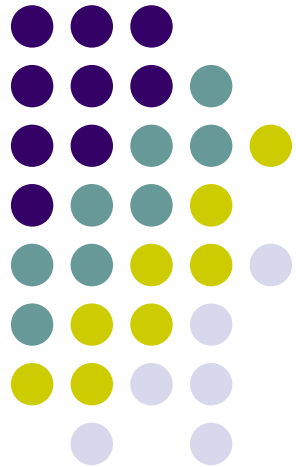
The CLARA Project

Calculations Related to Accidental Spills at Sea



Cedre Information Day,
18 March 2008,
INHES, Saint-Denis-La-Plaine

Overview of the CLARA project

Project partners

ÉCOLE DES MINES D'ALÈS
ALÈS • NÎMES • PAU

Cedre

Ifremer

METEO FRANCE

INERIS
maîtriser le risque pour un développement durable

- Project start date: 25/11/2003
- Project end date: 24/11/2006

Duration (months): 36	TOTAL BUDGET (k€)	REQUESTED BUDGET (k€)	
TOTAL	920	550	54%

Context

- Many incidents on European coasts involving chemical tankers
  - **ECE** (31-01-06) – 10,000 T phosphoric acid
  - **Bow Eagle** (26-08-02) – 200 T ethyl acetate
  - **Balu** (20-03-01) – 8000 T sulphuric acid
  - **Ievoli Sun** (30-10-00) – 4000 T styrene and 1000 T methyl ethyl ketone

- High level of maritime transport
- New "risks" (dispersions of toxic gases)
- Considerable media attention demanding rapid and efficient crisis management
- Poorly adapted modelling

Context

populations and public authorities aspire to quicker, more efficient management of spills to reduce the consequences

- tighter regulations
- strict controls
- more severe penalties

- efficient response means
- quantification of risks

Crisis management software

Context

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Crisis management software

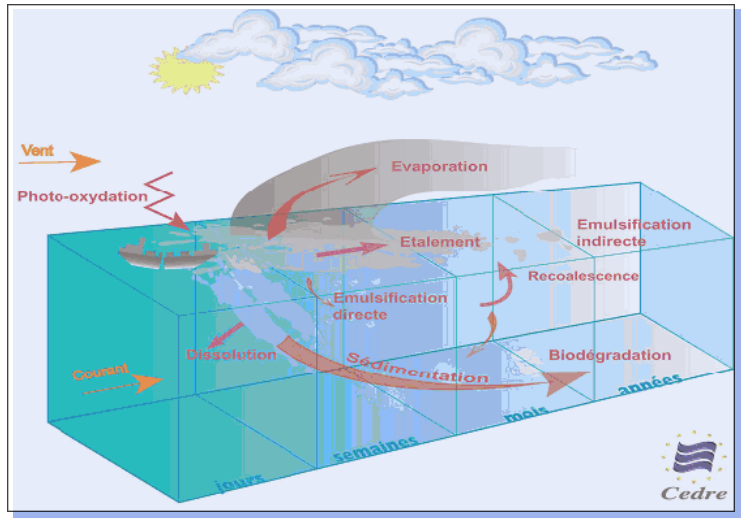
Aims

- Predict the evolution of the product in the marine environment

- Determine the concentrations and/or the location of dispersed chemicals

- Assess atmospheric evaporation and dispersion

- Assess the toxicological consequences on humans, and maritime flora and fauna



New computer-based decision support system for chemical spills at sea

Project structure

- Phase 1: State of the art review
- Phase 2: Characterisation of products
  - Physico-chemical properties
  - Toxicological properties
  - Product database
- Phase 3: Modelling
  - Hydrodynamic
  - Physico-chemical behaviour
  - Atmospheric dispersion
- Phase 4: IT integration
  - Data input interface
  - Results display interface
- Phase 5: Validation

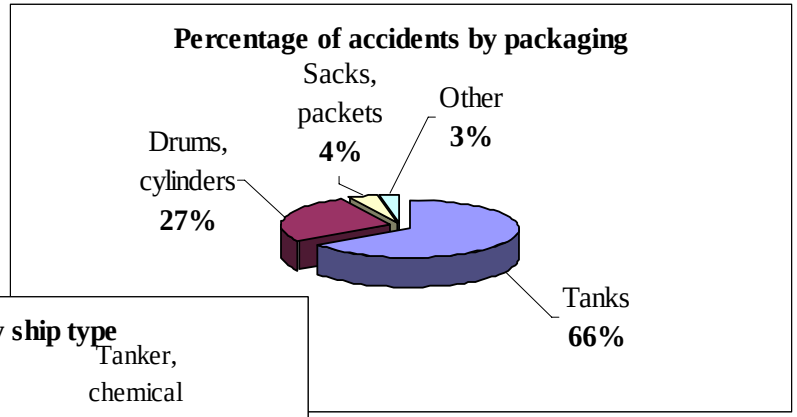
Analysis of maritime traffic

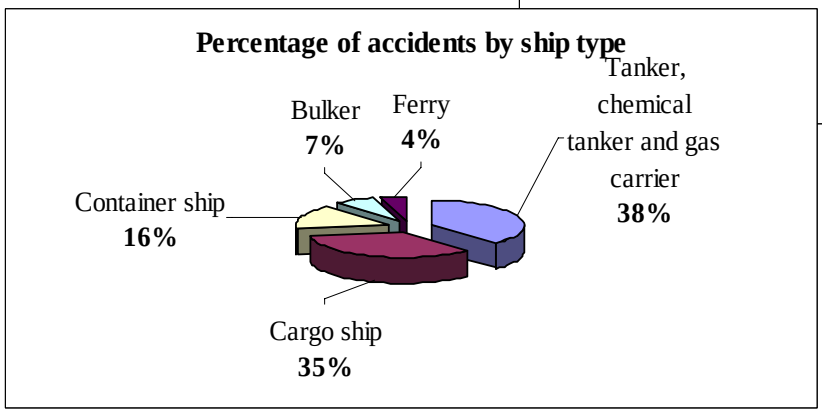
- Increase in transportation of chemicals in the Channel
  - 30 MT in 1998
  - 150 MT in 2000

