# UNLEADED GASOLINE

T: Toxic

F+: Extremely flammable

N: Dangerous for the environment

UN n°: 1203

CAS n°: 86290-81-5

CHEMICAL RESPONSE GUIDE

# UNLEADED GASOLINE

*PRACTICAL GUIDE*

*INFORMATION*

*DECISION-MAKING*

*RESPONSE*

This document was drafted by *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) with financial support from TOTAL S.A., the French Navy and MEEDDAT, and technical guidance from TOTAL S.A.

**Warning**

Certain data, regulations, values and norms may be liable to change subsequent to publication. We recommend that you check them.

Author:
François-Xavier Merlin

The information contained in this guide is the result of research and experimentation conducted by *Cedre*. *Cedre* cannot be held responsible for the consequences resulting from the use of this information.

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# Purpose of this guide

The diffusion of the results of studies, experimentation and feedback from accidents in the form of guides constitutes an important part of *Cedre*'s work, highlighted by its Strategic Committee.

This guide is intended for operational personnel liable to be confronted with a spill of unleaded gasoline in the marine environment or on a water body or course. This document does not deal with land pollution. It is designed to provide operational personnel with useful information on spill response and on the establishment of response plans in case of such a spill.

This guide is designed to allow rapid access to the necessary initial information (see chapter entitled "First line emergency data"), in addition to providing relevant bibliographical sources to obtain further information.

It contains the results of accident scenarios involving spills at sea, in a port and on a river. These scenarios are only intended to provide response authorities with indications of what to do in an emergency. Each real incident should be analysed individually and the response authorities should not underestimate the importance of taking *in situ* measurements (air, water, sediment and marine fauna) in order to determine exclusion areas.

This guide is primarily intended for specialists who are familiar with the techniques to use in the event of an emergency in addition to the relevant operational response measures. The main concern is to mitigate the consequences of a spill, however we cannot afford to overlook responder safety and human toxicology.

To contact the duty engineer at *Cedre* (24/7)
Tel.: + 33 (0)2 98 33 10 10

National toxicology surveillance system in the event of a major toxicological threat.

In France, a hotline is manned around the clock by Division 7 of the General Department of Health (SD7/DGS).

During opening hours please call:
Tel.: + 33 (0)1 40 56 47 95
Fax: + 33 (0)1 40 56 50 56

Outside normal working hours please call the relevant authority.

Poison Control Centres in France

Angers (Centre Hospitalier d'Angers) Tel.: + 33 (0)2 41 48 21 21
Bordeaux (Hôpital Pellegrin-Tripode) Tel.: + 33 (0)5 56 96 40 80
Grenoble (Hôpital Albert Michallon) Tel.: + 33 (0)4 76 76 56 46
Lille (Centre Hospitalier Universitaire) Tel.: + 33 (0)8 25 81 28 22
Lyon (Hôpital Edouard Herriot) Tel.: + 33 (0)4 72 11 69 11
Marseille (Hôpital Salvator) Tel.: + 33 (0)4 91 75 25 25
Nancy (Hôpital Central) Tel.: + 33 (0)3 83 32 36 36
Paris (Hôpital Fernand Widal) Tel.: + 33 (0)1 40 05 48 48
Reims (Hôpital Maison Blanche) Tel.: + 33 (0)3 26 78 48 21
Rennes (Hôpital de Pontchaillou) Tel.: + 33 (0)2 99 59 22 22
Rouen (Hôpital Charles Nicolle) Tel.: + 33 (0)2 35 88 44 00
Strasbourg (Hôpitaux Universitaires) Tel.: + 33 (0)3 88 37 37 37
Toulouse (Hôpital de Purpan) Tel.: + 33 (0)5 61 77 74 47

# Contents

# What you need to know about unleaded gasoline

## Definition

Unleaded gasoline (or petrol*) is a mixture of hydrocarbons (not or slightly miscible with water) and "oxygenates" (ethanol, substituted ethers...) more or less soluble in water. It is very pale yellow in colour, transparent, with a strong smell, readily flammable and highly volatile (vapour pressure: 35 - 90 kPa at 20°C).

## Uses

Unleaded gasoline is an engine fuel (spark ignition engines) mainly used for transport (automobiles, motorcycles, "95 and 98 octane rating gasoline" pleasure boats).

## Risks

- Toxicity:
  - irritation and burns (to eyes) by contact with the product or its vapours.
  - by inhalation at strong concentrations, effects on the central nervous system leading to possible loss of consciousness.
  - risk of severe pulmonary burns in the event of ingestion.
  - risk of intoxication by benzene in the event of prolonged or chronic exposure.
- Fire:
  - extremely flammable, risk of explosion by gasoline vapours in a confined environment.

## Behaviour in the environment

When spilt in water, gasoline floats (density of 0.72 - 0.78 at 15°C) and forms a slick at the surface, from which some of the compounds (mainly non-oil compounds) dissolve. Evaporation of the slick is rapid to very rapid according to the wind. If atmospheric turbulence is low, the gasoline vapours, which are heavier than air, move around at the water surface or at ground level.

Gasoline is toxic for aquatic organisms and may cause long term adverse effects on the aquatic environment. Gasoline is slightly but potentially bioaccumulable due to certain hydrocarbon compounds in its make-up.

## Response strategy

Gasoline represents above all a safety hazard (fire, explosion, accumulation of vapours in concentrated areas). From a point of view of clean-up, response will often simply involve leaving the product to naturally evaporate. Free pollutant can be recovered using sorbents in the case of very small spills or by pumping or skimming, possibly by concentrating or deflecting slicks using floating booms (large spills). In the latter case, for safety reasons, the recovery area can, where necessary, be covered with fire fighting foam to reduce evaporation.

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*The term "gasoline" is chiefly an American term and corresponds to the British term "petrol". To ensure clarity, the term "gasoline" will be used throughout this guide.

# First line emergency data

# First aid information

(ICSC, TOTAL MSDS)

## In the case of severe or persistent symptoms, call a doctor or seek emergency medical attention

### Inhalation

In the case of exposure to high concentrations of vapours, fumes or aerosols:
- transport the person into fresh air, outside of the contaminated area
- keep them warm and at rest
- supply oxygen or apply artificial respiration if necessary
- place under medical supervision
- transfer to hospital in the case of illness.

### Skin contact

- Remove contaminated clothing.
- Rinse and wash skin with plenty of water and soap for several minutes.

### Eye contact

- Rinse the eyes with plenty of water for several minutes (if possible remove contact lenses).
- Consult a doctor where necessary.

### Ingestion

- Rinse out the mouth.
- Do not induce vomiting (risk of aspiration into respiratory tract).
- Give the person plenty to drink.
- Keep the person at rest.
- Call a doctor or transfer immediately to hospital.

# ID card

| | |
|---|---|
| Synonyms | Unleaded petrol, unleaded, super unleaded, super plus, super 95, super 98, premium petrol, premium gasoline, E85 (85% ethanol), gas, pygas, mogas, motor fuel, motor spirit |
| Shipping name | Motor spirit (gasoline) |
| Identification | UN n°: 1203<br>NATO code: F-57<br>EC n°: 289-220-8<br>CAS n°: 86290-81-5 |
| Similar oil products (composition and behaviour) | Alkylate, reformate, reformulated gasoline, isomerate, naphtha, virgin naphtha, light/heavy crack spirit... |

## Product labels


T: toxic


F+: extremely flammable


N: Dangerous for the environment

NB: Unleaded gasoline replaces leaded gasoline (tetra-ethyl lead additive) used in Europe until 2000.

Unleaded gasoline belongs to a group more generally known as petrols or gasolines, a term which covers many products formulated for different applications (in particular solvents for products such as paints). We refer to light gasoline, heavy gasoline, A gasoline, C gasoline, special boiling point spirit... not to be confused with unleaded gasoline.

## EU Classification

**T: toxic**
**F+: extremely flammable**
**N: dangerous for the environment**

R12: extremely flammable
R38: irritating to skin
R45: may cause cancer
R46: may cause heritable genetic damage
R51/53: toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R63: possible risk of harm to the unborn child
R65: harmful: may cause lung damage if swallowed
R67: vapours may cause drowsiness and dizziness

S2: keep out of reach of children
S16: keep away from sources of ignition - no smoking
S23: do not breathe vapour
S24: avoid contact with the skin
S29: do not empty into drains
S45: in case of accident or if you feel unwell, seek medical advice immediately (show label where possible)
S53: avoid exposure - obtain special instruction before use
S61: avoid release to the environment. Refer to special instructions/safety data sheet
S62: if swallowed, do not induce vomiting: seek medical advice immediately and show this container or label

# Chemical composition

## Unleaded gasoline is a mixture of hydrocarbons and organic oxygenates, to which additives are added.

### Petroleum hydrocarbons

The main part of gasoline is generally made up of hydrocarbons. These are the light fractions (mainly $C_4 – C_{12}$) from the distillation of crude oil and/or other refining processes.
In terms of petroleum hydrocarbons, European regulations impose the following limits:

- benzene < 1 % in volume: non-substituted monoaromatic hydrocarbon* (< 2.5 % in Africa)
- toluene < 30 % in volume: substituted monoaromatic hydrocarbon*
- n-hexane < 5 % in volume: linear saturated hydrocarbon.

| Type of hydrocarbons | automobile gasoline % volume |
|---|---|
| n-paraffins & isoparaffins | 30 - 90 |
| cycloparaffins naphthenes | 1 - 35 |
| aromatics | 5 - 55 |
| olefins | 0 - 20 |

Table 1: Types of hydrocarbons in gasoline (Concawe)

### Oxygenates (see annex 1)

Known as "green gasoline", these components (ethers or alcohols) today represent a very significant proportion of gasolines and help to improve certain characteristics such as increasing the octane rating and reducing certain exhaust emissions.
National regulations determine or limit the content of these compounds in gasoline. For instance, recent French regulations (2007) now authorise a proportion of 85% ethanol in gasoline (80% in Brazil).

### Additives

Present in minimal quantities (1% or less), additives are intended to improve the properties and/or performance of premium grade gasoline (see annex 2).

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*Benzene and toluene make up, along with xylene, what is known as BTEX (benzene, toluene, ethylbenzene, xylene), toxic or harmful compounds subject to many regulations.

# Physicochemical data

**Conversion factors:**
1 ppm = 3 to 4.4 mg/m$^3$

Physicochemical data for unleaded gasoline vary according to its composition.

| | |
|---|---|
| Weight-density | 720 - 775 kg/m$^3$ at 15°C Total MSDS |
| Viscosity | 0.5 - 0.75 mm$^2$.s$^{-1}$ at 20°C Total MSDS |
| Vapour tension | 35 - 90 kPa at 20°C Concawe |
| Relative vapour density (air = 1) | 3 - 4 at 20°C Total MSDS |
| Boiling point (distillation range) | 30 - 210°C Total MSDS |

Solubility in water

- hydrocarbons in gasoline:
  - monoaromatic hydrocarbons (BTEX)* mainly dissolve (< 100 mg/L) Concawe.
- oxygenates in gasoline:
  - alcohols are totally miscible with water
  - MTBE has a high solubility of 51 g/L US-EPA
  - the other ethers have a low solubility (1 g/L) US-EPA (2.3 g/L) Lyondell MSDS.

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* The solubility of monoaromatics is highly dependent on their benzene content which, since 2000 in Europe, must be below 1% in weight.

