PHOSPHORIC ACID

EU classification:

C: corrosive

UN n°: 1805

MARPOL classification: Z
SEBC classification: D (dissolver)

CHEMICAL RESPONSE GUIDE

PHOSPHORIC ACID

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 and technical guidance from GPN.

Warning

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

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

Published in French: September 2008
English translation: November 2008

Translated by AlbaTraduction.com

Purpose of this guide

As part of the research funded by GPN (Grande Paroisse Nitrogen), *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) produces a series of response guides for chemical hazards. They can be used to assist in emergency response in the event of an incident involving a vessel carrying hazardous substances which may cause water pollution.

These guides are updates of the 61 "mini response guides" published by *Cedre* in the early 1990s.

These guides are 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.

They also contain the results of scenarios relating to incidents which have occurred in the Channel, the Mediterranean and in ports and rivers. 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. These guides are intended primarily for specialists who know about 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 phosphoric acid

Definition

At room temperature, chemically pure anhydrous phosphoric acid is a white solid. It melts at 42.4°C to form a colourless, viscous liquid. It is highly soluble in water.

In practice, users and even chemists employ the term "phosphoric acid" to refer to an aqueous solution of phosphoric acid. This common terminology will be used in this guide.

Phosphoric acid is generally transported diluted in liquid form by specialised vessels. When spilt in water, it sinks and mixes with the water to produce a diluted acidic, corrosive solution, giving off a small amount of heat.

Although this acid is neither flammable nor explosive, contact with certain metals releases hydrogen which can be a source of fire or explosion.

Phosphoric acid is not volatile, but inhalation of its aerosol can cause irritation of mucous membranes. Phosphoric acid is corrosive and causes burns which vary in severity according to the duration of contact and the concentration of the acid. It is harmful for the environment due to its corrosive nature.

Phosphoric acid exists at different levels of concentration and purity according to the manufacturing process and its application (see B.3).

The most commonly found phosphoric acid in maritime or river transport is the dark green acid referred to as commercial grade acid, also known as green acid.

Use (INRS, 1997; IFA, 2006)

Phosphoric acid is mainly used in the manufacture of fertilisers (around 85%), as well as in metal surface treatment, the pharmaceutical industry, fermentation, wastewater treatment, cleaning products, refractory binders, mineral chemistry and the food industry.

Risks (ICSC, 2000)

- Toxicity

  Phosphoric acid is corrosive to the eyes, skin and respiratory tract and corrosive upon ingestion.

  The risks for man and for the environment are therefore mainly due to the corrosive nature of phosphoric acid when in contact with this chemical. Concentrated solutions of phosphoric acid result in severe lesions of the tissues. Diluted solutions are only moderately irritating; repeated or prolonged contact with the skin can cause dermatitis.

  During combustion, toxic fumes form, consisting of phosphorous oxides.

  The substance breaks down when in contact with alcohols, cyanides, ketones, phenols, esters, sulphides and halogenated organic substances, producing toxic fumes.
- Fire and explosion

  Phosphoric acid is stable, non-explosive and non-flammable. However, because of its corrosive action on many metals, a reaction which releases hydrogen, phosphoric acid can be a secondary source of fire or explosion: hydrogen is a highly flammable and explosive gas when mixed with air.

  In the presence of strong bases, a lot of heat is released with a risk of projections.

Behaviour in the environment

Phosphoric acid is a triacid. Phosphoric acid transported by ship is miscible in any proportions with water, resulting in the release of heat, the amount of which will vary according to the acid's concentration.

Given its high density (d = 1.57 for a 75% aqueous solution of phosphoric acid), the acid sinks if there is no agitation before being diluted.
Its toxicity depends above all on the acidity of the substance and its effect on the pH: it is harmful for certain aquatic species whose survival requires a pH of at least 5.5.

However, it does not represent a risk in terms of bioaccumulation or bioamplification along the food chain.

Its acidic character will naturally be reduced in water by the minerals present, and the phosphate will be consumed as a nutritive salt.

Worldwide trade and transport

(IFA, 2006)

European manufacturers of phosphoric acid: Prayon, Kemira GrowHow, Thermphos, BASF, Helm, Febex CECA, Albright & Wilson, Amsterdam Fertilizers. Globally, Europe is an importer of phosphoric acid.

In 2007, the worldwide P_2O_5 production capacity was estimated at 43 Mt. Worldwide import-export transport of P_2O_5 reached 4.9 Mt in 2006. The main exporters are Morocco (number one, with the sites Safi and Jorf Lasfar), Tunisia, Senegal, South Africa and Jordan. The main importer is India (around 50%).

First line emergency data

First aid information

(ICSC, 2000; ERICARDS, 2007; INRS, 1997)

The corrosive action of phosphoric acid can appear after a certain delay: it is important to take immediate action.
Immediately remove all soiled or spotted clothes, including shoes.

Intoxication by inhalation

- Immediately move the affected person into the fresh air and away from the contaminated area.
- Where necessary, apply artificial resuscitation.
- Immediately obtain medical care.

Skin contact

- Remove contaminated clothing.
- Rinse the skin with plenty of water for at least 15 minutes or have a shower.
- Immediately obtain medical care.

Eye contact

- Rinse the eyes with plenty of water for at least 15 minutes (if possible remove contact lenses).
- Immediately obtain medical care and consult an eye specialist.

Intoxication by ingestion

- If the person is fully conscious, rinse out their mouth with water.
- Give the person plenty to drink.
- Do not induce vomiting.
- Immediately obtain medical care.

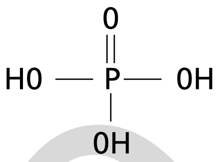
Where necessary, contact the nearest poison control centre (cf. page 4).

ID card[1]

Phosphoric acid

Gross formula: H_3PO_4

Semi-developed formula: $(HO)_3{-}P{=}O$



$$HO - \underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}} - OH$$

Synonyms (other names)

Orthophosphoric acid, white phosphoric acid, o-phosphoric acid, green acid.

EU Classification

C: corrosive

R34: Causes burns.

S1/2: Keep locked up and out of the reach of children.

S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S45: In case of accident or if you feel unwell, seek medical advice immediately (show label where possible).

CAS n°:	7664-38-2
EC N° (EINECS):	231-633-2
Index n°:	015-011-00-6

Classification for transportation

Phosphoric acid in solution
UN n°: 1805
Class 8

Solid phosphoric acid
UN n°: 3453
Class 8

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[1] Additional data in Annex 2

Physical data

Pure phosphoric acid (solid)

Molecular mass	98 $g.mol^{-1}$ INRS, 1997
Boiling point	260°C NPI, 2004; INRS, 1997
Melting point	42.4°C NPI, 2004; INRS, 1997; ECB, 2000
Vapour density	3.4 NPI, 2004
Relative density	1.864 at 25°C INRS, 1997
Vapour pressure/ tension	4 Pa at 20°C 16 Pa at 40°C 177 Pa at 80°C 487 Pa at 100°C INRS, 1997

75% phosphoric acid

Boiling point	133°C ECB, 2000; EFMA, 1996
Melting point (freezing point)	- 17.5°C EFMA, 1996; CSST, 2006; ECB, 2000
Critical temperature	N/A
Relative density (water = 1)	1.57 at 25°C ECB, 2000; CSST, 2006; DEKKER 1968
Vapour density (air = 1)	3.4 (*)
Solubility in seawater	100% (totally miscible)
Solubility in fresh water	100% (totally miscible)
pKa	pKa 1 = 2.15 pKa 2 = 7.09 pKa 3 = 12.32 HSDB, 2005
Vapour pressure/ tension (20°C)	267 Pa (75%) EFMA, 1996 290 Pa (85%) CSST, 2006
Viscosity at 20°C	24 cPo (75%) DEKKER, 1968
Olfactory threshold in air	Odourless
pH	< 1 EFMA, 1996

Pa.s = 1 Pl = 10 Po = 103 cPo
(*) approximate value: few references available

Composition and manufacturing processes

Phosphoric acid is made from phosphate ore which is either a sedimentary or magmatic rock depending on its origin. In addition to the predominant element phosphorus (P), phosphate rock naturally contains many other elements or impurities.

The main manufacturing process of phosphoric acid involves natural phosphate being attacked by sulphuric acid (wet process). After filtration and settling, this process produces a commercial grade phosphoric acid with a concentration of between 70 and 75% which contains residues of various elements and traces of impurities according to the original phosphate. This type of acid is black to dark green in colour (green acid).

Example of the composition of commercial grade phosphoric acid: table 2, page 13.

Technical grade, food grade and chemically pure phosphoric acid is obtained either from complementary purification and extraction treatments or through other thermal processes (furnace process) by the combustion of pure phosphorus followed by hydration. These acids are colourless.

Physical characteristics

At identical concentrations, the physical characteristics of phosphoric acid can vary slightly due to the residual impurities contained in the acid, which depend on the manufacturing process and the origin of the natural phosphate used.

Thus by way of comparison, wet process phosphoric acid (green acid) has a slightly higher density and viscosity and a lower boiling point and freezing point.