- Statistical analysis by CEPPOL over 10 years
  - 164 products identified
  - Certain products are transported more frequently and in greater quantities
    - Benzene
    - Vegetable and animal oils
    - Olefins (unsaturated hydrocarbons)
    - Alcohols
    - Xylene
    - Styrene

History of accidents at sea

- Between 1947 and 2002, 69 accidents at sea involving chemicals identified worldwide
- Cargo ships and chemical tankers most often involved
- Chemical pollution generally due to collision or explosion onboard
- Identification of 74 substances
  - **Sulphuric acid**
  - **Ammonium nitrate**
  - **Acrylonitrile**
  - **Phenol**





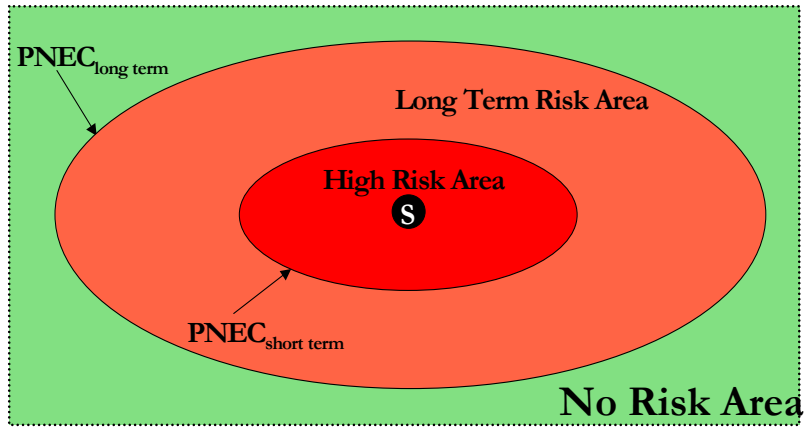
Selection of chemicals

- Greatest hazards (maritime traffic and past accidents)
- Short-term physico-chemical behaviour in the event of a spill (MARPOL classification),
- Presence or otherwise of priority substances
  - **OSPAR Convention**
  - **EU Water Framework Directive 2000/60/EC**
  - **Directive 76/464/EEC**
  - **Regulation 793/93/EEC**
- European classification (SEBC classification)

- Selection of 33 pure chemicals (no mixtures)
- Realisation of a database of physico-chemical properties

Toxicological analysis

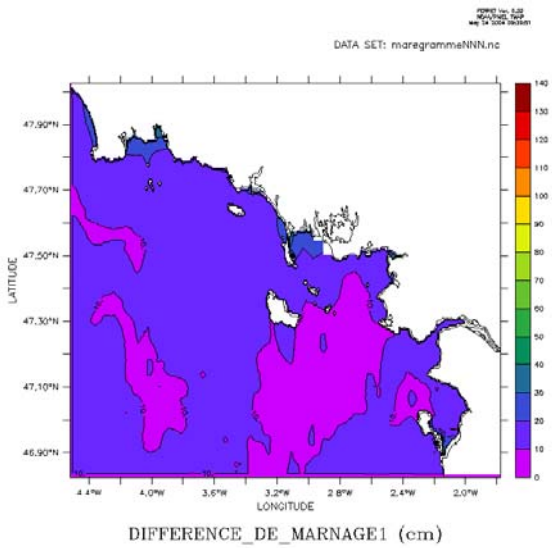
- Definition of high risk areas
- Methodology
  - **Collection of valid ecotoxicological data on pelagic organisms**
  - **Characterisation of PNEC (Predicted No Effect Concentrations)**
    - Short term exposure
    - Long term exposure



Hydrodynamic modelling

- Use of 5-day Météo-France weather forecasts
- Possibility of selecting homogeneous weather conditions if no forecast is available
- Assessment of current fields
- Definition of climatological structures
- Input data for physico-chemical models

- **2D and 3D model**
  - Results: tide, currents, temperature, salinity
  - Fine resolution
  - Calculation time complies with crisis management



Hydrodynamic modelling

Coupling of 2D/3D models with different resolutions

- Rank0: 2D, 5 km mesh size

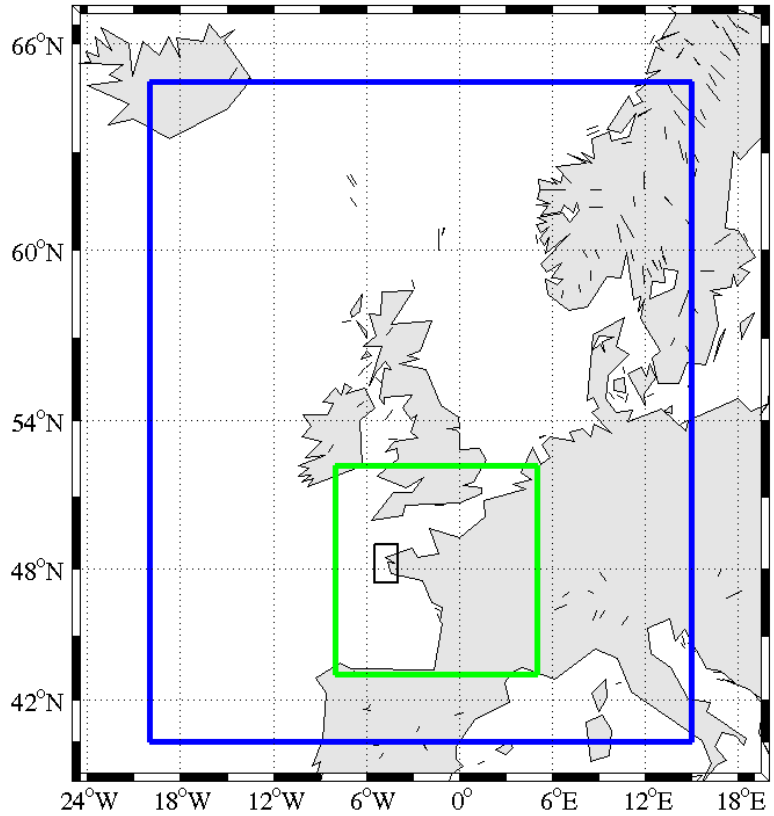
Tide boundary conditions: Atlas model or international tide model