For information, according to a source from Concawe:

- for 1.5% benzene in weight:
  - benzene concentration: 18 - 90 mg/L
  - gasoline concentration: 30 - 100 mg/L
- for 3 % benzene in weight:
  - benzene concentration: 60 mg/L

# Flammability data

**Flash point** Concawe, Total MSDS
< - 40°C

**Self-ignition point** Total MSDS
> 300°C
(lowered to 250°C to 260°C in the presence of catalytically active substances such as copper, finely divided substances...).

**Flammability or explosive limits (% in air)**
- Lower limit: 1.4 % Concawe, Total MSDS
- Upper limit: 7.6 % Concawe, 8.7 % Total MSDS

**Dangerous products of decomposition** Total MSDS
Incomplete combustion and thermolysis produce gases with a varying degree of toxicity, such as carbon monoxide, carbon dioxide, various hydrocarbons, aldehydes as well as soot.

**Stability and reactivity** Total MSDS
- Stability: stable product at storage, handling and usage temperatures.
- Conditions to be avoided: heat, sparks, sources of ignition, flames, static electricity.

**Particular risks** Total MSDS
- Extremely flammable: the vapours, which are heavier than air, can spread and linger at ground level, with a very high risk of explosion or flashback.
- Ignition from a distance is possible.
- The vapours mix well with air and explosive mixtures are rapidly formed.
- In the case of pumping, friction caused by the product flowing can create a charge of static electricity, which can lead to sparks resulting in ignition or explosion.

# Transportation, handling, storage

## Transportation

Identification n° (UN): 1203

**Land transport:** RID (rail) /ADR (road)

Danger n°: 3
Classification code: F1
Label n°: 3
Danger code: 33
Packaging group: II

**Transportation via inland waterways**: ADNR

Danger n°: 3
Classification code: F1
Label n°: 3
Packaging group: II

**Maritime transport**: IMO/IMDG

Danger n°: 3
Label n°: 3
Packaging group: II
Safety card: F-E, S-E
Marine pollutant: no

**Air transport**: ICAO/IATA

Danger n°: 3
Label n°: 3
Packaging group: II
Special provisions: ADR / RID / ADNR: 243 534

*Transport symbols*

## Handling and storage (Total MSDS)

Inspection, cleaning and maintenance operations require strict procedures to be followed and should only be carried out by qualified personnel from specialised companies.

- Handle in well ventilated areas.
- Prevent all sources of ignition, flames, sparks, hot spots and do not smoke.
- Avoid inhaling vapours and avoid contact with the skin and mucous membranes.
- Never prime a siphon by mouth.
- Prevent the formation of vapours and spray.
- Wear safety shoes and coveralls which do not generate sparks or electrostatic charges.
- Use fireproof material.
- Ensure equipotential connections between installations to prevent the generation of static electricity when pumping the product.
- Do not use compressed oxygen or air when transferring the product.
- Never pierce, grind, cut or weld a container or tank, even when empty.
- Do not remove the danger labels from containers even when empty until they have been cleaned and degassed.
- Only ever operate on cold, degassed, aerated tanks (risk of explosive atmosphere).
- Only use hydrocarbon resistant materials, joints, pipes, recipients etc.
- Avoid contact with strong oxidising agents.

# Identification - Analysis technique

The most frequently used separation and analysis technique is gas phase chromatography coupled with flame ionisation detection (GC-FID). Chromatography coupled with mass spectrometry (GC-MS) may also be an appropriate choice.

Given the large number of components, the interpretation should concentrate on certain specific compounds which are noteworthy because of their toxicological properties or their predominant nature.


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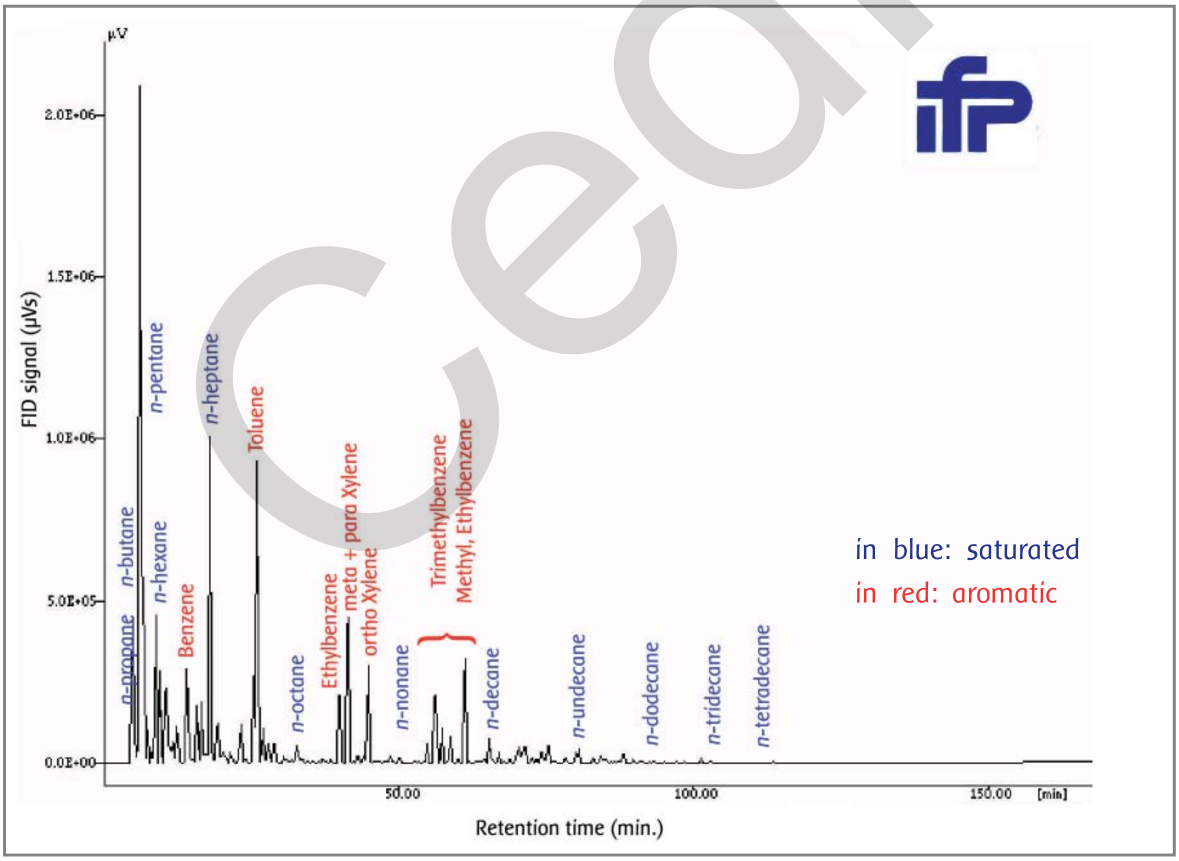
*Gas chromatograph coupled with a mass spectrometer (GC-MS)*



*Example of gasoline chromatogram (for petroleum hydrocarbons)*

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*Specialised software programmes (e.g. CARBURAN by IFP) exist which are able, in specific chromatographic conditions, to identify and quantify all 280-odd individual compounds which make up a gasoline.

# Toxicological data

The composition of gasoline is very variable, which makes its toxicity all the more difficult to evaluate: a petroleum based gasoline is very different from an 85% ethanol gasoline. A gasoline's toxicity will depend, among other factors, on its BTEX content and, in particular, its benzene content.

## Acute human toxicity

- By eye contact: burning sensation and temporary redness. Vapours and fog are irritating to mucous membranes.

- By inhalation: possible irritation of upper respiratory tract, with headaches, nausea, fainting. At high concentrations: effects on the central nervous system (headaches, dizziness, drowsiness, or even fainting sometimes with convulsive movements requiring emergency treatment).

- By ingestion: nausea, vomiting and stomach pains. If the product enters the lungs, it can cause severe burns (with pneumopathy due to inhalation developing in the following hours, necessitating medical surveillance for 48 hours).

- By skin contact: possible skin irritation.

## Chronic human toxicity

Prolonged and/or repeated exposure to gasoline vapours can cause intoxication by benzene. The liquid defats the skin. Frequent or prolonged contact with the skin destroys the lipoacid cutaneous layer and can cause dermatitis with a risk of secondary allergy. The substance can affect the central nervous system and the liver.

## Specific effects

The hydrocarbon part of gasoline contains benzene, a substance classed as carcinogenic and mutagenic. Gasoline is a possible carcinogen in humans (according to IARC).

As an indication, the following maximum exposure values are recommended:

- in the US Concawe:
  - for 8 hours:
    TLV-TWA = 890 $mg/m^3$ (300 ppm)
  - for 15 minutes:
    TLV-STEL = 1,480 $mg/m^3$ (500 ppm)
- in Sweden:
  - for 8 hours:
    TLV-TWA = 220 $mg/m^3$ (70 ppm)
  - for 15 minutes:
    TLV-STEL = 300 $mg/m^3$ (100 ppm)

## Olfactory thresholds CCHST Canada:

- perception: 0.57 $mg/m^3$
  (0.12 - 0.15 ppm)
- detection: 0.31 $mg/m^3$ (0.06 - 0.08 ppm)

It is important to note that the olfactory detection threshold in air is far lower than the exposure limit values.

# Ecotoxicological data

Gasoline is toxic for aquatic organisms and can lead to long term harmful effects (*Concawe* recommendations). The aromatic and saturated short chain components are toxic at concentrations of less than 100 ppm. A gasoline's toxicity results largely from its benzene content, benzene being the most soluble and toxic petroleum compound.

The hydrocarbon part is potentially bioaccumulable: octanol/water partition coefficient: log Pow between 2.1 and 6 (Total MSDS).

However, the effect of bioaccumulation can only be limited due to the rapid evaporation of the petroleum hydrocarbons. Nevertheless, in the event of a spill in confined waters (inland or coastal waters), temporary organoleptic changes in living resources can be observed.

The table below presents a few values from toxicity tests on gasolines of unspecified composition.

| | | | |
|---|---|---|---|
| Fish (*Alburnus alburnus*) | $LC_{50}$ (96 h) | = | 119 mg/L |
| Fish (*Cyprinodon varieatus*) | $LC_{50}$ (96 h) | = | 82 mg/L |
| Fish (*Salmo gairdneri*) | $LC_{50}$ (24 h) | = | 58 mg/L |
| Crustacean (*Daphnia magna*) | $EC_{50}$ (24 h) | = | 170 mg/L |
| Crustacean (*Nitocra spinipes*) | $LC_{50}$ (96 h) | = | 201 mg/L |
| Algae (*Selenastrum capricornutum*) | $EC_{50}$ (72 h) | = | 56 mg/L |
| | NOEC (72 h) | = | 10 mg/L |

Source: European Commission

# Behaviour in the aquatic environment

## General behaviour

Evaporation, spreading and dissolution for high ethanol content gasoline.

## Evaporation

Practically all types of compounds in gasoline have high vapour pressure, both in terms of hydrocarbons and oxygenates. Evaporation is therefore the predominant process in the event of a spill, possibly resulting, for a spill in the open air, in the disappearance of 80 to 90% of the gasoline in a few hours, and almost 100% in 12 to 24 hours. As an indication, experiments conducted by *Cedre* in the open environment within floating cells give evaporation rates of around 1 litre/m²/hour.