	Wet process (in %)	Purified wet process (in %)	Thermal process (in %)
Calcium monoxide	0.06	0.005	0.01
Fluoride	0.8	0.08	<0.0001
Aluminium oxide	1.7	0.01	0.0003
Iron oxide	1.23	0.007	0.004
Magnesium oxide	0.58	0.003	0.0002
Potassium oxide	0.01	0	0.0007
Sodium oxide	0.12	0.0025	
Silicon dioxide	0.07	0.1	0.0015
Sulphate	2.2	0.2	<0.002

Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York: John Wiley and Sons, 1982, 17,435 p.

Table 1: Variation in the composition of phosphoric acid

Concentrations and definitions

The concentration of phosphoric acid is often referred to as P_2O_5.

The conversion formula is as follows:

$[H_3PO_4] = [P_2O_5] \times 196 / 142$

Thus an acid given as 54 % P_2O_5 has a concentration of 74.5%.

Detailed composition of a given sample of phosphoric acid

Sample from OCP MAROC (source: laboratoire GPN Rouen 2006)

			Value
Main constituents	**Volumic mass**	kg/dm^3	1.624
	P_2O_5	%	52.6
	Total SiO_2	%	0.009
	CaO	%	0.1
	SO_3	%	1.8
	Al_2O_3	%	0.16
	Fe_2O_3	%	0.23
	MgO	%	0.95
	F	%	0.22
	Na_2O	%	0.13
	K_2O	%	0.12
Other elements/traces	Cl^-	mg/kg	180
	Arsenic	mg/kg	18
	Barium	mg/kg	1.7
	Boron	mg/kg	54
	Cadmium	mg/kg	9
	Cerium	mg/kg	< 0.1
	Chromium	mg/kg	164
	Cobalt	mg/kg	0.25
	Copper	mg/kg	35
	Europium	mg/kg	< 0.1
	Lanthanum	mg/kg	6
	Lead	mg/kg	< 0.1
	Lithium	mg/kg	3
	Manganese	mg/kg	19
	Molybdenum	mg/kg	5
	Nickel	mg/kg	21
	Organic carbon	mg/kg	200
	Selenium	mg/kg	< 0.1
	Silver	mg/kg	< 0.1
	Strontium	mg/kg	7
	Thorium	mg/kg	7
	Tin	mg/kg	0.5
	Titanium	mg/kg	53
	Uranium	mg/kg	176
	Vanadium	mg/kg	170
	Yttrium	mg/kg	20
	Zinc	mg/kg	183
	Zirconium	mg/kg	7

Table 2: Detailed composition of a given sample of phosphoric acid

Flammability data

Explosive limits: non-flammable product

Flash point: non-flammable product

Self-ignition point: non-flammable product

Thermal decomposition and dangerous decomposition products

(INRS, 1997; ICSC, 2000; EFMA, 1996)

As with all acids, flammable and explosive hydrogen is formed through the corrosion of metals.

Toxic gases and vapours (phosphoric acid vapours) can be released.

The acid can give off phosphorus oxides by thermal decomposition in the case of fire (over 200 to 300°C).

In 160°C heat, phosphoric acid loses water and turns into pyrophosphoric acid. At over 300°C, it turns into metaphosphoric acid then polyphosphoric acid.

At over 200°C, the polyphosphoric acids formed are very aggressive: all materials, including siliceous refractories, glass and enamels are rapidly attacked.

Wet process phosphoric acid (green acid) can release fluorine compounds when subjected to heat.

Behaviour when in contact with other products (INRS, 1997; ICSC, 2000)

- When water is poured on very concentrated phosphoric acid, considerable heat is produced causing a risk of projections.
- In the presence of strong bases, a lot of heat is released with a risk of projections.
- The substance breaks down when in contact with alcohols, cyanides, ketones, phenols, esters, sulphides and halogenated organic substances, producing toxic fumes.
- Violent reaction with nitrates, chlorates and calcium carbide, causing fire and explosion.

Definitions in glossary

Toxicological data

(INRS, 1997)

Concentrated solutions of phosphoric acid result in severe lesions of the tissues with which they come into contact, while diluted solutions of phosphoric acid are only moderately irritating. The intensity and nature of the lesions caused will depend on the concentration of the acid and the duration of exposure.

Acute human toxicity

- By inhalation: causes severe irritation of the upper respiratory tract, accompanied by a cough, burns, breathing difficulties and a risk of coma. Can cause irritation liable to trigger pulmonary congestion by chemicals and pulmonary oedema.
- By ingestion: causes acute pain, nausea, vomiting and diarrhoea. There is also a risk of haemorrhage of the digestive tract, which may lead to corrosion and permanent destruction of the tissues of the oesophagus and digestive tract.
- By skin contact: all contact with the liquid is corrosive and causes severe burns, redness and ulceration.
- By eye contact: risk of irreversible corneal lesions. Contact with this chemical is corrosive for the eyes and causes severe burns.

Chronic human toxicity

- Prolonged inhalation can cause inflammation of the respiratory tract and pulmonary lesions.
- Prolonged or repeated skin contact can cause dermatitis.
- Prolonged or repeated contact with the eyes can cause conjunctivitis.

Threshold toxicological values

Occupational exposure values
Code du travail, Arrêté du 30 juin 2004; EFMA, 1996; ICSC 2000
MEV (France)/OELV 8 hours: 1 mg/m^3
MEV (France)/OELV short term: 2 mg/m^3
TLV-TWA (ACGIH): 1 mg/m^3

Risk management values for the population
(ICSC, 2000; US DEPARTMENT OF ENERGY'S CHEMICAL SAFETY PROGRAM, 2005)
IDLH: 1 000 mg/m^3 (NIOSH, 2005)
TLV STEL (ACGIH): 3 mg/m^3 (EFMA, 1996)
TEEL 0: 1 mg/m^3
TEEL 1 (ERPG 1): 3 mg/m^3
TEEL 2 (ERPG 2): 5 mg/m^3
TEEL 3 (ERPG 3): 500 mg/m^3

Specific effects

Carcinogenic effects: not classed as carcinogenic by ACGIH

Genotoxicity: not considered as genotoxic

Mutagenic effects: classed as non-mutagenic

Ecotoxicological data

Acute ecotoxicity (ECB, 2000)

Fish (*Lepomis macrochirus*)	LC_{50} (96 h)	=	pH between 3.25 and 3.0
Fish (*Gambusia affinis)*	LC_{50} (96h)	=	pH between 3.5 and 3
Crustacean (*Daphnia magna*)	EC_{50} (12 h)	=	pH 4.6
Crustacean (*Daphnia pulex*)	EC_{50} (12 h)	=	pH 4.1
Crustacean (*Gammarus pulex*)	LC_{50} (12 h)	=	pH 3.4
Aquatic bacteria	EC_{50} = pH 2.55	=	270 mg/L

Chronic ecotoxicity

Recommended maximum limit of total phosphorus in order to prevent unwanted development of algae: 0.1 mg/L

Additional remarks

Increased acidity of the environment can lead to sublethal effects on fish such as interrupted reproduction, altered growth rate or skeletal malformations. Increased acidity can also be directly toxic for fish. A pH of less than 3 causes the coagulation of gill mucus, which can result in anoxia or breathing difficulties. For a higher pH, fish mortality is due to a decrease in chloride ions and sodium ions, as well as an increase in hydrogen ions in the blood. However, the toxicity can also be due to anions as well as to an increase in the acidity of the environment. A comparative study showed that sulphuric acid is the most toxic for fish, while nitric and hydrochloric acid are moderately toxic and phosphoric acid the least toxic. The different toxicities of these acids can be caused by anions produced during acid dissociation, however further investigation would be needed to come to a definitive conclusion.

- Alkahem, H.F. Effect of different acids on the freshwater fish, *Aphanius dispar. J. Biol. Sci. Res. Vol. 20, n° 3*, 1989, p. 537-545
- Ellgaard, E.G. ; Gilmore, J.Y. Effects of different acids on the bluegill sunfish, *Lepomis macrochirus* Rafinesque. *J. Fish Biol, Vol. 25, n°2*, 1984, p. 133-137

PNEC (Predicted No-Effect Concentration): No PNEC was able to be calculated as the buffering capacity, the pH and its fluctuation are very specific to the ecosystem in question. To estimate the effect of a phosphoric acid spill, the change in pH of the water must be calculated or measured. **Variation by one pH unit can affect flora and fauna.** The average pH of water can vary in seawater from 8 to 8.4 (stable pH with high buffering capacity) and in fresh water from 6 to 7.5.

Examples of pH in natural waters

Bay of Brest	Fos sur Mer	Fresh water
8	7.95	6 - 7.5

Definitions in glossary

Persistence in the environment

The risk presented by phosphoric acid for the environment is due to hydronium ions (pH effect). The effect of phosphoric acid therefore depends on the buffering capacity of the aquatic or terrestrial ecosystem. A pH of less than 5.5 is harmful for aquatic life. The effect of this ion is naturally reduced by dilution and in seawater by a buffering effect.

Risks for the environment

A high concentration of phosphoric acid in the water will increase the acidity of the water, which can be harmful for aquatic life.

In seawater, some types of algae can survive at a pH of 6, but cannot endure a decrease in pH to less than 5.5.

Fresh water fish cannot survive at a pH of less than 4.5. Marine organisms generally cannot endure significant variations in pH (see Figure 1).

Breakdown

The acidity of the water due to phosphoric acid may be rapidly reduced by the minerals present, and the phosphates will be consumed as nutritive salts.