- Rank1: 2D and 3D, 3 km mesh size

Tide boundary conditions: rank0 solutions

- Rank2: 3D, 800 m mesh size

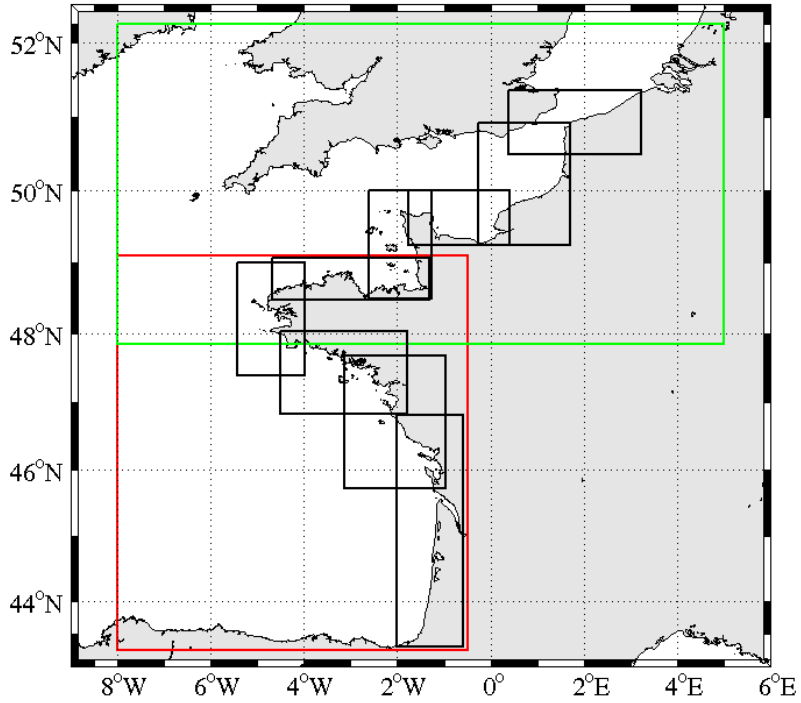
Tide boundary conditions: rank1 solutions



Hydrodynamic modelling

3D approach: overlap of models

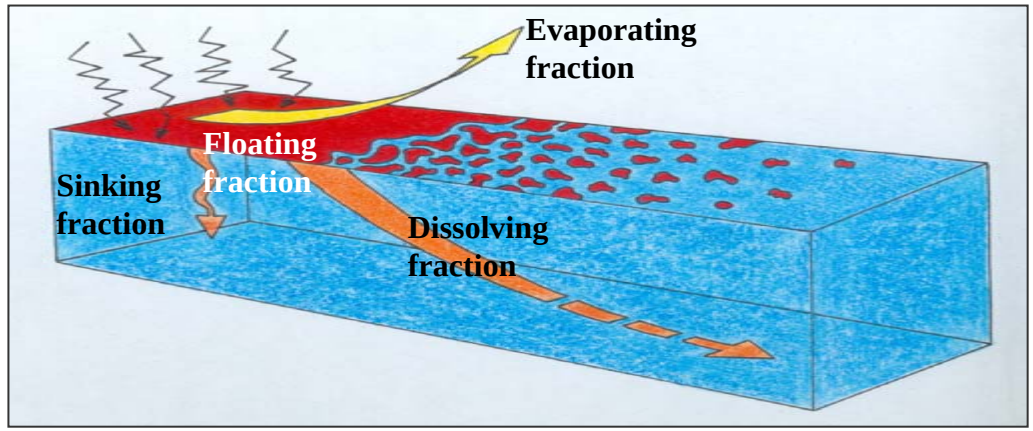
- Two 3D rank 1 models with a resolution of 3 km
  - **Channel** and **Gascogne**
- Nine 3D rank 2 models with a resolution of 800 m
  - **From the Landes region to Pas-de-Calais**
- 10 depth levels
- Validation of models
  - Currents
  - Temperature
  - Tide
  - Salinity



Physico-chemical modelling

Characterisation of the evolution of substances at sea

- Integration of 4 types of behaviour in the hydrodynamic models
  - **Sinking fraction**
  - **Floating fraction**
  - **Evaporating fraction**
  - **Dissolving fraction**