## Spreading

Gasoline, which has a very low viscosity and a density lower than that of water, spreads very rapidly on the water surface in the absence of barriers (dams, banks, shores...). The film soon transforms into sheen which then disappears due to evaporation.

## Dissolution

After being spilled into water, some of the compounds contained in the gasoline may dissolve. This process depends on the composition of the gasoline, in particular the types of proportion of oxygenates. Longer term, due to their vapour tension, the compounds dissolved in water can gradually evaporate into the atmosphere as vapours.

Solubility in water results from:

- oxygenates: mainly ethanol, which is totally soluble in water (like methanol and TBA) and, to a lesser extent, MTBE (solubility of 50 g/L) and ETBE (solubility of 2.1 g/L)
- other far less soluble oxygenates
- mono-aromatic hydrocarbons (BTEX) which are the most soluble hydrocarbons (but also the most toxic) in gasoline. The most soluble (and most toxic) of these compounds is benzene, with a solubility of approximately 1.8 g/L
- certain polycyclic aromatic hydrocarbons (PAH) with a low molecular weight (in particular naphthalene) which can dissolve rapidly in water at low concentrations.

## Dispersion

Dispersion (suspension of droplets in the water column) only occurs in the case of violent agitation (backwash, waterfall, supercritical flow). Furthermore, due to the low density of gasoline compared to water, dispersion is unstable and recoalescence at the surface is rapidly observed as soon as the agitation conditions subside sufficiently.

## Biodegradation

The hydrocarbons which form gasoline are light hydrocarbons and are in principal biodegradable in the absence of inhibitors (very low temperatures, presence of biocidal products...) The biodegradability of oxygenates is, however, highly variable. While simple primary alcohols (ethanol, methanol) are very readily biodegradable, branched structures are far less so. Branched esters (ETBE and MTBE) have components which are only slightly or non degradable in water (half-life of MTBE in the ground estimated at 2 years).

Source: FAYOLLE F., 2005

## Adsorption

Only the hydrocarbons in gasoline are liable to be adsorbed by sediments as well as mineral and organic particles is suspension. This fixation phenomenon is promoted when the pollutant is dispersed in the water column, as contact between the pollutant and the particles is thus facilitated (e.g. strong turbulence in a water course with supercritical flow). Hydrocarbons, for instance, can be trapped on clay particles, significantly slowing down their biodegradability. In high concentrations, the fixation mechanism of hydrocarbons on particles in suspension can result in a gradual transfer of pollutant to deposit areas.

*Cedre* is equipped with facilities enabling experiments to be conducted in a controlled natural environment. These facilities are in the form of floating units, placed in coastal or port areas, which separate the experimentation area from the free sea surface. These floating cells are subject to external environmental conditions, and can therefore be used for various trials in view of characterising the behaviour of pollutants spilled at sea.

*Floating cells in a port area*

*Simulation of an unleaded gasoline spill in a floating cell*

*Unleaded gasoline sheen*

# Persistence in the aquatic environment

The persistence of gasoline in the aquatic environment is very low as the majority of it evaporates. Pollution by gasoline can persist if the circumstances cause it to infiltrate sediments (bank, shore) as evaporation can no longer occur. In very specific conditions, a cold climate and an anoxic environment (absence of oxygen or low permeability), gasoline can subsist long term.

Persistence in the environment mainly concerns slightly or non degradable dissolved compounds, i.e. branched oxygenates (MTBE/ETBE) and/or hydrocarbons "trapped" on particles in suspension. When these particles charged with gasoline settle on the bottom, then can, in a number of specific cases, result in accumulations.

The product can infiltrate the ground and contaminate ground water.

# Environmental impacts following a spill

Gasoline pollution first and foremost generates safety hazards for individuals. These issues, which must be dealt with as a priority, are not addressed in this document, which is specifically dedicated to environmental aspects of the maritime environment and inland waters.

Gasoline, which is only slightly persistent in the aquatic environment, can cause a significant environmental impact by direct contact with the product or by exposure to its soluble compounds.

## Direct contact

As gasoline has a low density and in principal floats, the impact mainly concerns the flora and fauna (birds, mammals...) living at the water surface or on the banks or shores. Bottom-dwelling (benthic) organisms can be exposed to the pollutant in shallow waters. In the case of agitation (waves, backwash...) of fine sediments on the shore, the gasoline can be mixed with the sediment, or even buried below the surface. This contact with the sediment can affect living organisms there (burrowing organisms).

## Dissolution of toxic compounds

Light aromatic hydrocarbons (BTEX), the most toxic hydrocarbons, can be distinguished from oxygenates (ethers and alcohols). Generally speaking, the impact of the dissolution of the most soluble compounds is limited. Except in the specific case of gasoline with a high ethanol content (e.g. E 85), the proportion of these compounds in gasoline is relatively low. These products remain "volatile" and tend to form vapour in the atmosphere. The possibility of contamination of the water column should not be excluded in shallow waters (a few metres to a few dozen metres deep according to the size of spill). In the case of a low renewal rate and/or a confined environment, all aquatic organisms can be locally impacted.

### - Light aromatics

Light aromatic compounds are degradable and slightly bioaccumulable, but present significant toxicity. The most toxic of these compounds is benzene: $LC_{50}$ from five to a few dozen ppm.

### - Bioaccumulable oxygenates

Bioaccumulable oxygenates have moderate to low toxicity ($EC_{50}$ from 1,000 to 10,000 ppm for simple alcohols, 100 to 1,000 ppm for MTBE). Furthermore, although some of these compounds are not biodegradable, they are, on the other hand, only slightly bioaccumulable.

These compounds can give water an unpleasant odour and taste (acrid).

# Potential impacts on different environments

## Coral reefs

As coral reefs are mainly immersed, their exposure to a pollutant can only be caused by the dissolution of the toxic compounds found in gasoline. This impact is all the more significant when corals are near the surface, in waters with a low renewal rate. Corals are fragile, vulnerable animals whose mucus can absorb toxic organic compounds.

## Mudflats, lake marshes and marine marshes

For marshes (vegetated areas), impact by direct contact between the pollutant and the vegetation should be anticipated. Furthermore, gasoline may pollute the sediment, both for mudflats and marshes, in particular if the water body is agitated or if the tides cause the pollutant to be deposited on the substrate. In this case, this contamination which affects the surface layer can spread deeper due to burrowing organisms (bioturbation for mudflats), or through transfer along root networks, for marshes. The buried pollutant can therefore be a durable source of contamination as evaporation is no longer possible. Furthermore, muddy and marshy substrates are most often anaerobic environments, which reduces the biodegradation of the pollutant.

## Mangrove swamps

Gasoline can affect the mangrove swamp's shrub cover through simple contact with the adventitious roots of mangroves and can also affect the associated fauna (crustaceans...).
Like in the case of marshes and mudflats, if there is direct, prolonged contact with the sediment (e.g. tides), there may be a risk of contamination for the substrate.

## Seagrass beds

Only the dissolved toxic compounds can affect seagrasses in the event of a gasoline spill. This is only possible in the event of a major spill in confined, shallow coastal waters.

## Rocky foreshores

In the case of rocky foreshores, a spill of unleaded gasoline in theory should not have any serious repercussions as the biomass is limited. For exposed shorelines, the mixing action of water promotes the continual remobilisation of pollutant as well as its evaporation and dispersion. Direct impact on organisms fixed at the water surface is nevertheless possible (e.g. limpets).

## Sandy foreshores

On sandy shores, the agitation of waves and the tides can cause substantial quantities of gasoline to infiltrate the sediment. In this case, the impact of the pollution will depend on the ecological wealth of the site, which is generally low, bar a few exceptions (e.g. turtle egg-laying sites).

## Cold or frozen waters

In cold climates, evaporation may be slower, allowing the pollutant to remain in contact with the environment for longer, thus increasing the risk of infiltration into the substrate or the layer of ice. In this case, the pollutant may remain trapped until the ice melts.

## Spawning grounds and hatcheries

A spill can have serious repercussions if it occurs during spawning or hatching periods of a species. Reproduction can be affected or the growth of larvae or fry jeopardised. As with seagrass beds, these phenomena can only be observed in the event of a major spill in shallow waters and/or waters with a low renewal rate.

## Commercial benthic species (including crustaceans)

In shallow coastal waters, a spill can affect the various species fished more or less visibly. The tainting of these species, potentially making them unsuitable for sale, is one of the possible effects.

## Birds

Gasoline, a volatile, floating pollutant, can affect sea birds which come into contact with surface slicks. Like all fatty products, gasoline alters birds' feathers, and they can die of hypothermia or by ingestion of pollutant when cleaning themselves.

Mudflat

Seagrass bed

Muddy/sandy foreshore

Mangrove swamp

# Potential impacts on economic resources

## In water, MTBE can be detected by smell between 15 and 180 µg/L and by taste between 24 and 135 µg/L (Health CANADA)

### Aquaculture

In the event of a spill, the presence of dissolved compounds (BTEX, oxygenates) or of gasoline dispersed below the surface by agitation can generate various effects on farmed species, ranging from lethal effects to the simple tainting of produce, making it unsuitable for human consumption.

### Salt pans

The polycyclic aromatic hydrocarbons (PAH) in gasoline can contaminate the salt produced in these pans in the event of a spill. However the risk remains low in as far as a salt pan is a walled area which can be closed off to prevent a floating pollutant from entering. Furthermore, PAH levels (mainly naphthalene) remain relatively low in gasoline.

*Salt pans*

### Tourist beaches

In addition to the safety aspect, gasoline pollution on a beach can result in a temporary interruption to tourist activities. Evaporation can, if the gasoline infiltrates the sand, be impeded and require the sediment to be aerated (e.g. harrowing) to accelerate the process.

### Industrial water intakes

- Cooling water intakes: gasoline is generally at a low risk of wide-spread penetration into cooling systems, whose intakes are usually positioned deep below the surface. However the quality of the water can be significantly altered due to the presence of dissolved compounds. This is the case for aromatic compounds and more so for oxygenates (in particular MTBE with its low degradability and persistence). In the case of a gasoline with added ethanol or methanol, the water quality can also be altered as these products dissolve very quickly and almost completely, but are not persistent.
- Water supply intakes: in the case of significant pollution, there is a risk of contamination of the intake by soluble compounds, potentially causing it to be closed (possibly as a preventative measure).

# Results of accident scenarios

# Reminder of properties

Gasoline is a liquid mixture of volatile hydrocarbons, with very low or no solubility in water, and compounds known as "oxygenates", which are also volatile and can have very low solubility (ETBE), moderate solubility (MTBE) or complete solubility (methyl and ethyl alcohol).

The properties and short term fate of such a mixture depend on the nature of the compounds present and their proportion.

On a water body, a gasoline, mainly composed of hydrocarbons and slightly soluble oxygenates, will remain at the surface in free air and will therefore rapidly evaporate.

Longer term (a few days), fractions dissolved in the water will in most cases (when the water body in question is in the open air) gradually evaporate to form vapours in the atmosphere. The remaining dissolved product will gradually biodegrade in the case of alcohols or light aromatics (BTEX). However, certain oxygenates (ETBE, MTBE) are particularly non-biodegradable and can cause long term contamination when dissolved in more or less captive waters (ground water or interstitial water...).

In the specific case of an 85% ethanol gasoline, the product will dissolve rapidly in water due to the high solubility of ethanol. The floating residue (the 15% hydrocarbon part) will evaporate rapidly.