Bioaccumulation

Phosphoric acid is a substance which does not bioaccumulate along the food chain.

Indirect pollution

Although the phosphate ions formed by the dissociation of phosphoric acid are nutritive salts for aquatic organisms, concentrations of over 0.1 mg/L of inorganic phosphorus can act as fertilisers for macroscopic or microscopic algae, causing objectionable effects in areas of low aeration or semi-closed areas (decrease in oxygen content).

Phosphoric acid is an acid which cause the release of the metal ions contained in the mud or sediments present at the base of the water column (case for lakes and ports).

Partition coefficient for octanol and water (Log Kow): 0.31 (CHEMMAP database).

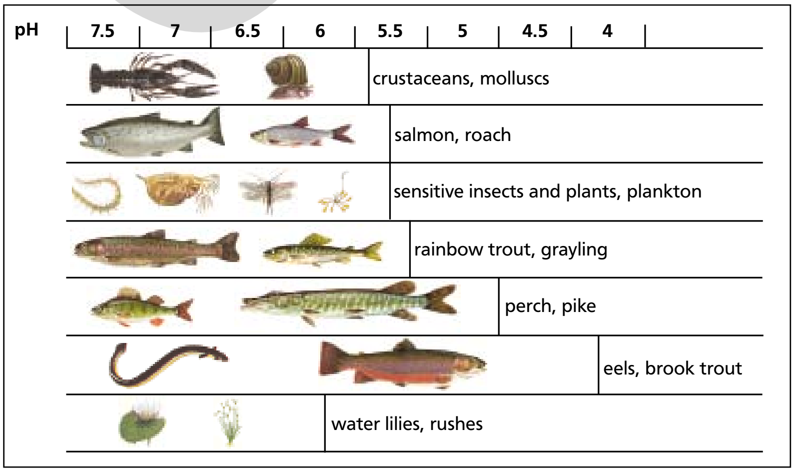


Figure 1: Degrees of acidity tolerated by the fresh water environment
(Diagram designed based on the Atmosphere, Climate & Environment Information Programme)

Classification

IBC classification (IMO, 2007)

- Hazards: S/P (safety/pollution risk)

- Ship type: 3

- Tank type: 2G (integral gravity tank)

- Tank vents: open

- Controlled venting:
  no particular requirements

- Electrical equipment:
  class i’’’: NF (non-flammable)

- Gauging: O (open type)

- Vapour detection: no

- Fire protection: no

- Emergency equipment:
  no particular requirements

SEBC classification: D (dissolver)

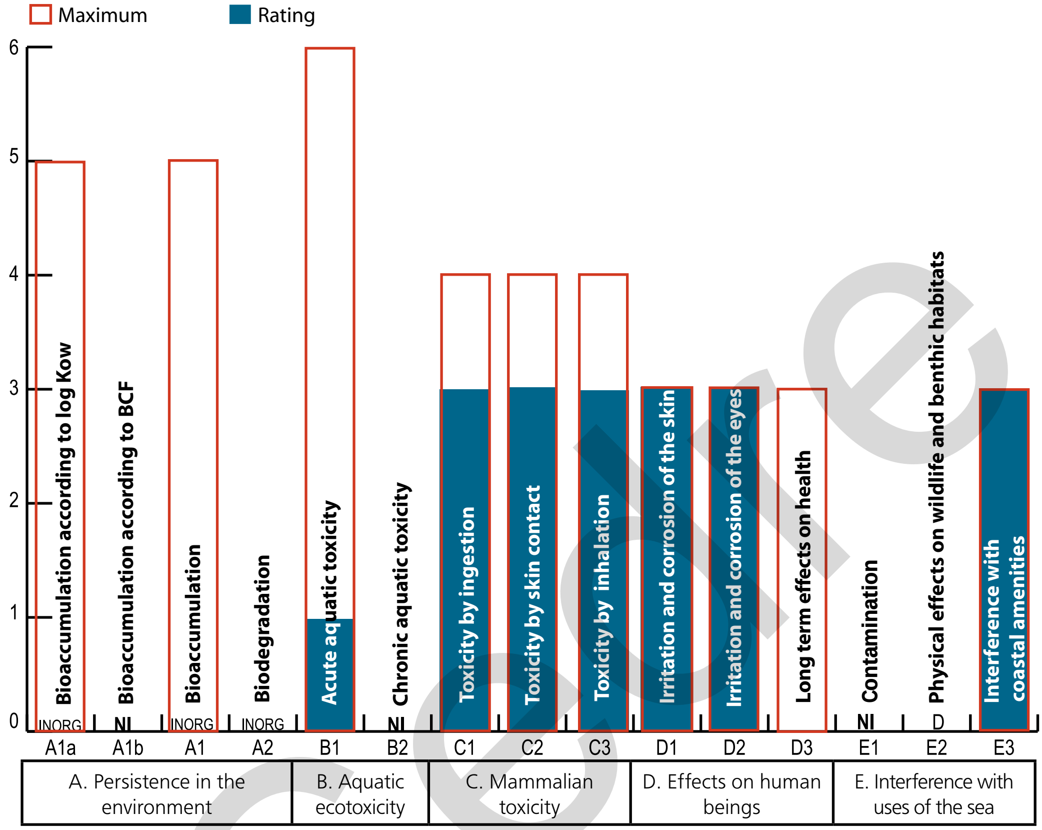
MARPOL classification: Z
(see Annex 4)

EU classification:

C: corrosive

R34	Causes burns.
S1/2	Keep locked up and out of the reach of children.
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S45	In case of accident or if you feel unwell, seek medical advice immediately (show label where possible).
EC n° (EINECS)	231-633-2

GESAMP classification of (purified) phosphoric acid: (GESAMP, 2007)



Graph 1: GESAMP classification of phosphoric acid

A1a:	inorganic substance
A1b:	**N**o **I**nformation
A1:	inorganic, non-bioaccumulable product
A2:	inorganic product
B1:	practically non-toxic
B2:	**N**o **I**nformation
C1:	relatively high toxicity through ingestion by mammals.
C2:	relatively high toxicity through skin contact with mammals.
C3:	relatively high toxicity through inhalation by mammals.
D1:	severely irritating or corrosive to the skin
D2:	severely irritating to the eyes
D3:	no long term effects
E1:	**N**o **I**nformation
E2:	substance which dissolves (**D**issolves)
E3:	highly objectionable, closure of amenity.

Particular risks

Danger (CEFIC ERICARD, 2007)

- Heating the recipient provokes an increase in pressure with a risk of shattering.
- Release of corrosive and irritating vapours in the case of fire.
- Possibility of metals being attacked and hydrogen being produced, possibly forming an explosive mixture with air.
- The vapours are invisible and heavier than air. They spread out across the ground and can infiltrate sewer systems and basements.

Stability and reactivity (INRS, 1997; CSST, 2006; DEKKER, 1968)

- Stable at room temperature and in normal conditions of use.
- Phosphoric acid is a corrosive substance (effect varies according to the concentration). It attacks most metals (in particular iron, zinc and aluminium). Its corrosivity increases with the temperature and when the acid contains impurities such as fluorine and chlorine products (technical grade phosphoric acid).
- Phosphoric acid reacts energetically with bases and violently with nitrates, chlorates and calcium carbide, causing fire and explosion.
- Due to heat action, phosphoric acid undergoes dehydration from 160°C and becomes pyrophosphoric acid. At over 300°C, it turns into metaphosphoric acid then polyphosphoric acid.
- Dangerous products of decomposition: at over 200 to 300°C, phosphoric acid, due to heat action, breaks down, giving off corrosive vapours and toxic gases (phosphorus oxides).
- Upon contact with sulphides, cyanides, carbonates, fluorides and phosphides, phosphoric acid solutions can produce highly toxic and flammable gases.
- Phosphoric acid solutions can react with chemicals such as aldehydes, amines, amides, alcohols and glycols. Phosphoric acid in solution can accelerate the violent polymerisation of certain compounds such as epoxides and accelerate the breakdown of unstable compounds such as nitrate compounds.
- Solid or very concentrated phosphoric acid: hygroscopic product which absorbs water from damp air.

Transportation, handling, storage

Transportation

Identification n° (UN): 1805

Land transportation:

RID (rail) /ADR (road)
Proper shipping name: liquid phosphoric acid
Danger n°: 80
Class: 8
Packaging group: III
Classification code: C1 (liquid inorganic acid)
Danger labels: 8
Tunnel restriction code: E

Transportation via inland waterways:

ADN/ADNR
Class: 8
Classification code: C1 (liquid inorganic acid)
Danger labels: 8
Packaging group: III
Tunnel restriction code: E

Maritime transport: IMDG

Class or division: 8
Packaging group: III
Marine pollutant (MP): No
Danger labels: 8

Air transport: IATA

Class or division: 8
Subsidiary risk: -
Packaging group: III
Hazard label: corrosive

Handling (INRS, 1997)

The recommendations relating to storage areas are applicable to areas where phosphoric acid or its aqueous solutions are handled.