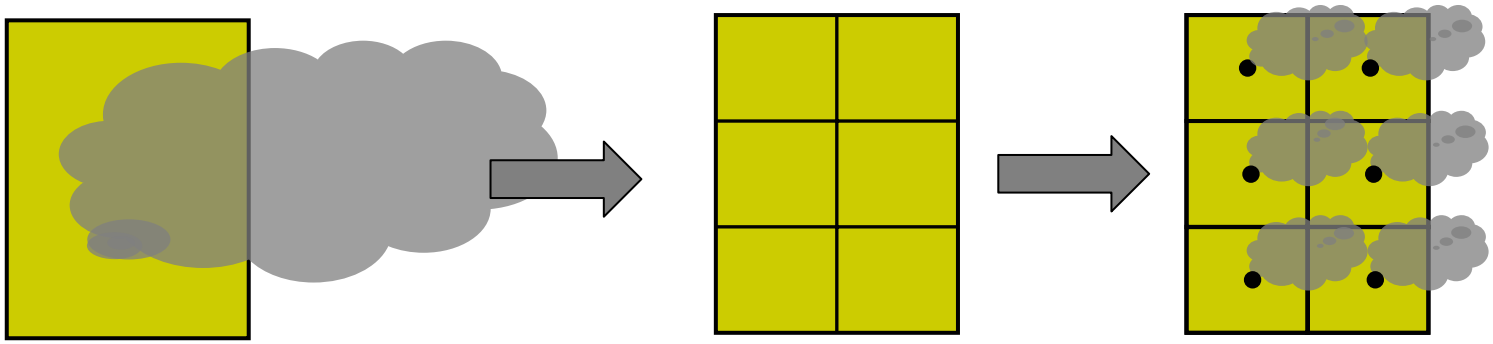


- Results
  - Lagrangian approach for dispersed parts (Spillet)
  - Eulerian approach for concentrations (concentration fields)

Atmospheric dispersion modelling

Simple, rapid and reliable assessment of potential effects on humans in the event of a spill of an evaporating chemical

- Gaussian "puff" model
- Discretisation of the evaporation surface into *n* surfaces
- Transposition of total rate *Q* into *n* rates with the value *Q/n*
- Application of evaporation rates to each "spillet"
- Assessment of IDLH to characterise the level of toxicity for humans



Continuous flow: Q *spatial discretisation* *n local flows*

Phase 4: IT integration

- Results display interface
- Predetermined pollution thresholds (PNEC, IDLH)
- Concentration graphs
- Mapping of concentrations (aquatic and atmospheric)
  - Maps saved in jpeg format
  - Possibility of exporting results as GIS (shape format)
  - Customisable concentration scale
- Visualisation of dispersed parts (spillet)
- Visualisation of wind fields
- Realisation of animations (avi format)
- Possibility of zooming in on a particular area
- Integration of map

Conclusion

- Realisation of a decision support system for chemical spills at sea

  - Assessment of results over 5 days:
    - Current field
    - Physico-chemical behaviour
    - Effect on marine flora and fauna
    - Atmospheric dispersion
    - Toxicological risk for humans

- Software designed for crisis management and setting up appropriate exclusion zones

- Continuation of development for Mediterranean coasts (CLARA II Project)

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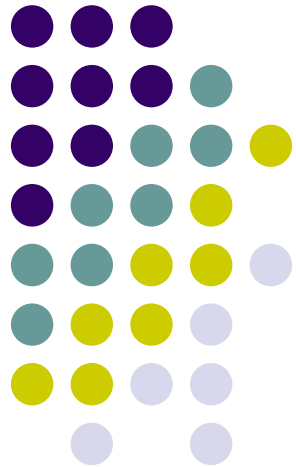

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VIII. Modelling tools

CLARA: chemicals

Name	CAS n°	Name	CAS n°
ETHYL ACETATE	141-78-6	ETHYLENE GLYCOL	107-21-1
VINYL ACETATE	108-05-4	SODIUM HYDROXIDE	1310-73-2
ACETIC ACID	64-19-7	METHYLENEDIPHENYL DIISOCYANATE	26447-40-5
PHOSPHORIC ACID	7664-38-2	METHANOL	67-56-1
SULFURIC ACID	7664-93-9	METHYL ISOBUTYL KETONE	108-10-1
ETHYL ACRYLATE	140-88-5	METHYL tert-BUTYL ETHER	1634-04-4
ACRYLONITRILE	107-13-1	NAPHTHALENE	91-20-3
AMMONIUM HYDROXIDE	1336-21-6	NONYL PHENOL	25154-52-3
BENZENE	71-43-2	o-CRESOL	95-48-7
BIPHENYL	92-52-4	PHENOL	108-95-2
VINYL CHLORIDE	75-01-4	STYRENE	100-42-5
DIOCTYL PHTHALATE	117-81-7	TOLUENE	108-88-3
1,2-DICHLOROETHANE	107-06-2	1,1,1-TRICHLOROETHANE	71-55-6
DICHLOROMETHANE	75-09-2	1,1,2-TRICHLOROETHANE	79-00-5
n-DODECYLBENZENE	123-01-3	UREA	57-13-6
alpha-EPICHLOROHYDRIN	106-89-8	XYLENES	1330-20-7
ETHYLBENZENE	100-41-4		