# Accident scenarios

The accident scenarios presented here are simply intended to provide an indication. In the event of a real spill, the extension and fate of the pollution may be different due to the surrounding conditions, but also due to the very nature of the gasoline involved (aromatic, high ethanol content...).

These scenario case studies were elaborated using 2 software programmes: the CHEMMAP* model (MTBE and ethanol) and the SIMPAP* model for hydrocarbon compounds in gasoline.

The results of these simulations were combined to assess the extension of the pollution and its fate in the 3 phases (atmosphere, water surface and water column), taking into account the initial composition of these gasolines (15% MTBE or 85% ethanol blends).

These summer and winter simulations were realised taking into consideration marine currents, the only fluctuating data being the temperature and the wind speed.

## Warning

These scenarios are digital simulations predicting the evolution of each spill. We must bear in mind that these predictions are not necessarily identical to what would happen in the case of a real spill. The results presented here have been systematically rounded up. The grids of models used in these scenarios are too large to model the immediate surroundings of the spill location (vessels, wrecks, pipes).

Consequently, data relative to the flammability zone, necessarily very close to the source, does not appear. Given the vapour pressure of gasoline (between 35 and 90 kPa at 20°C, compared with atmospheric pressure of 100 kPa), flammability conditions can be expected above and around the slick for as long as gasoline remains at the surface.

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*The modelling software programmes CHEMMAP and SIMAP are simulation models for chemical spills (CHEMMAP) and oil spills (SIMAP), developed by ASA (Applied Science Associated, Inc. - US), able to model the movement and fate of products spilt in fresh or marine waters.

## High sea scenarios

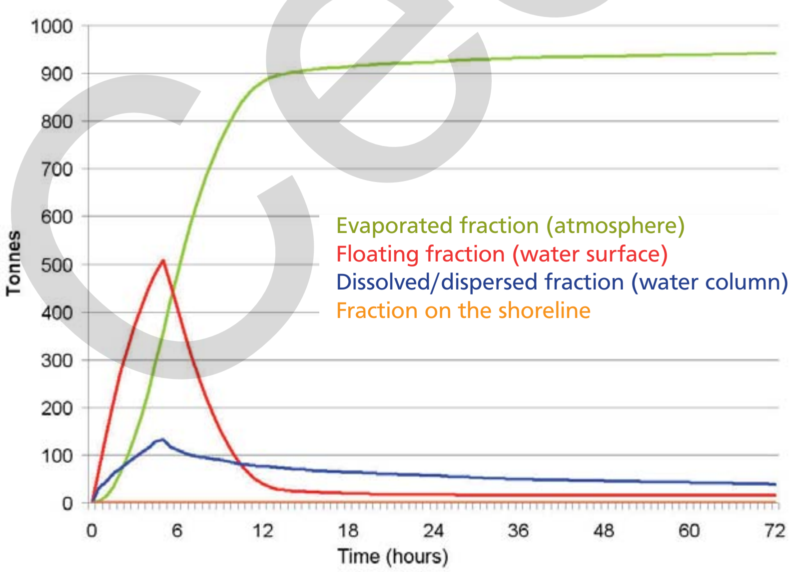
### Spill of 1,000 tonnes of gasoline following a collision

- Standard gasoline: mineral origin gasoline with 15% oxygenates (MTBE)
- Quantity: 1,000 tonnes
- Spill duration: 5 hours
- Model time step: 10 min
- Location: Channel, 70 km NW of Guernsey
- Air temperature
  - summer scenario: 20°C - winter scenario: 5°C
- South wind
  - summer scenario: 3 m/s - winter scenario: 10 m/s

### Weighted evolution of unleaded gasoline in the 3 environmental compartments (atmosphere, water surface and water column)

The majority of the pollution evaporates in around 12 hours in summer and 6 to 8 hours in winter. The wind promotes the passage of the pollutant into the water column, but dissolution nevertheless remains limited (around 8 to 10% in winter).

#### Summer scenario: 15% MTBE gasoline



Graph 1: weighted evolution of 15% MTBE gasoline - summer scenario

*In air:* evaporation is very rapid. By the end of the 5 hour spill of 1,000 tonnes, the gasoline surface slick only represents 500 tonnes (giving a mean evaporation rate of 1.3 t/min). As the MTBE forms a solution or evaporates, the remaining 500 tonnes are only hydrocarbons. Evaporation continues at a high rate, reaching around 90% of the total volume spilt after 12 hours.
Although the model does not provide information on the high concentrations of gasoline vapours around the spill point, simulations conducted in parallel indicate that the vapours may reach 1/10th of the Lower Explosive Limit (LEL) around 2.5 km downwind of the source.

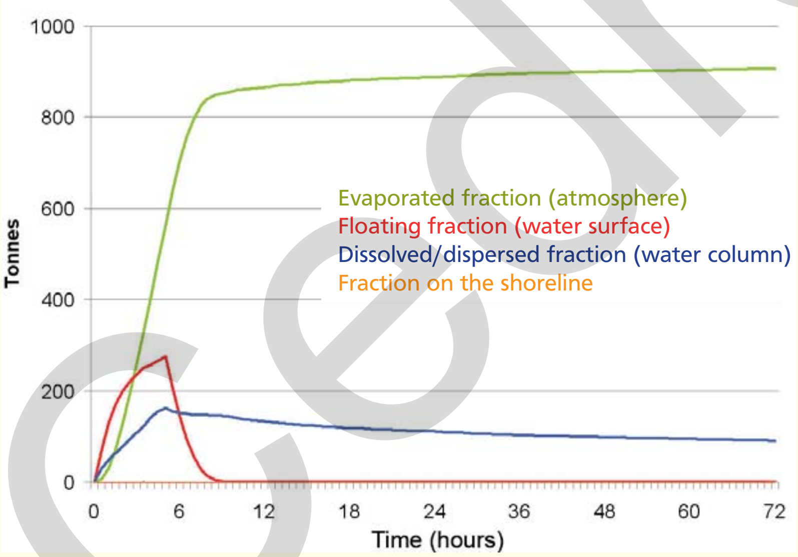
The Exposure Limit Value (ELV = 300 mg/m$^3$) is reached for a period of 7 hours up to 17 km from the source and the Mean Exposure Value (MEV = 200 mg/m$^3$) is reached for 8 hours up to 19 km from the spill location. Gasoline odours ($c > 0.3$ mg/m$^3$) are detected for 24 hours and MTBE odours persist for 6 to 7 days (gradual evaporation of dissolved MTBE).

*In water:* after 5 hours, around 130 tonnes of gasoline pass into the water column (90 tonnes of hydrocarbons and 40 tonnes of MTBE).

Thereafter, the concentrations in the water gradually decrease: at a faster rate for the MTBE (boiling point = 55°C) than for the hydrocarbons (boiling point of lightest aromatics: benzene = 80°C, toluene = 111°C).

After 72 hours, around 40 tonnes of gasoline remain in the water column at low concentrations: 2 and 1 ppm of hydrocarbons respectively up to 18 and 23 km from the source, 30 and 70 hours after the spill. MTBE is found up to 18 km from the spill location at concentrations of over 15 µg/l.

### Winter scenario: 15% MTBE gasoline



Graph 2: weighted evolution of 15% MTBE gasoline - winter scenario

*In air:* evaporation is far faster than previously due to stronger winds. Five hours after the beginning of the spill, the quantity of gasoline forming a surface slick therefore only reaches 280 tonnes (mean evaporation rate > 2 t/min). Thereafter, evaporation continues, reaching 85% after 9 hours.

The model does not indicate at what distance the LEL is reached, but it assesses the area in which the ELV and MEV are reached. The ELV is reached up to 10 km from the spill location for 5 hours. The MEV is reached up to 17 km from the spill location for 9 hours.

*In water:* around 160 tonnes of gasoline pass into the water column after 5 hours (90 tonnes of hydrocarbons and 70 tonnes of MTBE). Thereafter, the concentrations gradually decrease, but after 72 hours, 70 tonnes of hydrocarbons and 17 tonnes of MTBE remain in the water column. Nevertheless, the concentrations decrease rapidly: 2 and 1 ppm of hydrocarbons up to 15 and 21 km respectively from the source after just over 30 hours. MTBE is found up to 24 km from the spill location at concentrations of over 15 µg/l.

## Port scenarios

### Instantaneous spills of 100 tonnes of gasoline, following a loading incident

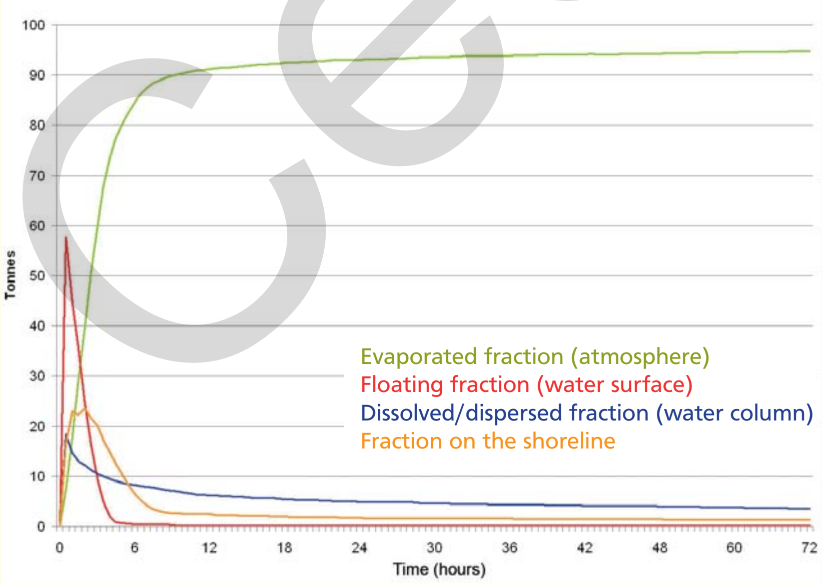
- Standard gasoline: mineral origin gasoline with 15% oxygenates (MTBE)
- Quantity: 100 tonnes
- Spill duration: instantaneous
- Model time step: 5 min
- Location: Channel, port of Cherbourg
- Air temperature
  - summer scenario: 20°C - winter scenario: 5°C
- South wind:
  - summer scenario: 3 m/s - winter scenario: 10 m/s

NB: Model run without tidal currents

### Weighted evolution of unleaded gasoline in the 3 environmental compartments (atmosphere, water surface and water column)

The majority of the pollution evaporates in around 6 hours in summer and in winter. The wind promotes the passage of the pollutant into the water column, but dissolution nevertheless remains limited (around 8 to 10% in winter).

