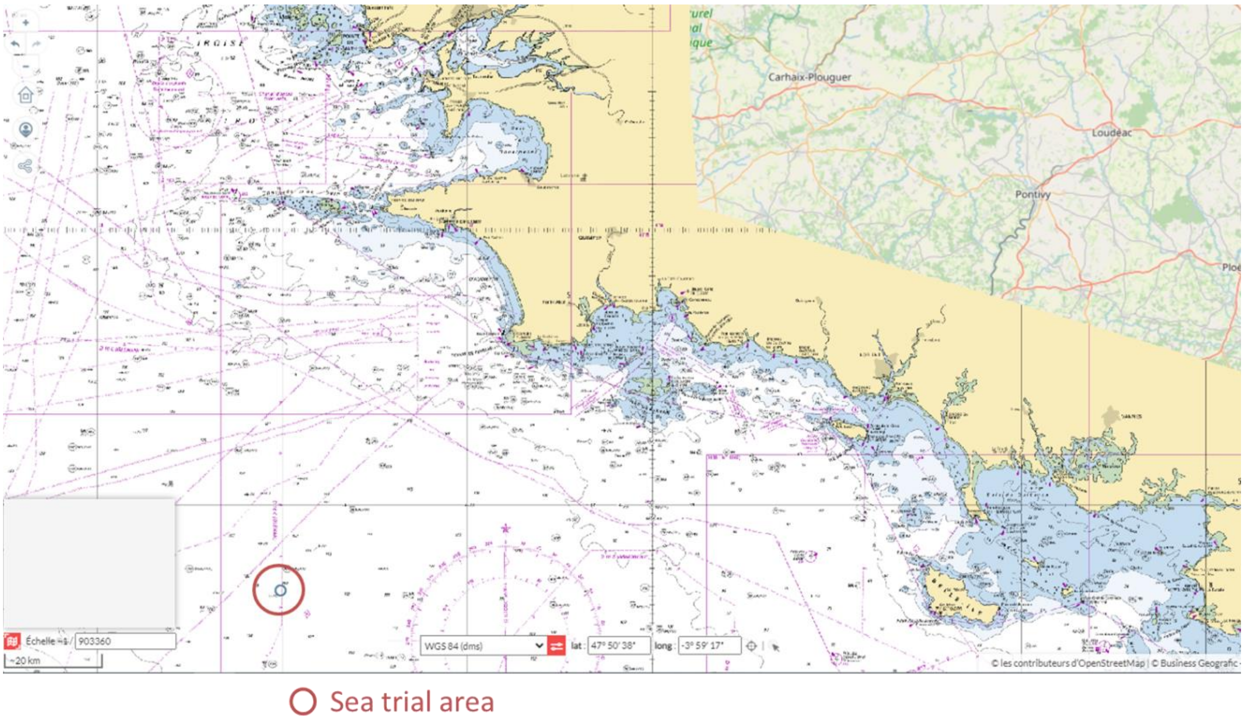


Figure 5: area of MANIFESTS sea trial

Weather conditions during the trial were particularly calm: clear skies, light breezes and flat seas (Less than Beaufort 2 during the first 2 days).

3.2.2. Selection of chemicals

In collaboration with CEPPOL (French Navy), some chemicals of interest were identified (Table 1), taking into account their SEBC behaviour, their intrinsic hazard(s) and risks in case of human approach after an accidental release and their frequency of transport in bulk (ECHA).

Chemicals with the short-term behaviour F (floating) and E (evaporating), based on behaviours of the SEBC classification were preferred. Acetone was selected to calibrate ONERA's SIMAGAZ sensor (multispectral detection).

Table 1: names of chemicals for the MANIFESTS sea trial, type of conditioning, volume discharged and CAS number

Name of chemical (SEBC)	Type of conditioning	Volume (m^3)	CAS number
Butyl acetate	IBC RSX electrostatic	2	123-86-4
Acetone	IBC RSX electrostatic	3	67-64-1
N-propyl acetate	IBC RSX electrostatic	2	109-60-4
Isopropyl acetate	IBC STAINLESS STEEL solvent	2	108-21-4
Methyl Ter Butyl Ether (MTBE)	IBC STAINLESS STEEL solvent	2	1634-04-4
Toluene	IBC RSX electrostatic	1	108-88-3
Xylenes	IBC RSX electrostatic	2	1330-20-7 90989-38-1
Soyabean oil	IBC RSX electrostatic	3	67701-30-8

The soyabean oil was kindly offered by the BUNGE Company in order to improve the response at sea in case of spillage of vegetable oil. Acetone and toluene required a declaration of final destination, in accordance with the European regulations in force.

Properties of chemicals are presented in ANNEX I.

3.2.3. Participants

Participants boarding SAPEUR vessel are listed in Table 2:

Table 2: participants on board SAPEUR during the MANIFESTS sea trial

Name	Organism	Position
CF Raphaël Fachinetti	CEPPOL, Navy (FR)	Director, MANIFESTS Advisory board
CF Rouat	CEPPOL (FR)	Air coordinator
Adrien Feltz	SEA OWL France (FR)	Captain of SAPEUR vessel
William Giraud	CEDRE (FR)	Engineer
Nicolas Loaec	CEDRE (FR)	Operator
Laura Cotte	CEDRE (FR)	Engineer
Thomas Le Bihan	CEDRE (FR)	Engineer

Roland Domel	ONERA (FR)	Engineer
Stéphane Langlois	ONERA (FR)	Engineer
Evi Cleynenbreugel	Belgian civil protection (BE)	Engineer
Steve Schets	Belgian civil protection (BE)	Operator
Eric Donnay	DG Environment (Ministry, BE)	Engineer, MANIFESTS Advisory board

3.2.4. Aircraft involved

Three aircraft were involved during the sea trials, directly under supervision of public organisations (French custom and RBINS, Belgium) or rented by a partner (ONERA, France). The organisations and corresponding models of the aircraft are summarised in Table 3.

Table 3: aircrafts involved during the MANIFESTS sea trial.

French custom with aircraft Beech 350 ER/FC SURPOLMAR

RBINS with aircraft Britten Norman Islander (BN2), a high wing Short Take Off and Landing (STOL) aircraft, with immatriculation OO-MMM

ONERA (France) flying with IMAO company on aircraft Piper-aztec PA03

Participants boarding French custom aircraft are listed in Table 4

Table 4: name, organism and position of participants boarding French custom aircraft during the MANIFESTS sea trial.

Name	Organism	Position
Dominique Pinel	French custom	Captain
Patrick Rideaux	French custom	Pilot
Didier Ménard	French custom	Technical expert
Philippe Béteille	French custom	Technical expert
Laurent Buignet	French custom	Technical expert on maritime pollution
Anne Le Roux	Cedre	Engineer, observer

Participants boarding IMAO aircraft are listed in Table 5:

Table 5: name, organism and position of participants boarding IMAO aircraft during the MANIFESTS sea trial.

Name	Organism	Position
Pierre-Yves Foucher	ONERA (FR)	Engineer
Philippe Déliot	ONERA (FR)	Engineer
Laurent Meignan	IMAO	Engineer

Participants boarding Belgian coastguard aircraft are listed in Table 6:

Table 6: name, organism and position of participants boarding Belgian coastguard aircraft during the MANIFESTS sea trial.

Name	Organism	Position
Ward Van Roy	RBINS (BE)	Technical expert
Pieter Janssens	RBINS (BE)	Technical expert
Geert Present	Defence Ministry (BE)	Pilot
Pieter Janssens	Defence Ministry (BE)	Pilot

3.2.5. Sensors used for chemical detection

Different sensors were tested to detect the HNS slick at sea surface and the associated gas cloud. Sensors were either on board SAPEUR, either airborne on the different aircraft. They are short-listed below:

- Two handled IR thermal camera: FLIR E75 42° owned by Cedre and FLIR P660 owned by DG Environment.
- The SIMAGAZ infrared multispectral camera implemented by ONERA (France) and fixed above the bridge of the SAPEUR vessel. It uses longwave IR (LWIR), in the range 6-13 cm^{-1}, and is dedicated to the detection of gases and should allow the visualisation, and possibly quantification, of volatile chemicals in the atmosphere. Such gas cloud will be present following accidental spill of evaporating liquid or gas at sea.
- The SIGIS 2 Scanning Infrared Gas Imaging System, owned by the Belgian Civil Protection and commercialised by Bruker Company. The SIGIS 2 is an infrared spectrometer with a single element detector and a scanner system. The detection is short wave IR (SWIR) in the range 680 - 1500 cm^{-1}, with a maximum spectral resolution of 0.5 cm^{-1}.

The different systems to detect chemicals are presented in Table 7:

Table 7: sensors used on the different platforms during the MANIFESTS sea trial.

Platform	Type of sensor	
	SLAR	IR
SAPEUR vessel		x (Cedre) x (DG env.) x (SIGIS2, BE Civil Protection) x (SIMAGAZ, multispectral)
PA 23 IMAO for ONERA (France)		x (SIMAGAZ, multispectral)
Beech 350 ERFC SURMAR French Customs*	x	x
BN-02 Belgian coastguard (RBINS)	x	x

* the aircraft was actually equipped with SLAR RADAR and scanner, but without the FLIR camera and the OM400 RADAR, which were removed to the benefit of other unit’s needs.

3.2.6. Buoys used to follow drift

Two types of buoys were used to follow drifting of the slick (Figure 6):

- **MargeT II buoys**, commercialised by CLS Company, France. It is resin coated, with notches for attachment, waterproof, and a range of operating temperature between -20°C and +50°C. Localisation is possible thanks to an ARGOS GPS, triggered by induction. It is equipped with a lithium-ion battery, LEDs, and is announced to have 30 days autonomy.

- **Homemade buoys**, with a SPOT brand tracker. The GPS tracker is wedged into screw-top HDPE bottle, ballasted with sand and tightly closed with high visible orange tap.

Figure 6: reparation of MargeT II buoys and homemade buoys on board SAPEUR vessel.

A goniometer (Figure 7) was also used to relocalise the CLS buoys at the end of the experimentation.

Figure 7: setting up goniometer to localise the CLS buoys dropped at sea.

3.2.7. Conditions related to discharge

3.2.7.1. Chronology of discharge

For a similar solubility, the less volatile is a chemical (low vapour pressure), the more persistent it will be. Following this postulate, the discharge order of chemicals was defined to allow the discharge of the most persistent products first, i.e. at increasing vapour pressure value. With this approach, in addition to the observation of the gas cloud of the last chemical observed, it was possible to observe in the background a continuation of the evaporation of the chemicals discharged previously.

Information on the conditions of discharge, including name and volume of chemical, time and position of discharge, and weather conditions (wind and current speed), are reported in ANNEX II. A sum up of the chemicals discharged and the corresponding volume for each slot is presented in Table 8:

Table 8: number of slot for discharge of chemical with corresponding date, name and volume for each chemical

Slot#	Day	Name of the chemical	Volume (m^3)
1	**31 May**	Soyabean Oil	3
		N-propyl acetate	1
		N-butyl acetate	1
		Isopropyle acetate	1
2	**31 May**	N-propyl acetate	1
		N-butyl acetate	1
		Isopropyle acetate	1
		Acetone	1
		MTBE	1
3	**01/06/2022**	MTBE	1
		Acetone	2
		Xylene	1
		Toluene	2

Before each discharge, an IBC filled with water coloured with fluorescein was discharged. To do so, an empty HDPE IBCs was first filled with seawater using the on board fire system.

3.2.7.2. Organisation with aircraft

The discharge of each chemical is triggered when the aircraft is at 5 min 30 (18 mN) from the slick so that the entire content of the IBC is released when the aircraft fly vertically over the slick. The correspondence between slots and aircraft involved is presented in Table 9.

Table 9: period and number of slot with corresponding aircraft involved.

	Tuesday 31th May	Wednesday 1st June
Morning	**Slot #1** IMAO French custom	**Slot #3** IMAO
Afternoon	**Slot #2** RBINS	

The different slots initially planned were actually modified due to the unavailability of French Customs aircraft on the 1st June.

3.2.7.3. Use of buoys

Three homemade buoys and three commercial buoys were deployed during the discharge of soyabean oil: one at the front, one at the middle and one at the end of the slick. Soyabean oil slick is illustrated in Figure 8.

Figure 8: slick of soyabean discharged in sea water.

3.2.7.4. Modelling

During the sea trial it was deemed interesting to obtain results from available modelling tools. For that purpose, METEO-FRANCE was asked to perform a drift forecast for the soybean oil using MOTHY. Still for soybean oil, as well as acetone and toluene, individual runs were performed using CHEMMAP software (RPS ASA).

Useful information related to the conditions of discharge of the different chemicals were collected carefully and include for each chemical: name, volume discharged, start/end time and location and environmental conditions (wind and current speed/direction). All these information are reported in ANNEXE II.

3.3. Results

3.3.1. Drift of vegetable oil

Before take-off of aircraft for slot 1, a volume of 3 m^3 was discharged at 10h30 local time on the 31th May. Immediately after, a forecast drifts were launched using Mothy and CHEMMAP.

During flight for slot 1 the crew in the French custom aircraft was able to visually localise yellow traces at seawater surface, corresponding to the soyabean oil. During the same period, the IMAO aircraft was unable to relocate the slick.

In the afternoon, during slot 2, the IMAO aircraft could finally relocate the slick at 14h27 local time visually and with the help of the SIMAGAZ camera.

Commercial drifting buoys were retrieved at the end of the experimentation while homemade buoys were leaved at sea and retrieved when stranded on the shore.

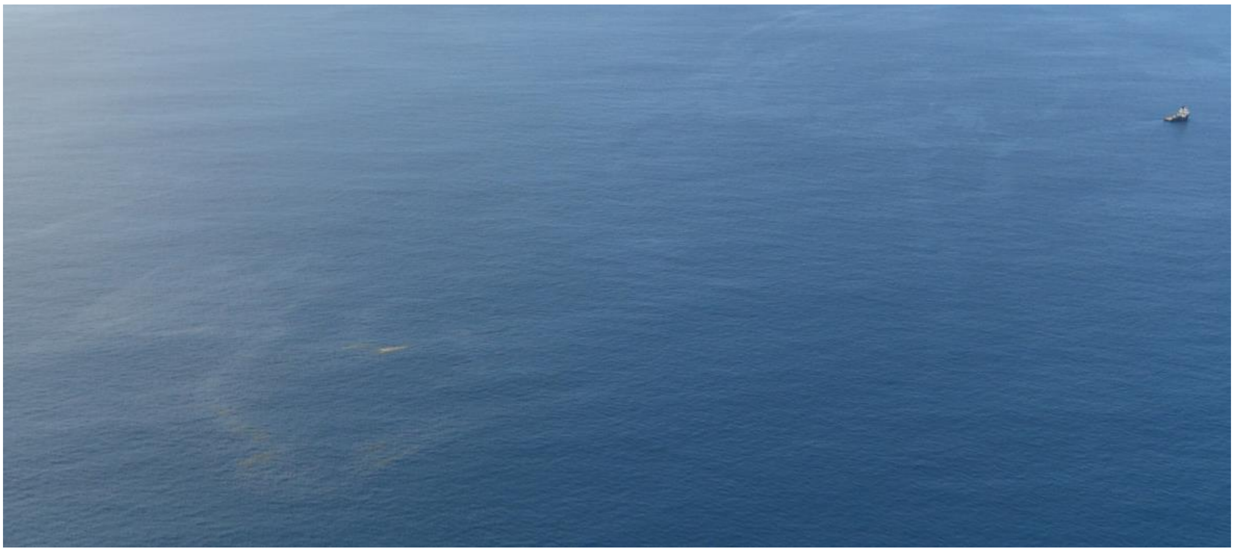
3.3.1. Detection by aircraft

French customs and RBINS operated flights during two different slots, respectively 1 and 2, on the 31th of May. Considering that sea state conditions during the whole day were not favourable to use SLAR (too calm), IR imagery was available for RBINS and UV/visible and HR imagery for both aircraft. Excepted soyabean oil, all chemicals discharged were uncoloured and it was not possible do detect them easily from the aircrafts. Examples of observation for both aircraft are presented hereafter.

RBINS

Full report provided by RBINS on the MANIFESTS sea trial is in ANNEX III.

As already stated in this report, the weather conditions were sub-optimal to make high quality SLAR recordings of the different slicks. Therefore the crew decided to focus on HR pictures of the different slicks and some FLIR imagery to check if their IR camera was able to detect the products on the sea surface. As a result the crew was not able to provide areas of the different slicks over time. The contribution of the Belgian coastguard Aircraft is focussed on HR pictures which may be useful for documentation purposes (Figure 9).



HR picture of soyabean slicks and SAPEUR vessel (©MUMM/BMM/UGMM)

HR picture of overall soyabean slicks (above image) and detail (below) in which buoys look to drift inside (©MUMM/BMM/UGMM)

Figure 9: examples of HR pictures acquired by the Belgian coastguard Aircraft.

Figure 10 presents screenshots of the IR camera and provides an impression of the possibilities to record the spilled chemicals with FLIR:

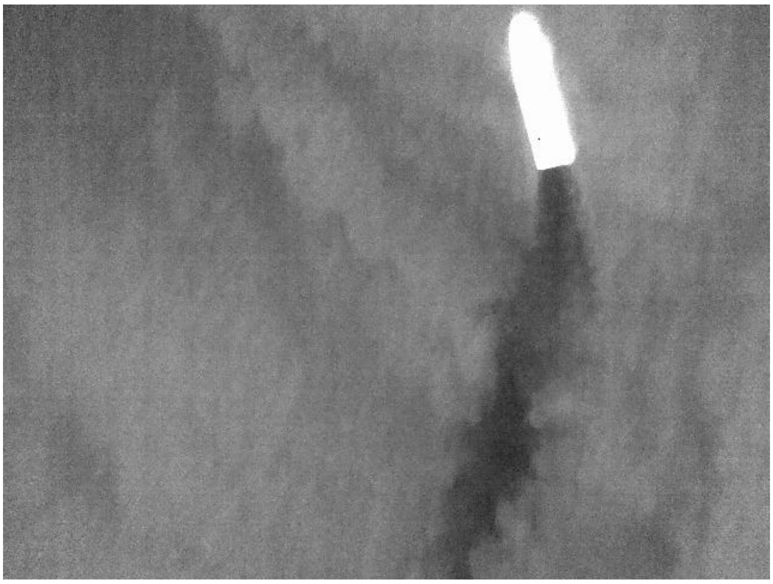


Figure 10: screenshot of the IR camera after discharge of MTBE (©MUMM/BMM/UGMM)

French custom

Full report provided by French Customs on the MANIFESTS sea trial is in ANNEX IV.

As presented in Figure 11, only soyabean oil was clearly detected by French customs aircraft. In addition, an illustration of the non-relevant use of SLAR in the condition of the sea trial is provided in Figure 12. A third example is presented in Figure 13 in to illustrate the very limited capacity of classical sensor to detect chemicals.

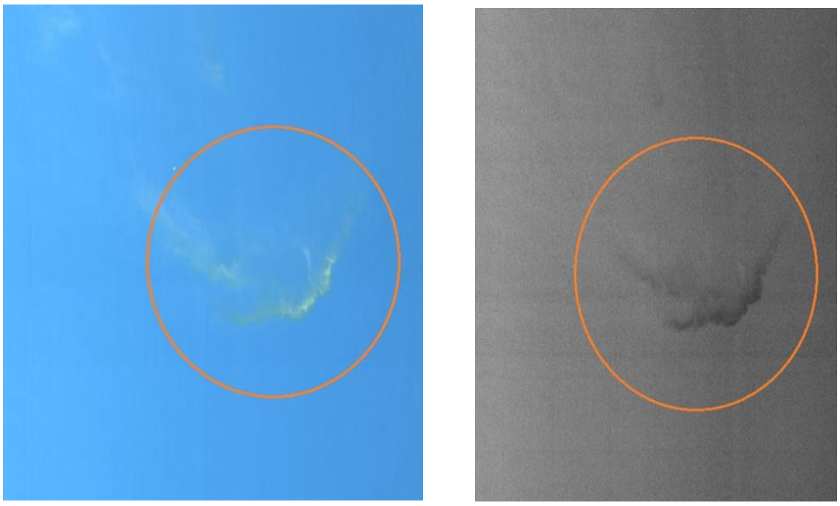


Figure 11: HR picture (left) and UV picture (right) of soyabean oil detected by scanner.

Avion : 47° 08' 45", -005° 09' 12"

Curseur : 47° 15' 17", -005° 07' 03"

Figure 12: SLAR detection after discharge of soyabean oil.

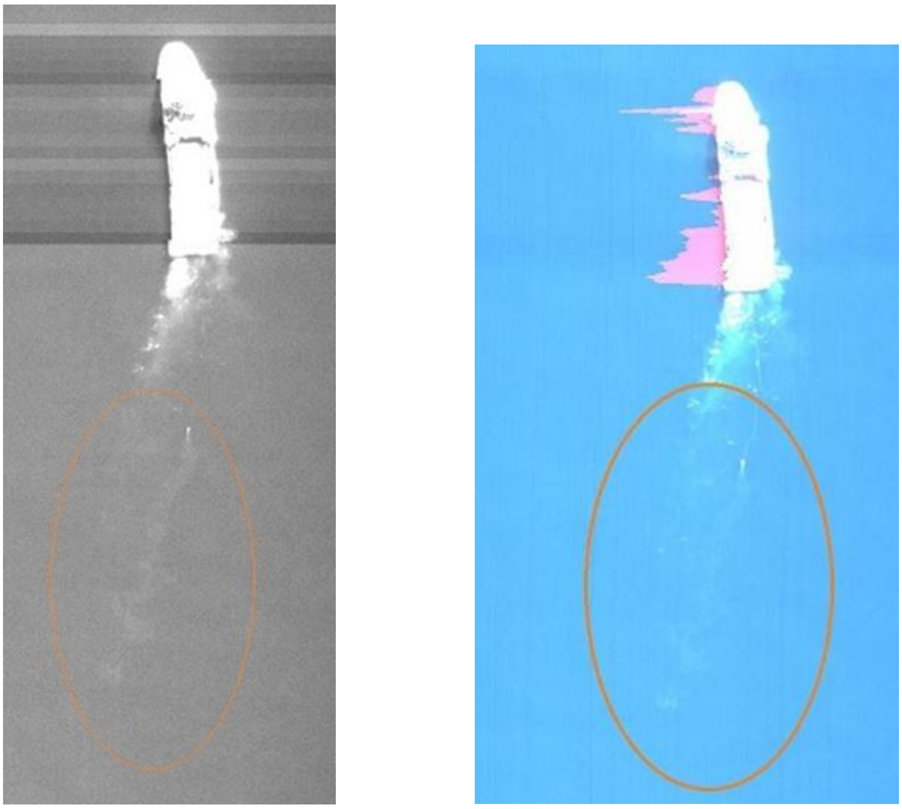


Figure 13: UV detection (left) and visible (right) after discharge of N-butyl acetate.

3.3.2. Detection of chemicals with handled thermal IR cameras

Almost all of chemicals discharged at sea could be observed with the two IR handled thermal cameras. Main results are presented below.

For the most persistent chemicals in the MANIFESTS sea trial, namely butyl acetate (FED), N-propyl acetate (ED), isopropyle acetate (ED), toluene (E), and xylenes (FE), the formation of a slick on the water surface resulted in a clear apparent temperature difference between the water and the chemical. This behaviour of the chemicals made it possible to observe significantly the presence of a chemical slick, excepted for acetone which was only detected with the FLIR portable E75 42° camera.

In addition, vapours from the slick into the atmosphere were also detected for butyl acetate (FED), N-propyl acetate (ED), isopropyle acetate (ED).

FLIR portable E75 42° camera - Cedre

The gas cloud of isopropyle acetate was observed but the contrast was lower compared to the observation made by FLIR of DG ENV, probably because of both technical specifications of the camera and adjustment of the device. As presented in Figure 14, enlargement using zoom allowed to obtain a better contrast but with a lower resolution.

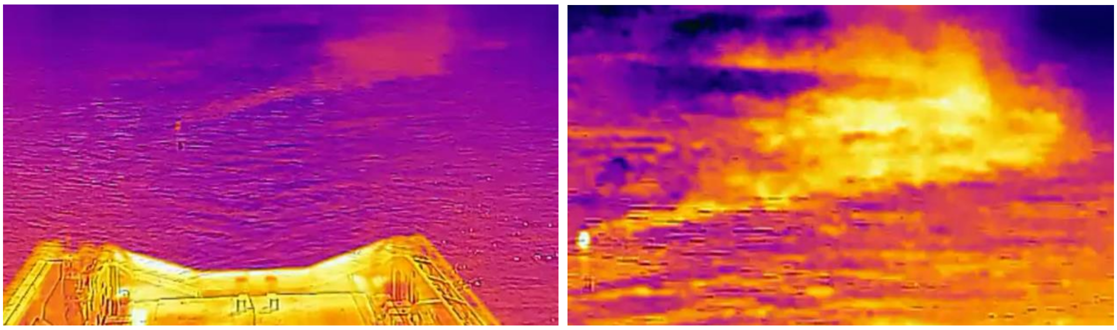


Figure 14: screen captures, without zoom (left) and zoomed (right) of observation done by the FLIR E75 42° for isopropyle acetate during slot 2.

Observation of acetone was very limited as it was punctual and localised at the outlet of the discharge system (Figure 15).

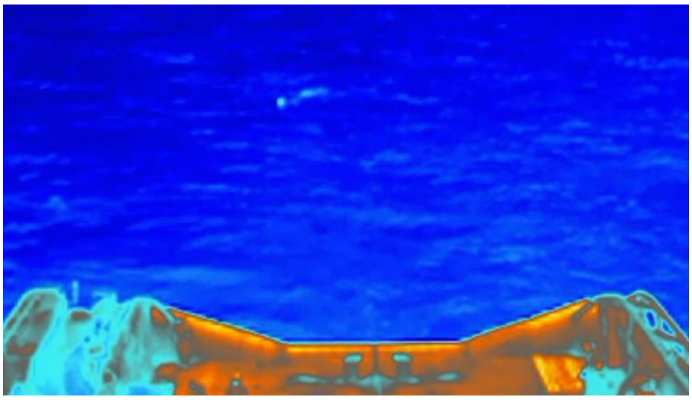


Figure 15: screen capture of observation done by the FLIR E75 42° for acetone during slot 3.

Observation of MTBE was clear and allowed to visualise both slick (darker on image in Figure 16) and gas cloud. Wind conditions created a cloud covering sea water surface (light pink on the upper right on the image in Figure 16).

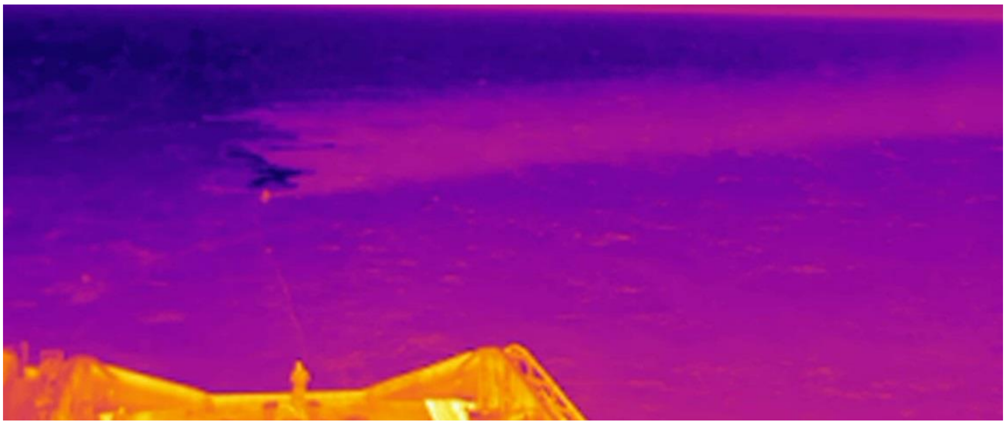


Figure 16: screen capture of observation done by the FLIR E75 42° for MTBE during slot 3.

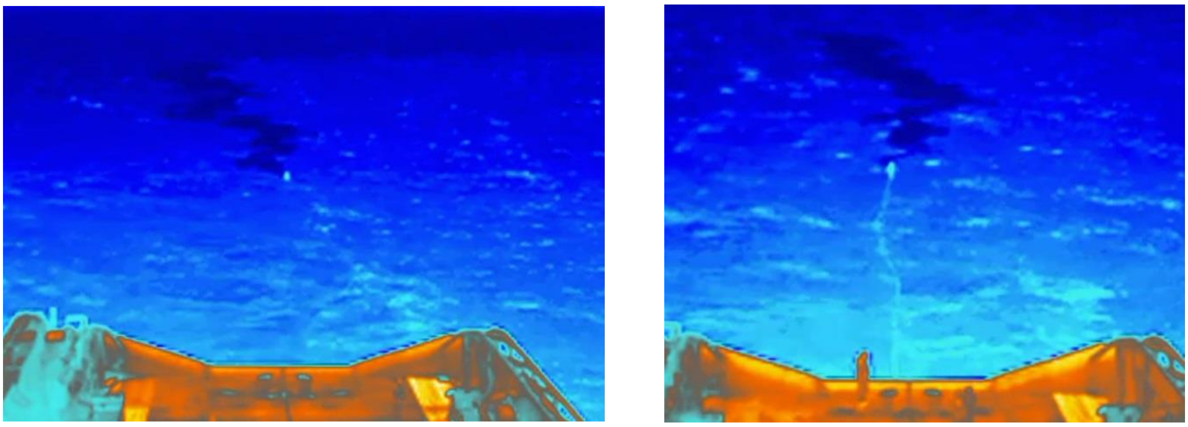


Figure 17: screen capture of observation done by the FLIR E75 42° for toluene (left) and xylenes (right) during slot 3.

FLIR P660 owned by DG Environment.

This handled thermal IR camera allowed to clearly observe both slick and vapours of N-propyl acetate (Figure 18) and isopropyl acetate (Figure 19).

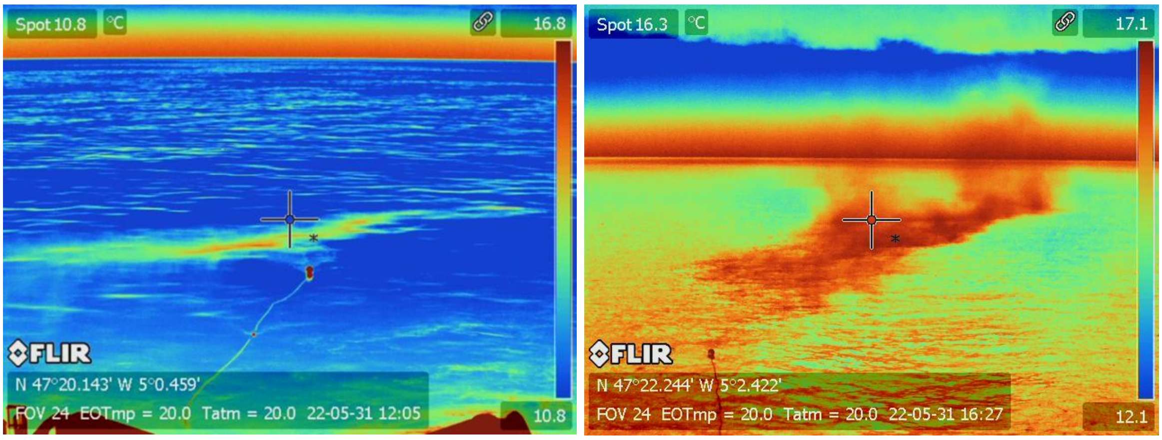


Figure 18: screen capture of observation done by the FLIR P660 for N-propyl acetate during slot 1 (left) and slot 2 (right).

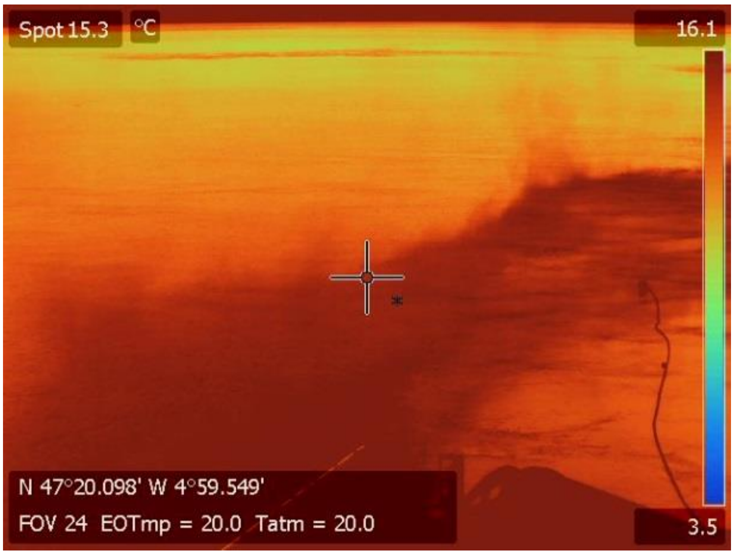


Figure 19: screen capture of observation done by the FLIR P660 for isopropyl acetate during slot 1.

For the most persistent chemicals, especially toluene and xylenes, slicks were observed with high contrast. Vapour cloud was also visible with less contrast compared to other fast evaporating chemicals (Figure 20).

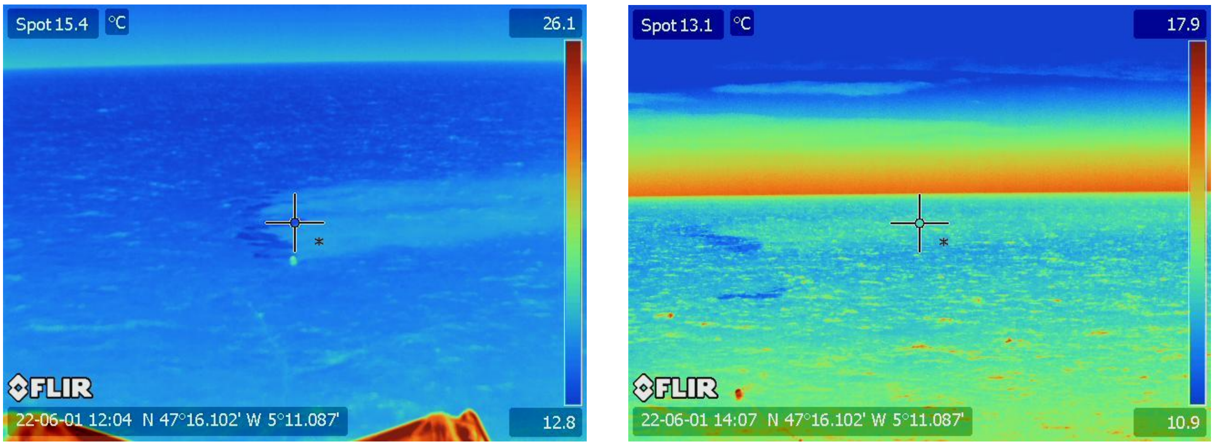


Figure 20: screen capture of observation done by the FLIR P660 for xylenes (left) and toluene (right) during slot 3.

3.3.1. Detection of chemicals with SIGIS2

Full report provided by Belgian civil protection on the MANIFESTS sea trial is in ANNEX V.

Two types of view were used during the test. For the first view, a correlation was made between experimental and recorded spectra. The lighter the colour (up to white) was the greater the similarity between the two spectra. The other view used was for identification by the system where red spots appear when a substance (sometimes more than one) is positively identified over a correlation threshold. Figure 21 illustrates these views. Complementary information is displayed on the screen with mention of the name(s) of substance(s) identified with level of certainty.