- Inform personnel of the risks presented by the product, precautions to be respected and measures to be taken in the event of a spill.
- Avoid inhalation of vapours and aerosols when the product is being heated. Wherever possible, carry out industrial operations in closed apparatus. In all cases, capture emissions at their source. Provide nearby respiratory protective apparatus and protective equipment suitable for short periods of work, of an exceptional nature, or for emergency response.
- Avoid contact of the product with the skin and eyes. Provide personnel with protective clothing, boots, gloves and safety goggles. Keep equipment in good condition and clean after use.
- Provide safety showers and eye fountains systematically in workplaces where the product is handled.
- When transferring, diluting, dissolving etc. the product, be sure to prevent localised overheating, projections of liquid and vapour emissions. Never prime a siphon using the mouth, rather use specially designed equipment for this purpose.
- Never conduct operations on or in tanks containing or having contained phosphoric acid or its aqueous solutions without taking the necessary precautions.
- Do not release phosphoric acid solutions into the sewer system. Discharge may only be disposed of after neutralisation by alkaline agents and dilution.
- Dilute the product immediately in plenty of water in the event of a leak or small spill. If the quantities spilt are significant, evacuate the personnel and only leave trained and equipped response teams to conduct response.
- Store waste in specially designed containers and tanks. To dispose of this waste, dilute and neutralise it at appropriate facilities.

When the quantities needing destroyed are significant, dispose of them according to the conditions set out by the regulations (processing by a specialised company or centre).

Storage (INRS, 1997)

- Store phosphoric acid in a cool, well ventilated place, out of direct sunlight and away from all sources of heat or ignition and products liable to react with it.
- Keep away from all metal or metal object liable to react when in contact with phosphoric acid to give off hydrogen.
- Store on impermeable ground in the form of a retention tank so that in the event of a spill the solutions do not spread outside the storage facility.
- Containers should be tightly closed and clearly labelled. Relabel in the event of damage to packaging.
- Provide protective equipment nearby and outside of the storage facility, in particular self contained breathing apparatus, a high flow water supply, safety showers and eye fountains, in case of accident.

Use

Eliminate all sources of ignition at metal tank openings. Phosphoric acid is non-flammable, however its corrosive action on many metals can result in the release and accumulation of hydrogen.

Incompatible products

A violent reaction can be generated upon contact with metals, strong bases and with nitrates, chlorates and calcium carbides.

Phosphoric acid can also react with aldehydes, amines, alcohols, glycols, cyanides, ketones, phenols, esters, sulphides and halogenated organic substances.

Recommended packaging materials

(INRS, 1997; DEKKER, 1968)

Commercial phosphoric acid solutions are generally stored in stainless steel containers (type 316) or containers lined with an acid resistant coating (coated steel: ebonite, natural rubber, butyl, neoprene), or in containers made of polyethylene, polyester or glass fibre reinforced PVC. Glass can also be used for small quantities; in this case cylinders can be protected by a more resistant, suitably adjusted metal envelope.

Results of accident scenarios

Reminder of properties

Transportation

Phosphoric acid is transported in liquid form in bulk by chemical tankers.

Vapour density and tension

- Relative density: 1.57 to 25°C
- Vapour density: 3.4
- Vapour tension: 267 Pa at 20°C

Solubility

Totally soluble product.

Behaviour of phosphoric acid when spilt in water

A 75% solution of phosphoric acid is miscible in water. When spilt in water, it sinks (density 1.57) and mixes with water, giving off rapidly absorbed heat.
The mixture of the acid with seawater acidifies the water (H_3PO_4 has three acid functions), but this is more or less buffered by the slightly alkaline seawater (pH 8).
Dissolution in water produces $H_2PO_4^-$, HPO_4^{2-} (dominant species at $7 < pH < 12$) and PO_4^{3-} ions.

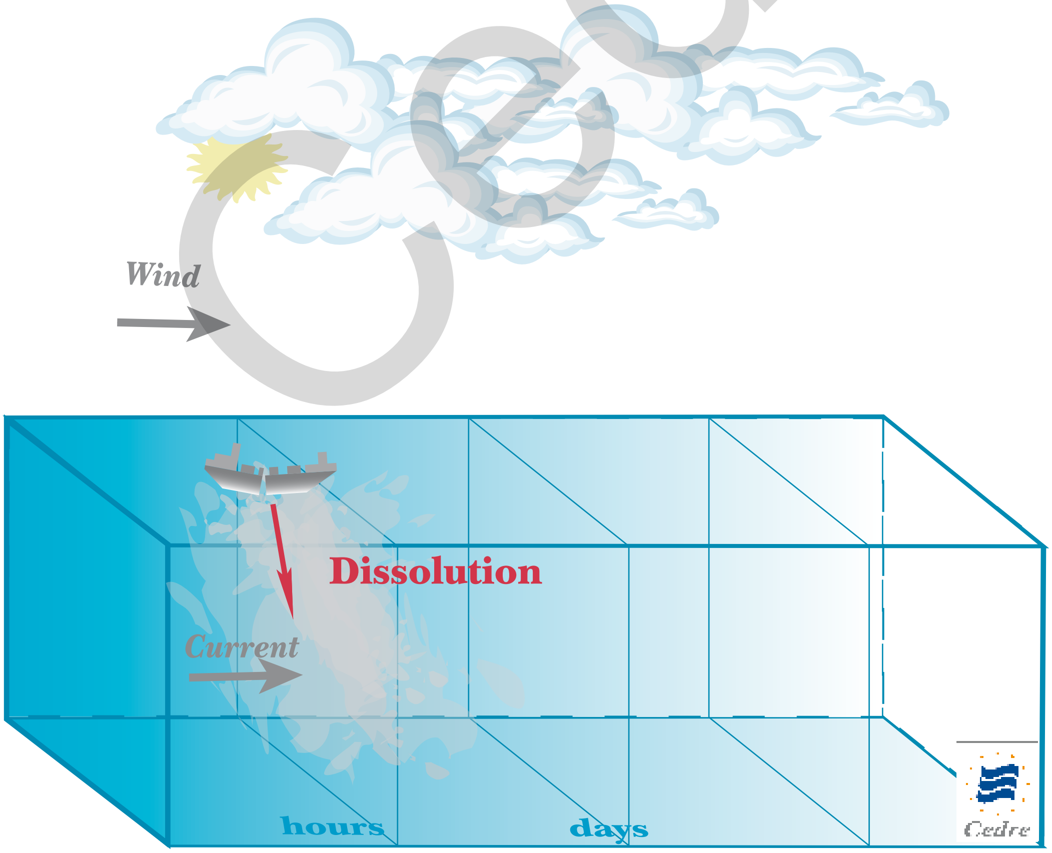


Figure 2: behaviour of phosphoric acid when spilt in water.

Accident scenarios

The scenarios defined here are simply designed to give an indication of the possible behaviour of phosphoric acid. In the event of a real spill, the results of simulations will naturally be different from those given here. We used CHEMMAP and ALOHA behaviour models, the emergency response models available to *Cedre*. Other more sophisticated models exist, but require response times which are incompatible with an emergency situation.
Four phosphoric acid spill scenarios are given here with different quantities of spilt acid:

- an **open sea scenario** (Channel) with three different spill rates:
4 t/h
20 t/h ➔ 5 hours
500 t ➔ instantaneous
- a **wreck scenario** (Channel) with two different spill rates:
100 t/h
200 t/h ➔ 5 hours
- a **port scenario** (Cherbourg) with an instantaneous spill of 200 t.
- a **river scenario** with a spill rate of 4 t/h for 5 hours.

The scenarios

A Channel scenario

- Location: 50°N; 3°W
- Air and water temperature: 10°C
- Two wind speeds: 3 and 10 m/s (NW)
- Tidal currents
- Spill depth: 1 m
- Model time step: 15 minutes.
- Duration of spill:
  - 5 hours
  - instantaneous

B Wreck scenario

- Location: 49°27N; 3°15W
- Air and water temperature: 10°C
- Wind speed: 10 m/s (NW)
- Tidal currents
- Spill depth: between 80 and 90 m
- Model time step: 15 minutes.
- Duration of spill: 5 hours

C Port scenario

- Location: port of Cherbourg
49°39,08 N; 1°36,67 W
- Air and water temperature: 15°C
- Wind speed: no wind
- No current
- Spill depth: at the surface
- Model time step: 15 minutes.
- Duration of spill: instantaneous

D River scenario

- Depth: 4 to 5 m; width: 150 m
- Air and water temperature: 15°C
- Wind speed: 3 m/s
- Current speed: 0.12 m/s
- Model time step: 15 minutes.
- Duration of spill: 5 hours

Modelling

CHEMMAP and ALOHA software was used to model hypothetical spillages of phosphoric acid in the aquatic environment.

ALOHA is a Gaussian atmospheric dispersion model, developed by NOAA and US EPA. This model is used to estimate the spread of the gas cloud.

CHEMMAP is a chemical spill model designed by ASA (Applied Science Associates, Inc - USA) which predicts the movement and fate of the spilt product in fresh and sea water. This model indicates both the movement of the product on the water surface and its distribution in the environment (evaporation, dissolution in the water column...). The time step used for the calculations is fifteen minutes.

Example of results obtained after a spill of 500 t of phosphoric acid in the Channel.