VIII. Modelling tools

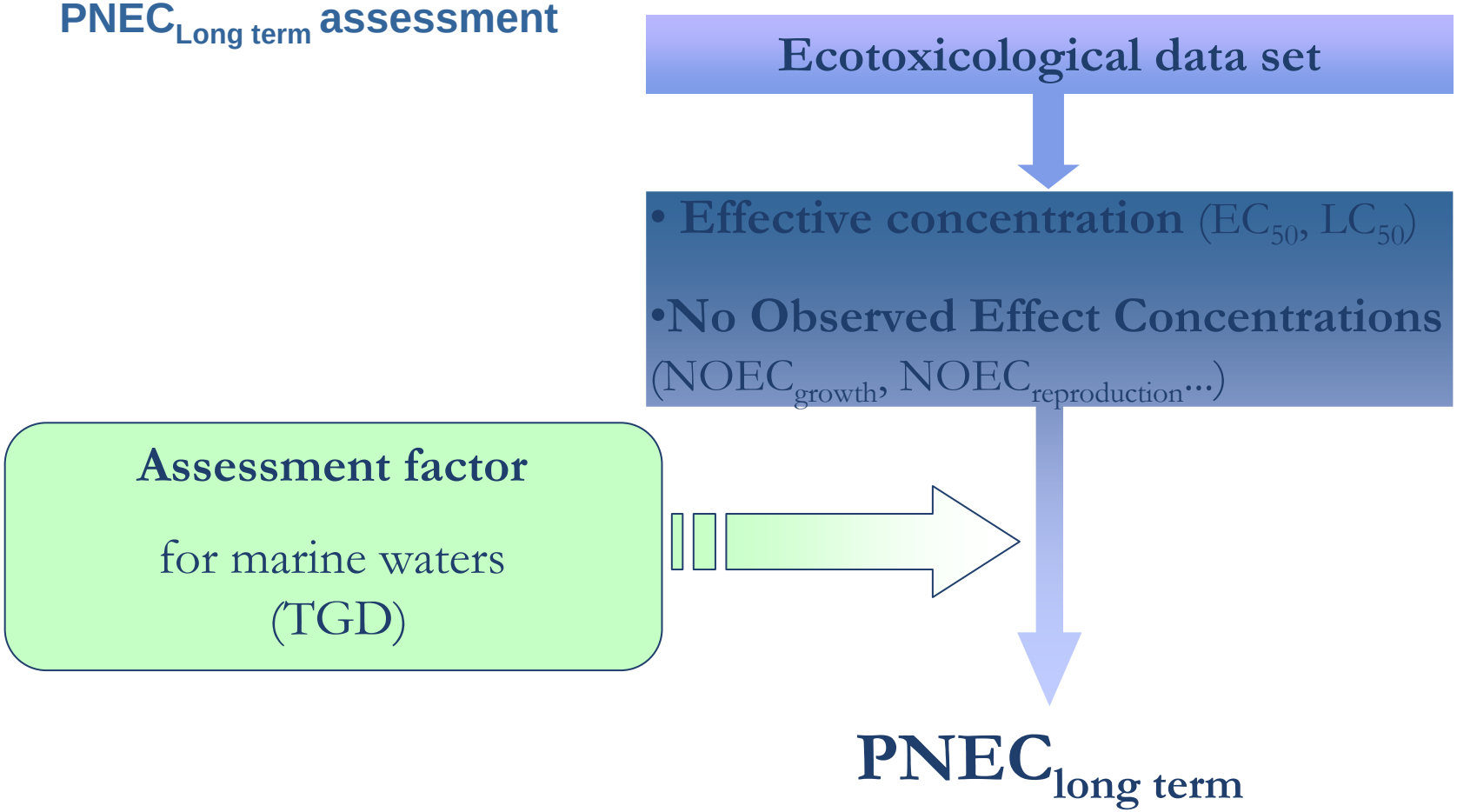
CLARA: physico-chemical and toxicological properties

Water solubility		Half-life of biodegradation	Characterization of biodegradation
Normal melting point	Characterization of physical state	Octanol-Water coefficient (Kow)	Characterization of bioaccumulation by marines organisms
Density at 20°C vs water at 4°C	Characterization of sinking part	bioconcentration factor (BCF)	
Viscosity	Characterization of floating part	organic carbon-water coefficient (Koc)	Capability of absorption
Surface tension	Characterization of floating part	Boiling temperature	Characterization of vaporisation tendency
hydrolysis degradation constant	Characterization of hydrolysis tendency	Specific heat of solid at 25°C	
Half-life hydrolysis		Heat of vaporization	
Photolysis degradation constant	Characterization of Photolysis tendency	Vapour density	
Half-life photolysis		Critical pressure	
Biodegradation constant	Characterization of biodegradation	Henry coefficient	