Summer scenario: 15% MTBE gasoline



Graph 3: weighted evolution of 15% MTBE gasoline - summer scenario

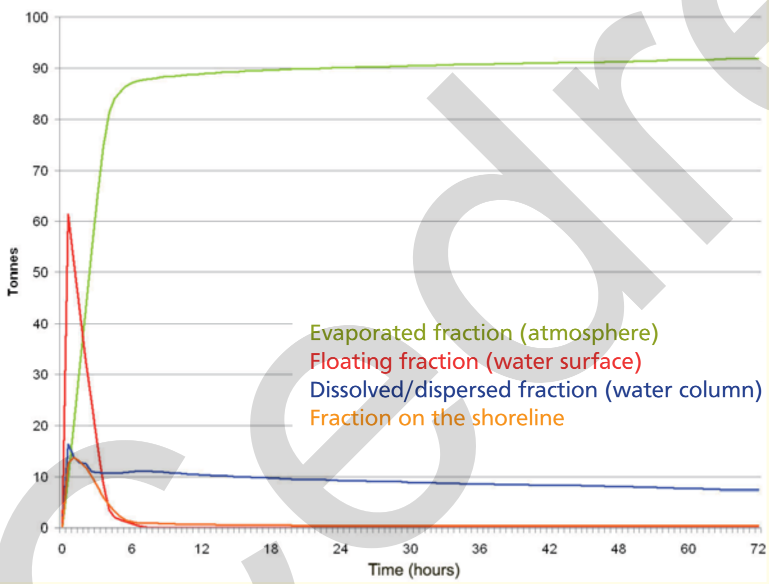
*In air:* for the first 5 hours, evaporation is very rapid, with an average of over 250 kg/min (maximum 400 kg/min). Thereafter, evaporation continues at a more moderate rate, reaching 90% after 10 hours, after which time evaporation is slower. The gasoline fractions which first dissolved gradually evaporate.
The model does not provide information on the potential presence of flammable or explosive concentrations in the area immediately surrounding the source.

The ELV (300 mg/m$^3$) and MEV (200 mg/m$^3$) can be detected for around 5 hours and they can extend to a maximum distance of 1 to 3 km from the source.

*In the water column:* the majority of the MTBE passes into the water column (almost 90 %), unlike the hydrocarbon fractions (6%). Thereafter, the MTBE passes directly into the atmosphere. Concentrations greater than or equal to 2 ppm for the hydrocarbons (acute toxicity threshold reached after 96 h) and 15 ppm for MTBE (olfactory detection threshold) extend up to 3 km from the source for a duration of 6 to 7 days.

*On the shoreline*: around 20 tonnes of gasoline arrive on the shore in the first half hour, then disappear rapidly by evaporation almost completely in the first 8 hours.

### Winter scenario: 15% MTBE gasoline



Graph 4: weighted evolution of 15% MTBE gasoline - winter scenario

*In air:* due to the wind, evaporation of the slick at the water surface is even more rapid than previously, around 300 kg/min, and reaches 80% in less than 4 hours, after which time practically no gasoline is left at the surface. Thereafter evaporation slows down. This deceleration corresponds to dissolved (or emulsified) gasoline fractions passing directly from the water column into the atmosphere. Although there is no information on the potential presence of flammable or explosive atmospheres, the model predicts that the ELV and MEV will be reached up to around 2 km from the source, for a duration of 4 hours (period during which evaporation is rapid).

*In the water column:* the majority of the MTBE passes into the water column (around 75%), unlike the hydrocarbons (6%). Thereafter, the dissolved MTBE evaporates slowly: 72 hours after the spill, around 50% (7.4 t) remains in the water column. Concentrations greater than or equal to 2 ppm for the hydrocarbons (acute toxicity threshold reached after 96 h) and 15 ppm for MTBE (olfactory detection threshold) extend up to 11 and 19 km for a duration of 35 and 60 hours respectively.

*On the shoreline*: around 14 tonnes of gasoline reach the shoreline during the first hours following the spill, before evaporating in 5 to 6 hours.

## River scenarios

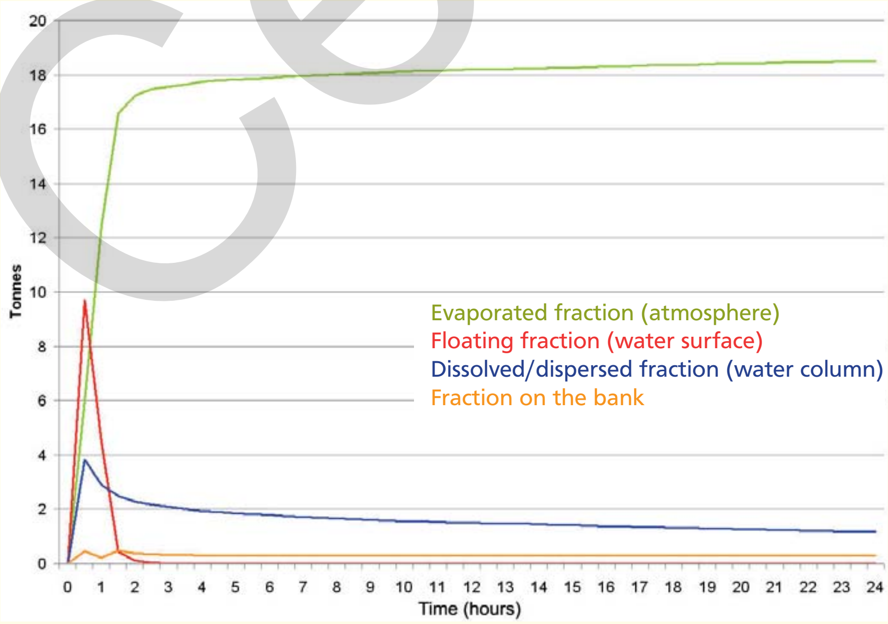
### Instantaneous spill of 20 tonnes of gasoline in a water course

- Scenario 1: Standard gasoline: mineral origin gasoline with 15% oxygenates (MTBE)
- Scenario 2: E85 gasoline, with 85% ethanol and 15% mineral compounds (petroleum fractions)
- Quantity: 20 tonnes
- Spill duration: instantaneous
- Model time step: 5 min
- Location: fictional river
- Air temperature: 20°C
- Wind speed: 10 m/s in an upstream direction
- River: current 0.5 m/s; width: 150 m; depth: 5 m

### Weighted evolution of unleaded gasoline in the 3 environmental compartments (atmosphere, water surface and water column)

The behaviour is completely different according to whether the gasoline spilt is with MTBE additive or 85% ethanol: while the first mainly evaporates, the second passes into the water column (dissolution of the ethanol).

### Scenario 1: 15% MTBE gasoline



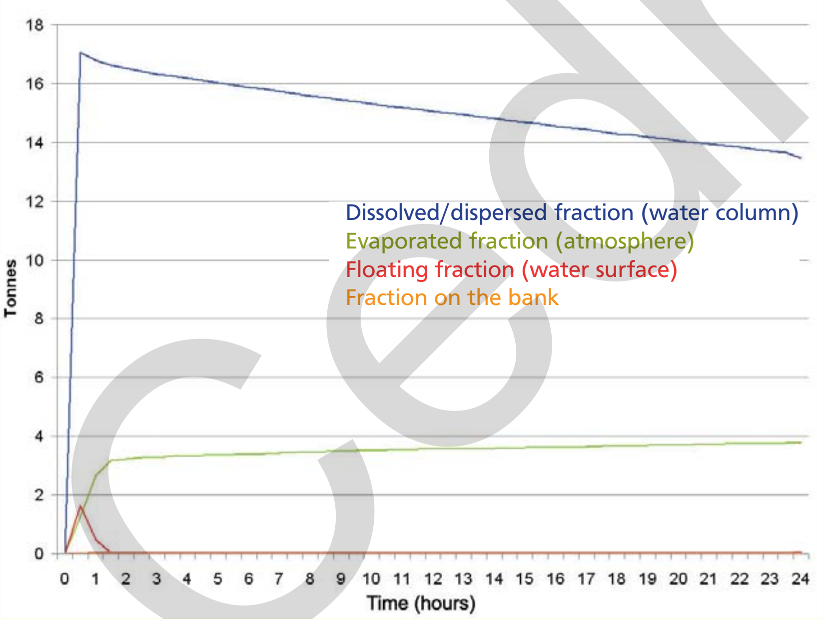
Graph 5: weighted evolution of standard gasoline with 15% MTBE - scenario 1

*In air:* like the previous scenarios, the gasoline evaporates very rapidly, with 80% evaporation, around 17 tonnes, in 1.5 hours. The evaporation rate for the first hour is approximately 200 kg/min. The model indicates a maximum atmospheric concentration of 250 ppm, with 200 ppm subsisting for 1 hour over a distance of more than 4 km from the spill location. Gasoline odours (c > 0.3 mg/m$^3$) are detected for over 5 hours. Although it is not predicted by the model, the possibility of explosive vapours temporarily occurring near the spill location should not be excluded.

*In the water column:* a maximum of 4 tonnes (20%) rapidly passes into the water column, mainly the MTBE. This quantity decreases quite quickly: 2 tonnes remain 3 hours after the spill, then slowly: 1.2 tonnes remain after 24 hours. The plume dissolved in the water column, with detectable MTBE concentrations (15 µg/L), extends up to 16 km and lasts for over 24 hours (duration of simulation). This plume is driven downstream by the current.

*On the banks*: the contamination remains moderate considering the quantities spilt: 0.5 tonnes in the first half hour, then 0.3 tonnes (1.5%) after 24 hours.

### Scenario 2: 85% ethanol gasoline



Graph 6: weighted evolution of E85 gasoline with 85% ethanol - scenario 2

*In air:* evaporation is very rapid immediately after the spill (45 kg/min), but far more limited than for the MTBE scenarios. Around 3 tonnes (15%) have evaporated after an hour and a half, i.e. as long as gasoline remains at the surface. This time, the maximum atmospheric concentrations do not exceed 22 mg/m$^3$ during this first phase. Thereafter, evaporation slows down due to the passing of the dissolved fractions into the atmosphere.

*In the water column:* the ethanol dissolves almost immediately and completely in the water column (i.e. 85% of the volume spilt). Thereafter, the dissolved ethanol is diluted and gradually evaporates. After 24 hours, 14 tonnes remain in the water column. This widespread dissolution creates a plume of polluted water with a concentration of 100 mg/L up to at least 8 km around the source and for at least 8 hours. This plume is gradually evacuated downstream by the current.

*On the banks*: the banks remain largely untouched, no or little gasoline is deposited.

# Consumption scenarios

The hydrocarbon fraction of unleaded gasoline is mainly composed of:

- either products with a low solubility and volatility
- or soluble and volatile products which are biodegradable.

On the other hand, oxygenates, in particular ETBE and MTBE, are soluble: 2.1 g/L for ETBE (LYONDELL MSDS) and 51 g/L for MTBE (US-EPA, SYMPOSIUM ON FUEL OXYGENATES 2002). These compounds have a very low biodegradability and can, at low concentrations (ppb), taint the taste or smell of water (e.g. 15 µg/L for MTBE). The persistence of these products can impose restrictions, in the medium term, on the consumption of contaminated water.

Due to the very low tendency of unleaded gasoline to bioaccumulate along the trophic chain, it is unlikely that this product will exist in sufficiently large quantities to have an impact on humans who consume contaminated fish or seafood.

# Spill response

# Examples of gasoline spills

## Generalities

The analysis of gasoline spills, of mainly mineral blends, highlights the following characteristics:

1) Gasoline spills represent first and foremost a **safety hazard in terms of fire and explosion**.
2) **Evaporation** of spilt gasoline is very rapid in the open air. For small spills (a few tonnes), 80 to 90% evaporates in the first 2 hours. For large spills, similar evaporation is obtained in 6 hours. Due to this rapid evaporation, gasoline is not a persistent substance.
   However, if gasoline infiltrates closed spaces or the ground, evaporation can be almost completely prohibited and the product can remain in the environment for several months.
3) In the absence of obstacles (dam, boom, bank), gasoline **spreads** on water very rapidly. The slicks rapidly turn into patches of sheen, accelerating the product's evaporation.
4) Surface spills of gasoline **do not generate problems of clean-up** (water body, banks...). However pumping operations are often implemented to recover the product where it naturally accumulates and/or has been contained.
5) The **impact** of gasoline spills on aquatic fauna is more often feared than observed. Up until now, the main concern has been the impact of light aromatic hydrocarbons (the most soluble hydrocarbons). However, there is a lack of data on gasolines with added soluble oxygenates (such as ethanol or MTBE).
6) In terms of **human protection**, other than physical evacuation of people, responders are often protected from vapours, in particular benzene vapours (masks) and their exposure should be monitored.