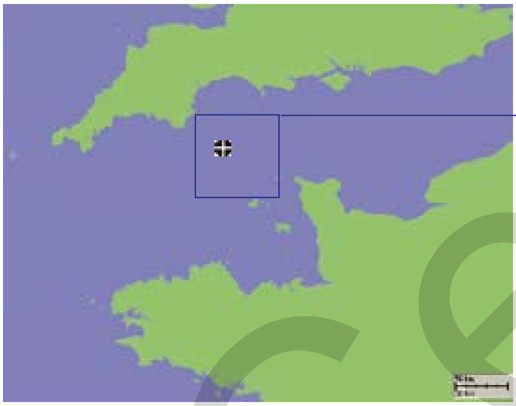


Figure 3: location of a hypothetical spill in the Channel

Figure 4: view of the dissolved part after 48 hours

⊕ Spill location

The CHEMMAP model does not take into account the buffering capacity of seawater. Graphs therefore had to be drawn up (cf. Annex 1) in order to obtain the pH values in the aquatic environment according to the concentration of phosphoric acid spilt in this environment (cf. Tables 3 and 4).

mg/m^3	seawater	g/L	pH
1 to 10,000	🟧	10^{-6} to 10^{-2}	little change from initial pH
10,000 to 15,000	🟨	10^{-2} to 1.5×10^{-2}	little change from initial pH
15,000 to 60,000	🟩	1.5×10^{-2} to 6×10^{-2}	7 > pH > 6
60,000 to 170,000	🟩	6×10^{-2} to 0.17	6 > pH > 5
170,000 to 400,000	🟦	0.17 to 0.4	5 > pH > 2
400,000 to 10,000,000	🟦	0.4 to 10	pH < 2

Acceptable concentrations (pH > 7)

Table 3: Concentrations of dissolved phosphoric acid and corresponding pH ranges in seawater

mg/m³	fresh water	g/L	pH
1 to 3,000	🟧	10^{-6} to 0.3×10^{-2}	little change from initial pH
3,000 to 27,000	🟨	0.3×10^{-2} to 2.7×10^{-2}	6 < pH < 7
27,000 to 44,000	🟩	2.7×10^{-2} to 4.4×10^{-2}	5 < pH < 6
44,000 to 62,000	🟩	4.4×10^{-2} to 6.2×10^{-2}	4 < pH < 5
62,000 to 150,000	🟦	6.2×10^{-2} at 0.15	3 < pH < 4
> 150,000	🟦	> 0.15	pH < 3

Acceptable concentrations (pH > 6)

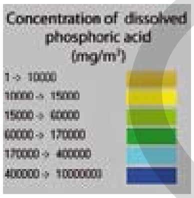
Table 4: concentrations of dissolved phosphoric acid and corresponding pH ranges in fresh water

Key used in this guide

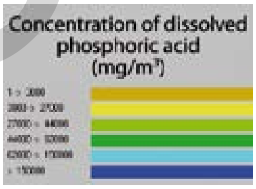
- for the graphs

— Quantity dissolved — Quantity decayed

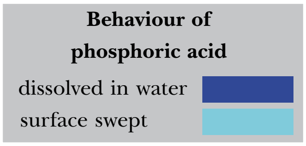
- for seawater concentrations



- for fresh water concentrations



- for the behaviour of phosphoric acid



- for the illustrations

⌖ Spill location

🟥 Observation point

— Section line

A- Results of the Channel scenario

Maximum concentrations according to the spill rate, with a wind speed of 3 m/s

	Maximum concentration of phosphoric acid found	Time after the spill	Distance from spill location
4 t/h for 5 hours	C_{max}* = 1,650 mg/m^3	15 min	620 m
20 t/h for 5 hours	C_{max} = 8,200 mg/m^3	15 min	620 m
500 tonnes spilt instantaneously	C_{max} = 660,000 mg/m^3	15 min	500 m
	C_{accept}** < 15,000 mg/m^3	3 h 30	1.5 km

Maximum concentrations according to the spill rate, with a wind speed of 10 m/s

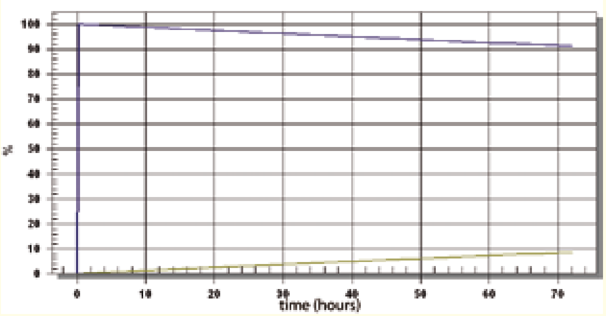
	Maximum concentration of phosphoric acid found	Time after the spill	Distance from spill location
4 t/h over 5 hours	C_{max}* = 1,450 mg/m^3	15 min	650 m
20 t/h over 5 hours	C_{max} = 7,300 mg/m^3	15 min	600 m
500 tonnes spilt instantaneously	C_{max} = 540,000 mg/m^3	15 min	650 m
	C_{accept}** < 15,000 mg/m^3	3 h 15	5 km

* Maximum concentration of phosphoric acid obtained in the water column

** Concentration at which the pH of the water remains acceptable (> 7) (see Table 3)

The spill scenarios involving spills of 4 t/h for 5 hours and 20 t/h for 5 hours do not cause any significant alteration to the pH of the surrounding environment: the maximum concentrations detected remain well below 15,000 mg/m^3 (concentration at which the pH is greater than or equal to 7). We will therefore **only study the consequences of the scenario involving 500 tonnes spilt instantaneously.**

Instantaneous spill of 500 tonnes of phosphoric acid, with a wind speed of 3 m/s.



Graph 2

— Quantity dissolved — Quantity decayed

From the beginning of the spill, we can see that all the phosphoric acid is found in the water column. After 72 hours, 90% of the phosphoric acid has dissolved, while the rest has been broken down.

Surface area covered by the phosphoric acid according to the wind

Wind speed	T + 24 h	T + 48 h	T + 72 h
3 m/s	158 km^2	281 km^2	355 km^2
10 m/s	590 km^2	1,300 km^2	2,170 km^2

Table 5

T = beginning of spill

The stronger the wind, the larger the surface area liable to be affected by the acid.

Behaviour of the 500 tonnes of phosphoric acid spilt instantaneously, according to the wind speed

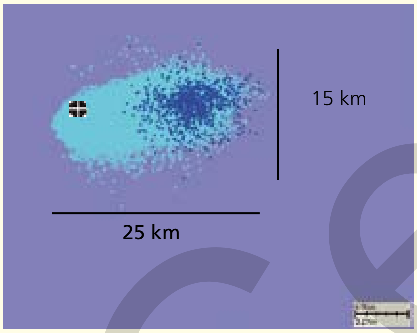


Figure 5: behaviour of the acid with a 3 m/s wind

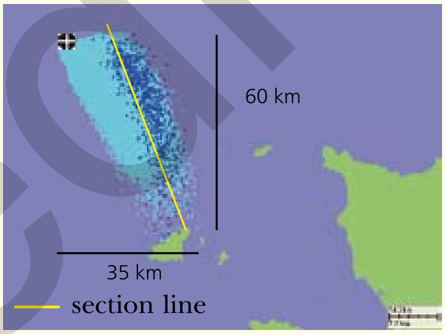


Figure 6: behaviour of the acid with a 10 m/s wind

With a 3 m/s NW wind, the surface area liable to be affected is 25 km by 15 km, for a 72 h simulation.

With a 10 m/s NW wind, the surface area liable to be affected is 60 km by 35 km, for a 72 h simulation.

Behaviour of phosphoric acid

dissolved in water 🟦
surface swept 🟦

— Section line
✚ Spill location

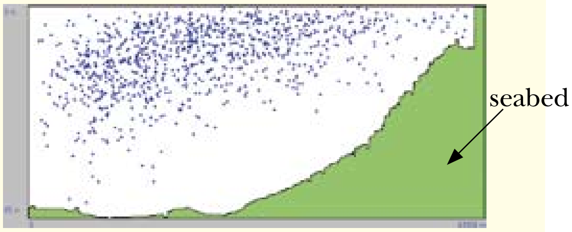


Figure 7: cross section of the water column

Figure 7 shows the depth of the water mass affected by the phosphoric acid with a 10 m/s wind. This acid spreads throughout the entire depth of the water column once it has dissolved. The water mass is influenced by the wind.

Concentrations of phosphoric acid dissolved in the water column and area where the pH is less than 7, according to the wind speed

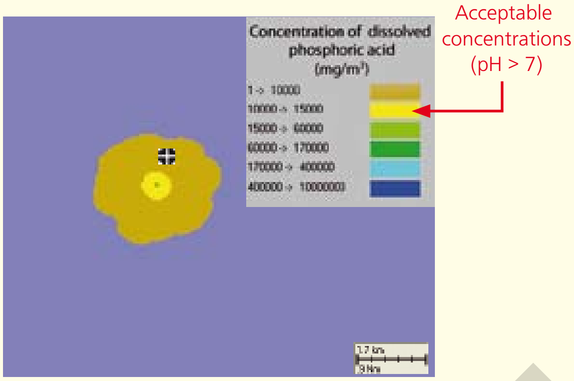


Figure 8: aerial view of dissolved part with a wind speed of 3 m/s

For a wind speed of 3 m/s, an area where the pH is less than 7 is detected up to 3 hours and 30 minutes after the beginning of the spill. The maximum extension of this area is 3.2 km south of the spill location, 2 hours after the beginning of the spill.