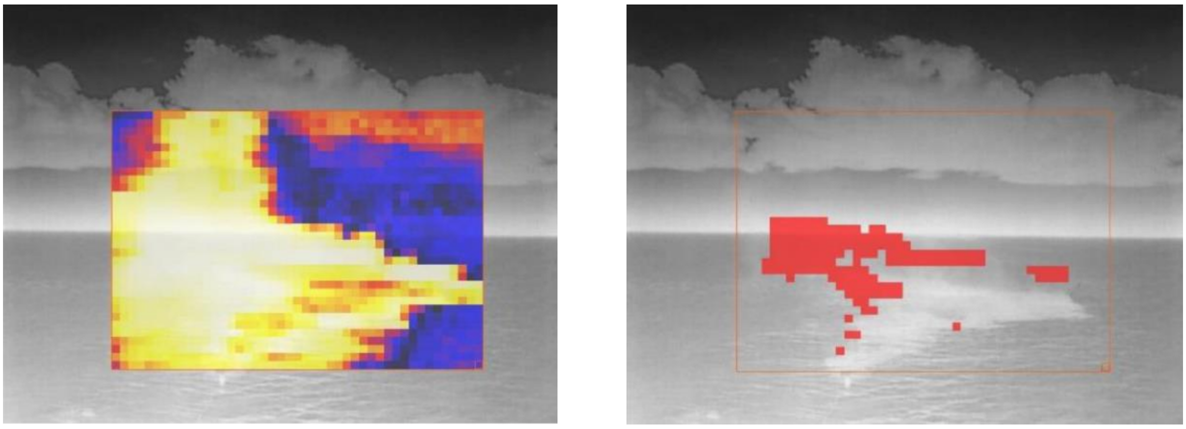


Figure 21: Types of view used with SIGIS2 system: correlation (left) and identification (right)

Table 10 presents an overview on the results obtained by SIGIS2 related to the detection of the different chemicals discharged during the MANIFESTS sea trial.

Table 10: Level detection by SIGIS2 for the different chemicals discharged

Slot #	Name of chemical	Level of detection
1	Soybean Oil	/
1	N-propyl acetate	Good correlation, no positive detection
1	N-butyl acetate	Positive after enhanced analysis
1	Isopropyl acetate	Positive after enhanced analysis
2	N-propyl acetate	Positive after enhanced analysis
2	N-butyl acetate	Live positive result
2	Isopropyl acetate	Positive after enhanced analysis
2	Acetone	No result
2	MTBE	Live positive result

3	MTBE	Live positive result
3	Acetone	No result
3	Xylene	No result
3	Toluene	Positive after enhanced analysis

The device was tested for the first time at sea with live releases of large amounts of hazardous substances. A majority of the released substances were detected (live or with the enhanced analysis) and a good view was obtained for the stains of the substances on the water and the formation of clouds. The negative measurements for the acetone might be explained through its solubility and no explanation is provided for xylenes at the time writing the report.

3.3.2. SIMAGAZ

Full report provided by ONERA (France) on the MANIFESTS sea trial is in ANNEX VI.

Table 11 and Table 12 summarise the main observations highlighted in the full report for observations with SIMAGAZ on SAPEUR vessel and airborne on IMAO aircraft.

All slicks of chemicals were detected with the airborne SIMAGAZ.

While all slicks of chemicals could be observed on the surface, vapours of 5 chemicals could be observed in the atmosphere. For the other gases, the SIMAGAZ filters are not suitable and only the slicks were observed.

The vapours of the gases for which the SIMAGAZ camera (Butyl acetate, Isopropyl acetate and N-propyl acetate) were observed for more than 30 min up to distances of more than 1 km. Persistence of other gases observed (acetone and MTBE) did not exceed 10 minutes, particularly in the presence of strong wind.

In the table below, the sign '-' is indicated in case of absence of detection or observation, and sign '+' for positive detection even if not very robustly and very dependent on the observation conditions. The sign ‘++ is indicated for positive detection, and '+++' for detections or observations depending on the robustness and the observations and detections made automatically with the current processing tool.

Table 11: summary of SIMAGAZ observations during the MANIFEST campaign - SAPEUR vessel

Chemical	Observation of the slick	Observation of gas cloud	Persistence of observation (min.)	Area of spreading (m)	Distance of observation (km)
Butyle acetate	+ “Cold” slick	+++ Observation, Detection and Quantification	> 30	> 500	1 (horizon)
Acetone	+ “Hot” slick	+ Observation, Detection and Quantification	5	100	0.3
MTBE	++ “Cold” slick	+ Observation, Detection	30	200	0.6-0.8
Isopropyl acetate	++ Observation “Cold” slick	+++ Observation, Detection and Quantification	>30	>500	1 (horizon)
N-propyl acetate	++ Observation “Cold” slick	+++ Observation, Detection and Quantification	>30	>500	1 (horizon)
Toluene	++ “Cold” slick	-	30	200	0.6-0.8
Xylenes	++ “Cold” slick	-	30	200	0.6-0.8

Table 12: summary of SIMAGAZ observations during the MANIFEST campaign – Airborne on IMAO aircraft

Chemical	Observation of the slick	Observation of gas cloud	Persistence of observation (min.)	Area of spreading (m)	Distance of observation (km)
Butyle acetate	+ “Cold” slick	+++ Observation, Detection and Quantification	> 55	> 2500	0.8
Acetone	+ “Hot” slick	+ Observation, Detection and Quantification	5	75	0.3
MTBE	++ “Cold” slick	+ Observation, Detection	5	200	0.3
Isopropyl acetate	+++ Observation “Cold” slick	+++ Observation, Detection and Quantification	>50	>1500	0.8
N-propyl acetate	++ Observation “Cold” slick	+++ Observation, Detection and Quantification	>30	>2000	0.8
Toluene	++ “Cold” slick	-	?	400	0.8
Xylenes	++ “Cold” slick	-	>30	800	0.8

4. Catalogue of sensors

4.1. Catalogue from bibliography

The *Marine HNS Response Manual, Multi-regional Bonn Agreement, Helcom, REMPEC*[2], produced in the framework of the West MOPoCo project, funded by DG ECHO, offers an interesting overview of existing sensors, especially as this manual includes a description of portable gas sensors for first responders (Fact sheet 5.25) and also a description of sampling techniques and protocols (Fact sheet 5.26). Considering state-of-the-art of existing technologies, the Fact sheet 5.27 of the West MOPoCo HNS Manual provides relevant information on chemicals detection and analysis methods and reminds applicability of the analytical techniques. This Fact sheet 5.27 also indicates main advantages and limitations such as sensing equipment that be miniaturized or chemicals excluded for detection. Fact sheets 5.25, 5.26 and 5.27 are presented in ANNEX VII.

4.2. Catalogue and features from field trial

Thanks to the IPOMAC and MANIFESTS sea trials, some observations have been carried out in the field by different sensors and are presented in Table 13.

Table 13: Main results from observation made by the different sensors during the IPOMAC and MANIFESTS sea trials

HNS	Detection on board vessel (handled or standoff)		Airborne detection (Aircraft or RPAS)	
	Slick	Vapours	Slick	Vapours
Acetone	IR M+	IR M+ (quantification)	IR, H M+	- M++
Butyl acetate	IR M+	IR M+++	IR, H M+	- M+

---

[2] https://www.westmopoco.rempec.org/en/project/specific-objectives-and-activities/hns-marine-response-manual

Heptane	IR M++	IR M	IR, H /	- /
Isopropyl acetate	IR M++	IR M+++	/ /	/ M+++
Methanol	IR M+	IR M-	IR, H /	- /
MTBE	IR M++	IR M+	/ /	/ M+
N-propyl acetate	IR M++	IR M+	/ M++	/ M+++
Soybean oil	IR, M -	M- -	/ -	/ M-
Toluene	IR M++	IR M-	IR, H M++	- M-
Xylenes	IR M++	IR M-	IR, H M++	- M-

/ is indicated for absence of experimentation

- is indicated for negative of detection

IR is indicated for positive detection using IR detection based tool

H is indicated for positive detection using hyperspectral detection based tool

Observations made with multispectral camera:

'**M-**': absence of detection or observation

'**M+**' low positive detection, dependent on the observation conditions

‘**M++**’: positive detection

'**M+++**': detections or observations with automatic detection made with the current processing tool

During the MANIFESTS sea trial, the **SIGIS2** sensor was mounted on the deck of the SAPEUR vessel and provided positive detection for all chemicals released, excepted for soyabean oil, acetone and xylenes. Live positive detection was obtained for MTBE and N-butyl acetate.

5. Conclusion and perspectives

Organisation of the MANIFESTS sea trial was done in safe conditions and provided interesting information from experimentation, both for scientists and responders, to improve the capacity to assess risks and impacts in case of evaporating or gaseous release at sea.

The participation of different aircraft has shown the limitation of current sensors used in routine to detect the presence of vapours or slicks of evaporating chemicals. Handled IR cameras are cost-effective and interesting tools at the moment to detect the presence of chemical slick in case of accidental release. For some chemicals, IR can also offer the possibility to visualise vapours in the atmosphere, however it remains limited and IR cameras cannot identify or quantify chemicals.

The use of multispectral camera during the MANIFESTS sea trial confirmed the possibility to observe, identify or even quantify chemicals discharged at sea. There is still fair amount of work, especially to develop algorithm, to provide reliable quantification of concentrations in the air. Such future developments are of high importance to improve existing forecast models. Further sea trial is thus not only recommended but necessary, especially to perform a specific “long term” observation of the evaporation of one chemical. Such experimental protocol should be adapted to the temporal monitoring of evaporating gases at sea and carrying out a dedicated observation campaign on the ground, on a boat or by airborne means (drone, plane or helicopter).

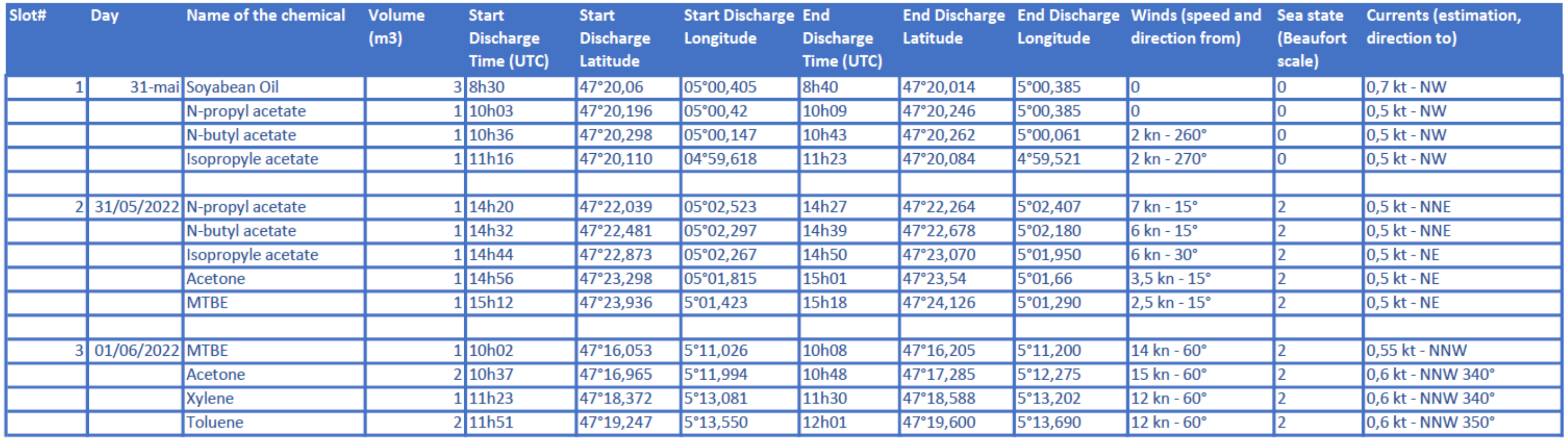
However, new challenges remain for this type of spill: how to take samples from both the water column and the atmosphere to validate the sensor observations and model predictions (evaporation, solubilisation, drift, etc.)? In the event of a sub-surface spill, how can we assess the behaviour of HNS in natural conditions when they rise into the water column in an open environment?

ANNEXES

ANNEX I - Properties of chemicals discharged during IPOMAC and MANIFESTS sea trials, including SEBC, are presented in ANNEX

Name of chemical	CAS number	UN number	Hazard category	Chemical formula	Hazard pictograms	SEBC	Molar weight (g.mol^{-1})	Explosive limits (%)	Specific gravity (20°C)	Boiling point (°C)	Flash point (°C)	Solubility (g.L^{-1} at 20°C)	Dynamic viscosity (mPa.s at 20 °C)	Vapour pressure (kPa at 20°C)	Vapout density	Ionisation potential (eV)	PID response coefficient (with lamp 10,6eV)	Coeff octanol/ water log $P_{o/w}$
Butyl acetate	123-86-4	1123		$C_6H_{12}O_2$		FED	116.16	1.7 - 7.6	0.879-0.881	125-127	22-26	7	0.732	1.2	4	10	2.6	1.81
Acetone	67-64-1	1090		C_3H_6O		DE	56.08	2.15 - 13	0.783	56.1	-18	Miscible	0.32	24.7	2	9.71	1.1	-0.24
N-propyle acetate	109-60-4	1276		$C_5H_{10}O_2$		ED	102.13	1.7 - 8	0.888	102	11.8	18.9	0.58	0.33	3.53	10.04	2.5	1.4
Isopropyle acetate	108-21-4	1220		$C_5H_{10}O_2$		ED	102.13	1.8 - 8	0.874	88.5	2	18	0.49	6.33	3.52	9.99	2.2	1.18-1.3
Heptane	142-82-5	1206		C_7H_{16}		E	99	1-7	0.710	90-100	-5	0.002	0.39	6	3.52	9.92	2.8	4.7
Methanol	67-56-1	1230		$CH_3\text{-}OH$		DE	32.04	6-37	0.791	64.6	12	Miscible	0.61	12.3	1.11	10.85	not detectable	-0.7
MTBE	1634-04-4	2398		$C_5H_{12}O$		ED	88.15	1.6-13	0.741	55.2	-28	48	0.35	26.8	3.1	9.24	0.9	1.06
Xylenes	1330-20-7 *90989-38-1*	1307		C_8H_{10}		FE	106	01-sept	0.86-0.88	136 - 144	23	< 20 mg.L^{-1}	0.6	0.89	3.7	8.44 - 8.56	0.39 - 0.46	3.2
Toluene	108-88-3	1294		C_7H_8		E	92.14	1.2 - 7	0.867	110-111	4	0.5	0.583	2.1	3.1	8.82	0.5	2.73
Soyabean oil	67701-30-8	/	/	Variable	/	F	920	/	0.919-0.925	"very high"	282	0	55	0	/	/	/	/

ANNEX II – Conditions of discharge during the MANIFESTS sea trial, including name and volume of chemical, time and position of discharge, and weather conitions (wind and current speed).



Slot#	Day	Name of the chemical	Volume (m3)	Start Discharge Time (UTC)	Start Discharge Latitude	Start Discharge Longitude	End Discharge Time (UTC)	End Discharge Latitude	End Discharge Longitude	Winds (speed and direction from)	Sea state (Beaufort scale)	Currents (estimation, direction to)
1	31-mai	Soyabean Oil	3	8h30	47°20,06	05°00,405	8h40	47°20,014	5°00,385	0	0	0,7 kt - NW
		N-propyl acetate	1	10h03	47°20,196	05°00,42	10h09	47°20,246	5°00,385	0	0	0,5 kt - NW
		N-butyl acetate	1	10h36	47°20,298	05°00,147	10h43	47°20,262	5°00,061	2 kn - 260°	0	0,5 kt - NW
		Isopropyle acetate	1	11h16	47°20,110	04°59,618	11h23	47°20,084	4°59,521	2 kn - 270°	0	0,5 kt - NW
2	31/05/2022	N-propyl acetate	1	14h20	47°22,039	05°02,523	14h27	47°22,264	5°02,407	7 kn - 15°	2	0,5 kt - NNE
		N-butyl acetate	1	14h32	47°22,481	05°02,297	14h39	47°22,678	5°02,180	6 kn - 15°	2	0,5 kt - NNE
		Isopropyle acetate	1	14h44	47°22,873	05°02,267	14h50	47°23,070	5°01,950	6 kn - 30°	2	0,5 kt - NE
		Acetone	1	14h56	47°23,298	05°01,815	15h01	47°23,54	5°01,66	3,5 kn - 15°	2	0,5 kt - NE
		MTBE	1	15h12	47°23,936	5°01,423	15h18	47°24,126	5°01,290	2,5 kn - 15°	2	0,5 kt - NE
3	01/06/2022	MTBE	1	10h02	47°16,053	5°11,026	10h08	47°16,205	5°11,200	14 kn - 60°	2	0,55 kt - NNW
		Acetone	2	10h37	47°16,965	5°11,994	10h48	47°17,285	5°12,275	15 kn - 60°	2	0,6 kt - NNW 340°
		Xylene	1	11h23	47°18,372	5°13,081	11h30	47°18,588	5°13,202	12 kn - 60°	2	0,6 kt - NNW 340°
		Toluene	2	11h51	47°19,247	5°13,550	12h01	47°19,600	5°13,690	12 kn - 60°	2	0,6 kt - NNW 350°

ANNEX III - Full report provided by RBINS on the MANIFESTS sea trial

ROYAL BELGIAN INSTITUTE OF NATURAL SCIENCES

OPERATIONAL DIRECTORATE NATURAL ENVIRONMENT

SCIENTIFIC SERVICE:
MANAGEMENT UNIT OF THE NORTH SEA
MATHEMATICAL MODELS (MUMM)

BE COASTGUARD AIRCRAFT PARTICIPATION IN THE MANIFEST SEATRIALS

31 MAY 2022 – MISSION REPORT

KOBE SCHELDEMAN & WARD VAN ROY

Table of Contents

1. Introduction

The Management Unit of the Mathematical Model of the North Sea (MUMM), a Scientific Service of the Royal Belgian Institute of Natural Sciences (RBINS), is recognized by Belgian Law as one of the legally competent authorities for the monitoring and follow up of MARPOL regulations at sea. For this, a Britten Norman Islander (BN2), a high wing Short Take Off and Landing (STOL) aircraft with immatriculation OO-MMM is used.

The Belgian Coastguard Aircraft took part in the MANIFEST (MANaging risks and Impacts From Evaporating and gaseous Substances To population Safety) sea trials near Brest on the 31th of May. For this project, the main categories of transported chemicals were identified and different sensors were tested for their ability to identify different substances. This was first done in a laboratory environment, but the ultimate test was a sea trial where sensors were tested on ships and on flying units. The focus here was on highly evaporating substances.

2. Crew

The crew on board consisted of aerial operators Ward Van Roy and Kobe Scheldeman (MUMM) and of pilots Geert Present and Pieter Janssens (Belgian Defence Ministry).

3. Routing and planning

The sea trials location of MANIFEST was located at 47°20'30.00"N - 5° 0'30.00"W. Quimper airport was the ideal base of operations for the aircraft during the trials.

Manifest sea trials	
LFRQ	47°58'29.00"N - 4°10'5.00"W
4_1	47°20'30.00"N - 5° 0'30.00"W
LFRQ	47°58'29.00"N - 4°10'5.00"W

4. Technical sheet of the OO-MMM air surveillance platform

Airborne platform
Model: Britten Norman Islander
Call sign: OO-MMM
Length: 10,9 m
Wingspan: 14,02 m
Height: 3,77 m
2 Lycoming engines (300 hp)
Mean cruising speed: 120 kts
Autonomy: 5 hrs

SLAR
Model: Terma SLAR 9000

Range: 20/20 nm (standard operations) up to 40/40 nm
Resolution on ground: 35m (20nm range); 75m (40 nm range)
With pixel per pixel georeferencing from Flight Management System (FMS)

GPS Positioning en Flight Management System
Model GPS: Garmin GTN650 (x2)
Model FMS: Garmin G600
Data-export of coordinates, course, airspeed, groundspeed, windspeed and direction, time, date, altitude (barometric), roll and pitch angle to control-unit
Built in Airband VHF radio-communication
1m accuracy

Controle-eenheid (Mission Management Unit)
Model: Optimare Medusa System
Integration and control van sensors and sensor-images
Equipped with ECDIS and Comar SLR200 AIS receiver
Equipped with UPS (model Mid Continent MD835)

Radar altimeter
Model: Bendix King KRA405B
Data-export from barometric altitude to control unit
Accuracy: 1m

VHF/FM Airborne transceiver
Model: Technisonic TFM-138B
Installed in control unit
Sound is recorded on video images

Satcom
Model: Garmin GSR 56
Controls integrated into Garmin G600 Flight Management System
Phone calls, text messages and weather information requests

Stormscope
Model: Goodrich WX-500

Traffic Advisory System
Model: Avidyne TAS600 S

Cockpit screen
Model: Avalex AVM 4095
Screen diameter: 8.4 inch
Resolution: 800x600
Analog video input: NTSC/PAL
Digital video input: SVGA

Sniffer System
Model: IGPS (Identification of Gross Polluting Ships) Sniffer System
Main instruments: SO2 (Thermo 43i TLE UV Fluorosensor), CO2 (LICOR 7200RS NDIR Spectroscopy) and NOx (Thermo 42i-TL) high accuracy gas sensors
Software: IGPS Present, Extract, Analysis, TCP-LOG

Digital Camera's
Model: Nikon D850+D800
Equipped with GPS connection

Video camera

IR

5. Weather conditions

The weather conditions were not optimal for SLAR recordings during slot 2 of the manifest sea trials. Due to a seastate below 2, the BE Coastguard Aircraft wasn't able to make usable SLAR recordings for the size estimation of the slicks during the slot.

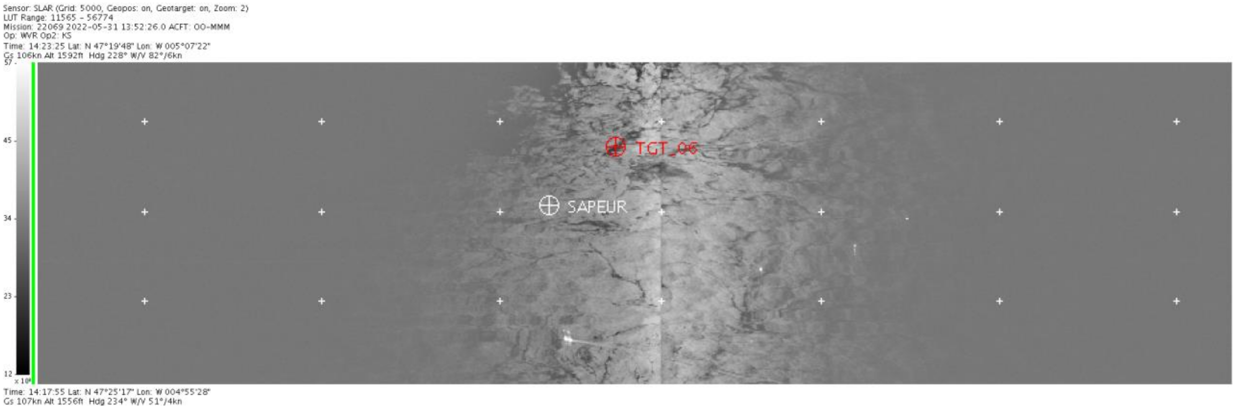


Fig 1: SLAR image of the sea area in the vicinity of the SAPEUR. Due to the low sea state it was not possible to record clear SLAR imagery of the different slicks.

6. Observation/detection summary

As stated before, the weather conditions were sub-optimal to make high quality SLAR recordings of the different slicks. Therefor the crew decided to focus on HR pictures of the different slicks and some FLIR imagery to check if our IR camera was able to detect the products on the sea surface. As a result we are not able to provide sizes of the different slicks over time. The contribution of the BE Coastguard Aircraft is focussed on HR pictures which may be useful for documentation purposes.

Timetable spills		
Spill	**Time**	**Remark**
-	1420	BCG AC entering zone
Spill 0	Unknown time spill	
Spill 1	1420 - 1427	N-propyl acetate
Spill 2	1432 - 1439	N-butyl acetate
Spill 3	1444 - 1450	Isopropyle acetate
Spill 4	1456 - 1501	Acetone
Spill 5	1512 - 1518	MTBE
-	1530	BCG AC leaving zone

HR pictures

The HR pictures are available through following download link:
https://share.naturalsciences.be/d/ac32c63b00c5436ba70a/

Manifest pictures			
Slick n°	**Picture n°**	**Time**	**Remark**
0	850_6300	1421	Vegetable oil + marker overview
0	850_6302	1421	Vegetable oil + marker overview
0	850_6312	1427	Vegetable oil + marker overview
0	850_6313	1427	Vegetable oil + marker overview
0	850_6314	1427	Vegetable oil + marker overview
1	850_6318	1430	Spill 1 at Sapeur
1	850_6320	1430	Spill 1 at Sapeur
1	850_6322	1430	Spill 1 at Sapeur
1	850_6323	1430	Spill 1 at Sapeur
1	850_6324	1430	Spill 1 at Sapeur
1	850_6326	1430	Spill 1 + marker
1	850_6327	1430	Spill 1 + marker
1	850_6328	1430	Spill 1 + marker
1	850_6330	1433	Spill 1 at Sapeur
1	850_6332	1434	Spill 1 at Sapeur
1	850_6333	1434	Spill 1 at Sapeur
1	850_6335	1434	Spill 1 at Sapeur
1	850_6336	1434	Spill 1 at Sapeur
	850_6338	1434	Marker
0	850_6339	1434	Vegetable oil detail
2	850_6343	1438	Overview Sapeur during spill 2
	800_7510	1440	Detail Marker
	800_7511	1441	Detail Marker
	800_7512	1441	Detail Marker

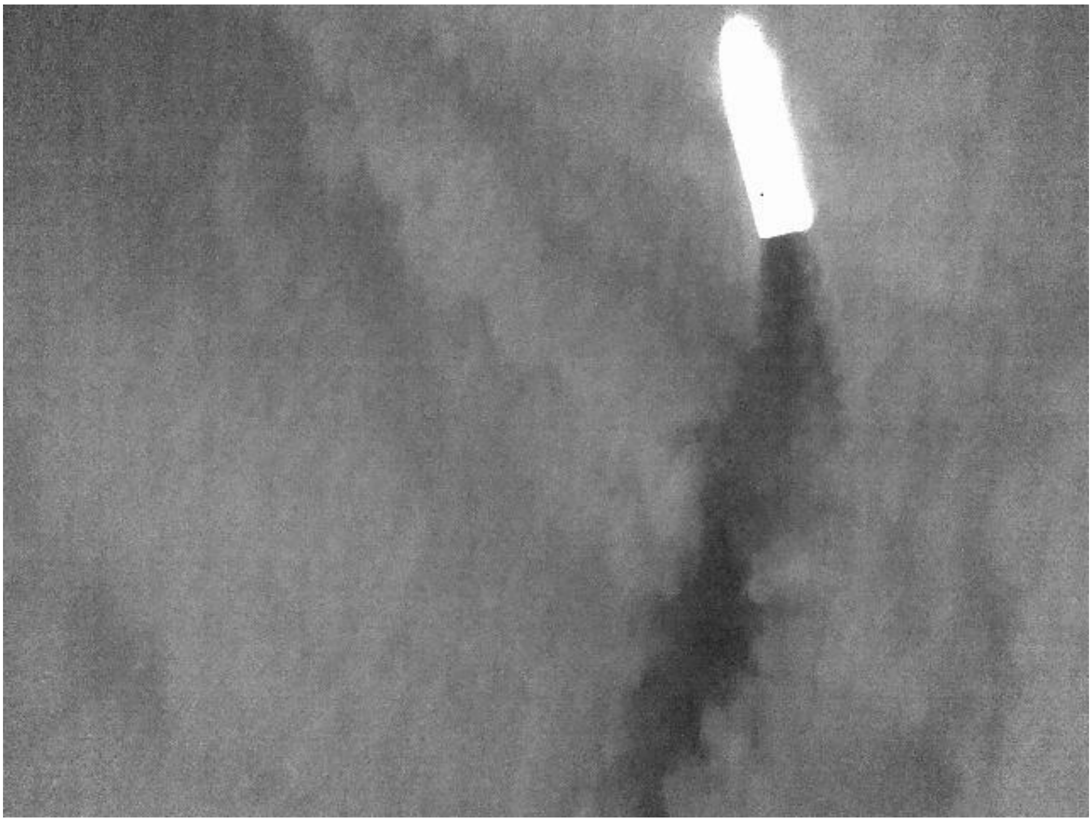
0	800_7513	1441	Vegetable oil + marker detail
0	800_7514	1441	Vegetable oil + marker detail
3	800_7516	1446	Sapeur during spill 3
3	800_7517	1446	Sapeur during spill 3
3	800_7518	1446	Sapeur during spill 3
3	800_7519	1446	Sapeur during spill 3
2 + 3	850_6344	1446	Overview spill 2 and 3 (ongoing) from Sapeur
3	800_7520	1447	Sapeur during spill 3
3	800_7521	1447	Sapeur during spill 3
3	800_7522	1447	Sapeur during spill 3
3	850_6346	1449	Spill 3 at Sapeur overview
3	850_6348	1449	Spill 3 at Sapeur overview
3	850_6349	1449	Spill 3 at Sapeur overview
1 + 2 + 3	850_6351	1449	Wide overview spill 1, 2 and 3
0	850_6352	1451	Overview vegetable oil
0	850_6353	1451	Overview vegetable oil
0	850_6356	1502	Overview vegetable oil
0	850_6357	1503	Overview vegetable oil
4	850_6362	1507	Spill 4 at Sapeur
4	850_6364	1507	Spill 4 at Sapeur
	800_7523	1507	Sapeur detail
4	850_6366	1507	Spill 4 overview
	800_7525	1508	Sapeur wake detail
	800_7526	1508	Sapeur detail
	800_7527	1508	Sapeur detail
	800_7528	1508	Sapeur detail
	800_7530	1508	Sapeur detail
0	850_6368	1511	Vegetable oil overview
0	850_6369	1511	Vegetable oil overview
0	850_6371	1512	Vegetable oil detail
5	800_7531	1517	Spill 5 from Sapeur
5	800_7532	1523	Spill 5 from Sapeur
5	850_6373	1524	Spill 5 from Sapeur
5	850_6374	1524	Spill 5 overview
0	850_6376	1528	Vegetable oil overview

Table 1: Overview HR pictures OO-MMM of the spills during the MANIFEST Seatrials on the 31th of May, slot 2

IR footage

Following screenshots of the IR camera provide an impression of the possibilities to record the spilled chemicals with FLIR.