VIII. Modelling tools

CLARA: toxicological analysis

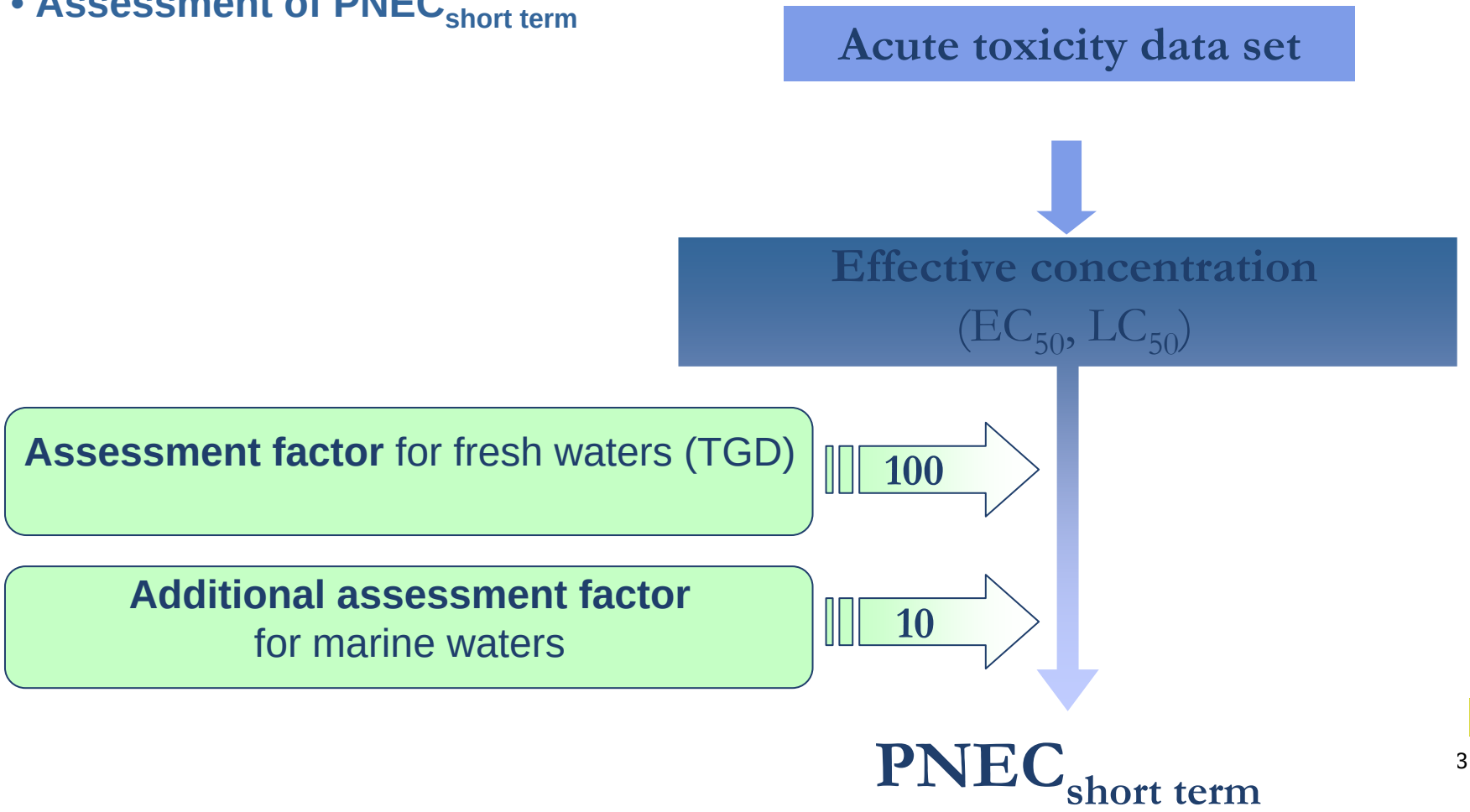
- $PNEC_{Long\ term}$ assessment

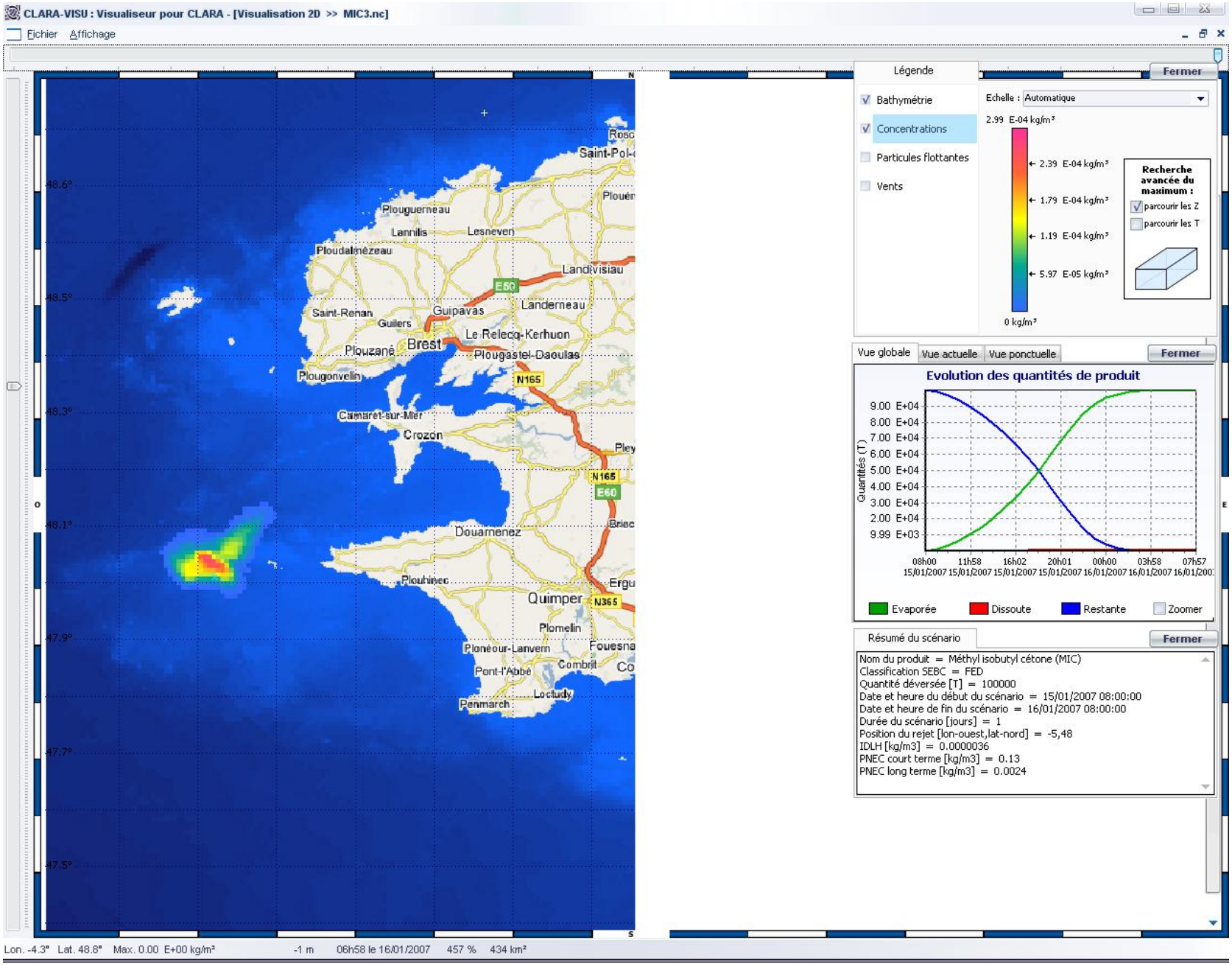