## A few examples of accidents

### 1993, Voulte-sur-Rhône

Following the derailing of 7 rail tank cars, 300 m$^3$ of gasoline were spilt into the Rhone and went on fire. Streams of gasoline in flames ran onto private land, reaching the first homes and generating a series of explosions in the sewer system. Some 500 people were evacuated and an exclusion zone of 300 m was established. Around 100 m$^3$ of gasoline infiltrated the ground, the rest having burnt off. After securing the area by inerting and cleaning the sewers, clean-up operations involved decontaminating the ground using several techniques: monitoring with piezometers, wells for beating down the slick, drains to stop the slick from entering basements and to extract floating gasoline and on site incineration of products recovered. Response operations took around 6 months (pumping from 130 boreholes) and monitoring of the site lasted 3 years. No significant impact was reported.

### 1990, *M/V Jupiter*

While unloading, the oil tanker *M/V Jupiter* exploded and went on fire on the Saginaw River (Michigan, US). The vessel grounded perpendicular to the river's flow. The hull broke, causing a spill of 3,100 $m^3$ of gasoline. The fire continued to burn intermittently for over 2 days before being definitively extinguished. Floating booms were deployed around the vessel to contain the slick. Around 50 $m^3$ of gasoline mixed with water were recovered by pumping and combustion residues deposited on the banks were collected manually. Three days after the accident, gasoline odours were detected in the nearby sewers, which were then rinsed and the outfall was monitored. Due to the presence of BTEX detected in low concentrations around the wreck located near a water treatment plant, an ozone water treatment operation was carried out as a precautionary measure. The environmental impact remained limited. It was mainly visible through fish mortality following the explosion onboard the vessel. The extinguishing agents (foam) used to fight the fire were probably more harmful than the gasoline itself.

### 1997, *Bona Fulmar*

This Bahamian oil tanker was in the North Sea in thick fog with a cargo of 60,000 tonnes of gasoline when it collided with another vessel. One of the *Bona Fulmar*'s tanks was ripped open and 7,000 tonnes of unleaded gasoline spilled out.

The vessels navigating in this area were warned of the fire and explosion risk. Six tugs were on site but no major response effort was organised as the majority of the gasoline spill evaporated and dispersed rapidly. There were no visible traces of pollution, the gasoline odour in the air was diluted and the leak was stopped by repairing the breach in the vessel. However, two divers who were inspecting the ship and carrying out emergency repairs were affected by the vapours.

### 2000, Volverine Pipeline Co

Due to corrosion and wear, a pipeline burst spilling 255 tonnes of gasoline which polluted a marshy area and a river feeding into Lake Michigan (US). As an initial response, the electricity supply was cut off around the affected area and 600 homes were evacuated. The water quality and benzene concentrations in the atmosphere were monitored. Clean-up operations involved preventing the pollution from spreading by deploying booms on the river and recovering the concentrated pollutant using vacuum trucks (recovery by suction). The local inhabitants were able to return to their homes 12 days later and the pipeline began operating again 15 days after the accident.

### 2000, *M/V Highland Faith*

A vessel loaded with 78,000 $m^3$ of gasoline grounded near the Port of New York (US). The vessel was towed from its distressing position to a terminal where a leak was detected, characterised by the presence of sheen. The main measures taken to correct the vessel's trim included the transfer between ballast tanks of the water-gasoline mixture, requiring the inerting and monitoring of the atmosphere in the ballast tanks, and the deployment of floating booms around the vessel. An extensive scenario study was carried out to predict the behaviour of the gasoline in the event of a major spill, as well as the related risks:

- persistence of the gasoline which can spread and rapidly form thin slicks (sheen or metallic appearance). If the slick were to reach the shore, it would simply form a greasy film, which would not require clean-up operations
- due to the presence of aromatic compounds (estimated here at 20 to 50% of the gasoline), impact generated by the toxicity of these dissolved compounds could be expected in calm, shallow areas where dispersion (natural dilution) could not take place
- in the vapours, aromatic compounds were expected to reach 15%, meaning that the exposure of personnel must be monitored.

# Response recommendations

All response efforts should be preceded by in-depth reflection on human safety (responders and third parties). The safety of the area must be ensured and human protection enforced. The following paragraphs lay out the basic elements of this reflection, which should be implemented throughout operations.

Unleaded gasoline is a transparent and almost colourless product, which complicates operations as it is always difficult to distinguish the outline and spread of the slick.

## Initial instructions

- Stop the spill if possible.
- Set up an exclusion zone.
- Secure the zone by prohibiting access to the polluted area and evacuating anyone within the zone.
- Prohibit all possible sources of ignition (use fireproof equipment, bronze tools...).
- Open and ventilate any closed or semi-closed spaces in the zone.
- Plug outflow pipes in contact with the polluted water body to prevent the product from spreading upwards and to reduce the risks of explosion in the pipes.

In all cases, involve professional fire fighters.
In the case of a spill on a river, suspend the use of water from downstream of the spill location (close water intakes, water supply channels...).

## Vapour and explosion monitoring measures

When responding to a spill, the first safety measure will be to control the percentage of gasoline vapours in the air (see B5) using an explosimeter. A safety margin is taken into account and response will be conducted if measurements correspond to less than 10% of the minimum flammability limit (1.4%) in air.
In the case of considerable evaporation, the presence of VOCs (some of which are very toxic) in air will be measured using detectors to ensure responder safety (e.g. HNU photo ionisation detector or Draëger tube for BTEX aromatic vapours).
The less ventilated or more enclosed the area (closed space, pipes, no wind...), the greater the risks of inflammation of gasoline vapours and intoxication of operators, due to the accumulation of vapours.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*Measuring vapours using an explosimeter.*

## A spill on fire

If the fire is too far on, the people within a sufficient radius must be evacuated. Fire fighting will take precedence over pollution response efforts.

For all response actions it is essential to:

- approach the spill from upwind and/or upstream of the current
- equip responders with explosimeters and personal protection equipment (see D4).

The extinguishing agents recommended are chemical foam, carbon dioxide snow or dry powder. Water may be ineffective in extinguishing the fire, but it can be used to cool tank sides and surfaces exposed to the fire. It is also possible to beat down the vapours with water spray. Never use a solid water stream as it disperses the flames. Tanks and parts exposed to the fire should be cooled with plenty of water. The fuel source must be isolated; according to the circumstances, let all the fuel burn off in a controlled manner or use the appropriate extinguishing agents.

**In all cases, the safety of the area must be ensured and protection of responders and local inhabitants enforced.**
**For fire/safety aspects, refer to specialised guidelines.**

*Fireproof boom*

## *In situ* burning

This technique can be applied to highly flammable gasoline blends in very specific situations, in particular in deserted areas, due to the related risks (fire and fumes). However, given the risks involved in this option, the potential consequences must be studied beforehand.

## Spill on water

### In the open sea

Given the evaporation rate of the product (a few hours) and whatever the scenario envisaged (see C2), the most appropriate solution is to leave the gasoline to spread and evaporate naturally.

### In coastal areas, ports, estuaries, water courses

In these cases, for safety reasons, natural evaporation and dispersion of the slick should generally be promoted, for example by mixing the pollutant at the surface using a fire hose with a solid water stream.

However, if the slick is at risk of drifting towards hot spots or an urban area, it should be deflected or contained. In this case, use fireproof equipment, contain with a fireproof boom where possible and cover the slick with a carpet of low to medium expansion foam to reduce the formation of flammable vapours. The pollutant is then recovered using a floating suction head, adapted for use on a carpet of foam. The storage tank for recovered pollutant is at risk of emitting flammable or explosive vapours. This emission must therefore be limited and all hot spots in the area eliminated. The combined use of a "fishtail" suction head and a sanitation or vacuum truck is, in this case, recommended. This type of truck, an ATEX certified ADR combined unit, is able to vacuum pump flammable products with a flash point lower than 61°C, and can store and transport the recovered product by road according to ADR regulations.

In the case of pumping, friction caused by the product flowing can create a charge of static electricity, which can lead to sparks resulting in ignition or explosion.
These operations should be carried out by trained professionals equipped with appropriate personal protective equipment (respiratory and skin protection - see D4).

## Warning

From an environmental point of view, a spill of this type of product results in the presence of significant quantities of toxic molecules in the water column. This phenomenon is all the more discernable in waters with a low rate of renewal and the use of a mixing technique will promote dispersion/dissolution. Furthermore, in turbid waters these molecules become adsorbed by matter in suspension then settle.

## Use of sorbents

For safety reasons, containment of volatile gasolines should be avoided and recovery on water by absorption is advised against. Doing so simply means transferring the risk of explosion from the water body to land, to used sorbent storage areas, from which the volatile gasoline recovered evaporates. Sorbents are therefore only used for very small quantities of product or for the final stage of response.

## Chemical dispersion

This technique is not appropriate as, on the one hand, gasoline is a light product which is unlikely to form a stable suspension and, on the other hand, dispersion promotes the dissolution of the soluble, toxic compounds in gasoline which can evaporate directly.

NB: in very specific cases (more or less confined atmosphere, e.g. sewer), attempts have been made to disperse gasoline using dispersants exclusively so as to decrease the concentration of hydrocarbon vapours and thus reduce the risk of explosion. Unless there is vigorous mixing action, the chances of this operation being successful are practically nil.

# Response techniques

## No response actions, leave alone

In most cases, natural evaporation of gasoline reduces the pollution. It is probably the most commonly used response option if safety allows it. This option nonetheless requires monitoring of the pollution, its spread, its movements, and, where relevant, the presence of soluble compounds of gasoline in the water column.

In some cases, such as confined or inland waters, this option does not exclude recourse to floating booms to protect specific areas from contamination by the slick (protection booms, deflection booms).

Generally speaking, slicks move with the current and the influence of the wind (100% of current, 3% of wind). On rivers, slicks therefore tend to accumulate and spread over the "downwind" banks.

## Mechanical recovery

This technique is often associated with containment using floating booms to concentrate the pollutant towards the skimmer head/pump. It is the second response option when the pollution cannot be left to evaporate. However, this option, which involves concentrating and handling gasoline, a highly flammable product, requires very strict safety measures throughout the treatment chain (explosive atmosphere, fire/intoxication, use of fireproof materials). These booms can also be used to deflect the movement of the slick towards a more suitable area (area where safety issues are less problematic or calmer area where recovery of the gasoline is possible...) or to prevent the gasoline from migrating towards an ecologically sensitive area (marsh...).