Fig2: IR screenshot from Slick 1



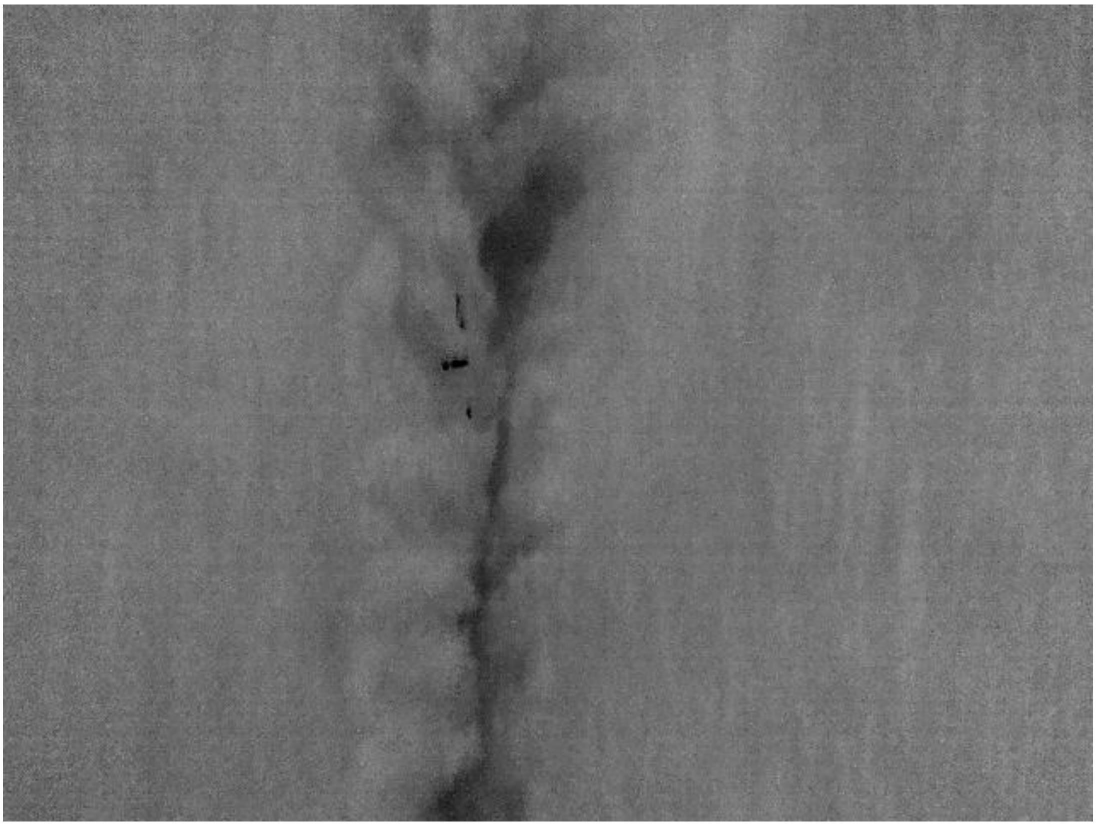


Fig3-5: IR screenshots from Slick 5

COLOPHON

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☒ final version
☐ revised version of document
☐ confidential

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☒ English
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https://odnature.naturalsciences.be/mumm/nl/aerial-surveillance/missions

ROYAL BELGIAN
INSTITUTE OF
NATURAL SCIENCES
OD NATURE

SCIENTIFIC SERVICE:
MANAGEMENT UNIT OF THE NORTH
SEA MATHEMATICAL MODELS (MUMM)

ANNEX IV - Full report provided by French customs on the MANIFESTS sea trial

EXERCICE MANIFESTS
C/R Equipage FDO 3302 (Beech 350 ER/FC SURPOLMAR)
Rédacteur : CP BUIGNET Laurent (Expert Polmar à bord)

Mardi 31/05/2022 (toutes heures en UTC)

0930 Décollage de LFRH
0948 On-Task
0950 CTC aircraft IMAO (FBVTP) sur VHF 122,025
1000 CTC Sapeur sur VHF 122,025
1002 T0 1er déversement
1009 fin de déversement
1 passage scanner UV+Visible (voie IR HS...)
1018 Montée 3000Ft, Passe SLAR, détection Sapeur+pollution à 13 Nm (Photos 1 à 4)
1036 début déversement produit 2
1037 Passe scanner (UV+Visible), détection déversement (Photos 4 & 5)
1043 Fin déversement
2 passages Scanner (UV+Visible) pas de détection
Montée à 3000Ft et éloignement à 10 Nm pour détection SLAR
aucune signature sur le Radar SLAR…
Information reçue du largage SOJA à 0830 UTC
1107 Position Bouée 1 « Soja » : 47°19,29N / 005°02,45W
1116 déversement produit 3
1123 fin de déversement
1er passage scanner à 1500 Ft aucune détection
Montée à 3000Ft pour détection SLAR, no joy
1143 Position Bouée 2 « Soja » 47°19,93N / 005°02,97W
1145 Visuel traces jaunâtres à proximité de la position Bouée 2
1154 Aircraft IMAO FBVTP quitte la Zone
Mise en descente à 1000Ft puis 500Ft pour prises de photos traces de Soja
1200 Passe scanner après détection visuelle traces jaunâtres
détection traces de SOJA sur voies UV et VIS (Photos 10 & 11)
1215 Fin exercice . Off-Task. RTB LBH
1300 Atterrissage à LFRH

Heures de vol effectuées =3h30min

-
Tuesday 05/31/2022
Crew FDO3302
All Hours in UTC Time

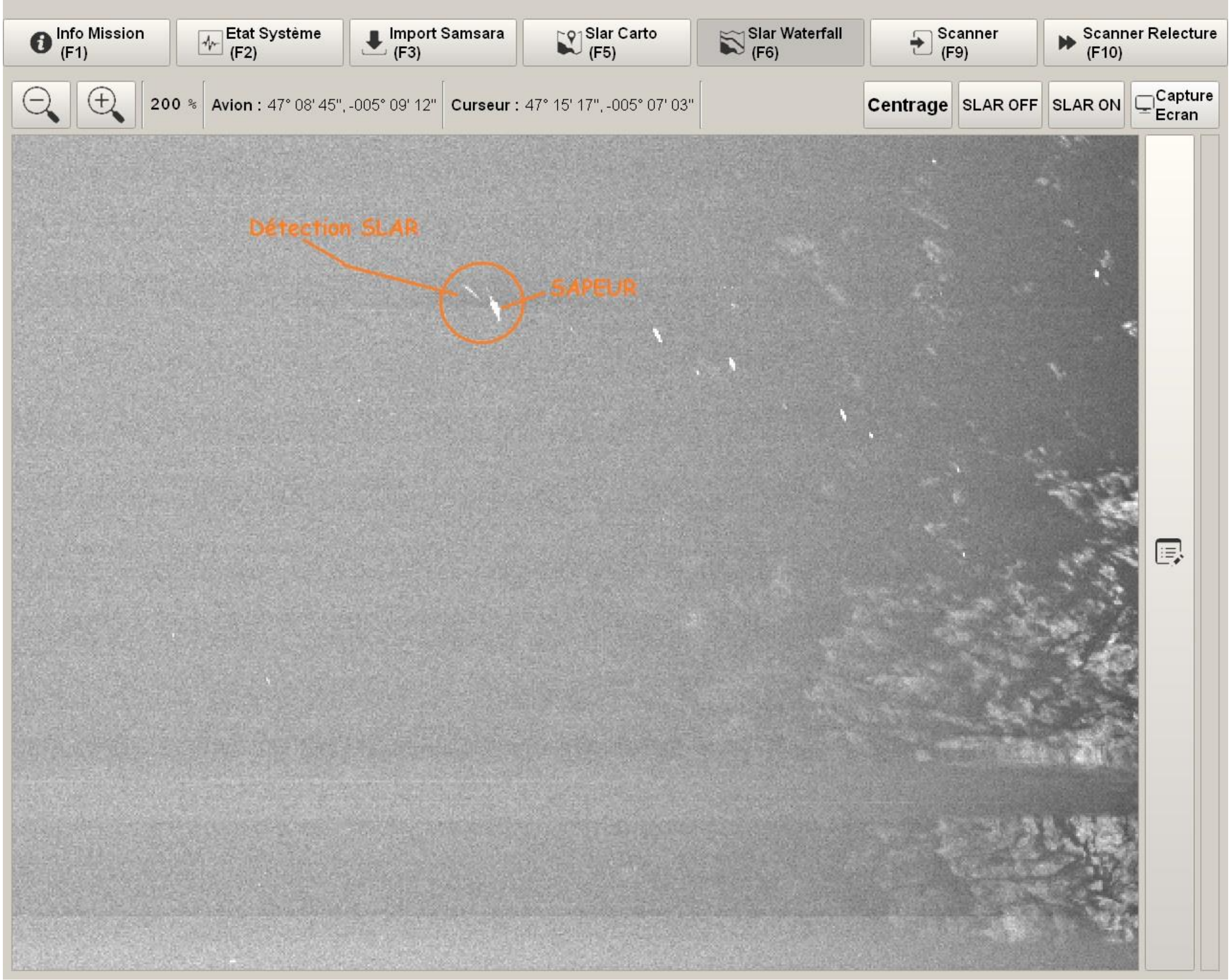
0930 Take of LFRH
0948 On-Task
0950 CTC aircraft IMAO (FBVTP) on VHF 122.025
1000 CTC Sapeur on VHF 122.025
1002 T0 Spill 1
1009 End of Spill
UV+Visible scanner pass (IR channel HS ...)
1018 Climb at 3000Ft, SLAR pass, detection Sapeur+pollution at 13 Nm (Pictures 1 to 4)
1036 T0 Spill 2
1037 Scanner (UV+Visible), spilling detection (Pictures 5 & 6)

1043 End of Spill 2
Scanner PASS(UV+Visible) no detection
Rise at 3000Ft and distance at 10 Nm for SLAR detection
No signature on the SLAR Radar…
Information received that SOJA was dropped at 0830
1107 Position Buoy 1 "Soja": 47°19.29N / 005°02.45W
1116 T0 spill 3
1123 end of spill3
One Scanner pass at 1500 Ft no detection
Rising to 3000Ft for SLAR detection, NO detection
1143 Position Buoy 2 "Soja" 47°19.93N / 005°02.97W
1145 Visual yellowish traces near position Buoy 2
1154 Aircraft IMAO FBVTP leaves the Area
Descending to 1000Ft then 500Ft to take photos of Soya traces
1200 Scanner Pass after detection of yellowish traces
detection SOYA traces on Scanner UV and VIS (Pictures 10 & 11)
1215 End of exercice. Off-Task. RTB LFRH
1300 Landing at LFRH

Total flying hours = 3h30min

Photos des différentes détections / Pictures of the different detections

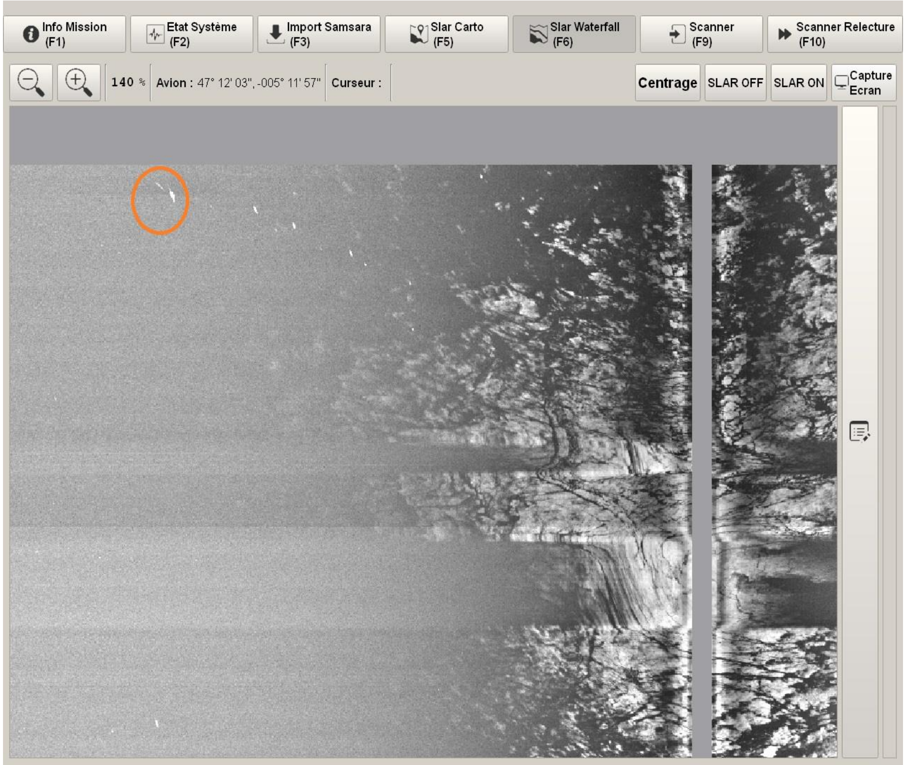
Ph1 : 10H21Z Détection SLAR sur premier déversement (1) Sapeur à gauche
10H21Z SLAR detection on first spill (1) Sapeur on the left



Avion : 47° 08' 45", -005° 09' 12"

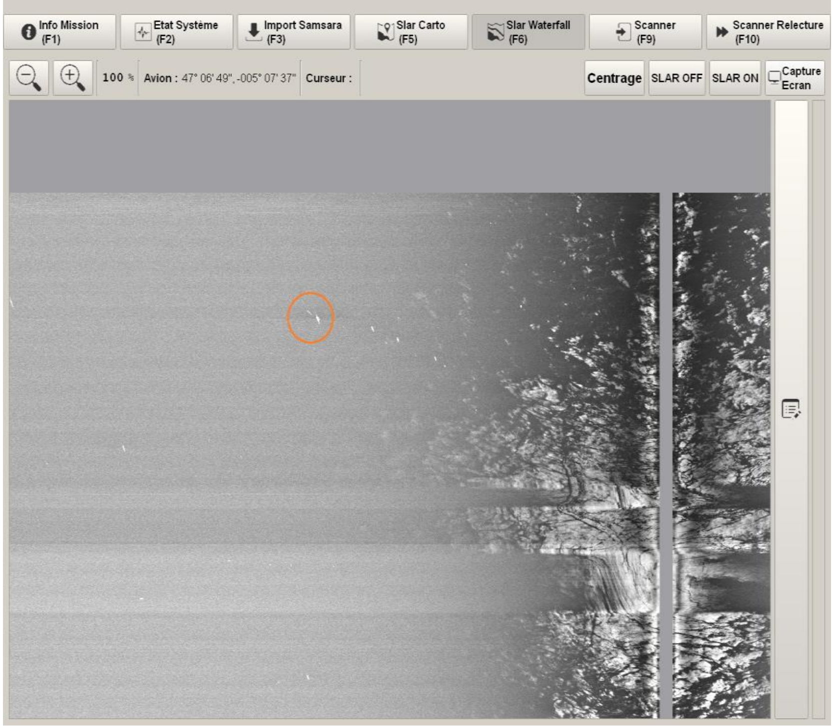
Curseur : 47° 15' 17", -005° 07' 03"

Ph2 : 10H21Z Détection SLAR sur premier déversement (1) Sapeur à gauche
10H21Z SLAR detection on first spill (1) Sapeur on the left



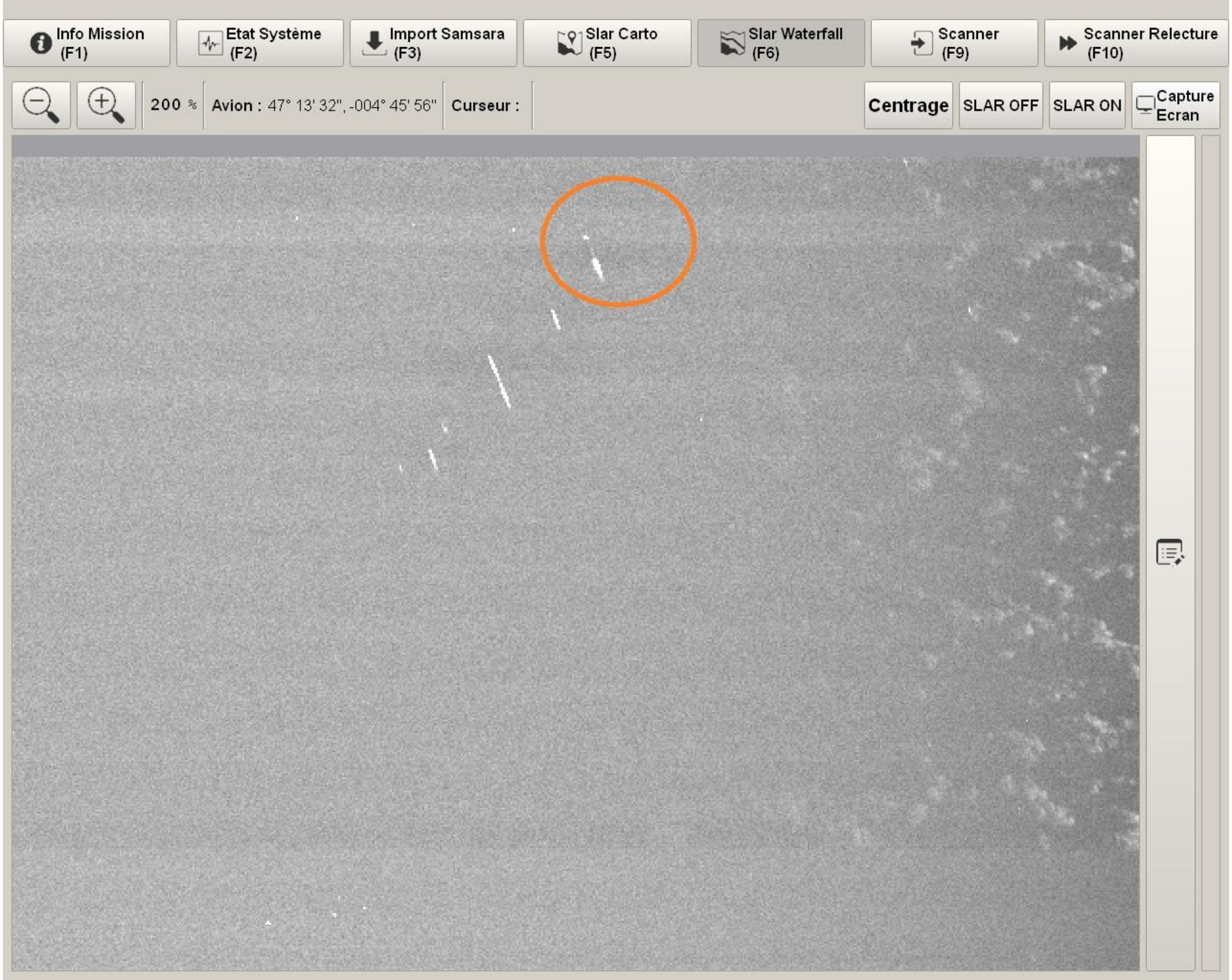
140 % Avion : 47° 12' 03", -005° 11' 57" Curseur :

Ph3 10H21Z Détection SLAR sur premier déversement (1) Sapeur à gauche
10H21Z SLAR detection on first spill (1) Sapeur on the left

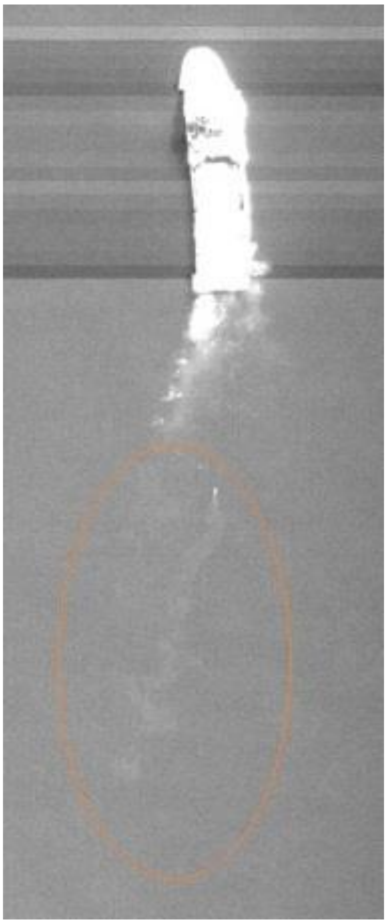


100 % Avion : 47° 06' 49", -005° 07' 37" Curseur :

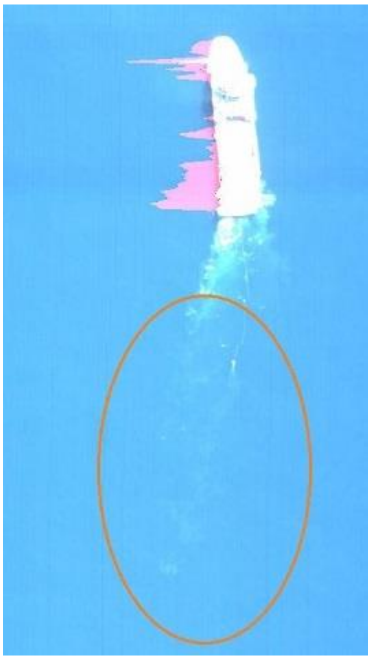
Ph4 : 10h28Z Détection SLAR, sapeur en haut
10h28Z SLAR detection, sapeur up



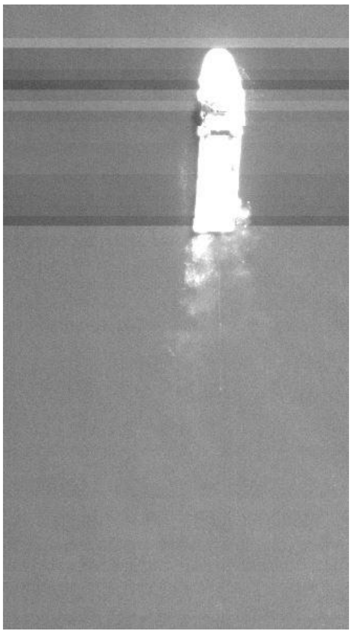
Ph5 1037Z détection déversement 2 lors de la passe Scanner voie UV
1037Z Spill 2 detection on Scanner UV Pass



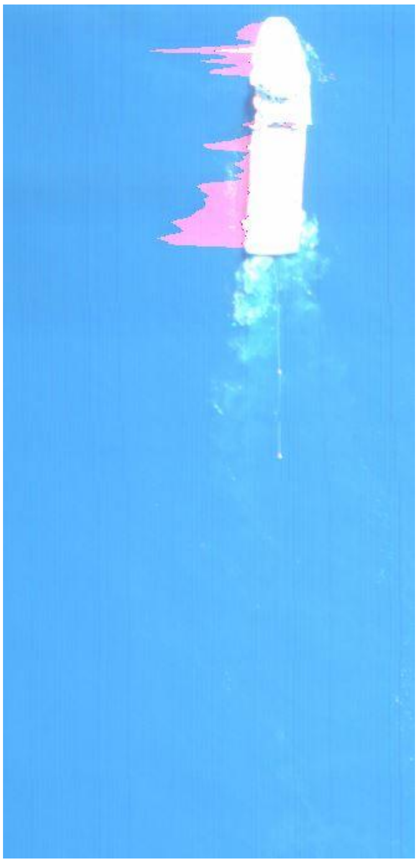
Ph6 1037Z détection déversement 2 sur passe Scanner voie visible
1037Z detection Spill 2 on Scanner Pass Visible



Ph7 : 1045Z déversement 2, Passe Scanner voie UV pas de détection
1045Z Spill 2 No detection on Scanner UV Pass



Ph8 1045Z déversement 2, pas de détection sur passe scanner voie Visible
1045Z Spill 2 No detection on Scanner Pass Visible



Ph9 : 1058Z déversement 2 Passe SLAR Pas de détection
1058Z Spill 2 No SLAR Detection

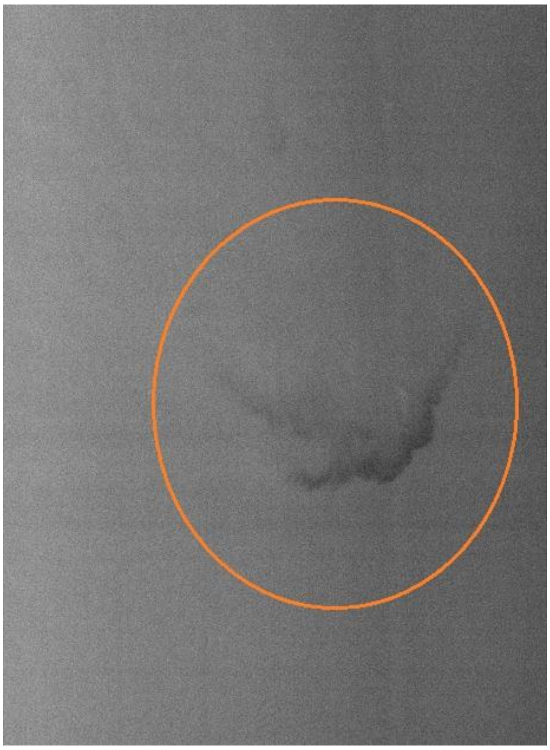
180 %

Avion : 47° 33' 44", -004° 59' 04"

Curseur :

Ph10 : 1200Z détection traces de Soja Scanner voie visible
1200Z Detection Soja on Visible Scanner Pass

Ph11 : 1200Z détection traces de Soja Scanner voie UV
1200Z Detection Soja on UV Scanner Pass



ANNEX V - Full report provided by Belgian civil protection on the MANIFESTS sea trial

Sea trail Manifests 2022

A detection team of the Belgian Civil Protection participated in the sea trails within the Manifests project from 30th of May until the 2nd of June 2022. The team used a SIGIS 2 system of Bruker to identify the released substances. This is a scanning imaging remote sensing system based on the combination of an infrared spectrometer with a single element detector and a scanner system. It is able to measure within a spectral range of 680 - 1500 cm^{-1} , with a maximum spectral resolution of 0.5 cm^{-1}. The device is capable of identify clouds of hazardous materials up to 1 km.

The images that follow will give a view of our results. We used two types of views during the tests.

First of all the correlation view of the SIGIS 2 system compares the measured spectrum against the spectrum of the pure substance in its library. The lighter the colour (up to white) the greater the similarity between the two spectra The other one is the identify view of the system. This shows the spots where it has positively identified a substance (sometimes more than one). To obtain a positive identification the similarity between the two spectra has to be above a certain threshold (correlation almost 1, inherent to the device). Each spot where this threshold is met gives a red square on the screen. On the right side of the screen is mentioned what was identified and how certain the system is of the result (one X is more or less sure, when there are three x's the system is very sure of the positive result. Figures 1 and 2 are examples of both views of the same measurement.

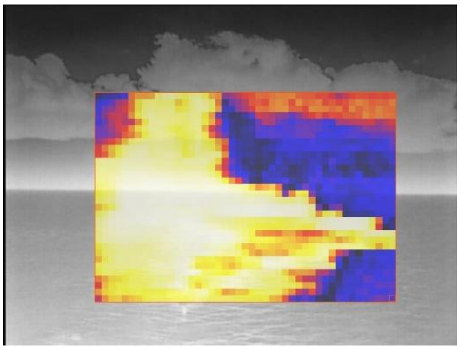


Figure 2: correlation view of the software of the SIGIS 2 system

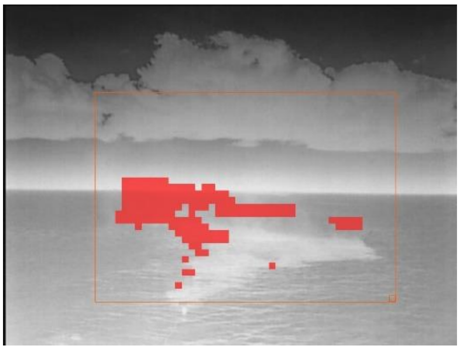


Figure 1: identification view of the SIGIS 2 system

The device was placed on the top of the ship SAPEUR from which hazardous materials were released.

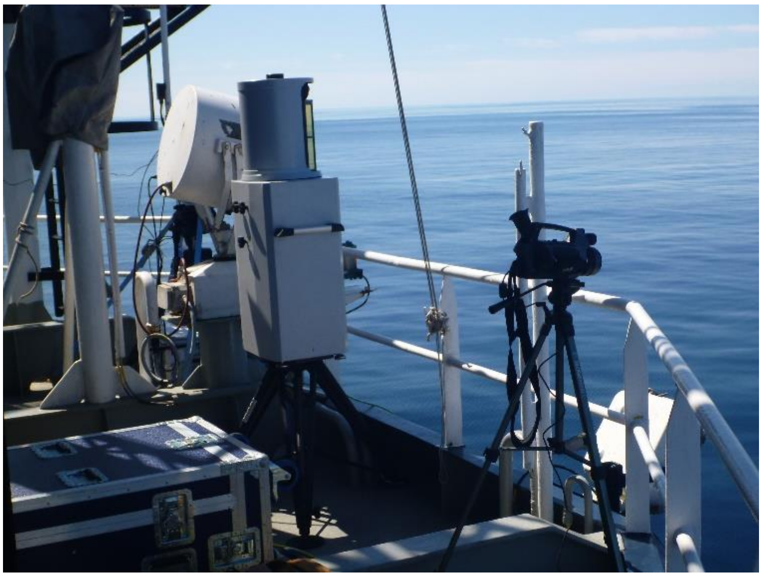


Figure 3: SIGIS-2 from the Belgian Civil Protection on the SAPEUR

Results:

Table 1: Time of detection of the substances with SIGIS 2

Day	Name of the chemical	Volume (m3)	Start Spill Time (UTC)	End Spill Time (UTC)	Detection Time (UTC)	Remarks	Image
31/05/2022	Soybean Oil	1	8:30	8:40	NA	/	/
	N-propyl acetate	1	10:03	10:09	/	Good correlation, no positive detection	Figure 4
	N-butyl acetate	1	10:36	10:43	10:48	Positive after enhanced analysis	Figure 5
	Isopropyl acetate	1	11:16	11:23	11:25	Positive after enhanced analysis	Figure 6
	N-propyl acetate	1	14:20	14:27	14:23	Positive after enhanced analysis	Figure 7 Figure 8
	N-butyl acetate	1	14:32	14:39	14:41	Live positive result	Figure 9 Figure 10
	Isopropyl acetate	1	14:44	14:50	14:53	Positive after enhanced analysis	Figure 11
	Acetone	1	14:56	15:01	/	No result	/
	MTBE	1	15:12	15:18	15:15	Live positive result	Figure 12 Figure 13
1/06/2022	MTBE	1	10:02	10:08	10:04	Live positive result	Figure 14
	Acetone	2	10:37	10:48	/	No result	Figure 15
	Xylene	1	11:23	11:30	/	No result	Figure 16
	Toluene	2	11:51	12:01	11:57	Positive after enhanced analysis	Figure 17 Figure 18

Except for the Soybean Oil, all the other substances had spectra of their pure form within the SIGIS 2 extended library, and thus possible to detect with the device. During the tests however, was noticed that some of the components weren't found by the device. The table gives some information about the measurements that were found and the how the results were obtained. For some substances it took some extra analysis afterwards to find a positive identification, others were found live immediately. MTBE in particular was observed rather quickly after the release.

To visualise the measurements there are two cameras on the SIGIS 2, a normal black-and white camera and an infrared camera. Due to the properties of the released substances we used the infrared camera to visualise the stain on the water surface to have a better orientation of where to aim the device.

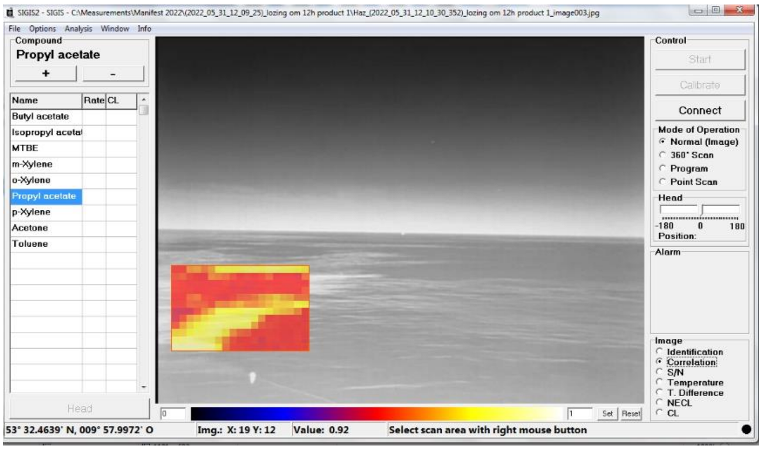
To make sure that the measurements wouldn't take too long only the spectra of the substances that were planned to be released were put in the live library.

The table gives a brief overview of the results. Below the results are discussed in more detail with images of the measurements.

Measurements 31st of May

N-propyl acetate (morning)

The first substance that was released and tested was N-propyl acetate. As mentioned in the table, we did have a positive detection (not even with the enhanced analysis option) at this stage. When you look at the correlation (showed in figure 4) you can see that the similarity of the spectra rises, but doesn't reach an acceptable level for a positive result (inherent to the device).



SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_05_31_12_09_25)_lozing om 12h product 1\Haz_(2022_05_31_12_10_30_352)_lozing om 12h product 1_image003.jpg

Compound: Propyl acetate

Mode of Operation: ● Normal (Image)

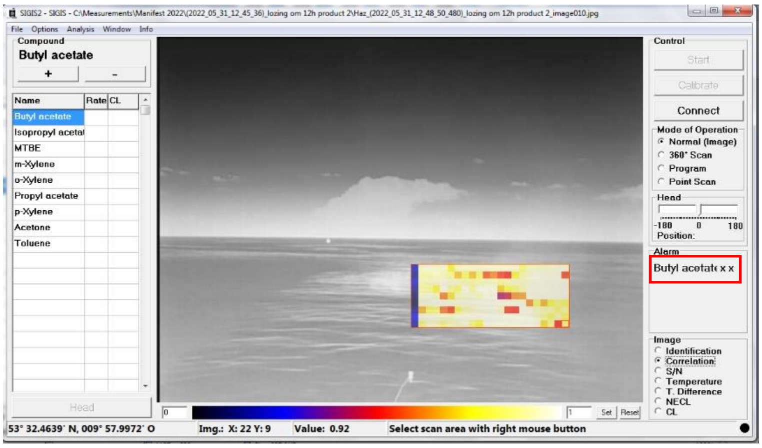
Image: ● Correlation

53° 32.4639' N, 009° 57.9972' O Img.: X: 19 Y: 12 Value: 0.92 Select scan area with right mouse button

Figure 4: results of the first release of N-propyl acetate

N-butyl acetate (morning)

Afterwards N-butyl was released. Figure 5 shows the correlation and the positive identification of the substance. These results were only seen after using the enhanced analysis function of the software. There wasn't a positive live result.



SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_05_31_12_45_36)_lozing om 12h product 2\Haz_(2022_05_31_12_48_50_480)_lozing om 12h product 2_image010.jpg

Compound: Butyl acetate

Mode of Operation: ● Normal (Image)

Alarm: Butyl acetate x x

Image: ● Correlation

53° 32.4639' N, 009° 57.9972' O Img.: X: 22 Y: 9 Value: 0.92 Select scan area with right mouse button

Figure 5: first N-butyl acetate result after enhanced analysis

Isopropyl acetate (morning)

The next figure (figure 6) shows the spots were isopropyl acetone was positively identified (after using the enhanced analysis tool of the software). Each red spot is a positive identification.

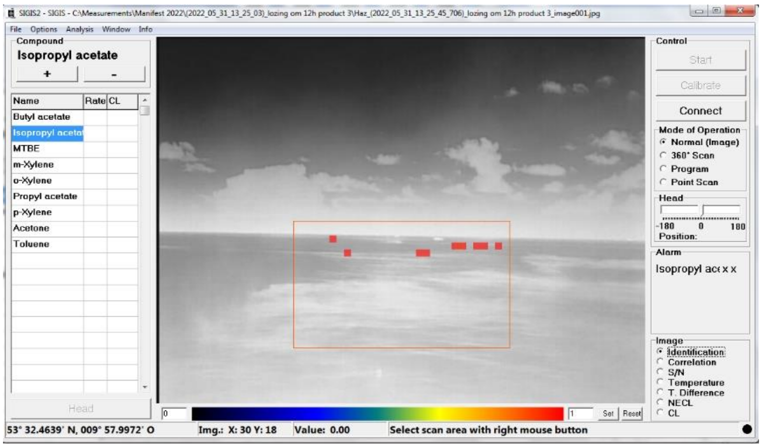


Figure 6: positive identification of isopropyl acetate

In the afternoon N-propyl acetate, butyl acetate and isopropyl acetate were released a second time along with some new substances (Acetone and MTBE).

N-propyl acetate (afternoon)

As in the morning we started off with N-propyl acetate. This time we saw a better correlation rather fast (figure 7) and were able to find a positive result after further analysis of the spectra (figure 8).

Figure 7: live correlation view of propyl acetate

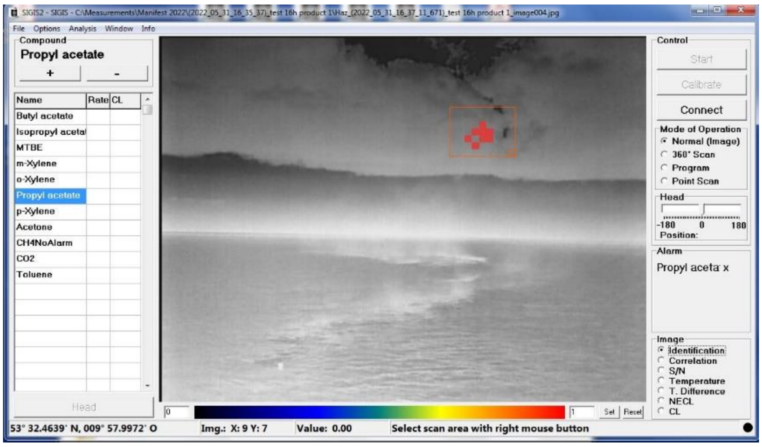


Figure 8: identification view of propyl acetate (enhanced)

N-butyl acetate (afternoon)

Afterwards N-butyl acetate was released. There was an immediate good correlation seen between the measured spectrum (figure 9) and the one in the library and thanks to the enhanced analysis a few minutes after the release we could positively identify the substance (figure 10).

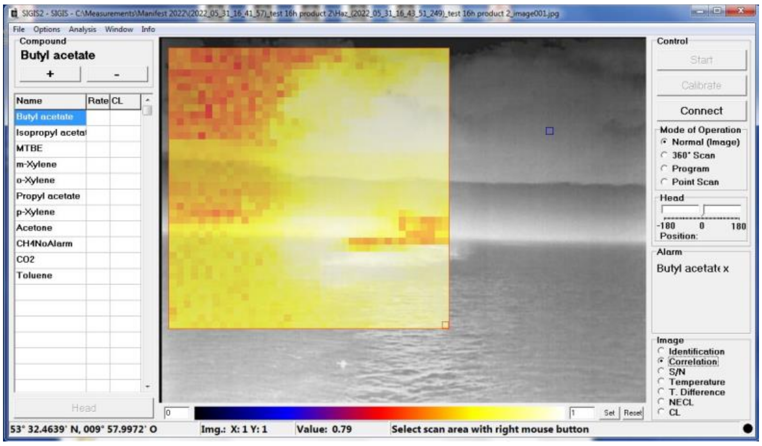


Figure 9: correlation for the N-butyl release

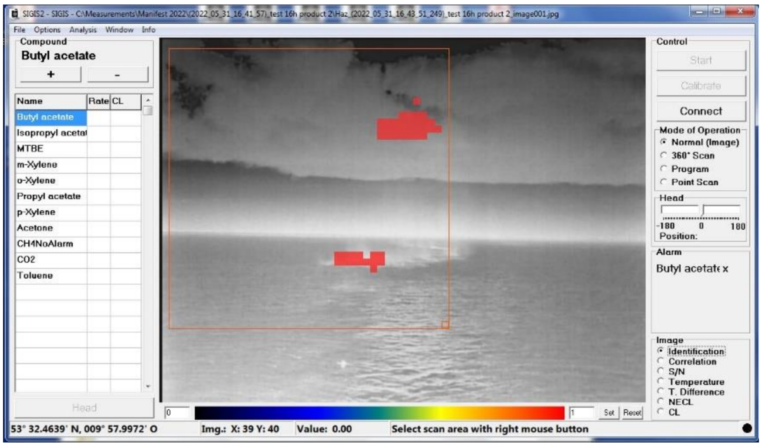


Figure 10: Identification of N-butyl

Isopropyl acetone (afternoon)

Then isopropyl acetate was released. During the release there wasn't a positive identification, but when we used the option to enhance our analysis we could identify the n-butyl-acetate and the isopropyl acetate (figure 11). The yellow squares in the figure are the spots where isopropyl acetate was identified, the red ones were n-butyl residues. This made us conclude that n-butyl acetate is easier to identify for our system than isopropyl acetate. If possible additional testing can provide us more information about the difference in results.