VIII. Modelling tools

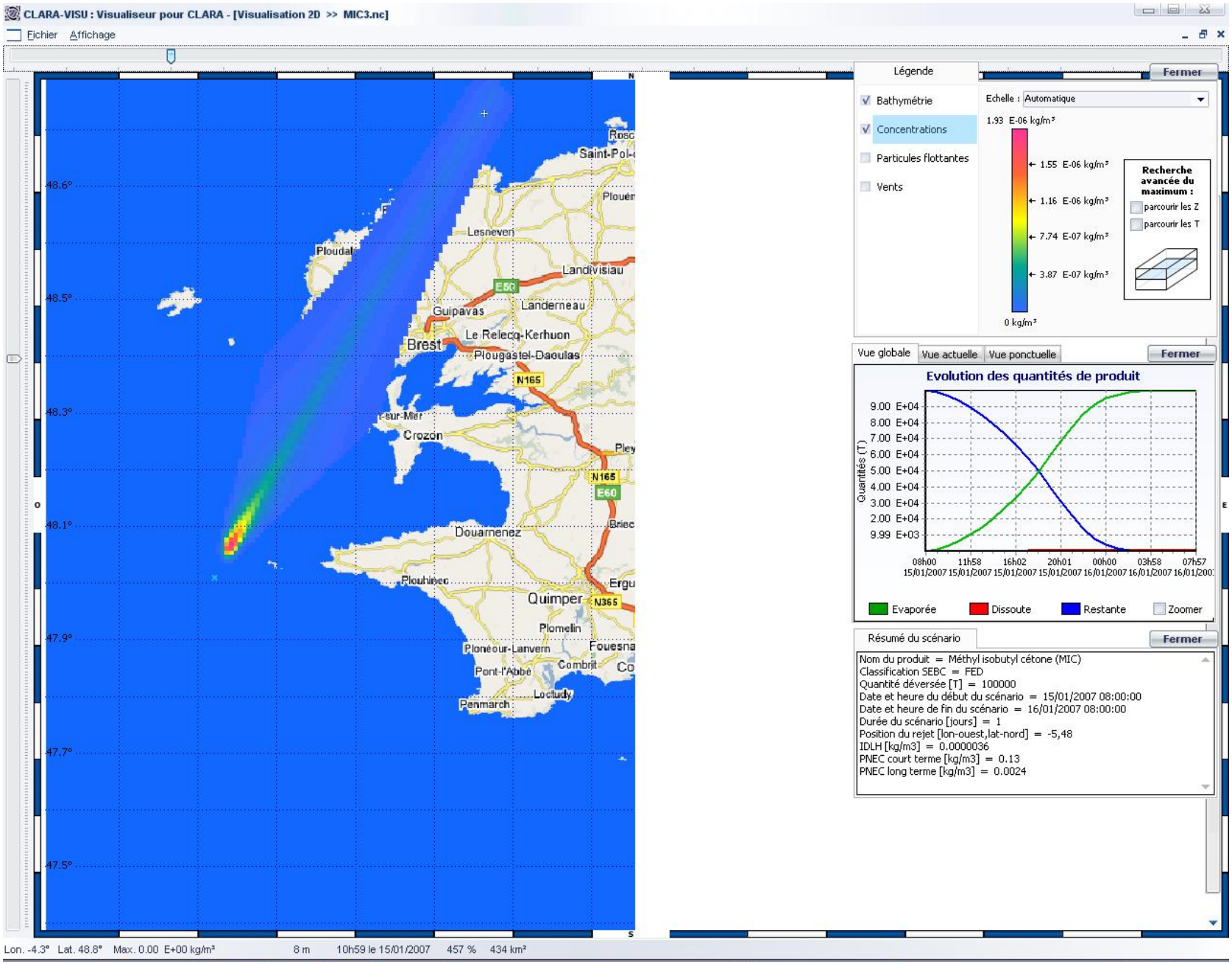
CLARA: toxicological analysis

- **Assessment of $PNEC_{short\ term}$**

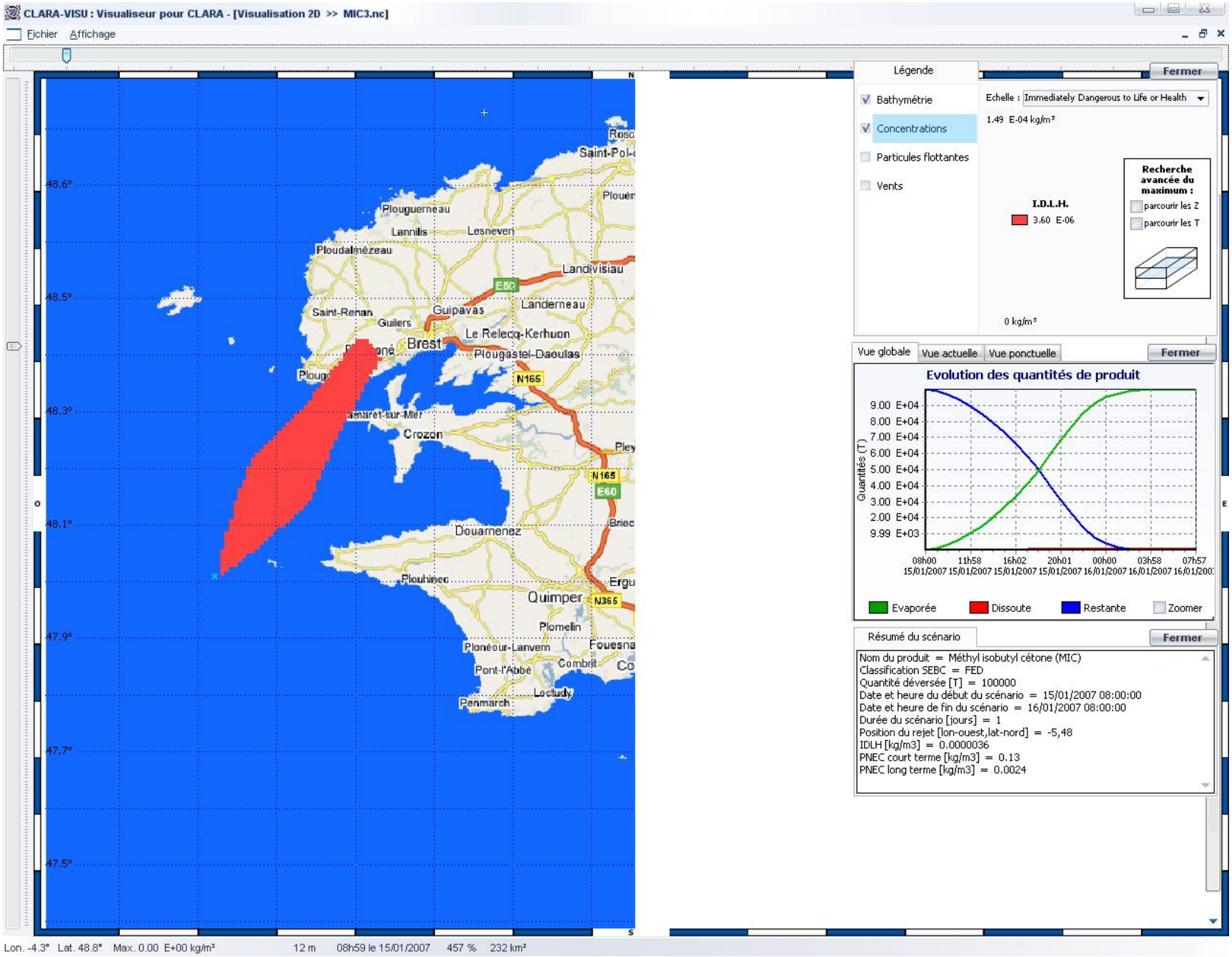