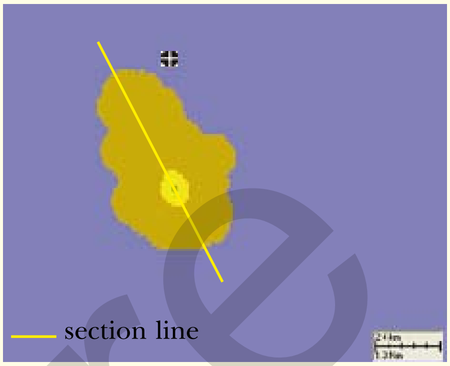


Figure 9: aerial view of dissolved part with a wind speed of 10 m/s

For a wind speed of 10 m/s, an area where the pH is less than 7 is detected up to 3 hours and 15 minutes after the beginning of the spill. The maximum distance reached by pH < 7 is around 5 km south of the spill location, 3 hours and 15 minutes after the beginning of the spill.

Figure 10: cross section of dissolved part with a wind speed of 10 m/s

Figure 10 shows the depth of the water column affected by the phosphoric acid, with a wind speed of 10 m/s. The depth reached 3 hours and 15 minutes after the beginning of the spill is around 23.5 metres.

B- Results of the wreck scenario

A wreck is lying on the seabed between 80 and 90 m below the surface not far from an inhabited coastline and begins to leak.

The leak causes the **continuous release of 500 tonnes (B1) or 1,000 tonnes (B2) of phosphoric acid over 5 hours from the tanks of the wreck.**

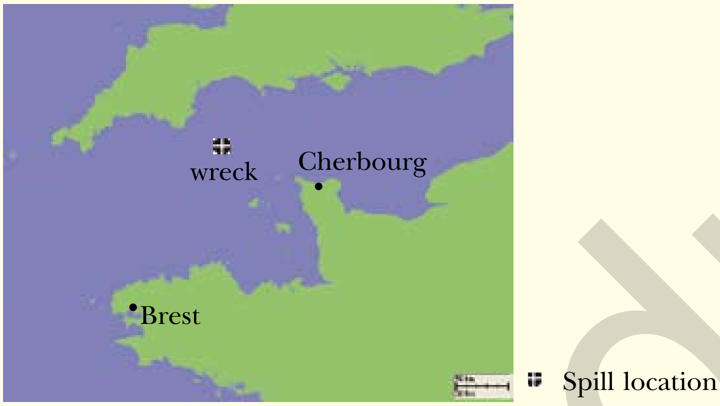


Figure 11: location of the wreck

B1- Spill of 100 t/h of phosphoric acid for 5 hours, with a wind speed of 10 m/s.

Concentrations of phosphoric acid dissolved in the water column, obtained 30 minutes after the beginning of the spill

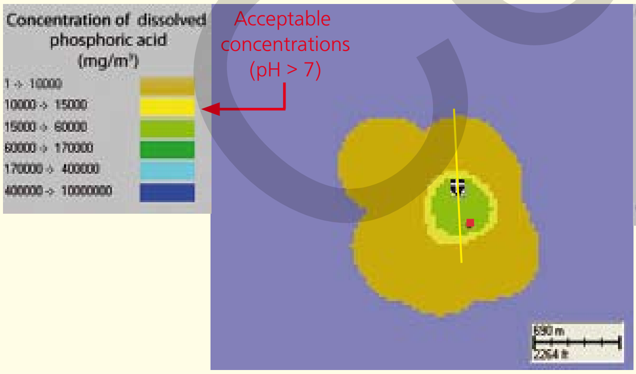


Figure 12: aerial view of dissolved part

Figure 13: cross section of dissolved part

- Spill location
- 🟥 Observation point
- — Section line

The phosphoric acid dissolves gradually but mainly remains on the seabed (from about 87 to 74 metres deep).

Maximum concentration at the observation point

	Maximum concentration reached for the duration of the scenario and corresponding pH	
Up to 350 m south of the spill location	3×10^{-2} g/L	6.8

Behaviour of phosphoric acid 48 hours after the spill

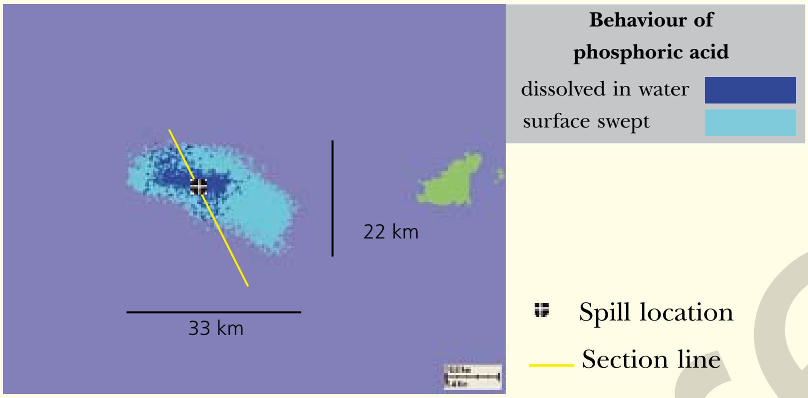


Figure 14: behaviour of the acid, aerial view

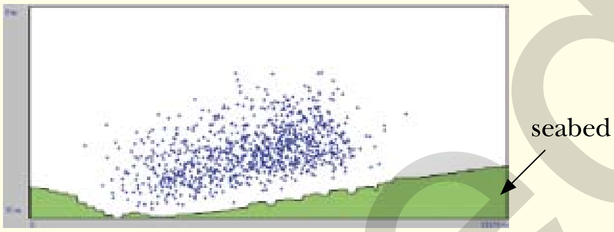


Figure 15: behaviour of the acid, cross section

The surface area swept by the phosphoric acid is around 33 km by 22 km. The spilt acid dissolves in the water column over a depth of around 60 metres from the seabed.

Concentrations of phosphoric acid dissolved in the water column, obtained 48 hours after the beginning of the spill

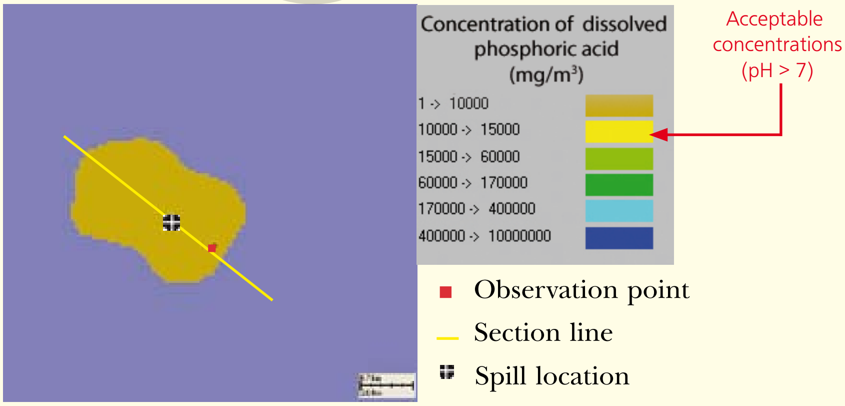


Figure 16: aerial view of dissolved part

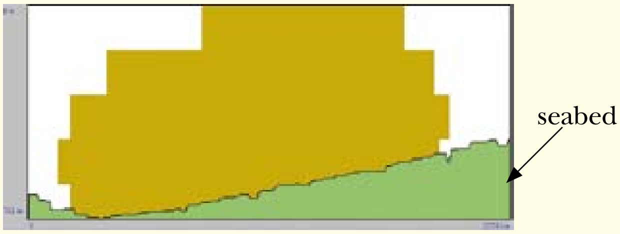


Figure 17: cross section of dissolved part

Forty-eight hours after the beginning of the spill, the maximum concentrations of phosphoric acid do not exceed 10,000 mg/m^3 (0.01 g/L), therefore the pH is greater than 7.

Maximum concentration at the observation point

	Maximum concentration reached for the duration of the scenario and corresponding pH	
Up to 7 km south east of the spill location	7×10^{-4} g/L	little change from initial pH

B2- Spill of 200 t/h of phosphoric acid for 5 hours, with a wind speed of 10 m/s.

Concentrations of phosphoric acid dissolved in the water column, obtained 30 minutes after the beginning of the spill

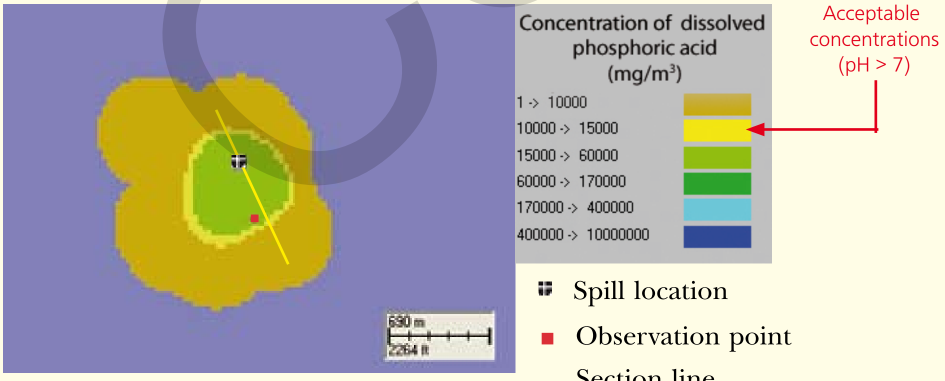


Figure 18: aerial view of dissolved part

Figure 19: cross section of dissolved part

The phosphoric acid dissolves gradually but mainly remains on the seabed (from about 87 to 74 metres deep).