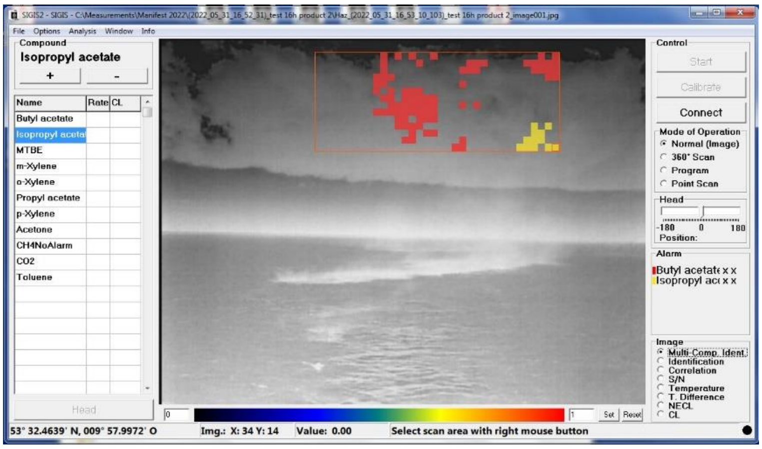


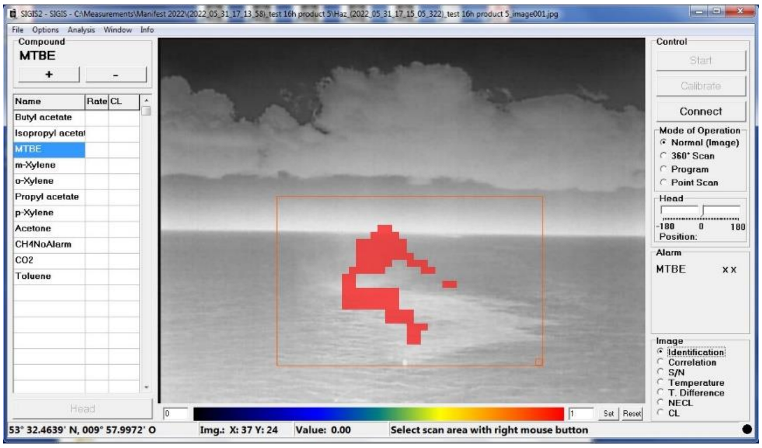
Figure 11: positive results for n-butyl acetate and isopropyl acetate after enhanced analysis.

Acetone

Acetone was the next substance that was released, but there were no results for this. There wasn't a stain in the water that we could see with the infrared camera of the SIGIS 2. Probably the solubility of the acetone made that there wasn't a positive measurement.

MTBE

Methyl tertiary-butyl ether (MBTE) on the other hand was identified instantly (figure 12). We could also get a good visualization of the cloud that was formed (figure 13). This was confirmed by the other IR visualization techniques that were used during the sea trail.


SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_05_31_17_13_58)_test 16h product 5\Haz_(2022_05_31_17_15_05_322)_test 16h product 5_image001.jpg

Compound: MTBE

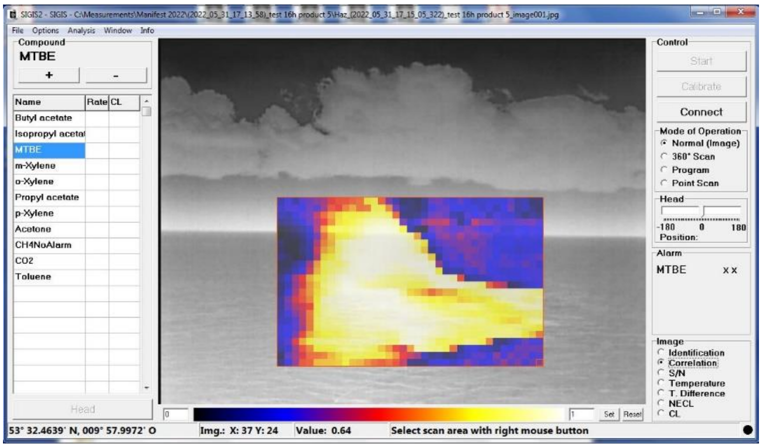
Mode of Operation: ● Normal (Image)

Alarm: MTBE xx

Image: ● Identification

53° 32.4639' N, 009° 57.9972' O Img.: X: 37 Y: 24 Value: 0.00 Select scan area with right mouse button

Figure 12: identification of MTBE


SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_05_31_17_13_58)_test 16h product 5\Haz_(2022_05_31_17_15_05_322)_test 16h product 5_image001.jpg

Compound: MTBE

Mode of Operation: ● Normal (Image)

Alarm: MTBE xx

Image: ● Correlation

53° 32.4639' N, 009° 57.9972' O Img.: X: 37 Y: 24 Value: 0.64 Select scan area with right mouse button

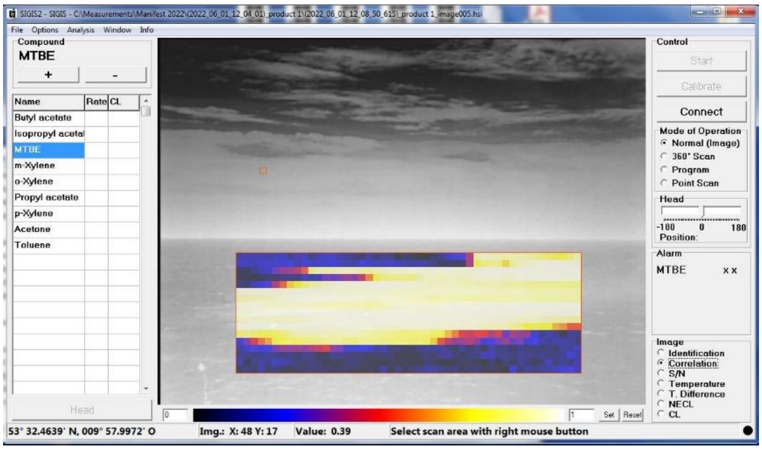
Figure 13: visualisation of the MTBE cloud.

Measurements 1st of June

On the 1st of June four other substances were released. MTBE and acetone were already tested on the 31st of May, toluene and xylene weren't.

MTBE

The first release was MTBE and as with the previous release of MTBE, we had a positive outcome within minutes after the initial release. Figure 14 shows the cloud that was formed. Due to the mild change in weather conditions (a bit more wind and swell on the water) the cloud was flattend.



SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_06_01_12_04_01)_product 1\(2022_06_01_12_08_50_615)_product 1_image005.hsi

Compound: MTBE

Mode of Operation: Normal (Image)

Alarm: MTBE x x

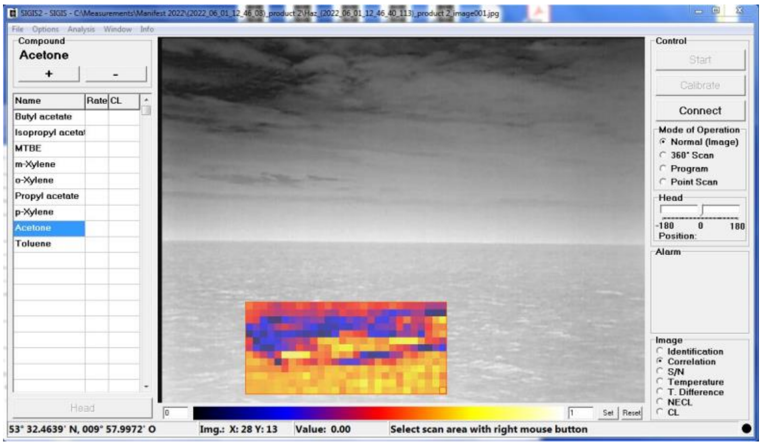
Image: Correlation

53° 32.4639' N, 009° 57.9972' O Img.: X: 48 Y: 17 Value: 0.39 Select scan area with right mouse button

Figure 14: cloud of MTBE on 1th of June.

Acetone

The second substance was acetone. And this was also a copy of the previous test. There wasn't a visualisation of the stain on the water and even after enhanced analysis the device did not give us a positive identification or a good correlation view (as is seen in figure 15).



SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_06_01_12_46_08)_product 2\Haz_(2022_06_01_12_46_40_113)_product 2_image001.jpg

Compound: Acetone

Mode of Operation: Normal (Image)

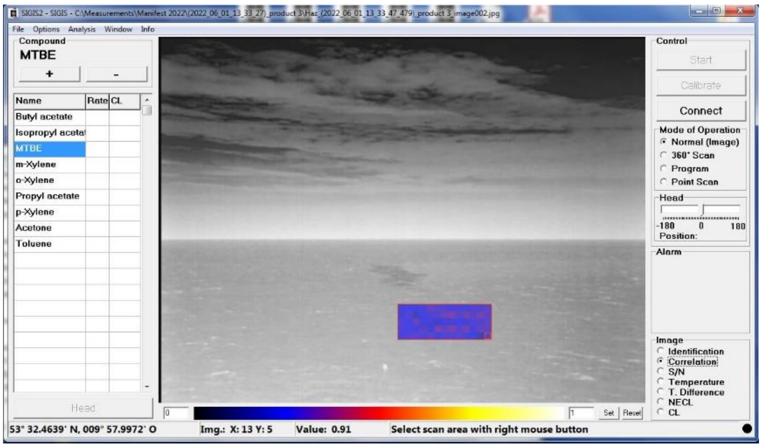
Image: Correlation

53° 32.4639' N, 009° 57.9972' O Img.: X: 28 Y: 13 Value: 0.00 Select scan area with right mouse button

Figure 15: image taken when acetone was released

Xylene

Then xylene was released and a stain was seen with the infrared camera of the SIGIS 2. Although there were three spectra in the system for xylene (the ortho, meta and para spectra were included), we didn't get a positive result. With the correlation view of the system (figure 16), there wasn't even a single spot were the measured spectrum showed resemblance with the three spectra in the library.



SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_06_01_13_33_27)_product 3\Haz_(2022_06_01_13_33_47_479)_product 3_image002.jpg

Compound: **MTBE**

Name	Rate	CL
Butyl acetate		
Isopropyl acetat		
MTBE		
m-Xylene		
o-Xylene		
Propyl acetate		
p-Xylene		
Acetone		
Toluene		

Mode of Operation
● Normal (Image)
○ 360° Scan
○ Program
○ Point Scan

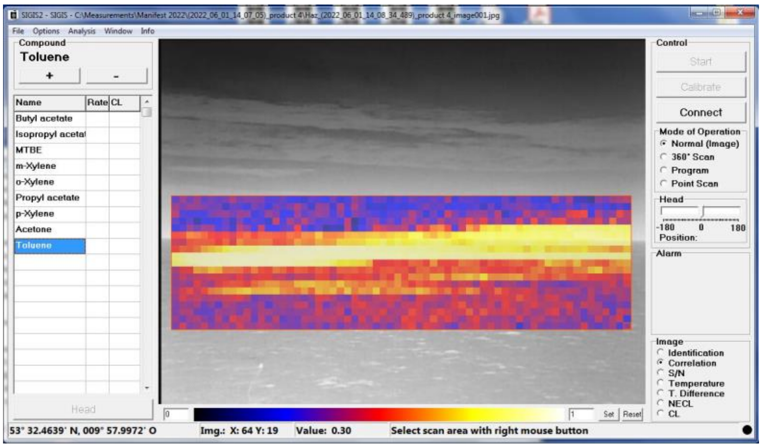
Image
○ Identification
● Correlation
○ S/N
○ Temperature
○ T. Difference
○ NECL
○ CL

53° 32.4639' N, 009° 57.9972' O | Img.: X: 13 Y: 5 | Value: 0.91 | Select scan area with right mouse button

Figure 16: results for xylene

Toluene

The last tested substance was toluene. During the tests only good correlation views were seen (figure 17), even during the release, but the positive identification was only found with the enhanced analysis (figures 18).



SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_06_01_14_07_05)_product 4\Haz_(2022_06_01_14_08_34_489)_product 4_image001.jpg

Compound: **Toluene**

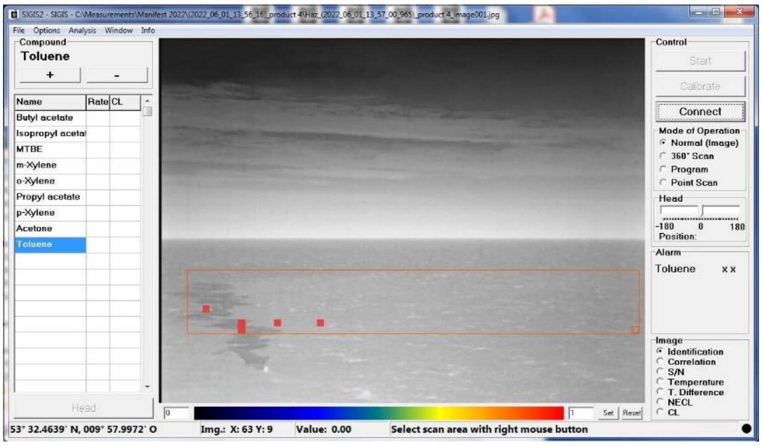
Name	Rate	CL
Butyl acetate		
Isopropyl acetat		
MTBE		
m-Xylene		
o-Xylene		
Propyl acetate		
p-Xylene		
Acetone		
Toluene		

Mode of Operation
● Normal (Image)
○ 360° Scan
○ Program
○ Point Scan

Image
○ Identification
● Correlation
○ S/N
○ Temperature
○ T. Difference
○ NECL
○ CL

53° 32.4639' N, 009° 57.9972' O | Img.: X: 64 Y: 19 | Value: 0.30 | Select scan area with right mouse button

Figure 17: live view of measurement with toluene in correlation view



SIGIS2 - SIGIS - C:\Measurements\Manifest 2022\(2022_06_01_13_56_16)_product 4\Haz_(2022_06_01_13_57_00_965)_product 4_image001.jpg

Compound: **Toluene**

Name	Rate	CL
Butyl acetate		
Isopropyl acetat		
MTBE		
m-Xylene		
o-Xylene		
Propyl acetate		
p-Xylene		
Acetone		
Toluene		

Mode of Operation
● Normal (Image)
○ 360° Scan
○ Program
○ Point Scan

Alarm
Toluene x x

Image
● Identification
○ Correlation
○ S/N
○ Temperature
○ T. Difference
○ NECL
○ CL

53° 32.4639' N, 009° 57.9972' O | Img.: X: 63 Y: 9 | Value: 0.00 | Select scan area with right mouse button

Figure 18: positive identification after enhanced analysis.

Outcomes

Our device was tested for the first time at sea with live releases of large amounts of hazardous substances. Therefor we were able to see the impact of the swell on the water on our measurements and most importantly the impact of doing measurements above seawater. It was a pleasant surprise to see all the positive outcomes. A majority of the released substances were detected (live or with the enhanced analysis) and we were able to have a good view of the stains of the substances on the water and the formation of clouds. The negative measurements for the acetone might be explained through its solubility, for xylene we are still searching.

Evi Van Cleynenbreugel

Captain of the Belgian Civil Protection

ANNEX VI - Full report provided by ONERA (France) on the MANIFESTS sea trial

RAPPORT FINAL

Télédétection aéroportée et sol de liquides chimiques évaporants en mer par l'instrument multispectral infrarouge SIMAGAZ - Campagne MANIFEST 2022

Auteurs : P.-Y. Foucher ; R. Domel ; S. Langlois ; P. Déliot

DÉPARTEMENT OPTIQUE ET TECHNIQUES
ASSOCIÉES

RF 1/32868 DOTA - Septembre 2022

Ref: n° 210890

DÉPARTEMENT OPTIQUE ET TECHNIQUES ASSOCIÉES

Rapport Final N° RF 1/32868 DOTA

Ref: n° 210890

Septembre 2022

Télédétection aéroportée et sol de liquides chimiques évaporants en mer par l'instrument multispectral infrarouge SIMAGAZ - Campagne MANIFEST 2022

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ONERA
THE FRENCH AEROSPACE LAB

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Ref: n° 210890

Emetteur : **DÉPARTEMENT OPTIQUE ET TECHNIQUES ASSOCIÉES**	Contractant : **CEDRE**	Référence du contrat : **Ref: n° 210890**
		Date : **Septembre 2022**

Titre : **Télédétection aéroportée et sol de liquides chimiques évaporants en mer par l'instrument multispectral infrarouge SIMAGAZ - Campagne MANIFEST 2022**

Auteur(s) : **P.-Y. Foucher ; R. Domel ; S. Langlois ; P. Déliot**

PROTECTION : Titre : AUCUNE Fiche : AUCUNE Document : AUCUNE	Calendrier de déclassification Titre : Sans objet Fiche : Sans objet Document : Sans objet

Résumé d'auteur :
Ce document est le rapport final concernant la prestation de mesure réalisée par l’ONERA pour le compte du le Centre de documentation de recherche et d'expérimentation sur les pollutions accidentelles des eaux (CEDRE) qui s’est déroulée dans le cadre des expérimentations en mer du projet Européen MANIFEST avec le soutien du Centre d’Expertise Pratique de lutte antipollution (CEPPOL). L’ONERA a été sollicité pour déployer deux instruments SIMAGAZ : une caméra à bord du navire SAPEUR du CEPPOL et une en configuration aéroportée. Cette campagne fait suite à la campagne IPOMAC qui s’est déroulée en 2021 où la caméra SIMAGAZ avait déployé avec succès à bord du Sapeur. L’objectif particulier de cette campagne pour l’ONERA est de voir en quelle mesure il était possible de visualiser des produits chimiques volatils en mer suite à des déversements accidentels de produits liquides évaporant lors du transport maritime avec l’instrument multispectral infrarouge SIMAGAZ intégré sur une plateforme avion à plusieurs centaines de mètres d’altitude. Ce rapport présente donc les résultats d’observation, de détection, d’identification et de visualisation quantitative des panaches s’évaporant des nappes déversées en surface obtenus lors des essais en mer réalisés les 31 Mai et 1er Juin 2022 au large de Brest. Cinq produits volatils parmi les sept testés ont pu être visualisés par la caméra SIMAGAZ sous forme gazeuse en configuration aéroportée et sol, les nappes de tous les produits ont aussi pu être observées.

Mots Clés :
GAZ ATMOSPHERIQUE ; NAPPE LIQUIDE ; SURFACE MARINE ; MULTISPECTRAL ; INFRAROUGE THERMIQUE

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TABLE DES MATIERES

1. INTRODUCTION

Ce document est le rapport final concernant la prestation de mesure réalisée par l’ONERA pour le compte du Centre de documentation de recherche et d'expérimentation sur les pollutions accidentelles des eaux (CEDRE) [DR1] qui s’est déroulée dans le cadre des expérimentations en mer du projet Européen MANIFEST [DR2] avec le soutien du Centre d’Expertise Pratique de lutte antipollution (CEPPOL). L’ONERA a été sollicité pour déployer deux instruments SIMAGAZ : une caméra à bord du navire SAPEUR du CEPPOL et une en configuration aéroportée. Cette campagne fait suite à la campagne IPOMAC [DR3] qui s’est déroulée en 2021 où la caméra SIMAGAZ avait été déployée avec succès à bord du SAPEUR. L’objectif particulier de cette campagne pour l’ONERA est de voir en quelle mesure il était possible de visualiser des produits chimiques volatils en mer suite à des déversements accidentels de produits liquides évaporant lors du transport maritime avec l’instrument multispectral infrarouge SIMAGAZ intégré sur une plateforme avion à plusieurs centaines de mètres d’altitude. Ce rapport présente donc les résultats d’observation, de détection, d’identification et de visualisation quantitative des panaches s’évaporant des nappes de produits déversés en surface obtenus lors des essais en mer réalisés les 31 Mai et 1er Juin 2022 au large de Brest. Cinq produits volatils parmi les sept testés ont pu être visualisés par la caméra SIMAGAZ sous forme gazeuse en configuration aéroportée et sol, les nappes de tous les produits ont aussi pu être observées.

2. DOCUMENTS APPLICABLES ET DE RÉFÉRENCE

[DR1] Contrat CEDRE – ONERA 2022

[DR2] https://wwz.cedre.fr/Projets/2021/MANIFESTS-2021-2022

[DR3] Rapport ONERA - Campagne IPOMAC 2021

3. CAMPAGNE DE MESURE

3.1. Instruments mis en œuvre

Les prototypes **Simagaz_Lwir** (nommés SIMAGAZ par la suite) ont été développés par l’ONERA dans le cadre du projet NAOMI en collaboration avec TOTAL et du FUI IMAGAZ (LYNRED, NOXANT, BERTIN, TOTAL, ONERA). Il s’agit de la première caméra compacte (1kg, 1L) multispectrale permettant d’offrir une visualisation quantitative d’un panache de méthane et de son évolution temporelle. La caméra (Figure 1) a été évaluée à de nombreuses reprises sur le site d’essai TADI (TOTAL) à Lacq sur des fuites maitrisées. Bien que développé à l’origine pour des aspects de sécurité industrielle, ce prototype s’est déjà montré efficace pour répondre aux besoins des équipes d’intervention en mer, dans le cas où des rejets accidentels de produits chimiques évaporant se produisent.

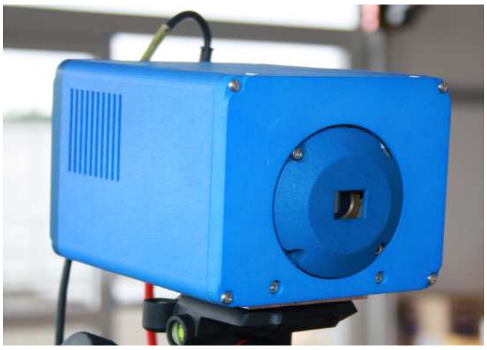


Figure 1: Caméra multispectrale infrarouge SIMAGAZ

3.1.1. SIMAGAZ sur le SAPEUR

De façon identique à la campagne IPOMAC de 2021, une première caméra est montée sur une tourelle Pan-Tilt associée à une centrale inertielle afin de stabiliser la ligne de visée et de limiter les déplacements sur l'image liés à la houle (Figure 2). Pour chaque essai, un logiciel de traitement déporté permet de visualiser en temps quasi-réel les cartes de détection en lien avec la scène observée permettant en particulier de sécuriser les zones d'intervention.

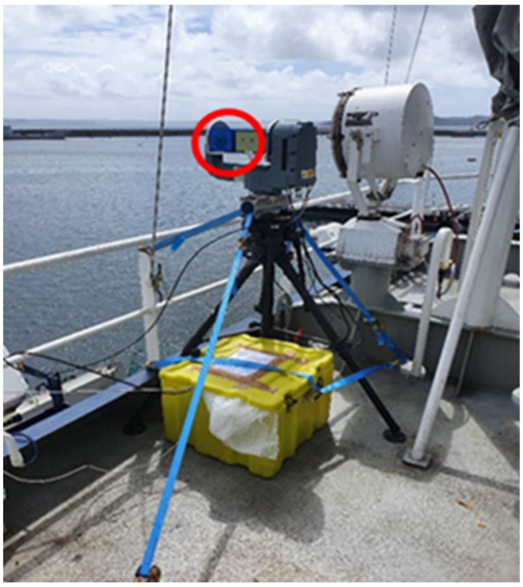


Figure 2: Instrument SIMAGAZ (en bleu entouré par un cercle rouge) disposé sur une plateforme stabilisée à bord du SAPEUR lors des essais en mer.

3.1.2. SIMAGAZ sur Beech Craft

Une seconde camera a été intégrée dans le Piper-aztec PA03 de la compagnie IMAO. L'ONERA a adapté une plateforme existante stabilisée pour assurer l'intégration de la caméra SIMAGAZ. La Figure 3 illustre ainsi le porteur et l'intégration de la caméra au niveau de la trappe photo de l'avion.

Figure 3 : Gauche : IMAO PA03, Droite : SIMAGAZ (en bleu entourée par un cercle rouge) intégrée sur la plateforme stabilisée au-dessus de la trappe photo.

Les acquisitions aéroportées ont eu lieu pour des créneaux bien définis (afin d'éviter des co-activités avec les autres partenaires du projet MANIFEST) pour des altitudes de 300 et 800 m. Un premier traitement des données a pu être réalisé à bord permettant de fournir une visualisation de la position des panaches de gaz vis-à-vis du bateau de la zone d'intervention potentielle des secours.

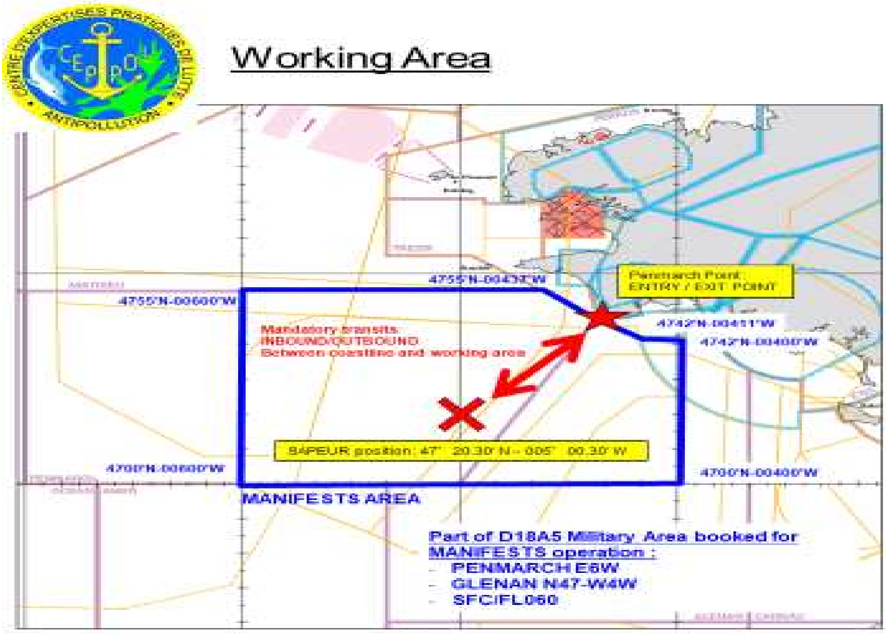


Figure 4 : Localisation de la zone de déversement

3.2. Déversement des produits liquides

Les essais se sont déroulées aux larges des côtes Bretonnes (Figure 4) entre le 31 Mai et le 1er Juin, sept produits chimiques évaporant ont été déversés depuis le BAAS SAPEUR sous la responsabilité du CEDRE et du CEPPOL. Les propriétés des produits déversés sont présentées dans Table 1. La Table 2 définit la position du SAPEUR au moment de chaque déversement. Ces déversements de 1 m^3 (excepté pour le Toluène et l'Acétone : 2 m^3) durent approximativement 5 min et le délai moyen entre deux déversements est d'une demi-heure.

Table 1 : Products properties

Product	N° CAS	Density	Vapor pressure	Solubility	Standard behaviour classification
		kg.m^{-3}, 20 °C	*kPa, 20 °C*	*g.L^{-1}, 20 °C*	
N-Butyl-acetate	123-86-4	0,880	1,2	7	FED (Floating, Evaporating, Diluting)
N-Propyl-acetate	109-60-4	0,888	0,33	18,9	ED
Isopropyl acetate	108-21-4	0,874	6,33	18	ED
Acetone	67-64-1	0,783	24,7	Miscible	DE
Methyl – Ter Butyl –Ether (MTBE)	1634-04-4	0,741	26,8	48	ED
Xylenes (isomers mixing)	1330-20-7 90989-38-1	0,87	0,89	< 0,02	FE
Toluène	108-88-3	0,867	2,91	0,5	E

Table 2 : Horaires et positions des déversements

Slot#	Day	Name of the chemical	Volume (m3)	Start Spill Time (UTC)	Start Spill Latitude	Start Spill Longitude	End Spill Time (UTC)	End Spill Latitude	End Spill Longitude	Winds	Sea
1	31-mai	Soyabean Oil	1	8h30	47°20,06	05°00,405	8h40	47°20,014	5°00,385	0	0
		N-propyl acetate	1	10h03	47°20,196	05°00,42	10h09	47°20,246	5°00,385	0	0
		N-butyl acetate	1	10h36	47°20,298	05°00,147	10h43	47°20,262	5°00,061	2 kn - 260°	0
		Isopropyle acetate	1	11h16	47°20,110	04°59,618	11h23	47°20,084	4°59,521	2 kn - 270°	0
2	31/05/2022	N-propyl acetate	1	14h20	47°22,039	05°02,523	14h27	47°22,264	5°02,407	7 kn - 15°	2
		N-butyl acetate	1	14h32	47°22,481	05°02,297	14h39	47°22,678	5°02,180	6 kn - 15°	2
		Isopropyle acetate	1	14h44	47°22,873	05°02,267	14h50	47°23,070	5°01,950	6 kn - 30°	2
		Acetone	1	14h56	47°23,298	05°01,815	15h01	47°23,54	5°01,66	3,5 kn - 15°	2
		MTBE	1	15h12	47°23,936	5°01,423	15h18	47°24,126	5°01,290	2,5 kn - 15°	2
3	01/06/2022	MTBE	1	10h02	47°16,053	5°11,026	10h08	47°16,205	5°11,200	14 kn - 60°	2
		Acetone	2	10h37	47°16,965	5°11,994	10h48	47°17,285	5°12,275	15 kn - 60°	2
		Xylene	1	11h23	47°18,372	5°13,081	11h30	47°18,588	5°13,202	12 kn - 60°	2
		Toluene	2	11h51	47°19,247	5°13,550	12h01	47°19,600	5°13,690	12 kn - 60°	2

3.3. Tableau récapitulatif du déroulement des acquisitions et observations

3.3.1. Acquisitions SIMAGAZ depuis le SAPEUR

Le tableau suivant répertorie les essais concernant la caméra SIMAGAZ montée à bord du SAPEUR avec le code couleur suivant :

Vert => produit recherché détecté automatiquement (et donc quantifiable)
Jaune => produit recherché visualisé mais difficilement détectable automatiquement
Orange=> produit recherché non visualisé

Les acquisitions SIMAGAZ durent ici en moyenne 5 minutes et de façon générale 2 acquisitions sont réalisées pendant et après le déversement.

Les plages horaires sont divisées en 3 « SLOT » identifiés Table 2 ci-dessus. Pour les SLOT1 et SLOT 2 tous les produits ont bien été identifiés et chaque acquisition SIMAGAZ. Pour le SLOT2 la direction du bateau étant très stable, les observations associées au produit N permettent alors d'observer le produit N-1 ce qui permet d'analyser la persistance dans le temps et avec la distance de l'observation des gaz évaporés. Pour le SLOT3, dans le cas de l'Acétone et du MTBE, dès la deuxième acquisition le produit gazeux n'est plus observé : la dynamique d'évaporation s'est révélée plus rapide que pour le SLOT2.

Table 3 : Acquisitions sur les HNS évaporant réalisées depuis le SAPEUR pour les différents SLOT

	N-propyl acetate	N-butyl-acetate	Isopropyl acetate	Acetone	MTBE
SLOT 1	CAGIR2-N-PROPYL-22-05-31-0003	CAGIR2-N-BUTYL-22-05-31-0004 CAGIR2-N-BUTYL-22-05-31-0005	CAGIR2-N-ISOPROPYL-22-05-31-0006 CAGIR2-N-ISOPROPYL-22-05-31-0007		
SLOT 2	CAGIR2-N-PROPYL-22-05-31-0008 CAGIR2-N-PROPYL-22-05-31-0009	CAGIR2-N-BUTYL-22-05-31-0010	CAGIR2-N-ISOPROPYL-22-05-31-0011	CAGIR2-ACETONE-22-05-31-0012	CAGIR2-MTBE-22-05-31-0013 CAGIR2-MTBE-22-05-31-0014
SLOT3				CAGIR2-ACETONE-22-06-01-0006 CAGIR2-ACETONE-22-06-01-0012	CAGIR2-MTBE-22-06-01-0001 CAGIR2-MTBE-22-06-01-0005

Les acquisitions durent en moyenne 10 minutes en visée fixe vers le point de déversement. Chaque produit a donc pu être suivi sur une période allant de 15 mn à 1h (tant qu'il n'a pas disparu ou que la trajectoire du navire ne change pas).

3.3.2. Acquisitions à partir du capteur SIMAGAZ embarqué sur porteur aéroporté

Le tableau suivant répertorie les essais du SLOT1 et du SLOT3 concernant la caméra SIMAGAZ aéroportée intégrée sur le beechcraft IMAO avec le code couleur suivant :

Vert => produit recherché détecté automatiquement (et donc quantifiable)
Jaune => produit recherché visualisé mais difficilement détectable automatiquement
Orange=> produit recherché non visualisé

Les lignes de vol s'étalent sur une distance de 3 à 6 km sur une largeur de 280 m pour les altitudes de vol de 300 m et sur une largeur de 750 m pour les altitudes de vol à 800 m. La visualisation de tous les gaz a été assurée avec néanmoins très peu de contraste concernant l'acétone pour lequel la détection automatique s'avère peu concluante.

Produit observé	Heure de fin de déversement (TU)	Nom de l'acquisition SIMAGAZ Aéroportée	Altitude d'acquisition (m)	Heure d'acquisition (TU)	Temps après la fin du déversement (min)	Visualisation	Détection automatique
N-propyl acetate	10h09	31-05-2022-MANIFEST-SLOT1_SEA0003	800 m	10:21:19.810	14	🟩	🟩
N-propyl acetate	10h09	31-05-2022-MANIFEST-SLOT1_SEA0004	800 m	10:24:09.940	17	🟩	🟩
N-propyl acetate	10h09	31-05-2022-MANIFEST-SLOT1_SEA0009	800 m	10:58:46.870	50	🟩	🟨
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0006	300 m	10:42:41.860	0	🟩	🟩
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0007	300 m	10:48:33.340	5	🟩	🟩
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0008	800 m	10:54:56.140	12	🟩	🟩
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0009	800 m	10:58:46.870	15	🟩	🟩
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0010	300 m	11:04:42.830	20	🟩	🟩
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0011	300 m	11:22:05.370	37	🟩	🟩
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0012	300 m	11:26:08.830	42	🟩	🟩
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0013	800 m	11:34:19.120	51	🟩	🟩
N-butyl acetate	10h43	31-05-2022-MANIFEST-SLOT1_SEA0014	800 m	11:38:40.250	55	🟩	🟩
Iso-propyl acetate	11h23	31-05-2022-MANIFEST-SLOT1_SEA0011	300 m	11:22:05.370	0	🟩	🟩
Iso-propyl acetate	11h23	31-05-2022-MANIFEST-SLOT1_SEA0012	300 m	11:26:08.830	3	🟩	🟩
Iso-propyl acetate	11h23	31-05-2022-MANIFEST-SLOT1_SEA0013	800 m	11:34:19.120	11	🟩	🟩
Iso-propyl acetate	11h23	31-05-2022-MANIFEST-SLOT1_SEA0014	800 m	11:38:40.250	15	🟩	🟩

Produit observé	Heure de fin de déversement (TU)	Nom de l'acquisition SIMAGAZ Aéroportée	Altitude d'acquisition (m)	Heure d'acquisition (TU)	Temps après la fin du déversement (min)	Visualisation	Détection automatique
MTBE	10h08	01-06-2022-MANIFEST-SLOT3_SEA0012	300 m	10:07:39.200	0	🟩	🟩
MTBE	10h08	01-06-2022-MANIFEST-SLOT3_SEA0015	800 m	10:22:32.650	14	🟧	🟧
Acetone	10h48	01-06-2022-MANIFEST-SLOT3_SEA0019	300 m	10:46:00.060	0	🟩	🟨
Toluene	11h30	01-06-2022-MANIFEST-SLOT3-SEA0033	800 m	12:01:05.270	0	🟩 Nappe uniquement	🟩
Xylene	12h01	01-06-2022-MANIFEST-SLOT3-SEA0034	800 m	12:06:23.080	5	🟩 Nappe uniquement	🟩
Xylene	12h01	01-06-2022-MANIFEST-SLOT3-SEA0036	800 m	12:15:27.730	14	🟩 Nappe uniquement	🟩
Xylene	12h01	01-06-2022-MANIFEST-SLOT3-SEA0037	800 m	12:20:12.980	19	🟩 Nappe uniquement	🟩
Xylene	12h01	01-06-2022-MANIFEST-SLOT3-SEA0038	800 m	12:25:32.290	24	🟩 Nappe uniquement	🟩

4. ANALYSE DES TESTS

4.1. Introduction – Signatures spectrales

Les acquisitions sont classiquement composées de 3 séquences : i) séquence « sans gaz », le tuyau de déversement est à l’eau, sa sortie est matérialisée par une bouée, ii) déversement du liquide sur une durée de 5 min pour 1 m^3 de produit, iii) fin du déversement, purge et remontée du tuyau sur le bateau.