Light refined products are characterised by a low viscosity. They therefore do not pose any particular problems for pumping, but do however tend to rapidly spread to form extremely thin slicks. The main difficulty is that of selectively recovering the gasoline without also collecting vast quantities of water. For this, auto-adjustable weir skimmers are suitable, as well as certain oleophilic skimmers (e.g. rope skimmers), as they are characterised by high selectivity but generally have a lower recovery rate. When the situation allows it, slick containment using a floating boom, towed or moored in the current, intended to contain and thicken the slick will significantly increase the efficiency of recovery and will sometimes even prove necessary. Finally, for small quantities of pollutant (a few litres, or even a few dozen litres, which can nevertheless represent large polluted areas), the use of sorbents will often be the most suitable solution for final clean-up.

# Choosing personal protective equipment (PPE)

## Choosing protective clothing

- Wear protective clothing covering as much of the body as possible.
- Facial and eye protection: wear chemical splash proof goggles. It may be necessary to wear a facial mask.
- Skin protection: wear protective gloves (oil resistant gloves: nitrile rubber, fluoropolymer and PVA), boots, coveralls and/or other oil resistant protective clothing.
- Rapidly remove all contaminated clothing which no longer effectively protects the skin.

## Choosing breathing apparatus

- In confined atmospheres, self-contained breathing apparatus must be worn due to the abundance of fumes and gases given off.
- Individual breathing apparatus must be worn if there is a risk of inhaling toxic vapours when concentrations near the Mean Exposure Value (MEV = 200 mg/m$^3$).


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*Full-face cartridge respirator*

# Gasoline resistance table

The fabrics used for protective equipment and materials must be resistant to gasoline.

The table below lists the compatibility of various plastomers and elastomers with gasoline and one of its oxygenates, ethanol.

| | | Unleaded gasoline | Ethanol |
|---|---|---|---|
| Acrylonitrile butadiene styrene | ABS | D | B |
| Ethylene propylene diene monomer rubber | EPDM | D | A |
| Fluorocarbonate rubber | FKM - Viton | A | B |
| Natural rubber | | D | A |
| Nitrile rubber | NBR - Buna Nitrile | A | C |
| Perfluoro rubber | FFKM - *Chemraz* | | A |
| Perfluoro rubber | FFKM - *Kalrez* | A | A |
| Polyester rubber | *Hytrel* | | |
| Polyvinyl chloride | PVC | C | C |
| Chlorinated polyvinyl chloride | CPVC | C | B |
| Polyvinylidene fluoride | PVDF - *Kynar* | A | |
| Polyamide | PA - *Nylon* | A | A |
| Polycarbonate | | A | B |
| Polychloroprene | *Neoprene* | B | A |
| Polychlorotrifluoroethylene | PCTFE-*Kel-F* | A | A |
| Polyepoxide | Epoxy | A | A |
| Polyetheretherketone | PEEK | | A |
| Chlorosulphonated polyethylene | CSPE - *Hypalon* | A | A |
| Low density polyethylene | LDPE | D | B |
| High density polyethylene | HDPE | C | A |
| Fluorinated polyethylene propylene | *Tygon* | C | C |
| Polyoxymethylene | Acetal | A | A |
| Polyphenylene oxide | *Noryl* | D | A |
| Polyphenylene sulphide | PPS - *Ryton* | A | |
| Polytetrafluorethylene | PTFE - *Teflon* | A | A |
| Polyurethane | | | D |
| Silicone | | D | B |

A excellent resistance (resists for years)

B good resistance (resists for at least a month)

C moderate resistance (signs of deterioration after a week)

D unsuitable

# Waste treatment

Gasoline spills can produce various types of waste.

## Polluted water

In the case of a mixture showing two distinct phases, water and gasoline, the insoluble, floating hydrocarbons should be separated by settling.

If this water/gasoline mixture is more or less dispersed, it is possible to filter with hydrophobic sorbents which will retain the gasoline part. For instance, for a small spill, pour the water/gasoline mixture into a tank containing bulk sorbents, such as polypropylene in the form of "spaghetti".

In the case of water contaminated by the soluble compounds from gasoline, the contamination will depend on the initial composition of the gasoline, in particular the proportion of BTEX and oxygenates (ETBE-MTBE or methanol and ethanol). These waters cannot be discharged into the natural environment. If the quantities are small and storage is possible, treatment of the contaminated water can be contracted to a specialised company.

Another alternative involves treating this water with activated carbon (1 kg for 3.5 kg of compounds in solution), before discharging it. In the case of large quantities for which this treatment is not possible, lagooning of this water is an option, preferably using a aerated system, in order to allow these volatile compounds to evaporate into the atmosphere over time. This process may also accelerate the biodegradation of the soluble and biodegradable compounds in gasoline, i.e. the light aromatics and alcohols, excluding ETBEs and MTBEs which are persistent.

## Polluted sediments

The sediments impregnated with gasoline are sent to industrial treatment facilities where they will be incinerated or possibly inerted by specific treatments (lime, clay...).

## Polluted sorbents

Oiled sorbents should be sent to industrial waste treatment plants for incineration.

# Further information

# Glossary

### Adsorption

Elevation of the concentration of a substance dissolved at the interface of a condensed phase and a liquid phase under the influence of surface forces. Adsorption can also occur at the interface of a condensed phase and a gas phase.

### Bioaccumulation

Continued retention of a substance in the tissue of an organism throughout the course of its existence (the bioaccumulation factor constantly increases).

### Biocide

An agent capable of destroying living organisms.

### Boiling point (measured at 1 atm)

Temperature at which a liquid begins to boil; more specifically, when the temperature at which saturating vapour pressure of a liquid is equal to standard atmospheric pressure (1,013.25 hPa). The boiling point measured depends on atmospheric pressure.

### Effective concentration 50 ($EC_{50}$)

Concentration causing a given effect (mortality, growth inhibition...) for 50% of a given population during a given period of time.

### Exposure limit value (ELV)

Ceiling exposure value measured for a maximum duration of 15 minutes.

### Flash point

The lowest temperature at which a substance generates vapours that ignite or burn immediately when in contact with a flame.

### Lethal Dose 50 ($LD_{50}$)

Dose of a substance deduced statistically which, when administered to a living organism, will cause the death of 50% of the organisms exposed.

### Lower Explosive Limit (LEL)

Minimum airborne concentration of a compound above which vapours ignite.

### Marine pollutant

Substance, object or matter likely to cause serious damage when released into the marine environment.

### Mean exposure value (MEV)

Value that has been measured or estimated for a work station lasting 8 hours and is intended to protect workers from long term effects. MEV can be exceeded for very short periods providing the ELV value (should there be one) is not exceeded.

### Median lethal concentration 50 ($LC_{50}$)

Concentration of a substance deduced statistically that should, during or after exposure and for a given period of time, cause the death of 50% of the animals exposed.

### N-octanol/water partition coefficient (Kow)

Ratio of the equilibrium concentrations of a substance dissolved in a two phase system made up of two solvents that virtually do not mix.

### Octane rating

Engine fuels and gasolines are characterised by their octane rating which indicates their combustion quality in spark ignition engines. Premium grade fuels have octane ratings of 95 and 98.

### Personal protective equipment

This refers to the respiratory and physical protection of humans. Protection levels, including both protective clothing and breathing apparatus have been defined and accepted by response authorities such as the US Coast Guard, NIOSH and the US EPA.

Level A: SCBA (self contained breathing apparatus) and fully air and chemical-tight suits.

Level B: SCBA and splash proof suits.

Level C: full face mask or goggles and splash proof suits.

Level D: coveralls without breathing apparatus.

### Relative density

Ratio of the weight-density of a substance to that of water for a liquid or to that of air for a gas.

### Relative vapour density

Weight of a volume of vapour or pure gas (without air) compared to that of an equal volume of dry air at the same temperature and pressure. A vapour density lower than 1 indicates that the vapour is lighter than air and will have a tendency to rise. When the vapour density is higher than 1, the vapour is heavier than air and will tend to stay near ground level and spread.

### Self-ignition temperature

Minimum temperature at which vapours ignite spontaneously.

### Solubility

Quantity of a substance dissolved in water. It will depend on salinity and temperature.

### Source of ignition

Examples of sources of ignition: heat, sparks, flame, static electricity and friction. Sources of ignition should always be prevented when handling flammable products or responding to an emergency in high risk areas (use explosion proof equipment e.g. pumps and VHF).

### Threshold Limit Value (TLV)

Average limit value (weighted as a function of time) that workers can be exposed to regularly for 8 hours a day, 5 days a week without experiencing noxious effects. This value was defined and determined by the American Conference of Governmental Industrial Hygienists (ACGIH).

TLV-STEL: Time-weighted average concentrations for 15 minutes that must never be exceeded at any time during the day.

TLV-TWA: Time-weighted average values for an 8 hour period per day and 40 hours a week.

### Upper Explosive Limit (UEL)

Maximum airborne concentration of a compound above which vapours will not ignite for lack of oxygen.

### Vapour pressure or tension

Partial pressure of gas molecules in a state of equilibrium with the liquid phase for a given temperature.

# Acronyms

| | |
|---|---|
| ADNR | European Agreement concerning International Carriage of Dangerous Goods by inland waterways |
| ADR | European Agreement concerning the International Carriage of Dangerous Goods by Road |
| BTEX | Benzene, Toluene, Ethylbenzene, Xylene (light aromatic compounds) |
| CAS | Chemical Abstracts Service |
| CEDRE | Centre of Documentation, Research and Experimentation on Accidental Water Pollution |
| ELV | Exposure Limit Value |
| ETBE | Ethyl Tert-Butyl Ether (branched oxygenates) |
| GC-FID | Gas chromatography - Flame Ionisation Detector |
| GC-MS | Gas chromatography - Mass spectrometry |
| IARC | International Agency for Research on Cancer |
| IATA | International Air Transport Association |
| IBC | International Bulk chemical Code |
| ICSC | International Chemical Safety Cards |
| IMDG | International Maritime Dangerous Goods |
| IMO | International Maritime Organization |
| LC | Lethal Concentration |
| LEL | Lower Explosive Limit |
| MEV | Mean Exposure Value |
| MSDS | Material Safety Data Sheet |
| MTBE | Methyl Tert-Butyl Ether (branched oxygenates) |
| MUC | Maximum Use Concentration |
| NOEC | No Observed Effect Concentration |
| PAH | Polycyclic Aromatic Hydrocarbon |
| ppb | Parts per billion |
| PPE | Personal Protective Equipment |
| ppm | Parts per million |
| RID | Regulations concerning the International Carriage of Dangerous Goods by Rail |
| SCBA | Self-Contained Breathing Apparatus |
| TAME | Tert-Amyl Methyl Ether |
| TBA | Tert-Butyl Alcohol |
| TLV-STEL | Threshold Limit Values - Short Term Exposure Limit |
| TLV-TWA | Threshold Limit Values - Time Weighted Average |
| UEL | Upper Explosive Limit |
| VOC | Volatile Organic Compound |

# Useful websites

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Available at: http://www.albina.com/Fuel/msds.htm

BARPI (Bureau d'Analyse des Risques et Pollutions Industrielles). ARIA [online].
Available at: http://www.aria.developpement-durable.gouv.fr

*Cedre* (Centre of Documentation, Research and Experimentation on accidental water pollution). [online].
Available at: http://www.cedre.fr

COLE-PARMER. Chemical Compatibility [online].
Available at: http://www.coleparmer.com/TechInfo/ChemComp.asp

CONCAWE (CONservation of Clean Air and Water in Europe). [online].
Available at: http://www.concawe.be/Content/Default.asp

CSST (Commission de la Santé et de la Sécurité du Travail). Les produits [online].
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Available at: http://www.cdc.gov/niosh/npg/
(consulted on 19.12.2008)