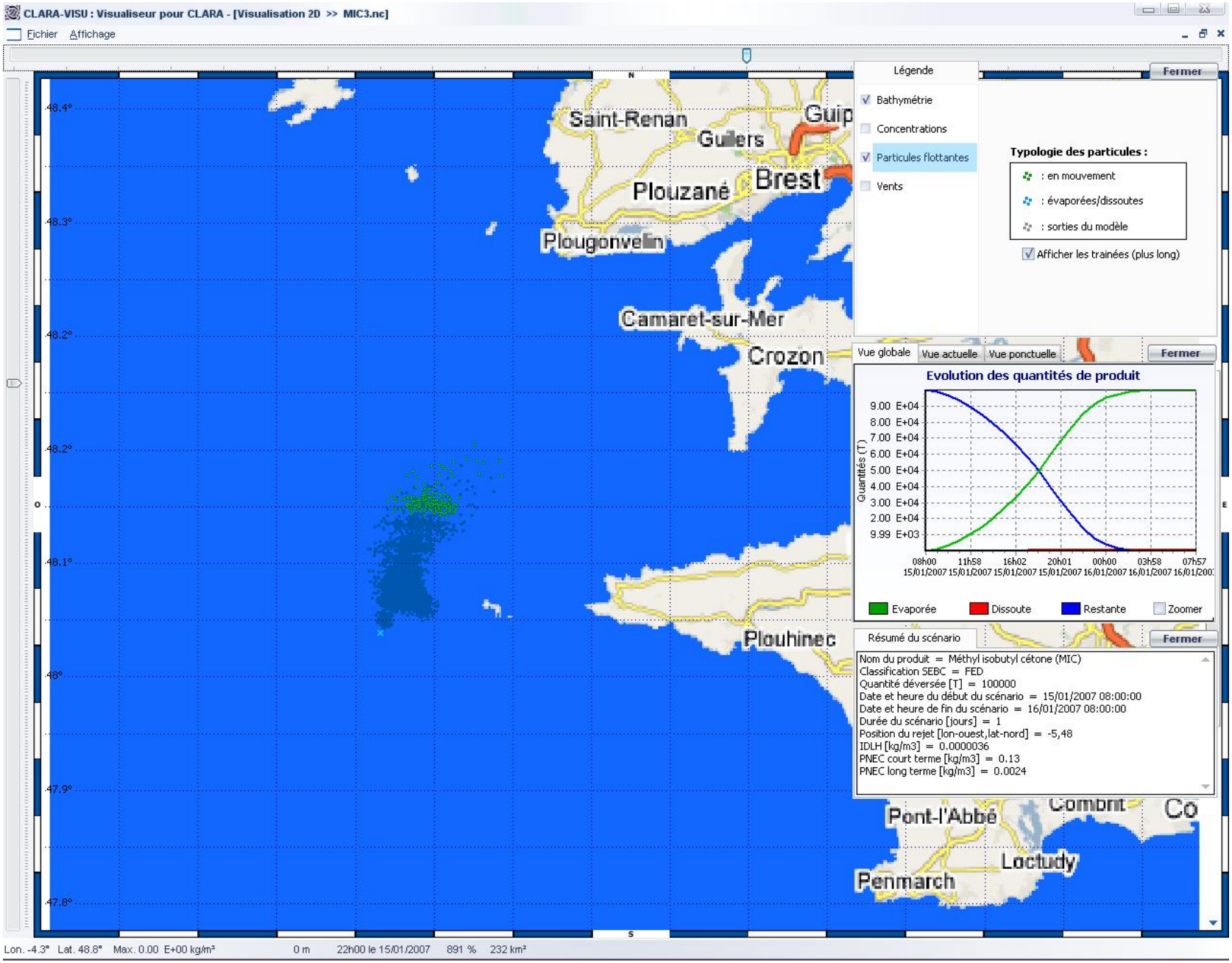
Aquatic concentration



Atmospheric dispersion



IDLH Concentration (Immediately Dangerous to Life or Health)



Floating fraction (Spillet)