Pour ces différentes séquences nous présentons les images de détection et de quantification, les durées et les étendues spatiales observées avec l’instrument SIMAGAZ pour les nappes et les produits s’évaporant.

Le déversement de produits chimiques est responsable de deux modifications de l’environnement thermique d’une scène que l’on peut observer en télédétection infrarouge : la nappe en surface et le gaz évaporant. Le produit à l’état liquide se repère par la création d’une nappe en surface d’aspect « lisse » du fait de l’atténuation des vagues de capillarité ayant une température apparente différente de celle de l’eau (pour les produits miscibles cette nappe n’est pas toujours visible). Cette signature est observable sur l’ensemble du spectre thermique infrarouge et donc par un instrument large bande. Les produits sous forme de gaz ne sont plus opaques et vont avoir un comportement très marqué spectralement en lien avec la position des raies d’absorption (base de données spectroscopiques connues a priori). Pour la plupart des gaz, cette signature locale est diluée lorsqu’on moyenne sur toute la bande spectrale, elle devient invisible pour un instrument large bande. Un instrument comme SIMAGAZ permettant de séparer l’information infrarouge pour différentes régions spectrales devient alors nécessaire pour détecter, identifier ou quantifier ces émanations.

Les signatures observables par un instrument donné vont dépendre donc du gaz, de sa quantité, de l’environnement, des filtres spectraux de l’instrument et de son rapport signal sur bruit. Nous présentons pour les différents produits de la campagne IPOMAC les signatures observables par SIMAGAZ et les quantités associées. Sur la figure ci-dessous sont indiquées pour chaque gaz, les valeurs de concentrations correspondantes à un contraste de 0.5 K observable par SIMAGAZ. Ces valeurs correspondent environ à 5 fois la valeur seuil de détection pour chaque gaz (associée à un contraste thermique de 2 K). La limite de détection se situant autour de 0.1 K.

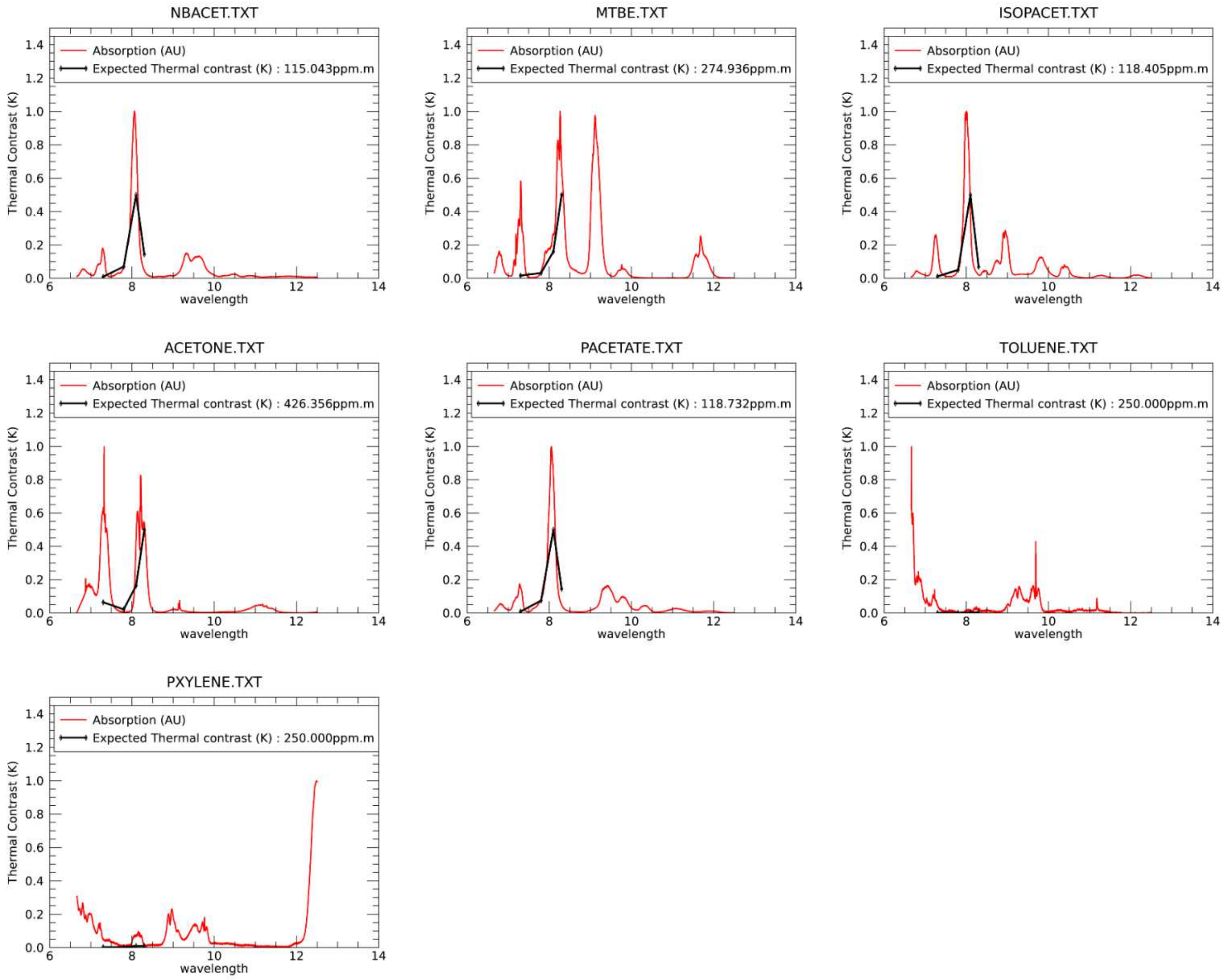


Figure 5 : Signatures spectrales (courbes noires) en Kelvin attendues pour SIMAGAZ pour les différents gaz étudiés comparées aux absorptions théoriques (rouge en unité arbitraire). Les valeurs en concentration intégrées en ppm.m sur les figures

correspondent (dans le cas où le gaz est détectable) à un contraste observable de 0.5K par SIMAGAZ (pour un contraste thermique de 2 K dans la scène)

Il y a donc plusieurs cas de figure :

- Acétate de Butyle, Iso-propyl acétate, N-propyly acétate, MTBE et Acétone : cas où les filtres SIMAGAZ sont bien placés par rapport aux absorptions maximales des gaz recherchés et les concentrations détectables sont faibles (de l'ordre de la centaine ppm.m). Néanmoins dans le cas de l'acétone on peut noter un seuil de détection (~ 100 ppm.m) correspondant à une concentration plus élevée que pour les autres gaz (25 - 50 ppm.m).

- Acétate de Butyle, Iso-propyl acétate, N-propyl acétate : gaz pour lesquelles les signatures spectrales sont très proche. Ainsi du fait des incertitudes liées à la prise de mesure il est fort probable que sans connaissance a priori supplémentaire il soit difficile voire impossible de séparer ces trois gaz à partir des images spectrales SIMAGAZ.

- P-Xylène : cas où les filtres SIMAGAZ sont mal placés par rapport aux absorptions maximales des gaz recherchés mais les concentrations très importantes pourraient être détectées.

- Toluène et O-xylène (non montré ici, absorption quasi nulle sur le domaine SIMAGAZ) : cas où les filtres SIMAGAZ sont mal placés par rapport aux absorptions maximales des gaz recherchés et où la probabilité d'observation du gaz est très faible.

4.2. Mesures depuis le navire

Les mesures depuis le SAPEUR confirment les résultats de la première expérimentation de 2020 : les panaches sont détectés et quantifiables dès le début du déversement et ont une étendue assez importante dans l'espace et dans le temps. Nous présentons donc brièvement des illustrations en composition colorée des différents déversements, des exemples de quantification et les signatures spectrales caractéristiques mesurées dans les panaches de gaz.

4.2.1. N-propyl-acétate

Il y a eu deux déversements de N-propyl-acétate qui ont été observés depuis le navire. Dans les deux cas le gaz a été observé de façon très nette. Les figures ci-dessous illustrent deux exemples de panaches observés pour le premier (SLOT1) et le deuxième essai (SLOT2). Lors du deuxième essai le gaz est observable au moins jusqu'au début du déversement suivant, le temps d'observation de l'évaporation est supérieur à 30 min malgré le déplacement relatif de la source par rapport à la caméra à bord du SAPEUR. Dans le cas du premier test, le navire a effectué un changement de cap vers la fin du déversement qui n'a pas pu permettre de continuer à suivre le gaz.

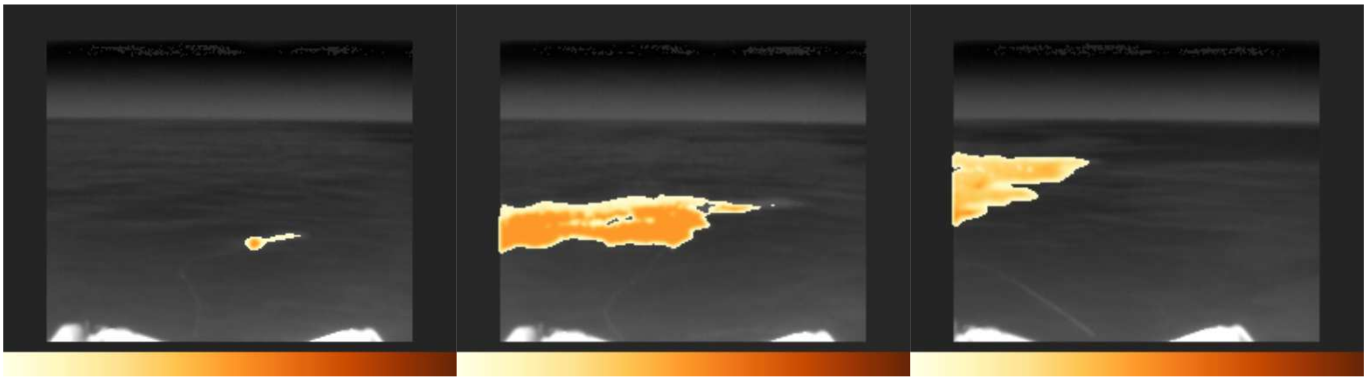


Figure 6 : Cartes en concentration (échelle 0-1000 ppm.m) de N-propyl-acétate surimposées sur le fond infrarouge observé par SIMAGAZ. De gauche à droite, on observe le début du déversement, 2 min et 5 min après (fin du déversement) pour le déversement du SLOT1 du 31-05-22. La dérive observée du produit est principalement due au changement de cap en cours du SAPEUR.

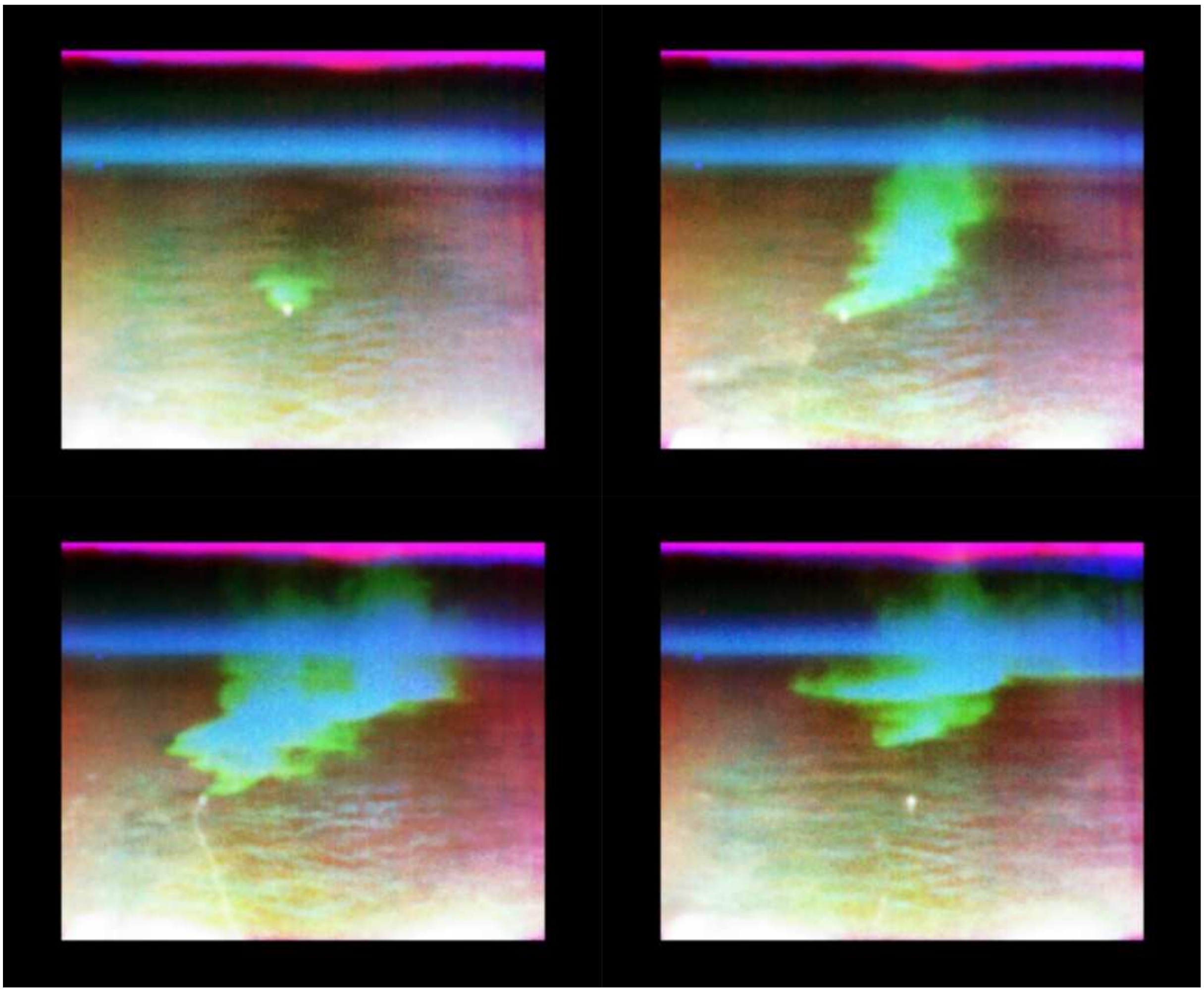


Figure 7 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement de N-propyl-acétate du SLOT2. De gauche à droite et de haut en bas, on observe le début du déversement puis 2, 5 min (fin du déversement) et 10 min après le déversement.

La Figure 8 et la Figure 9 illustrent un exemple de signature spectrale observée dans le panache comparées aux signatures attendues du fait de l’environnement extérieur caractérisé sur les images SIMAGAZ : température de l’air, température de surface, contenu en vapeur d’eau. Ces signatures attendues sont représentées dans la Figure 9 pour l’acétone et le MTBE et dans la Figure 8 pour les différents acétates. La première conclusion est que la signature attendue est proche de la signature observée compte tenu des incertitudes sur la composition de l’environnement et la géométrie de visée (distance au panache et épaisseur du panache en particulier), il est donc possible de façon automatique de rejeter par exemple la présence d’acétone ou de MTBE. Néanmoins les trois acétates comme indiqué précédemment seront difficilement discernables dans cette configuration d’observation (et pour une grande majorité des conditions d’observation).

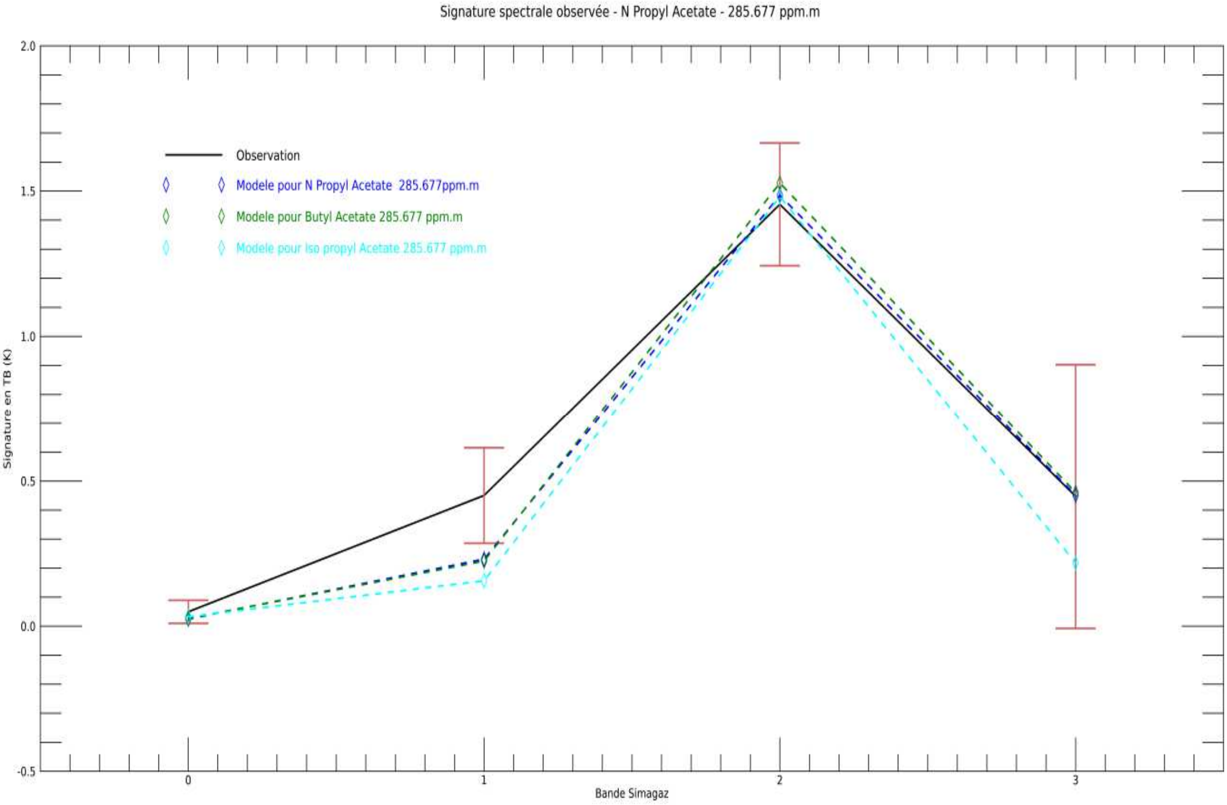


Figure 8 : Exemple de signature observée comparée aux signatures théoriques du gaz cible (N-propyl-acétate), du butyl-acétate et de l’iso-propyl-acétate

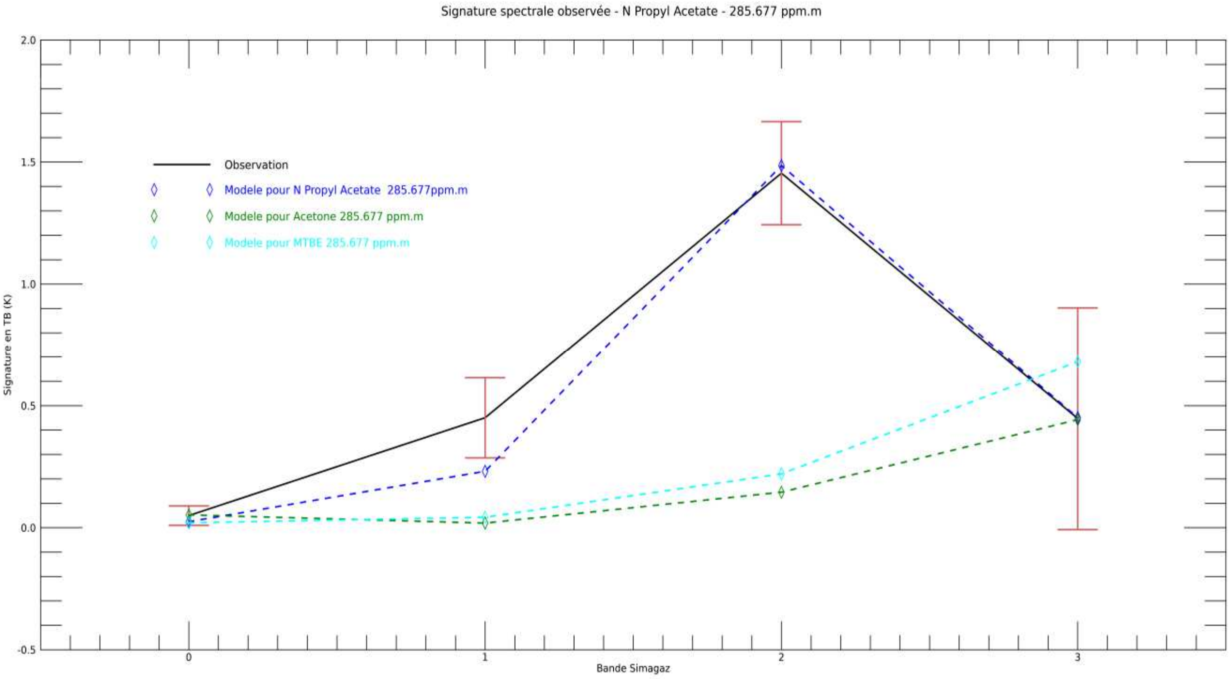


Figure 9 : Exemple de signature observée (moyenne sur 25 pixels dans le panache) comparée aux signatures théorique du gaz cible (N-propyl-acétate), du MTBE (cyan) et de l'acétone (vert) pour une concentration inversée moyenne de 285.7 ppm.m. La température de l'eau est estimée à 285 K et la température de l'air est estimée à 288 K.

4.2.2. Acétate de Butyle

Il y a eu deux déversements d'Acétate de Butyle qui ont été observés depuis le navire. Dans les deux cas le gaz a été observé de façon très nette. Les figures ci-dessous (Figure 10 et Figure 12) illustrent des exemples de panaches observés pour le premier (SLOT1) et le deuxième essai (SLOT2). On peut remarquer que le N-propyl-acétate (produit précédemment versé) lors du SLOT1 revient fugacement dans le champ de vue de la caméra environ 15 min après le début du déversement (Figure 10). Dans le cas du SLOT2, le N-propyl-acétate est bien encore présent dans le champ de vue avant le déversement de l'Acétate de Butyle (Figure 12) mais comme pour le SLOT1 (et comme attendu du fait des similarités spectrales), les deux gaz sont impossibles à discerner sur cette composition colorée. De plus ces gaz se mélangent ensuite dans le champ de vue de la caméra.

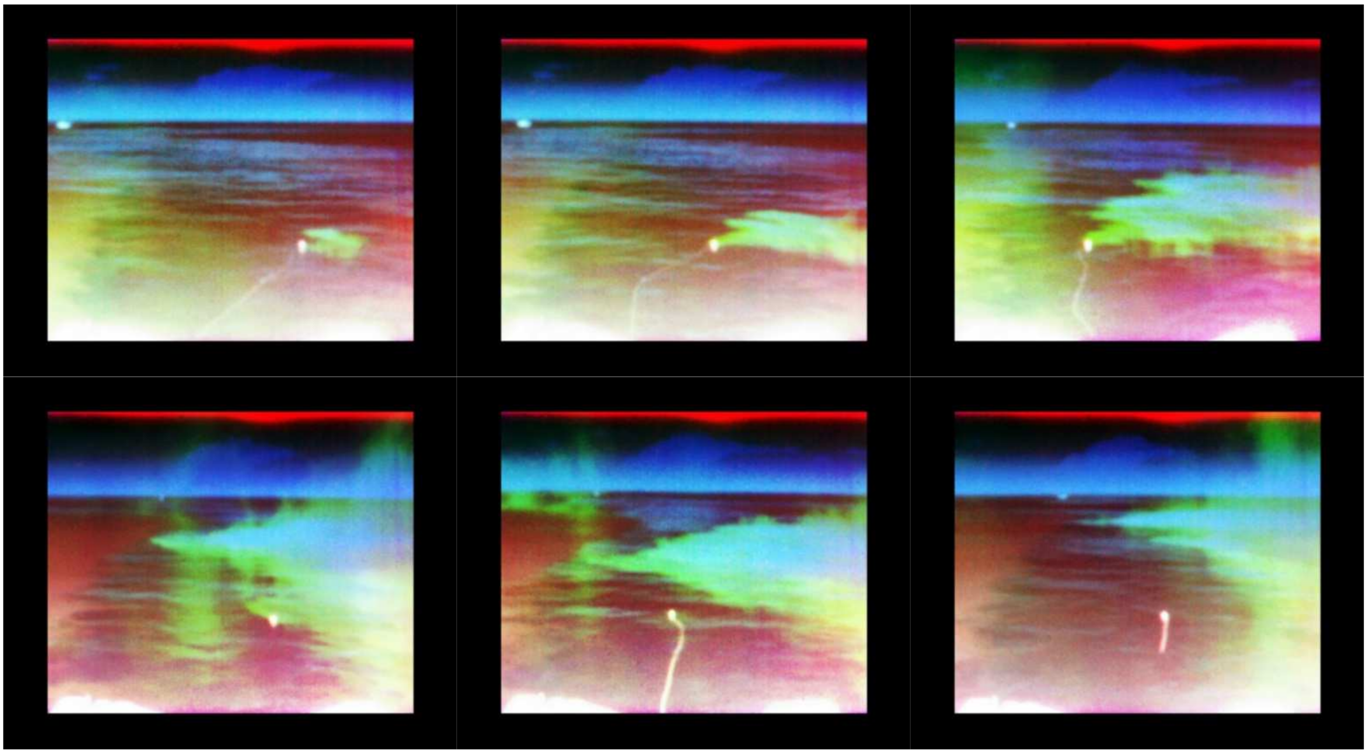


Figure 10 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement de N-butyl-acétate du SLOT1. De gauche à droite et de haut en bas, on observe le début du déversement puis 2, 5 min (fin du déversement),10, 15 et 20 min après le début du déversement.

La Figure 11 illustre un exemple de signature spectrale observée dans le panache comparée aux signatures attendues du fait de l’environnement extérieur caractérisé sur les images SIMAGAZ : température de l’air, température de surface, contenu en vapeur d’eau. Ces signatures attendues sont représentées pour l’acétone et le MTBE. La première conclusion est que la signature attendue est proche de la signature observée compte tenu des incertitudes sur la composition de l’environnement et la géométrie de visée (distance au panache et épaisseur du panache en particulier), il est donc possible de façon automatique de rejeter par exemple la présence d’acétone ou de MTBE et/ou de confirmer la présence d’acétate.

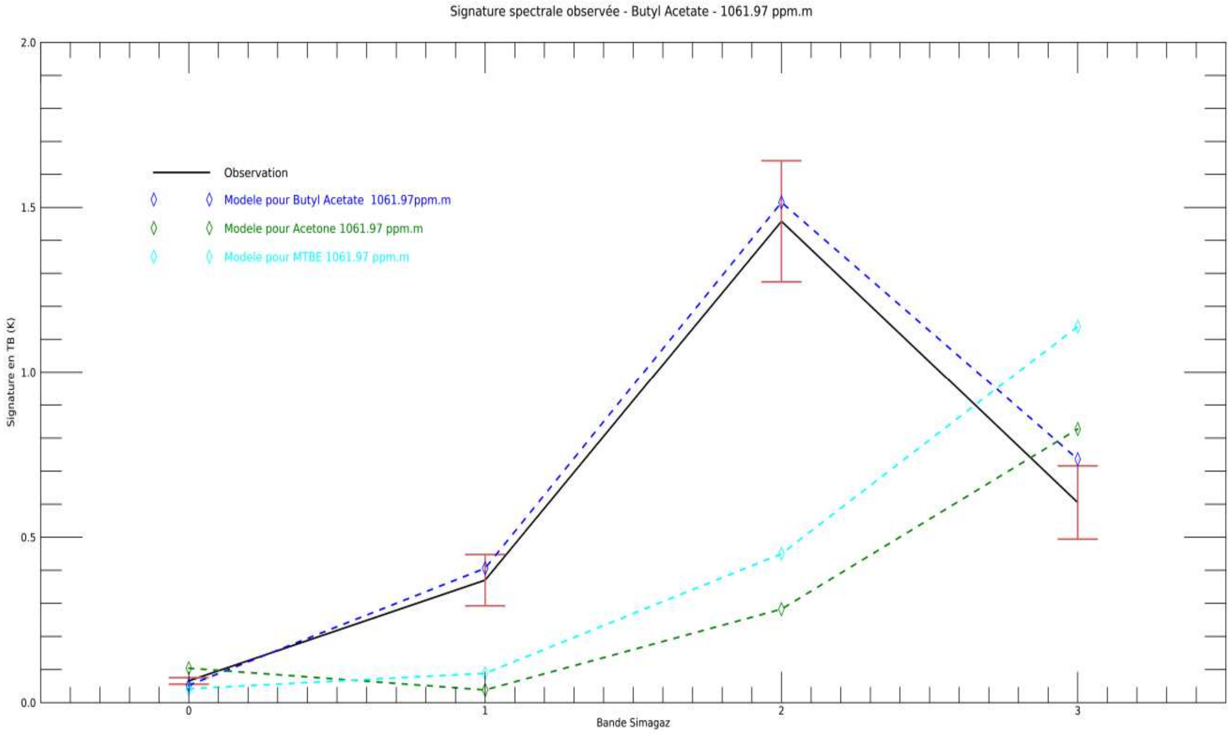


Figure 11 : Exemple de signature observée (moyenne sur 25 pixels dans le panache) comparée aux signatures théoriques du gaz cible (Butyl-acétate), du MTBE (cyan) et de l’acétone (vert) pour une concentration inversée moyenne de 1060 ppm.m. La température de l’eau est estimée à 285 K et la température de l’air est estimée à 288 K.

Figure 12 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement de N-butyl-acétate du SLOT2. De gauche à droite et de haut en bas, on observe avant le début du déversement puis 2 et 5 min (fin du déversement) après le début du déversement.

4.2.3. *Iso-propyl-acétate*

Il y a eu deux déversements d'Iso-propyl-acétate qui ont été observés depuis le navire. Dans les deux cas le gaz a été observé de façon très nette. Les figures ci-dessous (Figure 13 et Figure 15) illustrent des exemples de panaches observés pour le premier (SLOT1) et le deuxième essai (SLOT2). Dans les deux cas, l'Acétate de Butyle (produit précédemment versé) est bien encore présent dans le champ de vue avant le déversement de d'Iso-propyl-acétate mais comme constaté précédemment, les deux gaz sont impossibles à discerner sur cette composition colorée. De plus ces gaz se mélangent ensuite dans le champ de vue de la caméra en particulier dans le cas du SLOT2. Dans le SLOT1 on observe un panache provenant du déversement qui se dirige vers le bateau et qui va occuper tout le champ de vue. Les observations aéroportées pourront confirmer cette observation de déplacement du panache dans la direction du navire mais avec une vitesse de transport plus élevée.

La Figure 14 illustre un exemple de signature spectrale observée dans le panache comparée aux signatures attendues du fait de l'environnement extérieur caractérisé sur les images SIMAGAZ : température de l'air, température de surface, contenu en vapeur d'eau. Ces signatures attendues sont représentées pour l'acétone et le MTBE. La première conclusion est que la signature attendue est proche de la signature observée compte tenu des incertitudes sur la composition de l'environnement et la géométrie de visée (distance au panache et épaisseur du panache en particulier), il est donc possible de façon automatique de rejeter la présence par exemple d'acétone ou de MTBE.

Figure 13 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement de Iso-propyl-acétate du SLOT1. De gauche à droite, on observe avant le début du déversement puis 2 et 5 min (fin du déversement) après le début du déversement.

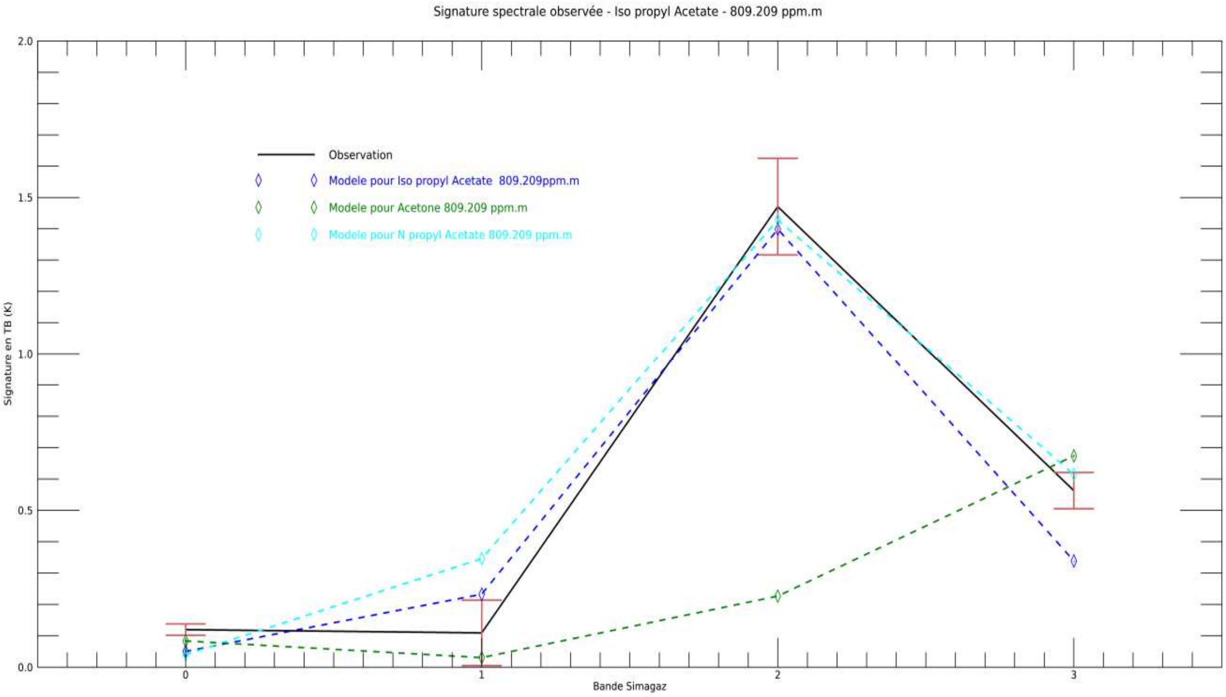


Figure 14 : Exemple de signature observée (moyenne sur 25 pixels dans le panache) comparée aux signatures théoriques du gaz cible (Iso-propyl-acétate), du N-propyl acétate (cyan) et de l'acétone (vert) pour une concentration inversée moyenne de 810 ppm.m. La température de l'eau est estimée à 285 K et la température de l'air est estimée à 288 K.