Maximum concentration at the observation point

	Maximum concentration reached for the duration of the scenario and corresponding pH	
Up to 450 m south of the spill location	5×10^{-2} g/L	6.3

Behaviour of phosphoric acid 48 hours after the spill

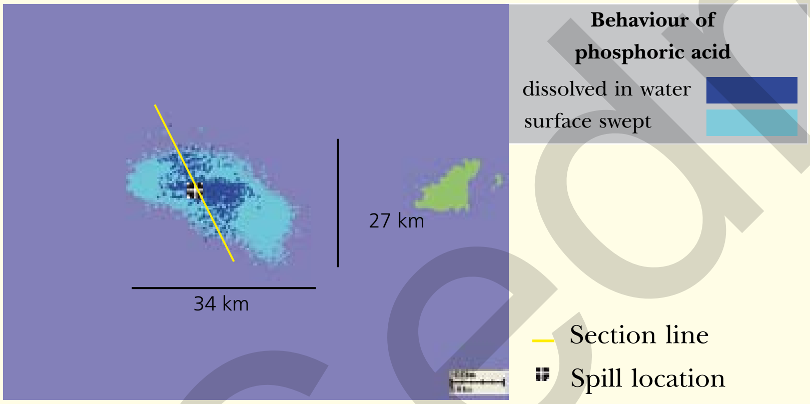


Figure 20: behaviour of the acid, aerial view

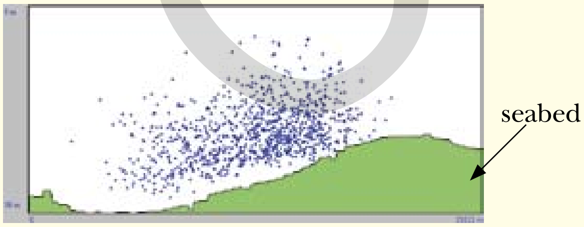


Figure 21: behaviour of the acid, cross section

The surface area swept by the phosphoric acid is around 34 km by 27 km. The spilt acid dissolves in the water column over a depth of around 80 metres from the seabed upwards.

Concentrations of phosphoric acid dissolved in the water column, obtained 48 hours after the beginning of the spill

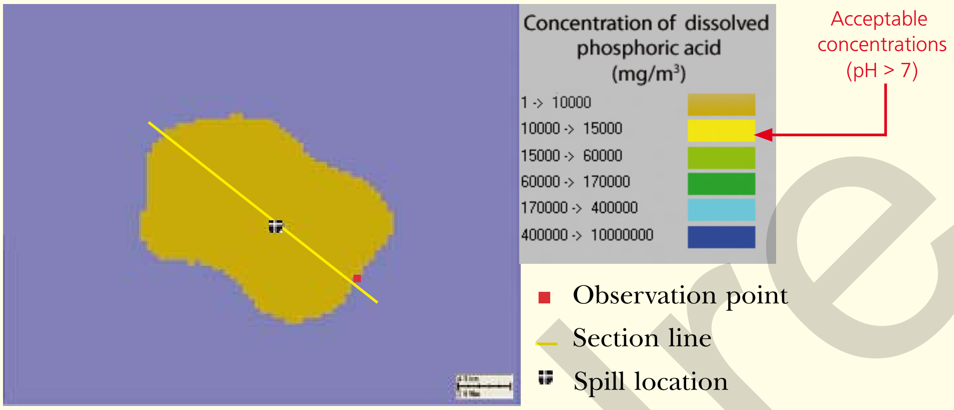


Figure 22: aerial view of dissolved part

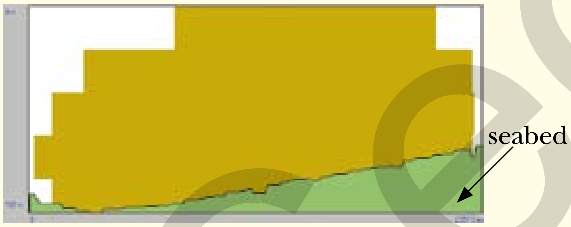


Figure 23: cross section of dissolved part

Forty-eight hours after the beginning of the spill, the phosphoric acid affects the entire depth of the water column. The maximum concentrations are lower than 10,000 mg/m³ (0.01 g/L). The pH is therefore greater than 7.

Maximum concentration at the observation point

	Maximum concentration reached for the duration of the scenario and corresponding pH	
Up to 9 km south east of the spill location	5×10^{-4} g/L	little change from initial pH

C- Results of the port scenario

Instantaneous spill of 200 tonnes of phosphoric acid on the surface, with no wind and no current.

Behaviour of phosphoric acid 48 hours after the spill

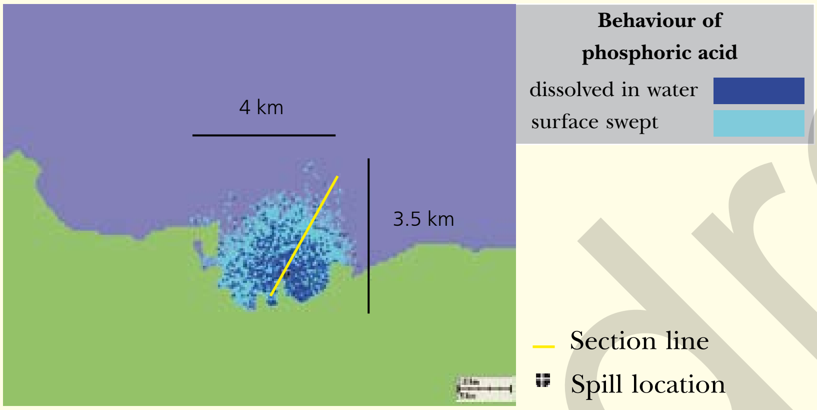


Figure 24: behaviour of the acid, aerial view

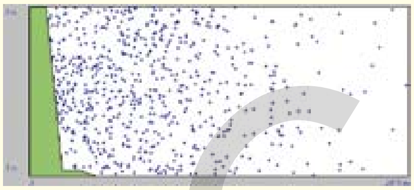


Figure 25: behaviour of the acid, cross section

The surface swept by the phosphoric acid is around 3.5 km north by 4 km from east to west. The spilt acid dissolved throughout the entire depth of the water column, i.e. 3 metres.

Concentrations of phosphoric acid dissolved in the water column, obtained 30 minutes after the beginning of the spill

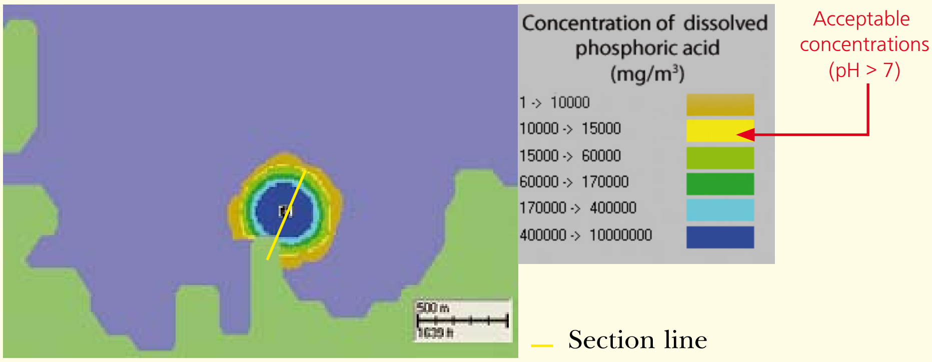


Figure 26: aerial view of dissolved part

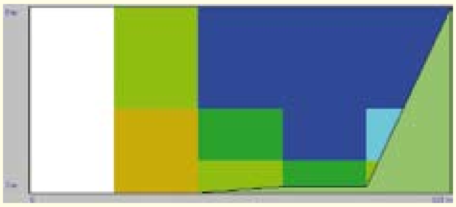


Figure 27: cross section of dissolved part

Thirty minutes after the spill, the maximum concentrations of phosphoric acid reach more than 10,000,000 mg/m^3 (10 g/L), over a diameter of around 650 metres. The pH of this area is less than 2.

Concentrations of phosphoric acid dissolved in the water column, obtained 48 hours after the beginning of the spill

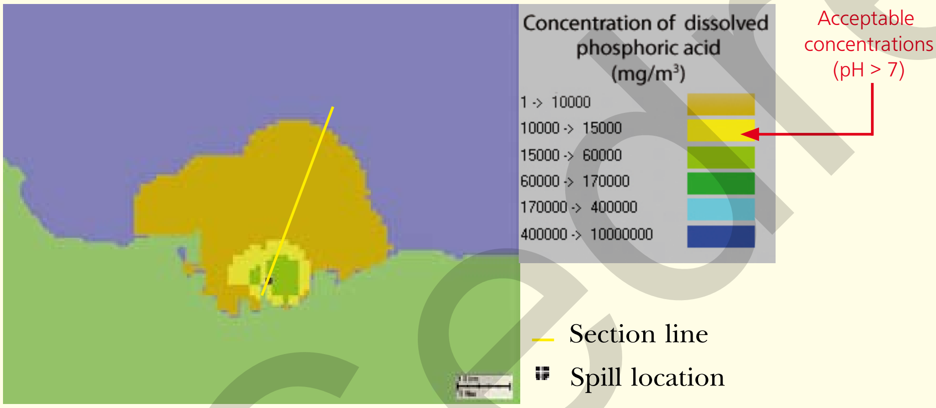


Figure 28: aerial view of dissolved part

Figure 29: cross section of dissolved part

Forty-eight hours after the beginning of the spill, the phosphoric acid affects the entire water column (3 metres). The highest concentrations are between 15,000 and 60,000 mg/m^3 (0.06 g/L) over an area of around 600 metres around the spill location. The pH is between 6 and 7.3. Lower concentrations, less than 15,000 mg/m^3 (0.015 g/L), are then observed up to 3 km from the spill location. Here, the pH varies little from the initial pH, i.e. is greater than 7.