**HEALTH CANADA**. Environmental and Workplace Health. Methyl Tertiary-Butyl Ether (MTBE) [online].
Available at: http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/mtbe/index-eng.php
(consulted on 19.12.2008)

**INRS** (Institut National de Recherche et de Sécurité pour la prévention des accidents du travail et des maladies professionnelles). Solvants naphta et solvants aromatiques, Fiche toxicologique n°106, 1999 [online].
Available at: http://www.inrs.fr/inrs-pub/inrs01.nsf/inrs01_ftox_view/D05611795E16522EC1256CE8005A1F2A/$File/ft106.pdf
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Available at: http://www.ultramar.ca/NR/rdonlyres/4CFD58AE-0791-43D0-8967-F9B5E47726BE/0/5100UnleadedGasolineRevisedFebruary2007.pdf
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# ANNEXES

## Annex 1:
Main oxygenates present in unleaded gasoline

## Annex 2:
Most common additives in premium grades

## Annex 3:
Fax format data card

# ANNEX 1: MAIN OXYGENATES PRESENT IN UNLEADED GASOLINE

### Main oxygenates in unleaded gasoline under French legislation

| Type | Compound | CAS n°: | Proportion in gasoline |
|---|---|---|---|
| Ether: | MTBE (Methyl Tert-Butyl Ether) | 1634-04-4 | |
| | ETBE (Ethyl Tert-Butyl Ether) | 994-05-8 | ETBE + MTBE < 20 % |
| | TAME (Tert-Amyl Methyl Ether) | 637-92-3 | < 13 % |
| Alcohol | Methanol | 67-56-1 | < 85 % |
| | Ethanol | 64-17-5 | < 3 % |
| | TBA (Tert-butyl Alcohol) | 75-65-0 | < 7 % |
| | Isopropyl alcohol | 67-63-0 | < 10 % |
| | Isobutyl alcohol | 78-83-1 | < 10 % |

### Other oxygenates used in other countries

| Type | | Compound | CAS n°: |
|---|---|---|---|
| Ether: | DIPE | Di Iso Propyl Ether | 108-20-3 |
| | TAEE | Tert-Amyl Ethyl Ether | 919-94-8 |
| Alcohol | TAA | Tert-Amyl Alcohol | 75-85-4 |

### Properties of oxygenates in unleaded gasoline

| Compound | Boiling point °C | Density | Solubility in water g/L |
|---|---|---|---|
| MTBE | 88 | 741 | 51 |
| ETBE | 102 | 752 | 1 |
| TAME | 102 | 764 | |
| DIPE | 102 | 724 | 2 |
| TAEE | 116 | N/A* | N/A* |
| TBA | 74 | 786 | Miscible |
| TAA | 88 | 805 | N/A* |
| Methanol | 32 | 791 | Miscible |
| Ethanol | 46 | 789 | Miscible |

Source: LESNIK B., 2002

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N/A*: data not available

# ANNEX 2: MOST COMMON ADDITIVES IN PREMIUM GRADES

| Time of incorporation | Additives | Type | Purpose | Concentrations in gasoline in ppm |
|---|---|---|---|---|
| Additives added to the mixture at refinery | Oxygenation inhibitors | Aromatic amines and other phenols | To inhibit oxidation and build-up of deposit in certain refinery transformation units. | 50 to 100 |
| | Metal deactivators | Chelating agent | To inhibit oxidation and build-up of catalysed deposit by certain metals, in particular copper | 5 to 50 |
| | Markers | Soluble compounds in oil | To identify the refined product (e.g. distinction between leaded and unleaded gasoline) | 5 to 50 |
| Additives added before leaving the refinery | Corrosion inhibitors | Carboxylic acids and carboxylates | To prevent the corrosion of iron in pipelines | 50 to 100 |
| Additives added at the sales outlet (fueling station) | Carburettor and injector detergent | Amines and amine carboxylates | To reduce deposit within the carburettor and the fuel injector orifice | 50 to 150 |
| | Deposit controller | Amine polybutane and amine polyethers | To eliminate and prevent deposit within the carburettor, collector entry, orifices and valves | 600 to 1000 |
| | Octane booster | Alkyl lead (for leaded gasoline) and manganese compounds | To increase the fuel's octane rating | 2000 to 3000 |
| | Demulsifiers | Polyglycolic derivatives and silicones | To prevent the formation of foam in particular when filling the tank | > 20 |
| | Antifreeze | Surfactants, alcohols and glycols | To prevent the formation of ice in the tank, the carburettor and the system | 1500 to 2500 |

# ANNEX 3: FAX FORMAT DATA CARD

## Synonyms

Unleaded petrol, unleaded, super unleaded, super plus, super 95, super 98, premium petrol, premium gasoline, E85 (85% ethanol), gas, pygas, mogas, motor fuel, motor spirit

## Shipping name

MOTOR SPIRIT (GASOLINE)

## Identification

UN: 1203
NATO code: F-57
EC n° (EINECS): 289-220-8
CAS n°: 86290-81-5

## Similar oil products

Alkylate, reformate, reformulated gasoline, isomerate, naphtha, virgin naphtha, light/heavy crack spirit...

## Product labels


T: toxic


F+: extremely flammable


N: dangerous for the environment

## First aid information

In the case of severe or persistent symptoms, call a doctor or seek emergency medical attention.

### Inhalation

- Transport the person into fresh air, outside of the contaminated area.
- Keep them warm and at rest.
- Supply oxygen or apply artificial respiration if necessary.
- Place under medical supervision.
- Transfer to hospital in the case of illness.

### Skin contact

- Remove contaminated clothing.
- Rinse and wash skin with plenty of water and soap for several minutes.

### Eye contact

- Rinse the eyes with plenty of water for several minutes (if possible remove contact lenses).
- Consult a doctor where necessary.

### Ingestion

- Rinse out the mouth.
- Do not induce vomiting.
- Give the person plenty to drink.
- Keep the person at rest.
- Call a doctor or transfer immediately to hospital.

## Physicochemical data

**Weight-density**: 720 - 775 kg/$m^3$ at 15°C
**Viscosity:** 0.5 - 0.75 $mm^2.s^{-1}$ at 20°C
**Vapour pressure**: 35 - 90 kPa at 20°C
**Relative vapour density** (air = 1) 3 - 4 at 20°C
**Boiling point** (distillation range): 30 - 210°C

**Solubility in water**

- hydrocarbons in gasoline:
  - monoaromatics (BTEX): < 100mg/L
- oxygenates in gasoline:
  - alcohols totally miscible with water
  - MTBE: 51 g/L
  - other ethers around 1 g/L

## Toxicological data

### Acute human toxicity

- By eye contact: burning sensation and temporary redness. Vapours and fog are irritating to mucous membranes.
- By inhalation: possible irritation of upper respiratory tract, with headaches, nausea, fainting. At high concentrations: effects on the central nervous system (headaches, dizziness, drowsiness, or even fainting sometimes with convulsive movements requiring emergency treatment).
- By ingestion: nausea, vomiting and stomach pains. If the product enters the lungs, it can cause severe burns (with pneumopathy due to inhalation developing in the following hours, necessitating medical surveillance for 48 hours).
- By skin contact: possible skin irritation.

### Specific effects

The hydrocarbon part of gasoline contains benzene, a substance classed as carcinogenic and mutagenic. Gasoline is a possible carcinogen in humans (according to IARC).

Maximum exposure values:

- in the US
  - for 8 hours: TLV-TWA = 890 mg/$m^3$ (300 ppm)
  - for 15 minutes: TLV-STEL = 1,480 mg/$m^3$ (500 ppm)

### Olfactory threshold

- perception: 0.57 mg/$m^3$ (0.12 - 0.15 ppm)
- detection: 0.31 mg/$m^3$ (0.06 - 0.08 ppm)

## Ecotoxicological data

Gasoline is toxic for aquatic organisms and can lead to long term harmful effects.

| | | | |
|---|---|---|---|
| Fish (*Alburnus alburnus*) | $LC_{50}$ (96 h) | = | 119 mg/L |
| Fish (*Cyprinodon variegatus*) | $LC_{50}$ (96 h) | = | 82 mg/L |
| Fish (*Salmo gairdneri*) | $LC_{50}$ (24 h) | = | 58 mg/L |
| Crustacean (*Daphnia magna*) | $EC_{50}$ (24 h) | = | 170 mg/L |
| Crustacean (*Nitocra spinipes*) | $LC_{50}$ (96 h) | = | 201 mg/L |
| Algae (*Selenastrum capricornutum*) | $EC_{50}$ (72 h) | = | 56 mg/L |
| | NOEC (72 h) | = | 10 mg/L |

## Flammability data

**Flash point:** < - 40°C
**Self-ignition point:** > 300°C (lowered to 250°C to 260°C in the presence of catalytic materials.
**Flammability or explosive limits (% in air)**
Lower limit: 1.4 %
Upper limit: 7.6 %

**Dangerous products of decomposition**

Incomplete combustion and thermolysis produce gases with a varying degree of toxicity, such as carbon monoxide, carbon dioxide, various hydrocarbons, aldehydes as well as soot.

**Stability and reactivity**

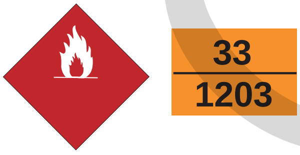
- Stability: stable product at storage, handling and usage temperatures.
- Conditions to be avoided: heat, sparks, sources of ignition, flames, static electricity.

**Particular risks**

- Extremely flammable: the vapours, which are heavier than air, can spread and linger at ground level, with a very high risk of explosion or flashback.
- Ignition from a distance is possible.
- The vapours mix well with air and explosive mixtures are rapidly formed.
- In the case of pumping, friction caused by the product flowing can create a charge of static electricity, which can lead to sparks resulting in ignition or explosion.

## Transportation

Identification n° (UN): 1203
**Land transport:** RID (rail) /ADR (road)
Danger n°: 3
Classification code: F1
Label n°: 3
Danger code: 33
Packaging group: II



*Transport symbols*

**Transportation via inland waterways:** ADNR
Danger n°: 3
Classification code: F1
Label n°: 3
Packaging group: II
**Maritime transport:** IMO/IMDG
Danger n°: 3
Packaging group: II
Label n°: 3
Safety sheet: F-E, S-E
Marine pollutant: no
**Air transport:** ICAO/IATA
Danger n°: 3
Label n°: 3
Packaging group: II
Special provisions: ADR / RID / ADNR: 243 534

## Handling, storage

- Handle in well ventilated areas.
- Prevent all sources of ignition, flames, sparks, hot spots and do not smoke.
- Avoid inhaling vapours and avoid contact with the skin and mucous membranes.
- Never prime a siphon by mouth.
- Prevent the formation of vapours and spray.
- Wear safety shoes and overalls which do not generate sparks or electrostatic charges.
- Use fireproof material.
- Ensure equipotential connections between installations to prevent the generation of static electricity when pumping the product.
- Do not use compressed oxygen or air when transferring the product.
- Never pierce, grind, cut or weld a container or tank, even when empty.
- Do not remove the danger labels from containers even when empty until they have been cleaned and degassed.
- Only ever operate on cold, degassed, aerated tanks (risk of explosive atmosphere).
- Only use hydrocarbon resistant materials, joints, pipes, recipients etc.
- Avoid contact with strong oxidising agents.