Figure 15 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement de Iso-propyl-acétate du SLOT2. De gauche à droite, on observe avant le début du déversement puis 2 et 5 min (fin du déversement) après le début du déversement.

4.2.4. *Acétone*

Il y a eu deux déversements d’Acétone qui ont été observés depuis le navire. Dans les deux cas le gaz a été observé de façon plus ou moins intense en fonction des conditions de vent. Les figures ci-dessous (Figure 16 et Figure 18) illustrent des exemples de panaches observés pour le premier (SLOT2) et le deuxième essai (SLOT3). Dans le premier cas, l’Iso-propyl-acétate (produit précédemment versé) est bien encore présent dans le champ de vue avant le déversement de d’Acétone et contrairement aux cas précédent, les deux gaz sont discernables sur cette composition colorée. Dans le SLOT3 on observe un panache provenant du déversement qui montre une dispersion très rapide du fait de la vitesse du vent (> 8 m.s^{-1}) et au bout de 10 à 12 min le gaz n’est quasiment plus observable.

La Figure 17 illustre un exemple de signature spectrale observée dans le panache comparée aux signatures attendues du fait de l’environnement extérieur caractérisé sur les images SIMAGAZ : température de l’air, température de surface, contenu en vapeur d’eau. Ces signatures attendues sont représentées pour l’acétone, le MTBE et l’acétate de butyle. La première conclusion est que la signature attendue est proche de la signature observée compte tenu des incertitudes sur la composition de l’environnement et la géométrie de visée (distance au panache et épaisseur du panache en particulier), il est donc possible de façon automatique de rejeter par exemple la présence d’acétate ou de MTBE.

Figure 16 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement d’acétone du SLOT1. De gauche à droite, on observe avant le début du déversement puis 2 et 5 min (fin du déversement) après le début du déversement.

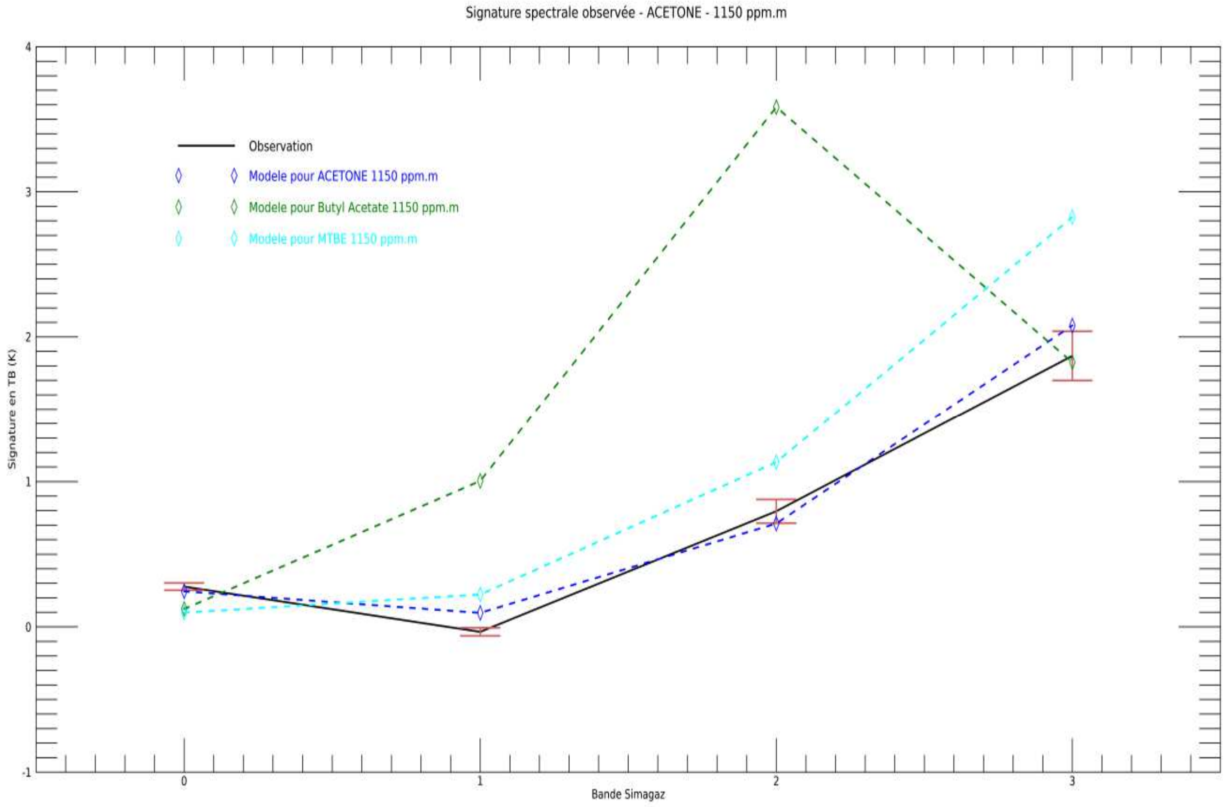


Figure 17 : Exemple de signature observée (moyenne sur 25 pixels dans le panache) comparée aux signatures théoriques du gaz cible (acétone), du MTBE (cyan) et de l'acétate de butyle (vert) pour une concentration inversée moyenne de 1150 ppm.m. La température de l'eau est estimée à 285 K et la température de l'air est estimée à 290 K.

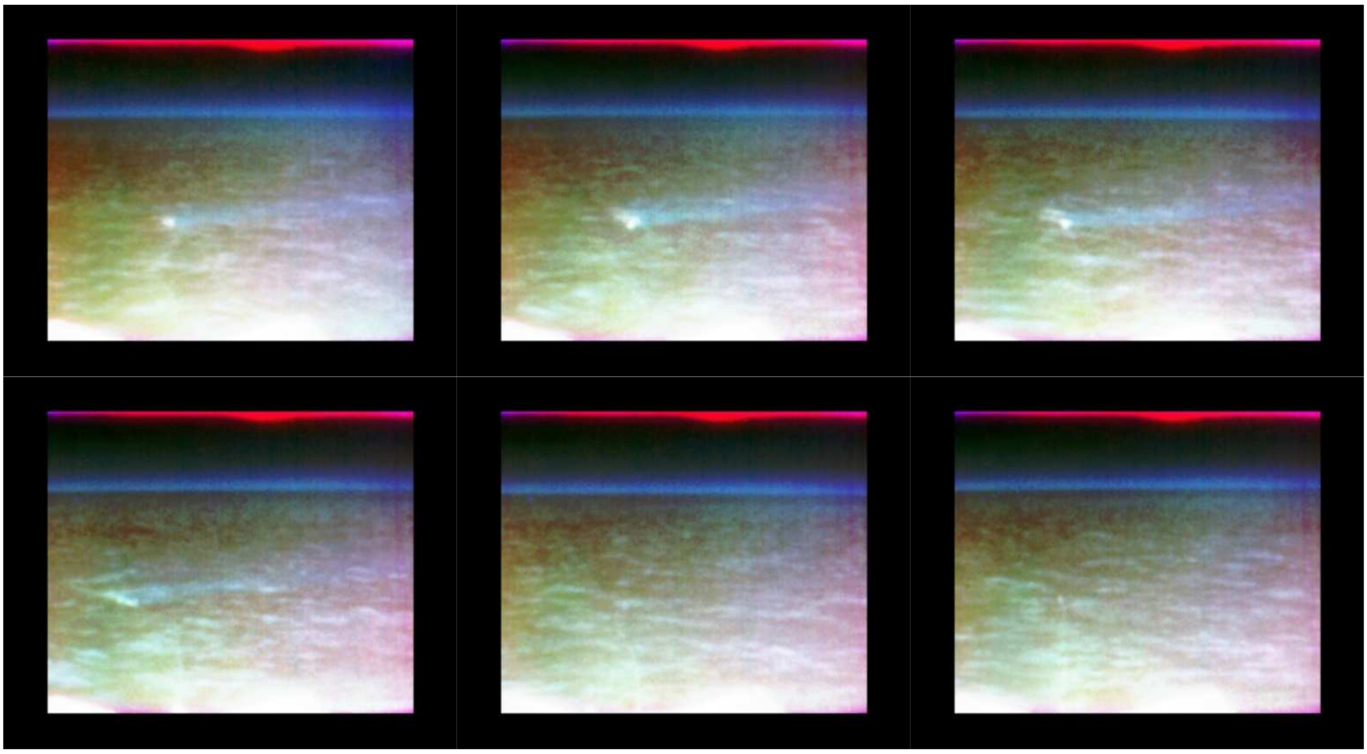


Figure 18 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement d'acétone du SLOT2. De gauche à droite et de haut en bas, on observe le début du déversement puis 2, 5 (fin du déversement), 7, 9 et 12 min après le début du déversement.

4.2.5. MTBE

Il y a eu deux déversements de MTBE qui ont été observés depuis le navire. Dans les deux cas le gaz a été observé de façon plus ou moins intense en fonction des conditions de vent. Les figures ci-dessous (Figure 19 et Figure 21) illustrent des exemples de panaches observés pour le premier (SLOT2) et le deuxième essai (SLOT3). Dans le premier cas, l'Acétone (produit précédemment versé) n'est plus encore présent significativement dans le champ de vue avant le déversement contrairement aux cas précédent. Dans le SLOT3 on observe un panache provenant du déversement qui montre une dispersion très rapide du fait de la vitesse du vent (> 8 m.s^{-1}) et au bout de 12 à 15 min le gaz n'est quasiment plus observable.

La Figure 20 illustre un exemple de signature spectrale observée dans le panache comparée aux signatures attendues du fait de l'environnement extérieur caractérisé sur les images SIMAGAZ : température de l'air, température de surface, contenu en vapeur d'eau. Ces signatures attendues sont représentées pour l'acétone, le MTBE et le N-propyl-acétate. La première conclusion est que la signature attendue est proche de la signature observée compte tenu des incertitudes sur la composition de l'environnement et la géométrie de visée (distance au panache et épaisseur du panache en particulier), il est donc possible de façon automatique de rejeter la présence d'acétate ou d'acétone. En particulier on confirme la séparabilité entre le MTBE et l'Acétone pour cette configuration d'observation.

Figure 19 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement de MTBE du SLOT1. De gauche à droite, on observe le début du déversement puis 2 et 5 min (fin du déversement) après le début du déversement.

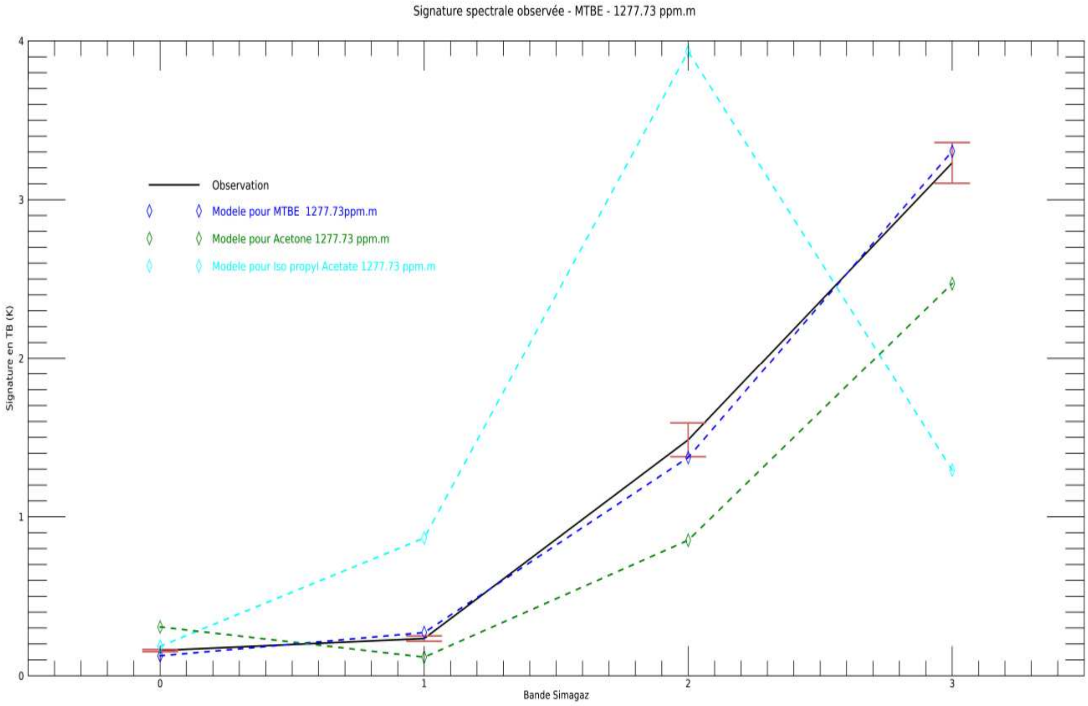


Figure 20 : Exemple de signature observée (moyenne sur 25 pixels dans le panache) comparée aux signatures théorique du gaz cible (MTBE), du Iso-propyl-acétate (cyan) et de l'acétone (vert) pour une concentration inversée moyenne de 285.7 ppm.m. La température de l'eau est estimée à 285 K et la température de l'air est estimée à 288 K.

Essai 2

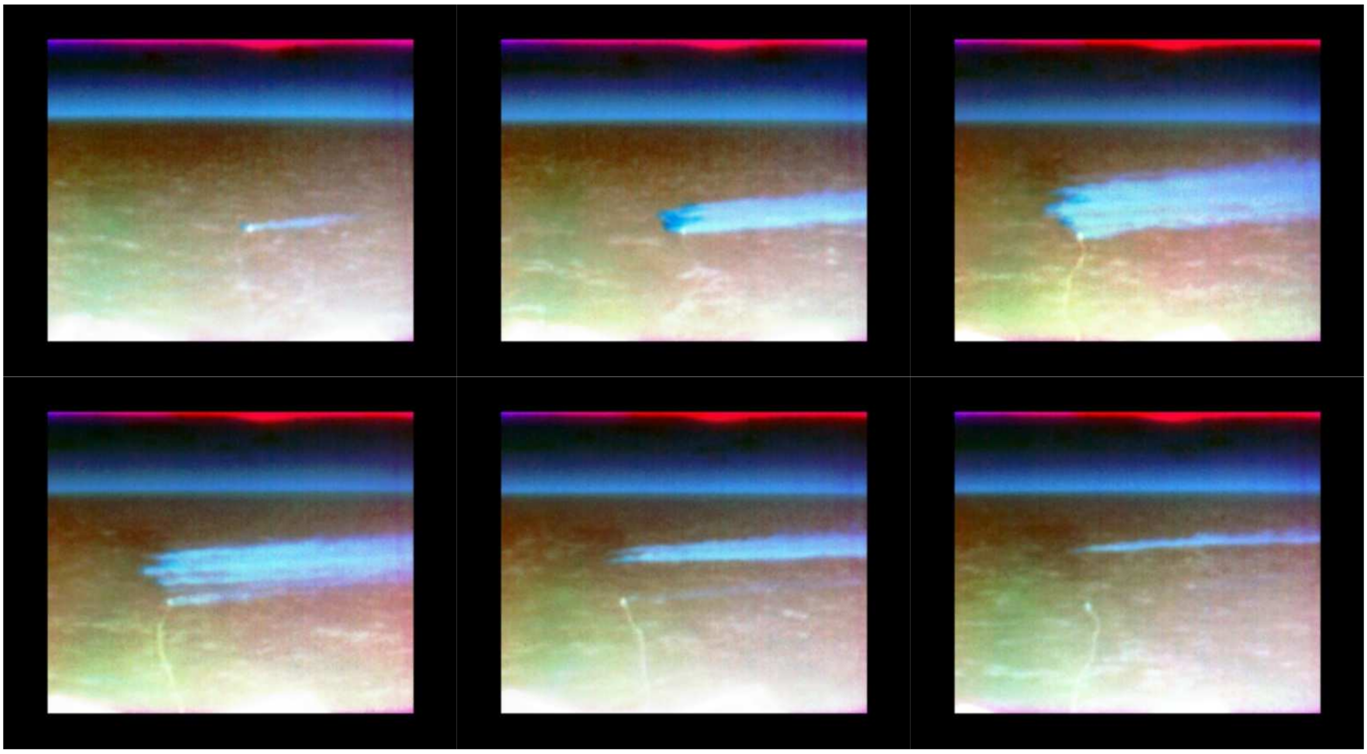


Figure 21 : Images en fausses couleurs issues des canaux SIMAGAZ pendant le déversement de MTBE du SLOT2. De gauche à droite et de haut en bas, on observe le début du déversement puis 2, 5 (fin du déversement), 7, 9 et 12 min après le début du déversement.

4.2.6. Toluène et Xylène

Concernant le toluène et le xylène, la sensibilité attendue est très faible. De plus les bandes de SIMAGAZ ne sont pas du tout adaptées pour ces gaz. Dans ces deux cas seule la nappe en surface est observée. La Figure 22 illustre bien la persistance des nappes pour ces deux produits réputés volatils. Comme pour le cas de l’acétate de butyle pour lequel on voit les émanations gazeuses, les produits sont visibles jusqu’à ce qu’ils se confondent avec l’horizon à des distances comprises entre 600 m et 800 m sur une durée de l’ordre de 30 min.

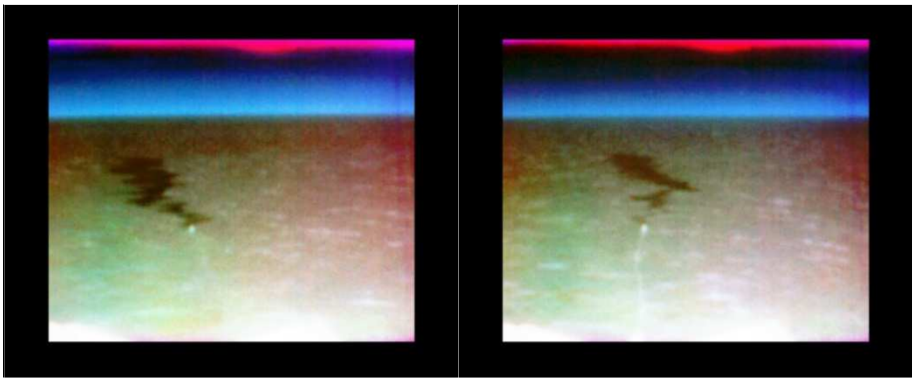


Figure 22:Images en fausses couleurs issues des canaux SIMAGAZ. Observations du Toluène (gauche) et du Xylène à la fin des déversements pour le SLOT3.

4.2.7. *Synthèse sol*

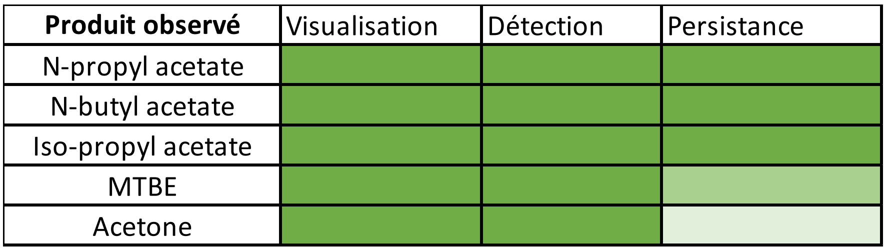
Les tableaux ci-dessous synthétisent les résultats obtenus dans le cas d’une mer calme et peu agitée (Table 4) et dans le cas d’une mer agitée mais ensoleillée (Table 5) pour les observations de la caméra SIMAGAZ à bord du SAPEUR.

La visualisation est quasiment toujours excellente (vert foncé) excepté peut-être pour l’acétone en condition agitée (vert clair).

La détection automatique se montre très robuste (vert foncé) excepté pour l’acétone en condition agitée (vert clair) où le taux de bonne détection sur le taux de fausses alarmes n’est pas toujours optimal.

La persistance est indiquée du vert foncé au orange (en passant par le vert clair), cela correspond respectivement à des persistances allant de 1h à quelques minutes.

Table 4 : Résultats en mer calme et peu agitée (vent < 3 m/s ensoleillé, pas de houle).



Produit observé	Visualisation	Détection	Persistance
N-propyl acetate	🟩	🟩	🟩
N-butyl acetate	🟩	🟩	🟩
Iso-propyl acetate	🟩	🟩	🟩
MTBE	🟩	🟩	▨
Acetone	🟩	🟩	░

Table 5: Résultats en mer agitée ensoleillée (vent > 6 m/s ensoleillé, houle marquée).

Produit observé	Visualisation	Détection	Persistance
MTBE	🟩	🟩	🟧
Acetone	▨	░	🟧

4.3. Mesures aéroportées

Les mesures aéroportées ont été nombreuses mais, comme indiqué dans le tableau de synthèse dans la section 3.3.2, dans un certain nombre de cas il n’a pas été possible d’ajuster la ligne de vol de façon optimale : le bateau, la nappe ou le nuage (ou les trois dans le pire des cas) ne sont pas présents sur les acquisitions. Les produits issus de l’analyse des images SIMAGAZ permettent de séparer le sillage du bateau, la nappe en surface et le gaz évaporant. Lorsque du gaz est détecté une estimation de la concentration pixel à pixel et de la masse totale présente est possible. La Figure 23 illustre le processus de traitement.

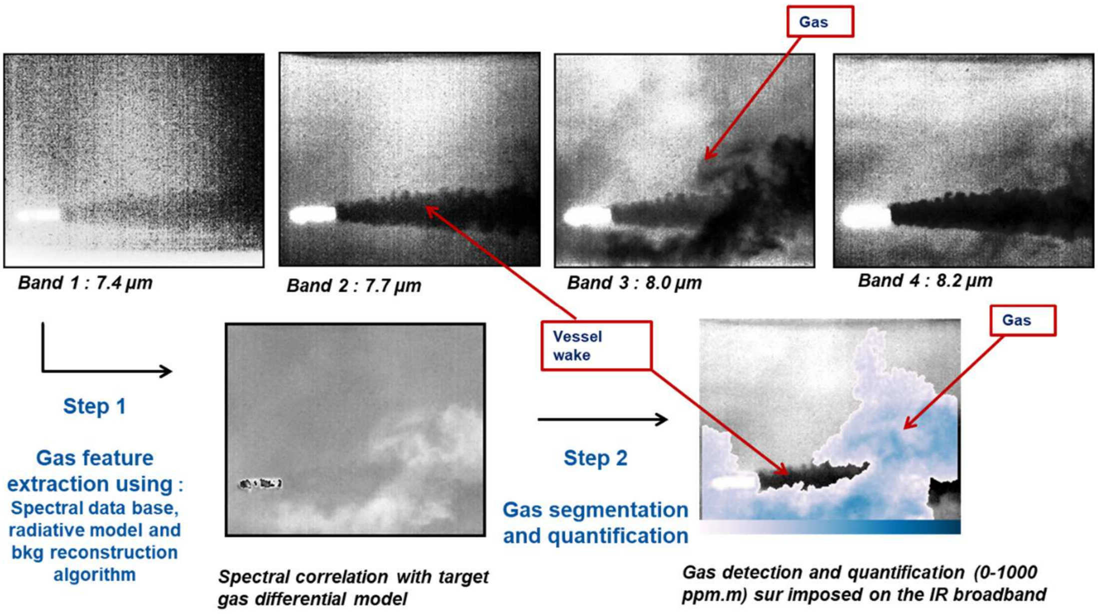


Figure 23 : Schéma de synthèse de l’algorithme de détection et de quantification de gaz SIMONET appliqué au cas aéroporté pour l’Iso-propyl-acétate.

4.3.1. N-propyl-acétate

Il y a eu deux acquisitions qui ont permis d’observer le dégazage du N-propyl-acétate lors du déversement du 31/05 autour de 10h (TU). Le gaz a ainsi pu être observé pendant 20 min, puis le navire a effectué un changement de cap : la nappe ne se situait plus sur l’axe de vol pris par l’avion pour observer les déversements suivants.

Comme indiqué dans le tableau récapitulatif des acquisitions, seul un déversement de 1m^3 de N-propyl-acétate a été réalisé en présence de SIMAGAZ aéroportée. Néanmoins nous avons observé l’évolution de ce déversement sur plusieurs acquisitions. Nous illustrons ci-dessous les principaux résultats obtenus sur le suivi de la nappe liquide en surface et sur le suivi du panache de gaz issu de l’évaporation du produit.

La première acquisition permettant d’observer le produit (SLOT1-0003) a eu lieu à 800 m d’altitude environ 10 min après la fin du déversement. La Figure 24 illustre ainsi par la concaténation de deux images la scène observée. Sur cette figure en fausses couleurs, correspondant à la projection de l’image multispectrale sur des vecteurs physiques correspondant à la signature du gaz et à la signature de la nappe en surface. Le gaz apparait alors en bleu clair, le fond de mer en rouge et la nappe en surface en vert sombre. Il est possible dans ce cas de dissocier le sillage du bateau (surface plus froide provenant de couches d'eau profondes remises en surface par la motorisation) de la nappe (à cet effet de température s'ajoute une baisse d'émissivité de surface) située à l'intérieur du sillage mais avec une signature plus sombre. La Figure 25 donne un exemple de segmentation automatique et de quantification en ppm.m du nuage de gaz.

Sur la Figure 24, on observe un étalement de la nappe de l'ordre de 400 m avec une fragmentation le long de l'axe de propagation, l'étalement transverse à l'axe du bateau est faible. La nappe observée en infrarouge thermique correspond aux zones d'épaisseurs importantes : typiquement des épaisseurs supérieures à 100 µm. Ainsi 10 mn après la fin du déversement, la surface observée de la nappe est de 950 m^2. Si on considère que 100% de la masse totale déversée est contenue sur ces 950 m^2, cela signifie que l'épaisseur moyenne est de l'ordre de 1 mm. Cette valeur est un majorant car du produit a disparu par évaporation et l'on sait que la partie de la nappe ayant une épaisseur inférieure à 100 µm n'est pas observable. Ainsi si on considère que 10% de la masse s'est déjà évaporée et que la nappe réelle est 3 fois plus grande, on obtiendrait une épaisseur moyenne de 0.3 mm.

On observe de plus un dégazage important en surface. Les sources de ce dégazage sont clairement associées aux zones les plus épaisses de la nappe décrites ci-dessous. L'étendue spatiale du panache est de l'ordre de 400 m au niveau de la source et de plus de 500 m dans la direction de propagation (direction du vent) qui est ici assez orthogonale au sillage. Dans cette direction l'étendue du gaz dépasse le champ de vue de l'instrument au moment de l'acquisition.

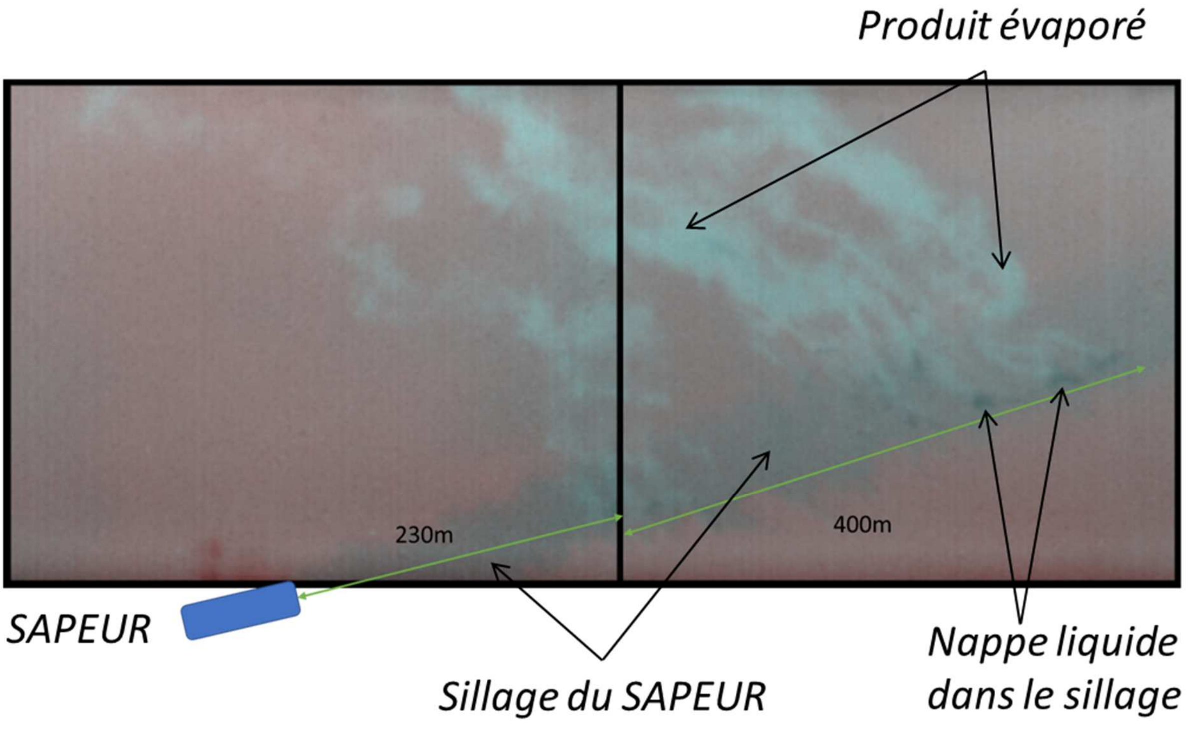


Figure 24: Visualisation pour le vol Slot-1-0003 de l'évaporation du N-Propyl-acétate.

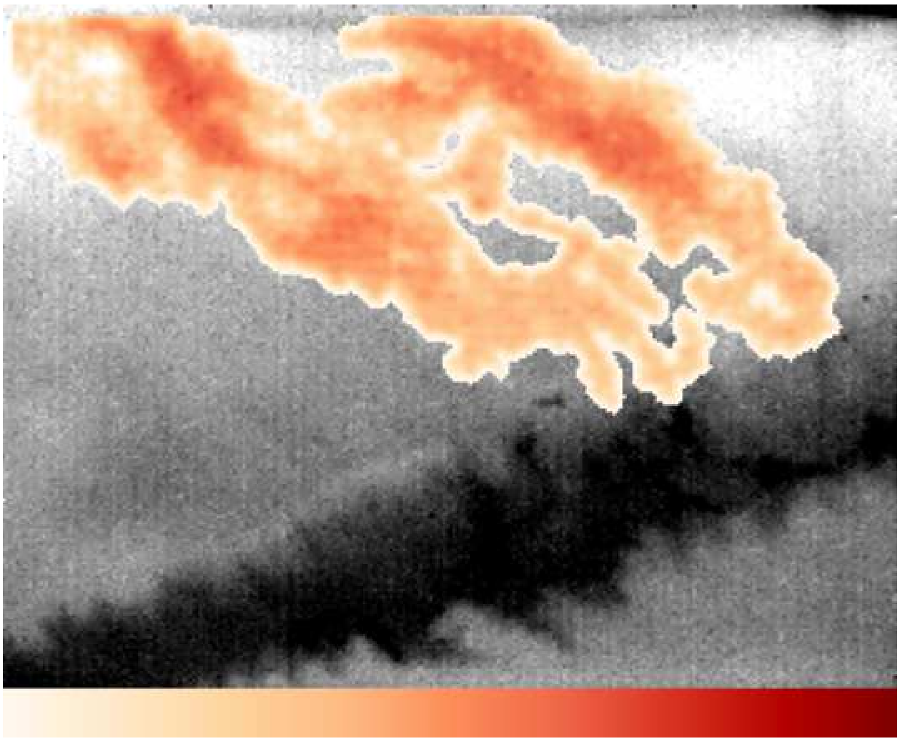


Figure 25: Carte en concentration (échelle 0-1000 ppm.m) de N-propyl-acétate. SLOT1-0003

Durant l’acquisition suivante (SLOT1-0004) toujours à 800 m d’altitude et trois minutes après, les observations sont assez similaires concernant la nappe, l’aire observable a néanmoins diminué en passant de 950 m^2 à 700 m^2. Le nuage de gaz a été observé toujours dans la même direction de propagation à plus de 800 m de distance de la source. On observe aussi sur la Figure 26 un phénomène d’accumulation du gaz à plusieurs centaines de mètres de la nappe liquide (bas à droite de la figure).

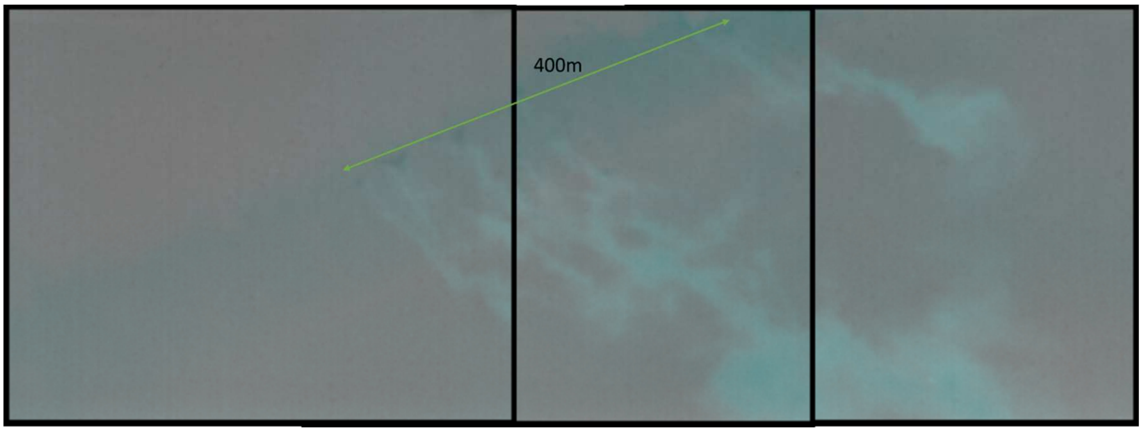


Figure 26 : Visualisation pour le vol Slot-1-0004 de l'évaporation du N-propyl-actétate. La largeur de chaque vignette est de 750 m.

Enfin le produit a pu être détecté lors de l’acquisition SLOT1-0009 qui a eu lieu près de 50 min après le déversement toujours à 800 m d’altitude. En effet le changement de cap du bateau a rendu impossible d’observer simultanément le déversement en cours et un précédent déversement sur la même ligne de vol rectiligne. La Figure 27 illustre le changement de cap par une modification assez brutale de 45° de la ligne de sillage (partie vert sombre sur les images) derrière le bateau. Le produit sous forme de nappe n'est plus distinguable vis-à-vis du sillage sur les acquisitions infrarouges mais le produit est toujours présent car son évaporation est toujours observée (gaz en bleu clair entourée en bleu foncé sur l'image), le point source est à environ 1800 m du bateau et le panache est détecté sur une étendue d'environ 100 m. On remarque que la direction du bateau et du vent sont alors identiques.

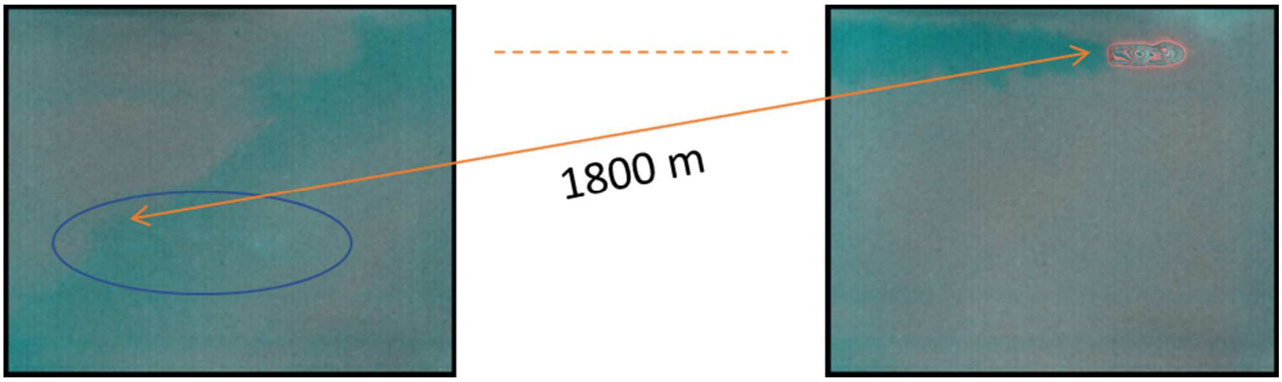


Figure 27 : Visualisation pour le vol Slot-1-0009 de l'évaporation du N-propyl-actétate.

4.3.2. *Acétate de Butyle*

Il s'agit du deuxième produit déversé lors des acquisitions du SLOT1 du 31 Mai. Le déversement a eu lieu en suivant du précédent et s'est terminé à 10h43. Une première acquisition a eu lieu dans la dernière minute du déversement, puis une grande partie des acquisitions suivante ont permis à nouveau d'observer la nappe et le panache de gaz une heure environ après la fin du déversement. La Figure 28 permet d'illustrer la formation de la nappe au milieu du sillage au moment du déversement à partir des acquisitions du vol SLOT1-0006. Les ondulations observées dans la queue de la nappe sont à l'origine du morcellement de la nappe avec la dérive et le vent. L'évaporation est très nettement observable sur la figure.

La taille de la nappe est de l'ordre de 200 m avec une aire estimée au moment de la fin du déversement de 1200 m^2. Ainsi en considérant que la totalité du volume déversé est observé et en négligeant ce qui a pu déjà être évaporé, on peut obtenir un majorant de l'épaisseur moyenne de l'ordre de 0.8 mm. On observe un phénomène intéressant du déplacement relatif entre le sillage et la nappe : au point source près du bateau le produit reste sur la partie haute du sillage alors que la queue de nappe a dérivé vers la partie basse du sillage (dans la direction du vent).

L'évaporation observée est assez similaire au cas précédent avec une zone source pas très homogène et liée aux accumulations locales de produits. On observe des filaments d'évaporation qui ont ensuite tendance à se rejoindre.

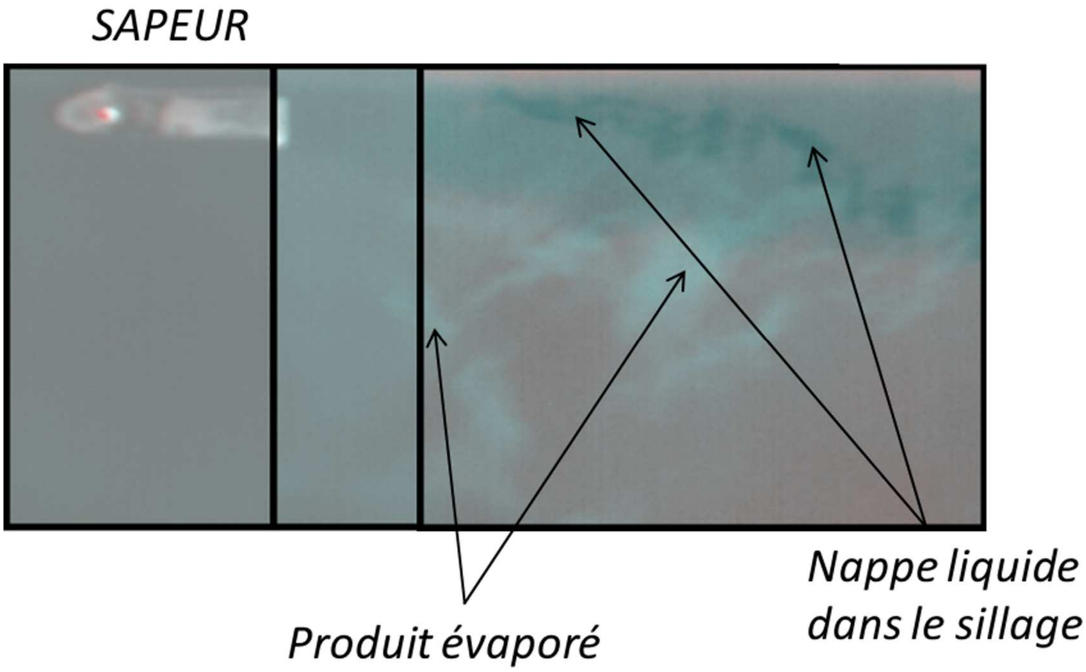


Figure 28 : SLOT1-0006 : à la fin du déversement. La largeur de chaque vignette est de 280 m.

La Figure 29 illustre les observations faites lors de l’acquisition suivante 5 min plus tard, toujours à 300 m d’altitude. Dans ce cas le bateau ne figure pas dans le champ de vue et la nappe liquide n’est pas observée entièrement. Néanmoins on observe un début de fragmentation de la nappe dès 5 min après la fin du déversement (ou 10 min après le début du déversement). Enfin, le panache formé par le gaz est déjà imposant et s’étale sur plus d’1 km en formant un système de bouffée (accumulations locales importantes lors du transport).

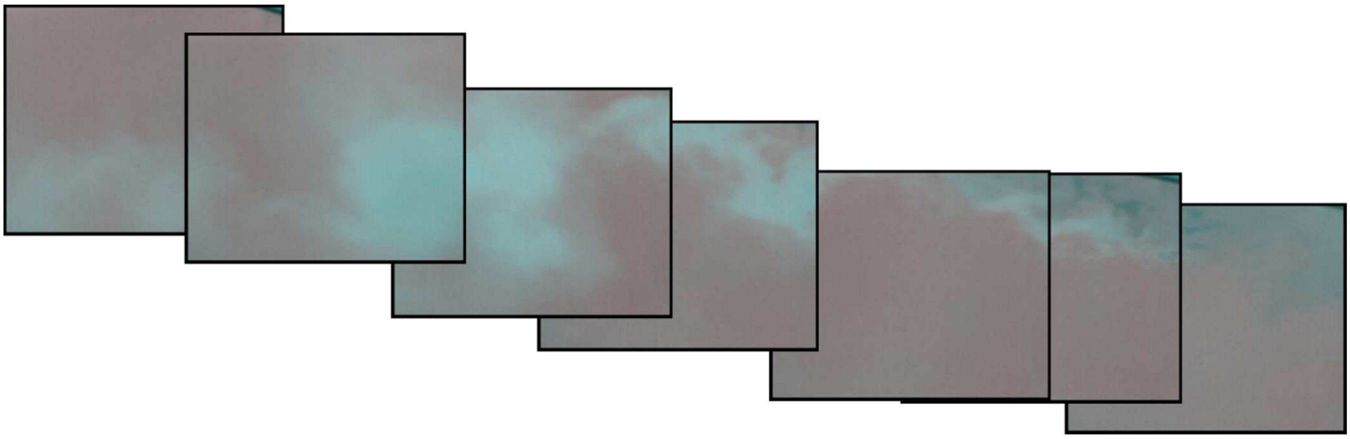


Figure 29 : SLOT1-0007. Image en fausses couleur. Superpositions d’extraits de traitement de la séquence SIMAGAZ à 300 m d’altitude. La largeur de chaque vignette est de 280 m.

La nappe a ensuite été observée à deux reprises (SLOT1-0011 et SLOT1-0013) dans sa totalité avec des surfaces observables de 600 m^2 avec des fragments étalés sur près de 500 m 40 min après le déversement et de 450 m^2 55 mn après le déversement. Le gaz a lui pu être observé sur toutes les acquisitions qui ont suivi, le panache n'a jamais pu être observé dans sa totalité du fait de son étendue sur plusieurs km. Sur la Figure 30 on peut observer que le gaz observé s'étend en effet sur plus de 1,5 km. Il faut noter que la direction de propagation du panache est parallèle au sillage et donc à la direction du bateau. On peut alors s'attendre à ce que le panache rattrape le navire.

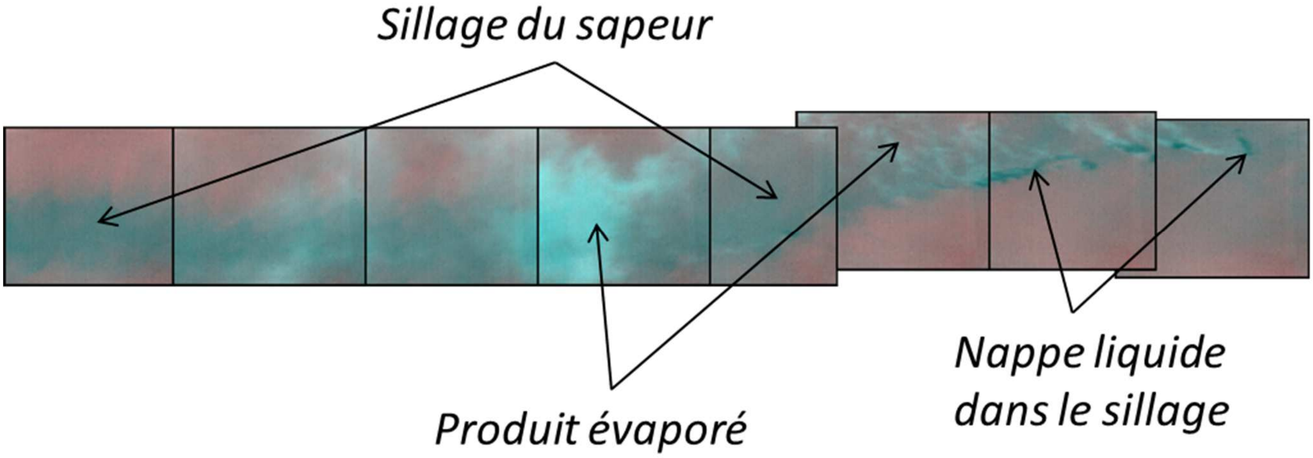


Figure 30 :SLOT1-0011. 300 m d'altitude. La largeur de chaque vignette est de 280 m.

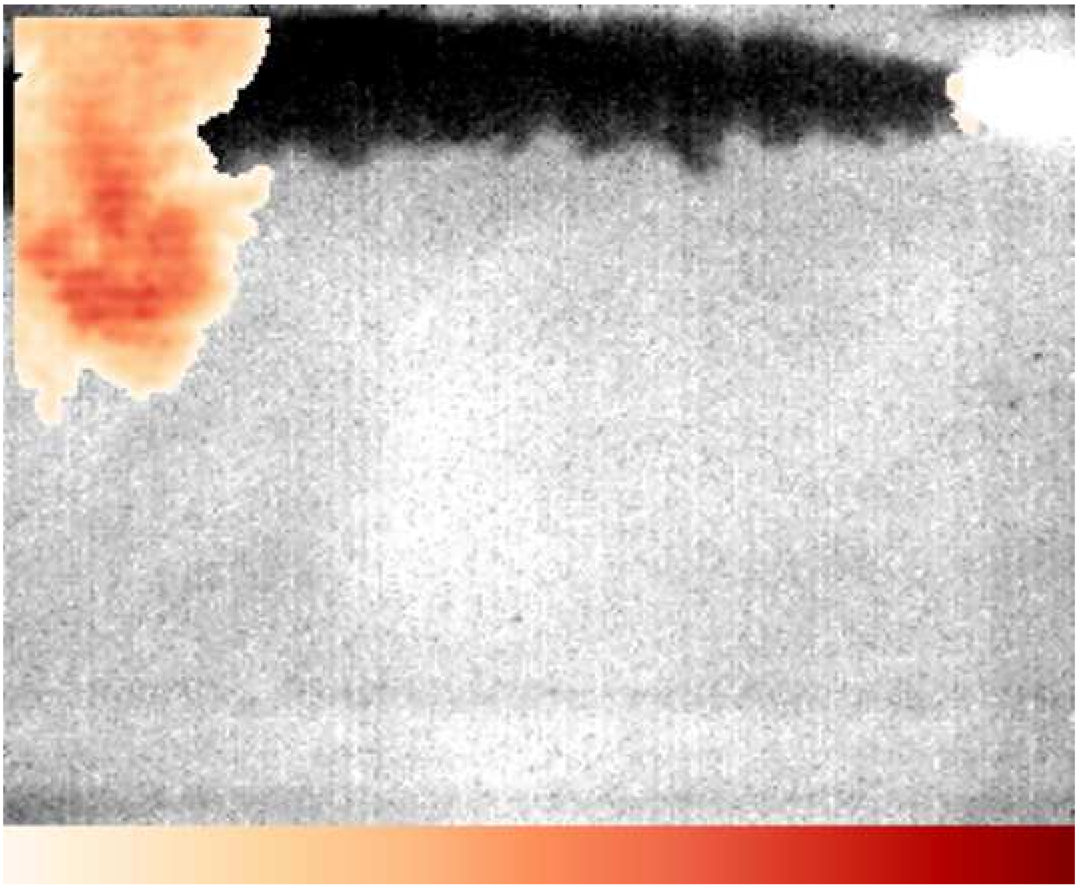


Figure 31 : Carte en concentration (échelle 0-1000 ppm.m) de butyl-acétate. SLOT1-0009. Le navire apparait en blanc (saturation de la visualisation) et le sillage en noir. La nappe n'est pas observable à l'œil sur cette image thermique.

4.3.3. Iso-propyl-acétate

Le dernier produit déversé lors du SLOT1 acquis est l'Iso-propyl-acétate, 1h20 environ après le premier déversement et 45 min après le précédent. Et ce qui était pressenti pour l'acétate de butyle se confirme : la trajectoire du navire est parallèle à la direction du vent et le panache de gaz évaporé est transporté avec une vitesse plus grande que celle du navire. Le navire est donc dans le gaz dès le SLOT1-0011 comme illustré sur la Figure 32 : dès la fin du déversement, la nappe est observable avec un comportement très similaire à l'acétate de butyle mais le dégazage se transporte dans la direction du navire qui se retrouve dans le nuage.

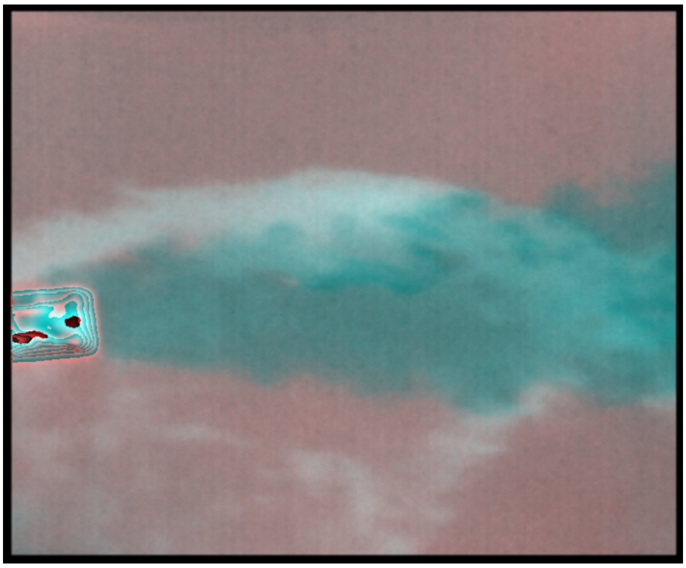


Figure 32: SLOT1-0011. La largeur de la vignette est de 280 m.

Dans les acquisitions suivantes ce phénomène s'observe de façon encore plus flagrante. De la Figure 33 à la Figure 36 nous illustrons ce phénomène en utilisant en outre les cartes de corrélation liées uniquement au gaz (Figure 34 et Figure 35). On observe bien qu'au fur et à mesure du temps, le gaz gagne de la distance par rapport au navire et se dilue assez lentement. Pour la dernière acquisition SLOT1-0014, on observe du gaz 1,5 km en aval du bateau alors que la nappe est située à ce moment à 1 km en aval.

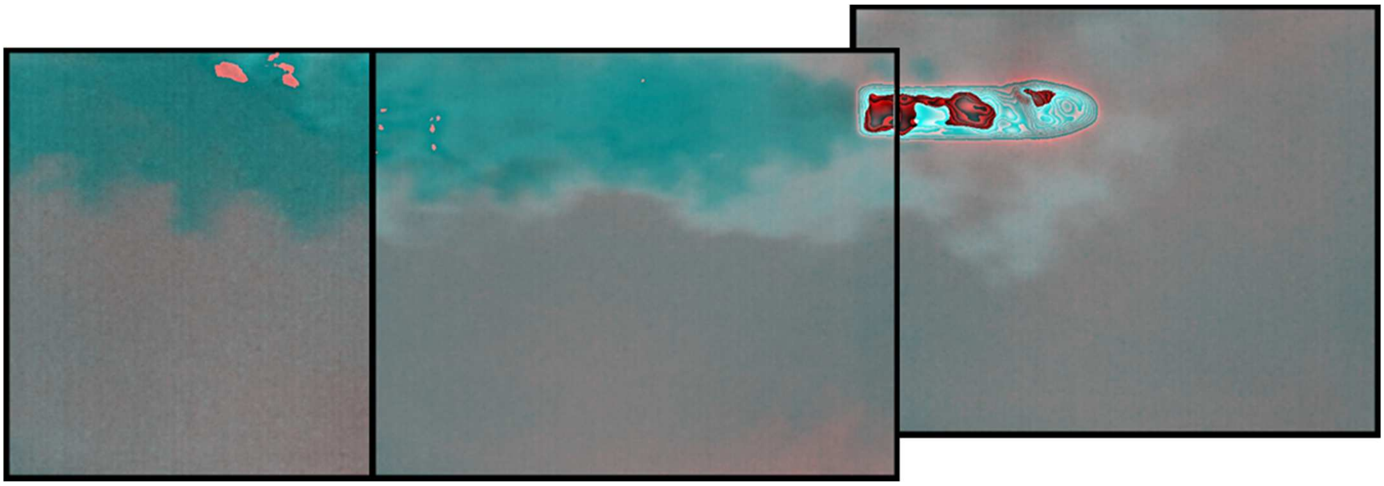


Figure 33: SLOT1-0012 à 300 m d'altitude. Produit : Iso-propyl-acétate. Image en fausses couleurs. La largeur de chaque vignette est de 280 m.

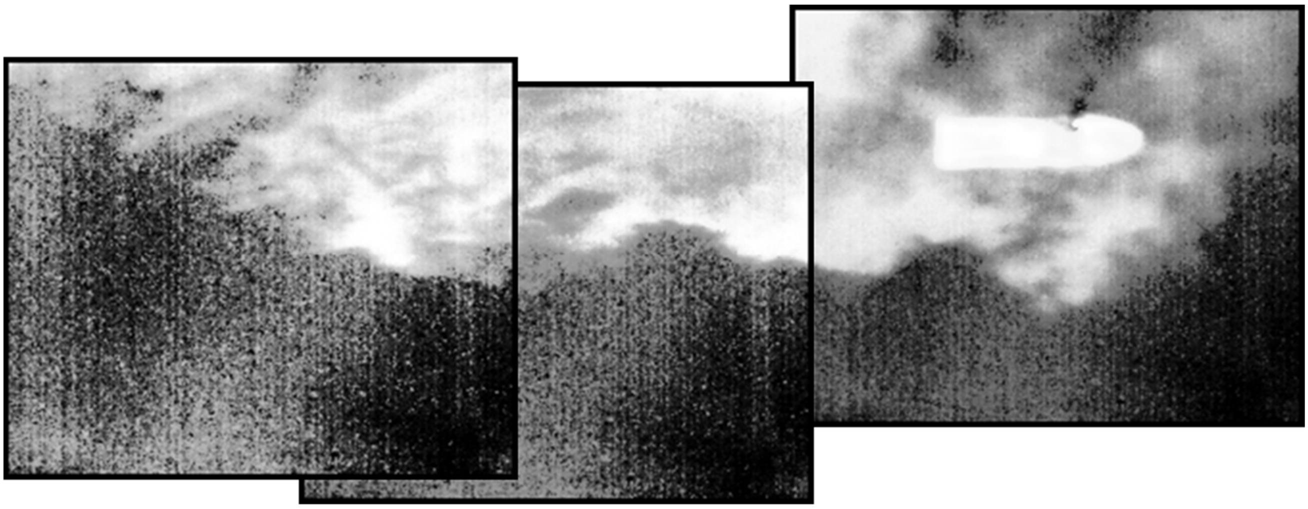


Figure 34 : SLOT1-0012 à 300 m d'altitude. Produit : Iso-propyl-acétate corrélateur dédié au gaz : la présence de gaz correspond aux parties les plus claires de l'image. La largeur de chaque vignette est de 280 m.

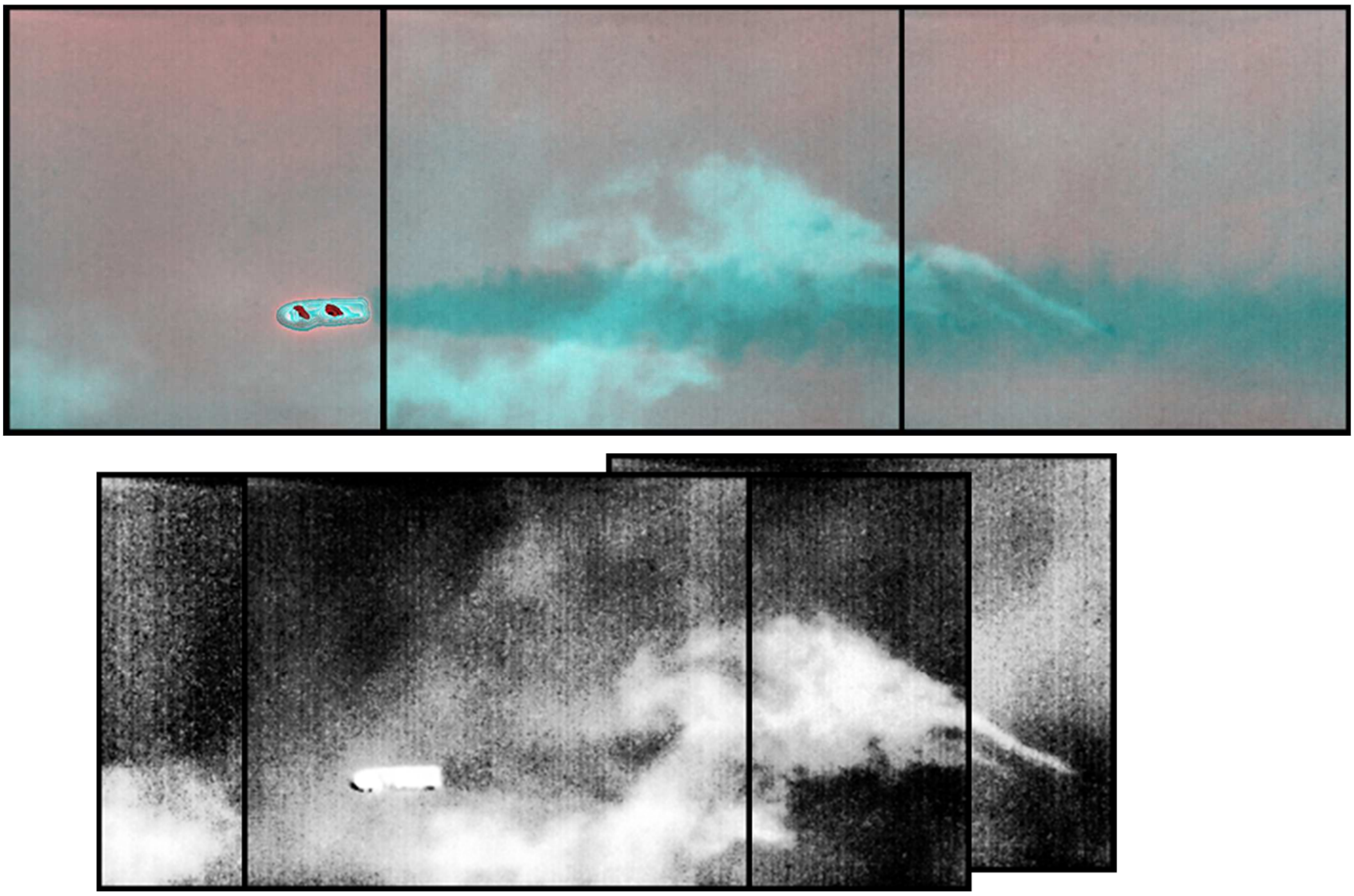


Figure 35: SLOT1-0013 à 800 m d'altitude. Produit : Iso-propyl-acétate. Haut : Produit RGB fausses couleurs. Bas : corrélateur dédié au gaz : la présence de gaz correspond aux parties les plus claires de l'image. La largeur de chaque vignette est de 750 m.

Figure 36: SLOT1-0014 à 800m. La largeur de chaque vignette est de 750 m.

La nappe observée à la fin du déversement a une surface de 1150 m^2 ce qui correspond à un majorant de l'épaisseur moyenne de 0.8 mm comme pour le cas de l'acétate de Butyle. Lors du SLOT1-0013, 10 minutes après la fin du déversement, la nappe observée a une surface estimée de 850 m^2. Il apparait ainsi que la nappe d'Iso-propyl-acétate en surface a une dynamique de disparition en infrarouge proche du N-Propyl-acétate mais peut être plus rapide que l'acétate de butyle pour lequel la nappe est observée sur des surfaces de l'ordre de 500 m^2 45 min après la fin du déversement. La colinéarité entre vecteur vent et vecteur de déplacement du navire, combinée à la persistance des gaz évaporant et leur faible vitesse de dispersion par la création de bouffées conduit au fait que les gaz se mélangent au-dessus du navire. De plus leur très forte ressemblance spectrale rend très difficile leur distinction par les traitements SIMAGAZ. Ainsi il est équiprobable que la bouffée observée sur la Figure 36 à droite à l'aval du navire soit de l'Iso-propyl-acétate ou du butyl-acétate. Les deux panaches, se déplaçant plus vite que le navire, ont une source qui s'éloigne du bateau (à la vitesse du navire) et quasiment dès leur déversement on peut observer des bouffées qui dépassent le bateau pour les deux gaz.

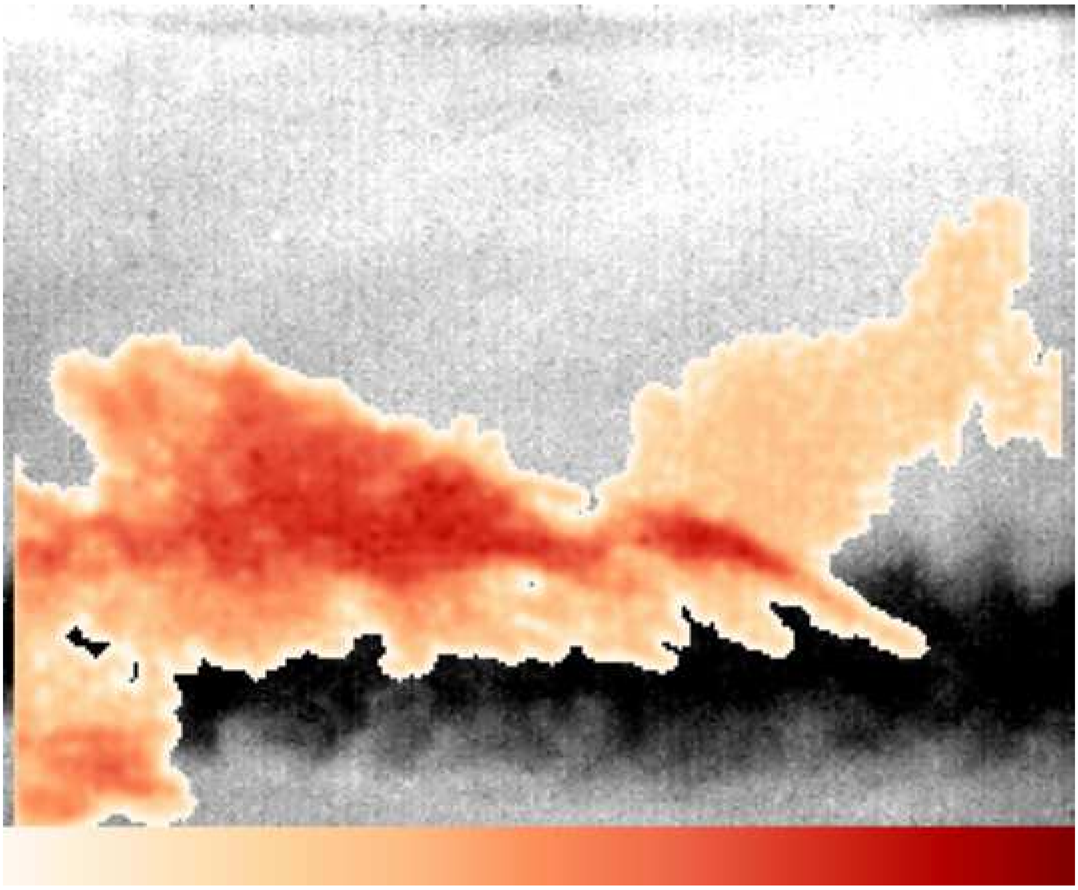


Figure 37 : Carte en concentration (échelle 0-1000 ppm.m) d'Iso-propyl-acétate. SLOT1-0013

4.3.4. MTBE

Il y a eu deux acquisitions exploitables pour le déversement de MTBE, le premier juste à la fin du déversement où la nappe et le gaz sont vus et le second 14 min après où l'on ne détecte rien. La Figure 38 montre que pour le SLOT3-0012 (et le SLOT3 de façon générale) le sillage était quasiment invisible en thermique. Cela s'explique par les conditions météorologiques et un état de mer radicalement différent de la veille : une houle de l'ordre de 1 à 2 m s'est formée et le vent est passé de 1à 2 m/s à 8-10 m/s. L'eau est naturellement brassée sur une couche bien plus épaisse : l'eau sous la surface et en surface ont les mêmes températures. La nappe observée pendant le déversement semble plus linéaire que pour les produits de la veille et plus compacte. Le gaz dans le champ de vue de la caméra reste fortement sous forme de filament très longiligne : la force du vent ne permet pas d'observer les phénomènes de bouffées et d'accumulation verticale vus pour les autres produits.

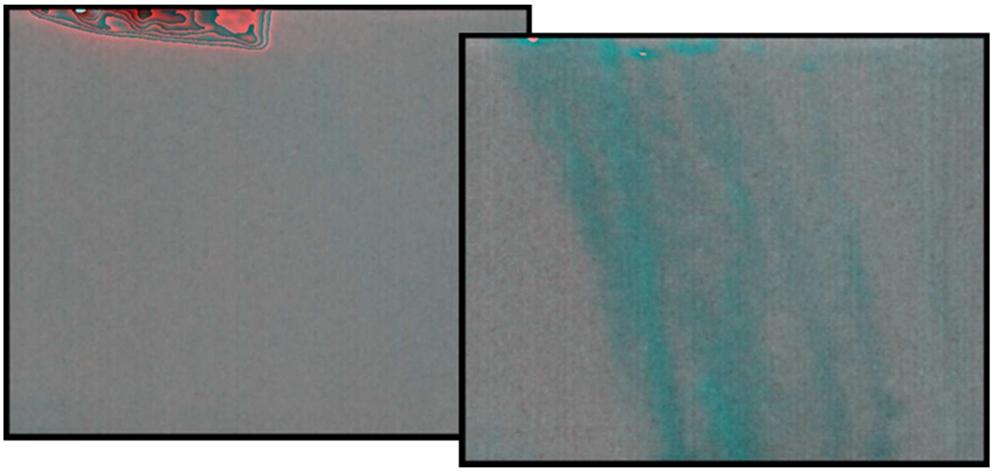


Figure 38 : SLOT3-0012 à 300m. Observation du MTBE. La largeur de chaque vignette est de 280 m.

La Figure 40 représente un fond infrarouge thermique sur lequel est plaqué le masque de détection et les concentrations obtenues sur une échelle de 0-1000 ppm.m.

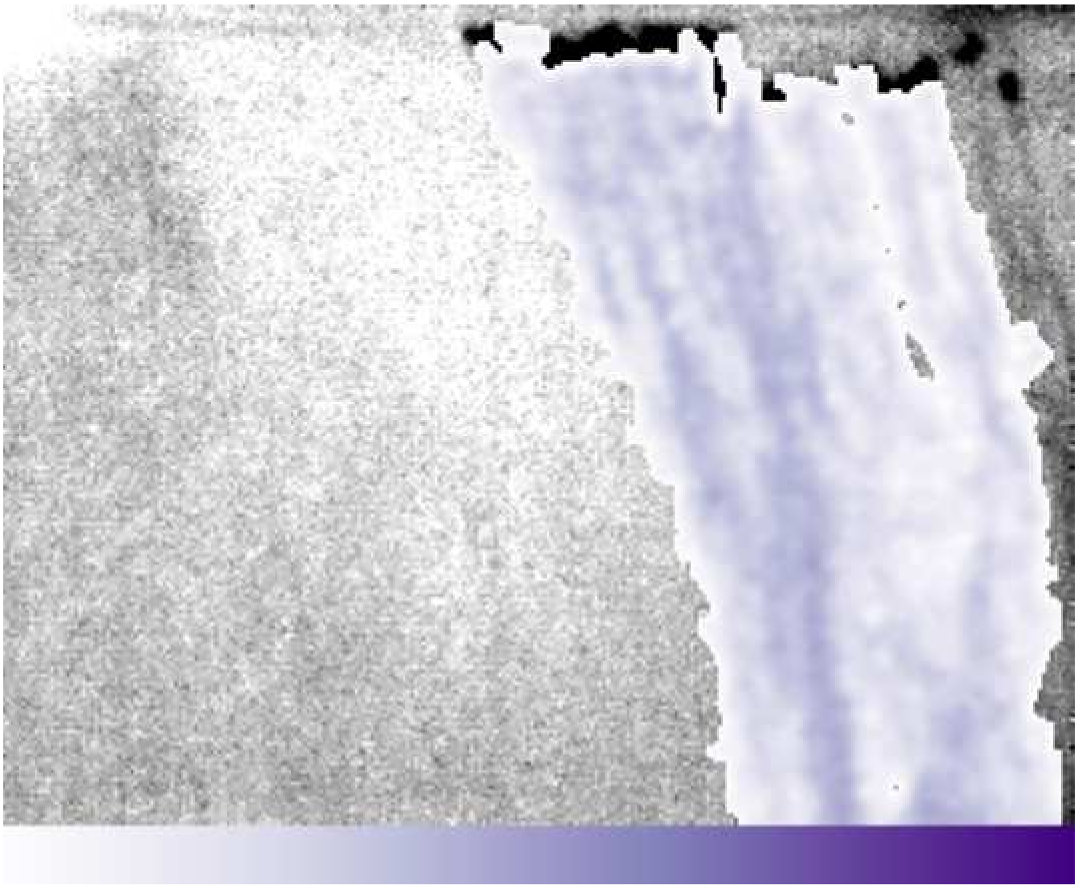


Figure 39 : SLOT3-0012 à 300 m. Observation du MTBE en concentration intégrée sur une échelle 0-1000 ppm.m.

4.3.5. Acétone

L'acétone n'a pu être observé que lors de l'acquisition SLOT3-0019 pendant le déversement. Ensuite le vent de travers a empêché la maîtrise de la trajectoire de l'avion pour assurer un passage dans le sillage du navire, couplé à une très faible signature du gaz dans les conditions d'observation. En effet sur la figure ci-dessous qui correspond à un produit intermédiaire de corrélation où la nappe apparait claire et le panache sombre, on peut voir que le gaz est difficilement discernable vis-à-vis du fond de mer. Il n'y a donc pas eu de détection automatique de l'acétone avec l'outil de traitement : dans ce cas, seule l'observation des films (la visualisation dynamique est un élément important pour la détection et difficilement transposable dans un rapport papier) par un opérateur averti permet à ce jour de détecter l'évaporation de la nappe.

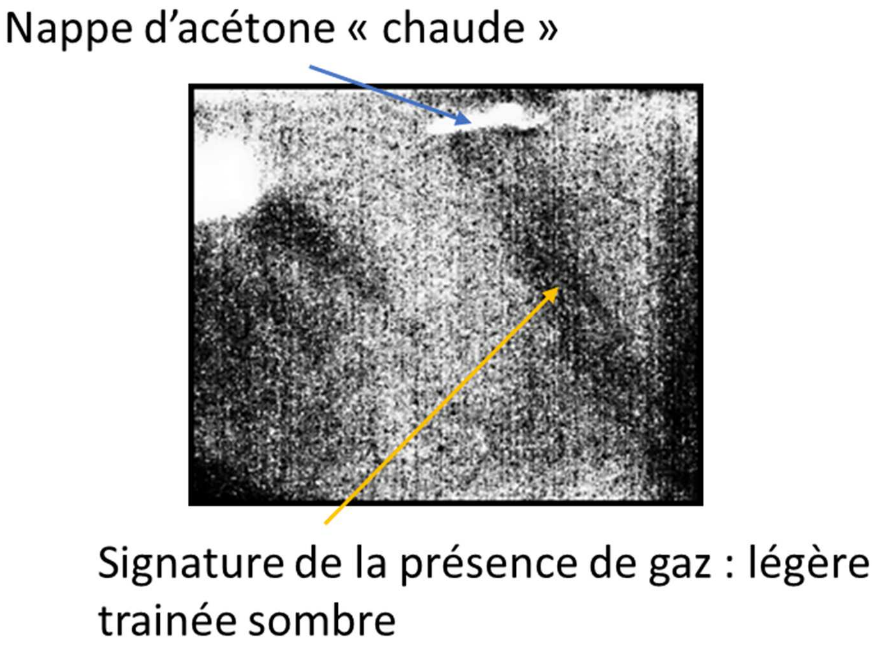


Figure 40 : SLOT3-0023 à 300m. La largeur de la vignette est de 280 m. Produit intermédiaire de corrélation : le gaz apparait sombre et la nappe ou le navire apparaissent clairs.

4.3.6. Toluène et Xylène

Pour le Toluène et le Xylène, comme attendu aucun dégazage n’a été observé : les filtres de la caméra SIMAGAZ ne correspondent pas aux longueurs d’ondes d’absorption et d’émission de ces deux produits à l’état gazeux. Néanmoins un suivi des nappes a pu être réalisé :

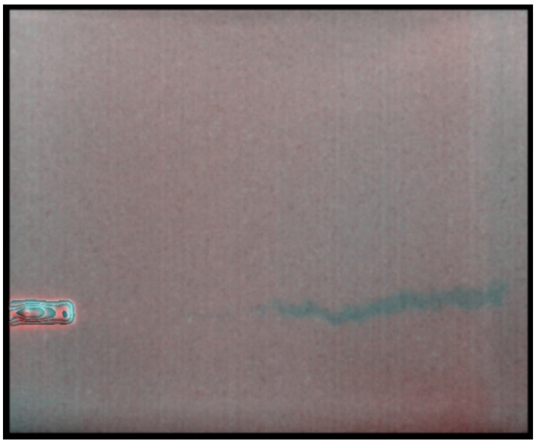


Figure 41: SLOT3-0029 Nappe de Toluène. Altitude 800 m. La largeur de chaque vignette est de 750 m. Image en fausses couleurs.

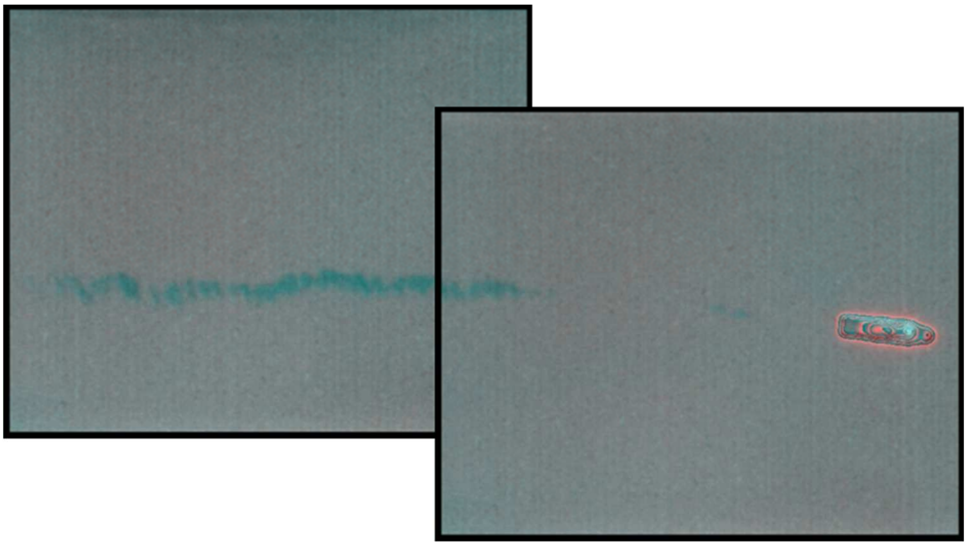


Figure 42: SLOT3-0034 Nappe de Xylène. Altitude 800 m. La largeur de chaque vignette est de 750 m. Image en fausses couleurs.

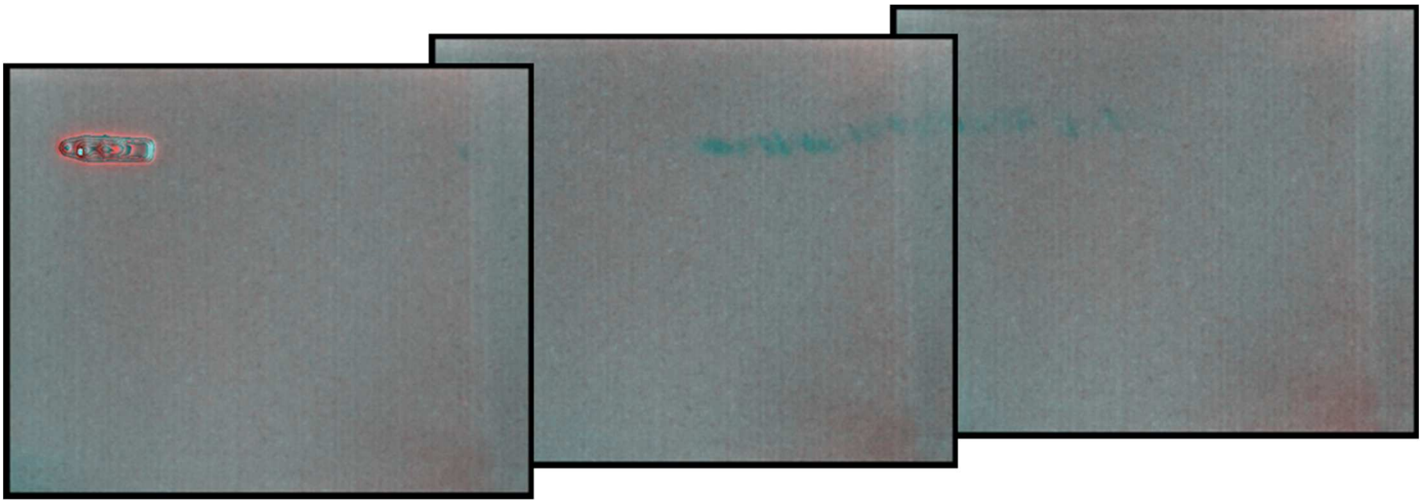


Figure 43: SLOT3-0035 Nappe de Xylène. Altitude 800 m. La largeur de chaque vignette est de 750 m. Image en fausses couleurs.

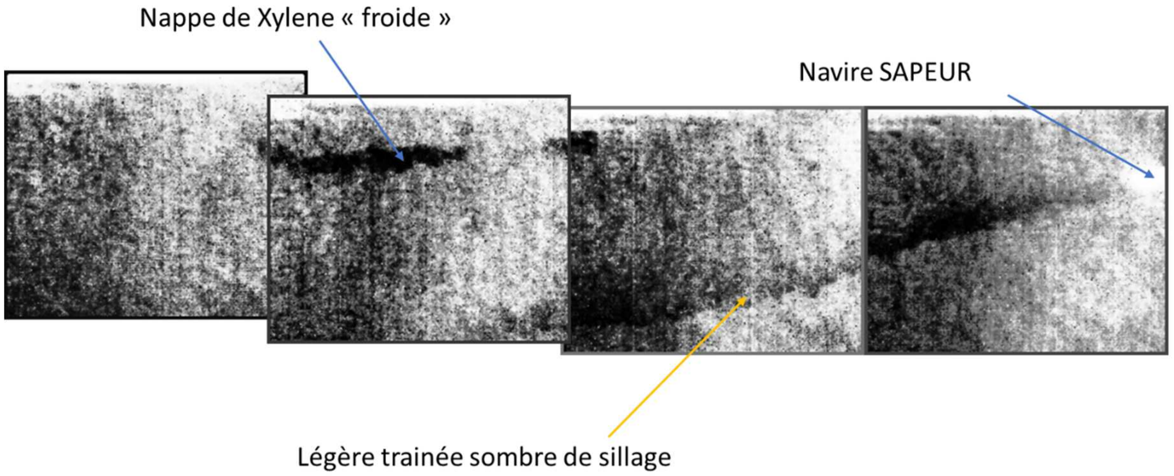


Figure 44: : SLOT3-0035 Nappe de Xylène. Altitude 800 m. La largeur de chaque vignette est de 750 m. Image en contraste thermique infrarouge dans la bande 2 de SIMAGAZ.

5. SYNTHESE - CONCLUSIONS – PERSPECTIVES

Les tableaux de synthèse ci-dessous reprennent les principales observations mises en avant dans ce rapport pour les observations sol et aéroportées. Si tous les produits ont pu être observés en surface, cinq produits gazeux ont été observés dans l'atmosphère. Pour les autres gaz, les filtres de SIMAGAZ ne sont pas adaptés et uniquement les nappes ont été observées. Les vapeurs des gaz pour lesquelles la caméra SIMAGAZ a le plus de sensibilité (Acétate de Butyle, Iso-propyl-acétate et N-propyl acétate) ont été observées pendant plus de 30 min jusqu'à des distances de plus de 1 km. Pour les autres gaz observés (acétone et MTBE), la persistance ne dépassait pas la dizaine de minutes en particulier en présence de vent important.

Dans ce tableau, l'absence de détection ou d'observation est représenté par le signe '-' et dans le cas positif on note '+' si cela s'est avéré possible mais de façon peu robuste et très dépendante des conditions d'observation. Dans le cas positif on note '++', puis '+++' les détections ou observation fonction de la robustesse et des observations et détections réalisées automatiquement avec l'outil de traitement actuel.

Tableau 1 : Synthèse des observations SIMAGAZ pour la campagne MANIFEST – Navire SAPEUR

Produit	Observation de la nappe en surface	Observation du panache de gaz	Persistance de l’observation (mn)	Etendue du produit observé (m)	Portée de l’observation du produit
Acétate de butyle	+ Nappe « froide »	+++ Observation, Détection et Quantification	> 30	> 500	1 km (horizon)
Acétone	+ Nappe « chaude »	+ Observation, Détection Quantification	5	100	300 m
MTBE	++ Nappe « froide »	+ Observation, Détection	30	200	600-800 m
Iso-Propyl-acetone	++ Observation Nappe « froide »	+++ Observation, Détection et Quantification	> 30	> 500	1 km (horizon)
N-Propyl-acetone	++ Observation Nappe « froide »	+++ Observation, Détection et Quantification	> 30	> 500	1 km (horizon)
Toluène	++ Nappe « froide »	-	30	200	600-800 m
Xylène	++ Nappe « froide »	-	30	200	600-800 m

.

Tableau 2 : Synthèse des observations SIMAGAZ pour la campagne MANIFEST – Aéroporté

Produit	Observation de la nappe en surface	Observation du panache de gaz	Persistance de l'observation (mn)	Etendue du produit observé (m)	Portée de l'observation du produit
Acétate de butyle	+ Nappe « froide »	+++ Observation, Détection et Quantification	> 55	> 2500	800 m
Acétone	+ Nappe « chaude »	+ Observation – Détection Quantification	5	75	300 m
MTBE	++ Nappe « froide »	+ Observation, Détection	5	200	300 m
Iso-Propyl-acetone	++ Observation Nappe « froide »	+++ Observation, Détection et Quantification	> 50	> 1500	800 m
N-Propyl-acetone	++ Observation Nappe « froide »	+++ Observation, Détection et Quantification	> 30	> 2000	800 m
Toluène	++ Nappe « froide »	-	?	400	800 m
Xylène	++ Nappe « froide »	-	> 30	800	800 m

Des travaux préliminaires de quantification ont été menés au sol et en aéroporté mais les résultats ne sont pas repris dans cette conclusion car ils nécessitent une consolidation et des travaux de validation en lien avec les efficacités d'évaporation des produits théoriques ou mesurés en laboratoire. De façon générale il semble que les concentrations volumiques mises en jeu dans les panaches observés sont de l'ordre de la centaine de ppm (partie par million) avec des débits compris entre la dizaine et la centaine de grammes par seconde. Ce travail peut s’avérer très important s’il permet de comparer aux modèles existant l’évolution des panaches en cas de déversement de produits en mer en fonction de leurs propriétés physico-chimiques.

Les perspectives envisageables sont de plusieurs types :

- Analyse comportementale et physique des scènes observées durant la campagne en lien avec le CEDRE, le CEPPOL et les acteurs du projet MANIFEST.
- Mise en place de protocoles d’expérimentations futurs adaptés au suivi temporel des gaz évaporant en mer et réalisation d’une campagne d’observation au sol, sur bateau ou en moyen aéroporté (drone, avion ou hélicoptère) dédiée.
- Mise en place d’évolutions logicielles dédiées aux applications maritimes de SIMAGAZ permettant notamment une détection couplée entre nappes liquides et leur produit évaporant.

ANNEX VII - Overview of existing sensors including a) a description of portable gas sensors for first responders, b) a description of sampling techniques and protocols and c) state-of-the-art of existing technologies, extracted respectively from Fact sheets a) 5.25, b) 5.26 and c) 5.27 of the West MOPoCo HNS Manual co-funded by DG-ECHO https://www.westmopoco.rempec.org/en

FACT SHEET 5.25

Portable gas detectors for first responders

BACK

Objective

To present a few examples of detectors used. Particular focus is placed on the key parameters to consider for the acquisition or usage of portable detectors, as well as a reminder on how to proceed when some threshold values are measured.

Context

Portable gas monitors allow readings to be taken and assessments to be made on the safety of implementing response operations at that time.

- It can be very difficult to identify hazards when dealing with an HNS incident, and as such, all measures that can help identify and reduce the risk of a hazard should be used. Portable gas monitors are a crucial piece of equipment for any first responder;
- Different portable gas monitors measure different gases and hence it is essential to check the substances involved in the incident and the monitor's manual to ensure the monitor can accurately measure the gas present.

What portable sensors should be used?

Portable sensors for the detection of hazards, especially gas, represent an incredibly worldwide market. Several experimental studies have been conducted to test sensors. One conclusion is that no detector meets the needs for first responders in full, which highlights the necessity to be trained and aware of its own detection device.

Above all, the different sensing technologies have both advantages and limitations ▶ 5.27 HNS detection and analysis methods and detector manufacturers develop equipment for which acquisition is generally the result of compromise between additional characteristics to be considered, including: being wearable (size and weight), single/multiple measurements, drop resistance, cost and other possible interesting options such as communication functionalities.

Type of detection	Picture
Portable Colorimetric Tubes (PCTs)	 © Cedre
Catalytic bead sensors (explosimeter)	 © Cedre
Thermal conductivity detector/ katharometer	 CO / H2S SO2 / ETO CH4 © SOBEGI
Photo Ionisation Detector (PID) instruments	 © Cedre

Table 51: Typically used portable detectors

What to measure

The table below describes different variables, reference measures and response actions, in brief and limited to some common issues related to gas. Further training on these variables and appropriate response actions should be provided to all first responders, including the use of gas monitors and confined spaces training.

Measure to be detected Gas detected	Ambient level	Action to be taken
O_2 (oxygen)	< 19.5%	Monitor wearing SCBA. *Caution: combustible gas readings are not valid in atmospheres with < 19.5% oxygen.*
	19.5% - 22%	Continue investigation with caution. SCBA not needed, based on oxygen content alone.
	> 22.0%	Discontinue inspection; fire hazard potential. Consult specialist.
CO_2 (Carbon dioxide)		Evacuate immediately if detected. Monitor only wearing SCBA.
H_2S (Hydrogen sulphide)	5 ppm	Monitor wearing SCBA.
	0.4-0.8% (10-20% LEL)	Continue on-site monitoring with extreme caution as higher levels are encountered.
	> 0.8% (>20% LEL)	Explosion hazards; withdraw from area immediately.
Organic and inorganic vapour/gases	Depends on chemical.	Consult toxicological refence values.
Concentrations		
Lower Explosive Limit (LEL) (For greatest safety reserve nonane is generally used for detecting unknown flammable substances)	< 10% LEL	Continue investigation.
	10% - 20% of LEL	Continue on-site monitoring with extreme caution as higher levels are encountered.
	> 20% LEL	Explosion hazards; withdraw immediately from the area.
Radiation	< 25 μSv/h - 30 μSv/h	Continue investigation. If radiation is detected above background levels, this signifies the presence of possible radiation sources; at this level, more thorough monitoring is advisable. Consult with a health physicist.
	> 100 μSv/h	Potential radiation hazard; evacuate site. Continue monitoring only upon the advice of a health physicist or medical personnel.

Table 52: Different variables, reference measures and response actions related to gas

Limitations of portable detectors

Certain factors may give rise to inaccurate readings:

Lower readings than actual concentrations, may be due to:
- The heat of combustion of the gas or vapour, e.g. carbon disulphide;
- Inappropriate substance used for calibration. For instance if a catalytic bead sensor is calibrated to detect a very sensitive gas, it will display lower readings than the substance's actual concentration;
- Polymer formation of the chemicals which can accumulate on the sensor (polymerising chemicals such as styrene, acrylonitrile). This problem can be anticipated for certain liquid chemicals since these are carried with inhibitor additions.

Invalid readings due to:
- An oxygen concentration < 19.5%;
- Problem of unit conversion: 1 Vol.-% = 10,000 ppm (mL.m-3) = 10,000,000 ppb

Gas meter failure due to:
- Corrosion or loss of catalytic functioning of the sensor caused by the spilled chemical, e.g. halogenated hydrocarbons, hydrogen sulphide;
- Expired validity for instance, if the shelf-life of the reagent has expired (for instance the colorimetric tubes).

Sampling techniques and protocols

BACK

Objectives

To provide advice on techniques and protocols for sampling spilled substances in the field.

Introduction to sampling

Two objectives for taking samples of spilled substances in the field are:

- To serve as a reference for operational needs (e.g. response options, fishery ban) or future scientific studies;
- To identify and characterise the pollutant to provide a reference as evidence for any future claims and to contribute to response strategies.

The protocol and method of sampling should be dictated by the overall objective for undertaking sampling, and the person(s) undertaking the sampling should be trained in the appropriate method.

Tracking the progress

To keep track of the progress of the sampling process, a **Chain of Custody form** is used. This form should be included in the contingency response plan and it should outline the appropriate sampling protocol for different situations and chemicals, including approved laboratories. The contingency response plan should also appoint a **Sampling Coordinator**, who is responsible for the transmission of samples to the appointed laboratories.

The **Chain of Custody form** should include several elements, which should be adapted for different groups of chemicals.

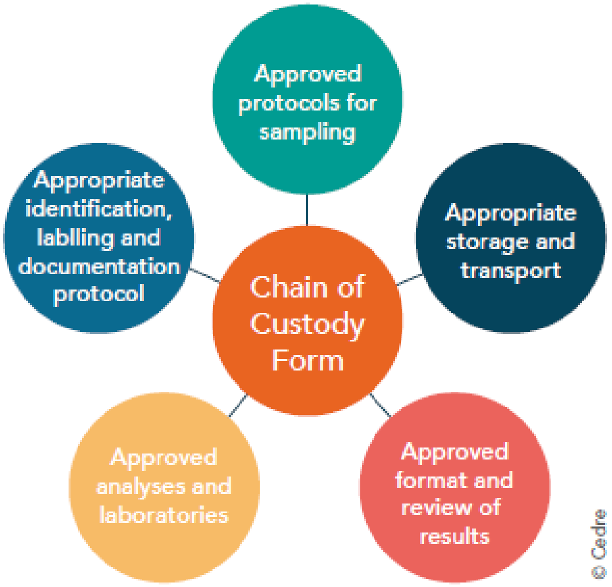


Figure 64: Chain of Custody Form

Key points

- **Objectives**: The final objective for taking samples should drive the process. This should be adaptable, if necessary and possible, to unexpected situations including harsh environments (weather, tide, current), equipment failure and other issues typical of sampling in the field.
- **Rigourous methods**: The protocols should be rigorously followed to reduce the risk of contamination and subsequently invalidating the results. This ensures the use of uncontaminated and clean equipment when sampling, as well as ensuring samples are not contaminated during storage and transport.
- **PPE**: Personal protective equipment (PPE) should be selected to enable sampling in safe conditions and to handle sampling equipment with ease.
- **Sampling kit maintenance**: The sampling kit should be maintained on a regular basis and items should always be replaced after each campaign in order to keep the kit operational.
- **Sampling kit materials**: The material for the sampling equipment should be suitable for the substance sampled. This typically consists of glass, polyethylene, polypropylene or a fluoropolymer (e.g. PTFE) which are known for their lack of interaction with analytical parameters. Section 7 of the ▶ 3.1 Safety Data Sheet for the chemical should be checked ahead of sampling to confirm compatibility.
- **Sample requirements**: The volume or weight of the sample required for analysis should be double-checked. The size of the required sample may differ depending on the type of substance, the type of analyses and the chosen laboratory.

Sampling methods

Sampling should be performed with proper equipment and techniques to ensure the integrity of the sampled substance and the subsequent reliability of analytical results.

Depending on the type of detection selected, some platforms such as ROVs may easily be equipped with in situ detectors. Other types of detection may require sampling prior to further analysis. The sampling technique should be properly performed in compliance with required standards and deterioration. For instance, organic compounds can adsorb to plastic containers, reducing the concentration in the sample, or substances such as PAHs are sensitive to degradation by ultraviolet (UV) radiation, requiring the use of amber glassware or by wrapping samples in foil.

▶ 4.5 Response vessels
▶ 5.24 Remotely operated vehicles
▶ 5.27 HNS detection and analysis methods

The frequency and quantity can vary depending on:

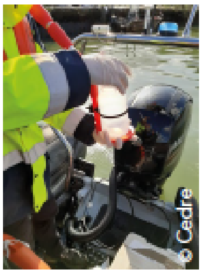
	Atmosphere	**Water**	**Sediments**	**Biota**
	 © SOBEGI *Air sampling kit*	 © Cedre *Bottle to sample water below sea surface*	 © ISPRA *Sampling sediments*	 © ISPRA *Sampling biota*
Sampling technique	In situ detection is preferable to sampling, especially due to potential explosive/flammable/toxic hazards, high spatial/temporal kinetics. Sampling bags should be made of a compatible chemical, tightly closed after sampling and the pollutant analysed rapidly. Air sampling can alternatively be implemented using an active carbon adsorber, followed by desorption in an analytical device such as a GC-MS.	At depths greater than 50m, water sampling can be undertaken using hydrographic sampling bottles, possibly with a PTFE internal lining.	Sediment samples can be collected using grabs or coring devices, or by means of ROVs deployed and controlled from a surface vessel. The choice of grab can be influenced by the type of sediment to be sampled. Corers are generally used to remove a core from the seabed to establish contaminant changes over time. If samples are taken from stable sediment areas, then increasing depth in the sediment (down the core from the sediment surface) represents an increase in time since the sediment was deposited.	The methods used for sampling biota will vary depending on the species of interest and the habitats with which they are associated.
Considerations	On-site monitoring needs to be carried out with extreme caution if explosive/flammable levels are encountered (10%-20% of the LEL). At levels higher than >20% of the LEL there is an explosion hazard and responders must withdraw from the area immediately.	Importance of understanding the vertical stratification in large water bodies and the effects of mixing in flowing streams.	Two main purposes: to assess if the pollutant is entering the sediments and to study changes in benthic communities and determine the impact on the seabed. In intertidal areas, sediment samples can be collected by hand.	In coastal areas, farmed fish/shellfish should also be prioritised for sampling. All contaminants in biota exhibit significant variability in concentrations between individuals and a number of fish and shellfish should be taken and analysed (if possible individually or as pooled samples) in order to reduce the level of uncertainty.

Table 53: Sampling techniques and considerations

Sample storage methods

To ensure good quality samples are submitted for analysis, there are several methods which can aid the preservation of samples and delay the degradation of the substance. These methods, which may include a pre-concentration technique, are listed in the table below.

Sample treatment	Description
Solid Phase Micro Extraction (SPME) or Stir Bar Sorptive Extraction (SBSE)	Solventless sample method using exposure on a fibre or on a magnetic stirring rod coated with extraction materials (polymer or sorbent).
Freezing	Reduces microbial action which may alter the concentration of the substance by biodegradation, for example.
Cooling	Reduces microbial action which may alter the concentration of the substance by biodegradation, for example.
Acidification	Decreases the pH ($pH < 2$) which preserves most trace metals and reduces precipitation, microbial activity and sorption losses to container walls.
Reagent addition	A high-grade reagent can chemically preserve the analytical parameters of the substance.
Solvent extraction	Extraction from sampling matrices based on their ability to be preferentially dissolved in a selected solvent. Also useful for concentrating the molecules involved to be analysed.
Filtration	Organic and inorganic contaminants can adsorb suspended matter in water. Filtration allows dissolved contaminant levels or contaminants associated with suspended matter to be determined.

Table 54: Sample storage methods

More information about sampling, preservation and holding times for commonly encountered chemicals can be found here: www.epa.vic.gov.au/about-epa/publications/iwrg701

FACT SHEET 5.27

HNS detection and analysis methods

BACK

Objective

How to choose the most suitable methods for HNS detection and analysis.

Considerations

- ✓ Account for the cost for acquisition, use and maintenance of necessary apparatus.
- ✓ Each device requires a trained operator.
- ✓ Think critically when analysing data and be aware of errors associated with the instrument.
- ✓ No single analytical method is applicable for all chemicals.

HNS detection method selection criteria

When deciding which sensor to use for HNS detection, several criteria need to be considered (Table 55).

Criteria	Explanation
Calibration	Means by which the sensor output is verified against known concentrations to enable confidence in measurements.
Sensitivity	The minimum concentration of a substance needed for a detectable sensor response. The sensitivity limit is the threshold below which a concentration cannot be detected.
Selectivity	Ability to detect the substance of concern in the presence of other substances.
Interference	Other substances/environmental parameters which might lead to false positives/ negatives.
Detection time	Time required to reach a measurement reflecting reality. Typically, the time for 90% of the signal response to be reached after exposure to the substance.
Recovery time	Time required to return to background levels once there is no more exposure to the measured substance.
Operation time	Time after which the sensor no longer outputs sufficiently reliable and accurate results, depending on the application.
Drift	Systematic change of the sensor baseline over longer timeframes as a result of instrument error in the absence of the measured substance.
Electricity consumption	Needs to be considered, especially in the field.

Table 55: Definition of the parameters characterising analytical equipment

The main detection devices are presented in following table with a description of working principle, including what species they target, a short description of their principle and the corresponding advantages and limitations.

HNS detection and analysis methods

Type of detection	Principle
Portable Colorimetric Tubes (PCTs)	A gas or vapour is pulled into a glass tube containing a sensitive reagent that reacts with the gas often causing a colour change, hence identifying the presence of a specific chemical and allowing a qualitative assessment of concentration. Can also be miniaturised on a chip.
Catalytic bead sensors (explosimeter)	When a catalyst-coated ceramic bead with an imbedded platinum coil is exposed to a flammable gas an oxidative reaction with oxygen on the bead surface causes a measurable change in the platinum wire resistance. This signal indicates the concentration of the gas in the air.
Thermal conductivity detector/ katharometer	The difference in thermal conductivity between a reference carrier gas and the measured gas is detected using the changing voltage across an electrode system.
Flame Ionisation Detector (FID) instruments	A gas sample is ionised in a hydrogen flame in the vicinity of an electrical cathode. Ions formed under an electrical potential are attracted and measured thanks to induced electrical current in an electrode system.
Surface Acoustic Wave (SAW)	SAW sensors use the interaction of sound waves with specific material coatings on a piezoelectric system to detect chemical vapours in the air. The material is chosen to detect specific chemical species. Different absorbed chemicals on the material produce a different electrical signal in the piezoelectric system caused by modulation of sound waves.
Infrared (IR) Sensors	Detection based on the absorption of infrared light by certain molecules which are detected by a decrease in transmitted radiation over a beam path. Compared with non-dispersive IR, selectivity can be improved used a FTIR detector.
Gas chromatography (GC) or High Performance Liquid Chromatography (HPLC)	The sample is introduced into a mobile phase in a column. Separation occurs along the column between a mobile phase and a stationary phase. The temperature of the column can be controlled to improve separation of chemicals. Different types of detectors can be used for the measurement or identification of separated chemicals at the outlet of the column.
Mass Spectrometry (MS)	Ionised chemicals are accelerated and then deflected by a magnetic field according to their mass-to-charge (m/z) ratio to separate the ions across a detector screen. MS is often coupled with a separation technique such as chromatography.
Ion Mobility Spectrometry (IMS)	Ionised molecules are separated in a buffer carrier gas as they travel through an electric field. Compounds are identified based on the time required for ionised molecules to drift. This separative technique is generally coupled with another detector type or mass spectrometry.
Inductively Coupled Plasma (ICP)	Ionisation technique using extremely hot plasma, usually made from argon gas. A “hard” ionisation technique as most of the molecules are atomised. A method known for its ability to detect trace metals and non-metals in liquid samples. Often combined with mass spectrometry and other spectroscopy.
Raman Spectroscopy	The substance is illuminated with infrared (IR) radiation thus interacting with the chemical bonds in the molecule and causing the IR radiation to be reflected. The reflected IR signal represents a characteristic signature spectrum of that molecular species and can be compared with reference spectra.
X-Ray Fluorescence (XRF)	The atoms in a molecule are excited by bombardment with x-rays and subsequently release energy including fluorescence and x-rays with specific wavelengths that are characteristic of certain elements. Can also be used as a remote sensor with laser-induced fluorescence.
Metal oxide semiconductor	Chemically resistant layer on a semiconductor chip that reduces a target substance hence inducing changes in conductivity or resistance that can be measured to indicate the concentration or identity of that target species. Different chemiresistors used in an array is called an ‘electronic nose’.

Electroanalytical detection	These techniques use electrode systems with a solution bridge and can use different characteristics of electrolysis to measure analyte concentrations that become dissolved in the solution. Different reactions at the electrodes can cause different electrical signals that can be measured to determine the concentration of a target species. Techniques include potentiometry, conductometry, voltammetry and amperometry.
pH meter	Monitoring of acids or bases can be done with a pH meter or with pH indicating paper. In the latter case, the paper is impregnated with an indicator which changes colour on contact with the water sample. The resulting colour is compared with a scale for pH value.

Table 56: Main detection devices - © Cedre

Operational considerations

Type of detection	Used for	Advantages	Limitations
Portable Colorimetric Tubes (PCTs)	Selected gaseous chemicals	- Simple presence/absence test - Cheap, intuitive and fast - Miniaturised version usable in inaccessible places or harsh environments	- Shelf-life - Possible interferences (e.g. water) - Often does not provide a quantitative measurement
Catalytic bead sensors (explosimeter)	H_2, CH_4, combustible gas	- Low cost and robust - Easy to calibrate - Small and easy to handle - Provides a quantitative measurement	- Concentration of oxygen below 12% may affect detection - Detection reduced by polymerising substances (e.g. chlorinated or fluoridated hydrocarbon substances, silicones, hybrid or sulphuric compounds) - Baseline calibration required - Low selectivity
Thermal conductivity detector/ katharometer	Organic or inorganic gaseous species	- High accuracy - Wide range of species detected	- Low sensitivity - Not selective - Less accurate with gases with a thermal conductivity close to air (NH_3, CO, NO)
Photo Ionisation Detector (PID) instruments	Volatile Organic Compounds (VOC)	- Can detect low concentrations - Can be used in explosive atmosphere - Inexpensive	- Calibration is required with isobutylene - Some gases not ionised using this method and hence cannot be measured
Flame Ionisation Detector (FID) instruments	Organic or inorganic gaseous species	- Commonly used in chromatography - Can detect low concentrations	- Non-selective - Cannot be used in explosive atmosphere - Very low detection for H_2S, CCl_4, NH_3, and some other gases - Cannot detect CO or CO_2.
Surface Acoustic Wave (SAW)	Selected gaseous chemicals	- Can detect very low concentrations - Wide range of species potentially measured - Can be miniaturised for portability	- Humidity, temperature or other chemicals may cause false positives/ negatives - Many sensors still in development stage
Infrared (IR) sensors	Hydrocarbon gases and vapours, NH_3, CO, CS_2, HCN, HF, H_2S	- Sensor not susceptible to contamination or poisoning - No calibration necessary - Not dependent on oxygen concentration	- Some chemical species not measurable - Expensive instrument - High energy consumption
Gas Chromatography (GC) or High Performance Liquid Chromatography (HPLC)	Wide range of compounds	- Flexible, customisable, high resolution and sensitivity - GC: wide range of species measurable - HPLC: many portable instruments capable of multiple analysis	- Appropriate detectors must be selected and calibrated - Slow detection time - GC limited by volatility of target species - HPLC not suited to field conditions

Mass Spectrometry (MS)	Wide range of compounds	- Existing portable mass spectrometers - Highly informative of chemical structure - Highly sensitive	- Expensive equipment - Usually not suited to field conditions - Slow detection time
Ion Mobility Spectrometry (IMS)	Molecules that can be ionised	- Low cost - High sensitivity - Fast response time - Portable	- Some detectors (not all) may use low energy radioactive source, authorisation required from nuclear safety authority - Limited selectivity
Inductively Coupled Plasma (ICP)	Wide range of compounds	- Some techniques can analyse liquid samples - Often used with Atomic Emission Spectroscopy (ICP-AES), with high accuracy	In ICP-AES, the sample must be dissolved in a strong acid: aqua regia, a mixture of hydrochloric acid and nitric acid
Raman spectroscopy	Hydrocarbon gases and vapours, H_2, NH_3, CO, CS_2, HCN, HF, H_2S	- Robust instrument for field use - Can detect through plastic, glass or water - High specificity - Low response time	- Interference by fluorescence or biological substances - Only suitable for higher concentrations
X-Ray Fluorescence (XRF)	Wide range of compounds	- Relatively cheap - Multi-elemental analysis - Low contamination risk	- Only suitable for larger atoms - Signal interference from other atoms - Complex equipment only suited to lab studies
Metal oxide semiconductor	Oxidising gases	- Fast response time - Cheap and reliable - Compact, with low power demands	- Low selectivity except when used in array as an *'electronic nose'* - Only suited to a limited amount of oxidising gases
Electroanalytical detection	Wide range of compounds	- Techniques are suited to liquid samples - In situ detection - Wide range of possible species measured - High degree of accuracy	- Sensitivity can depend on the materials used for the electrodes, which can vary - Possible interferences of other chemicals
pH meter	Acids and bases	- Intuitive visual result - Very simple and cheap equipment - Clear results	- Overly simple - Paper indicator is not a quantitative measurement

Table 57: Operational considerations related to detection - © Cedre