Analysis of maximum concentrations at several sample points

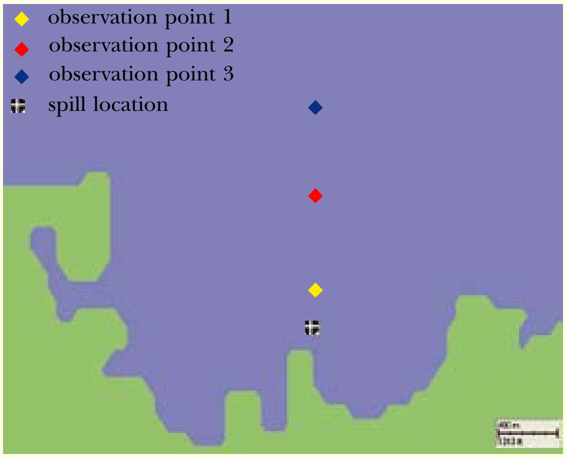


Figure 30: location of observation points

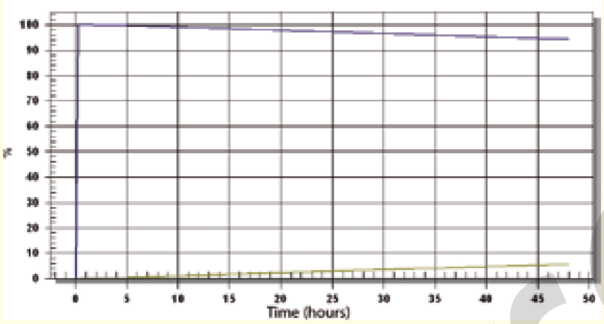
Maximum concentration at the observation points

	Distance from the spill location to the sampling point	Maximum concentration reached for the duration of the scenario and corresponding pH	
Point 1	200 metres	0.29 g/L	2.8
Point 2	900 metres	8.6×10^{-3} g/L	little change from initial pH
Point 3	1,500 metres	3.3×10^{-3} g/L	little change from initial pH

At point 1, the first concentrations of phosphoric acid are detected 15 minutes after the spill. At point 2, they are detected after 3 hours and 45 minutes and at point 3 after 7 hours and 30 minutes.

D- Results of the river scenario

Spill of 4 t/h of phosphoric acid for 5 hours, with a wind speed of 3 m/s and a current speed of 0.12 m/s



Graph 3

▬ Quantity dissolved ▬ Quantity decayed

From the beginning of the spill, we can see that all the phosphoric acid is found dissolved in the water column. Forty-eight hours after the spill, around 95% is found in the water column, while the rest has been broken down.

Behaviour of phosphoric acid 48 hours after the spill

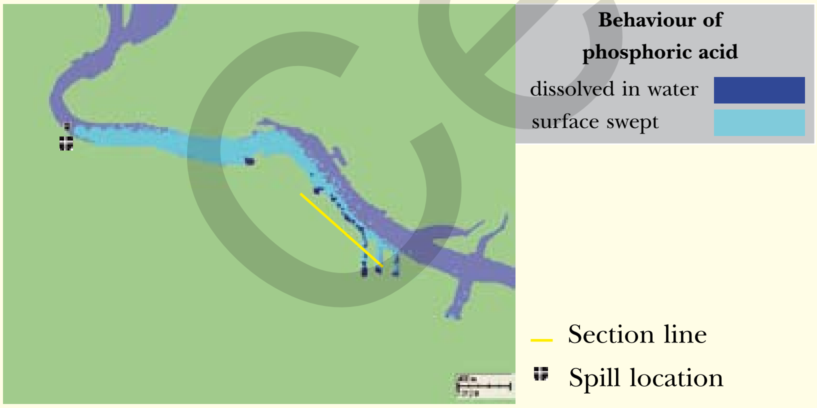


Figure 31: behaviour of the acid, aerial view

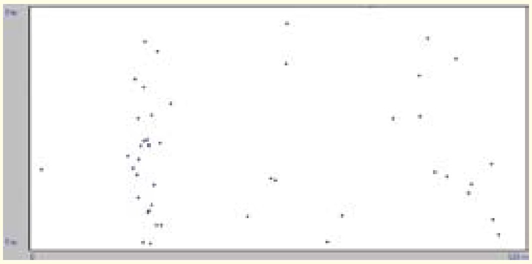


Figure 32: behaviour of the acid, cross section

The surface swept by the phosphoric acid is 3.5 km downstream of the spill location. The cross section shows that the chemical has spread throughout the water column (5 metres deep).

Concentrations of phosphoric acid dissolved in the water column, results obtained 48 hours after the spill

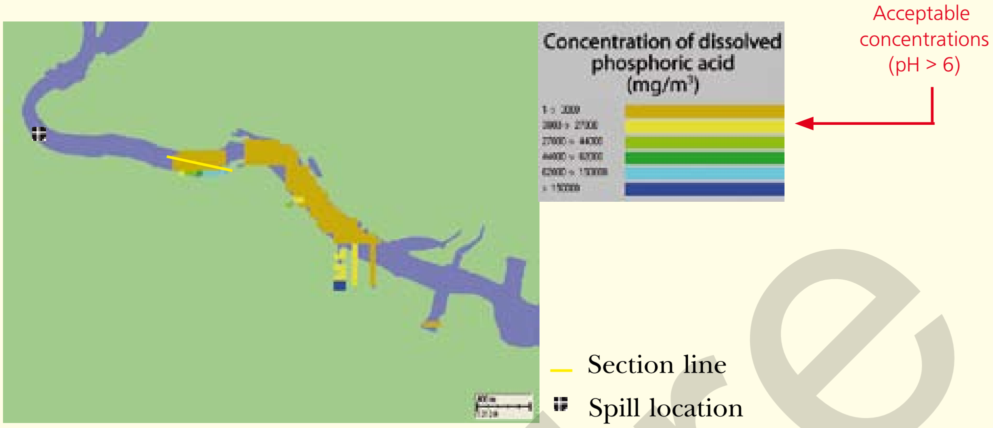


Figure 33: aerial view of dissolved part

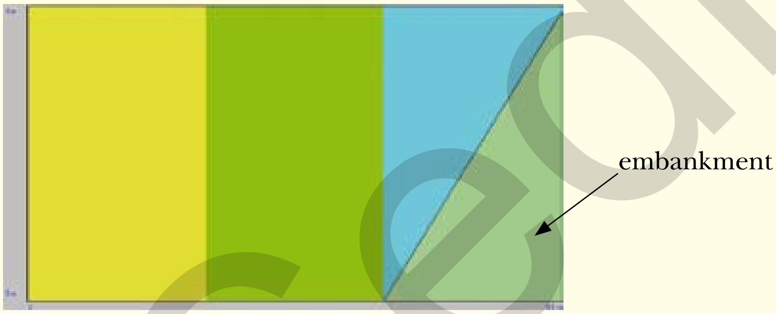


Figure 34: cross section of dissolved part

Forty-eight hours after the spill, the phosphoric acid dissolves up to 3.5 km downstream of the spill location and spreads throughout the entire water column (5 metres). The highest concentrations, greater than 15,000 mg/m³, are found at the most up to 3 km downstream of the spill location. The pH value corresponding to these concentrations is lower than 3.

Consumption scenarios

Phosphoric acid does not bioaccumulate and will not end up in the food chain. No impact on persons consuming sea produce having been exposed to phosphoric acid is expected.

Response

Experience feedback

(CEDRE, 2006; MARINE NATIONALE, 2006)

Collision of the *Ece* (Casquets traffic separation scheme, Channel, 31 January 2006)

Background

On the night of 30 to 31 January 2006, the Maltese bulk carrier the *General Grot Rowecki*, transporting 26,000 tonnes of phosphates collided with the Marshall Islands chemical tanker the *Ece* en route from Morocco. *Ece* is a double hulled chemical tanker built in 1988.

The accident occurred in an area located 50 nautical miles (90 km) west of Cherbourg, near the Casquet traffic separation scheme in international waters.

The *Ece*, transporting 10,000 tonnes of phosphoric acid, developed a leak and a 25° stabilised list to port and was no longer operating.

© Marine nationale

The regional marine rescue coordination centre (CROSS-Jobourg) coordinated the crew rescue operation in collaboration with the British Maritime and Coastguard Agency (MCA). The 22 crew members were safely evacuated to Guernsey.

Once the crew had been evacuated from the *Ece*, it was taken in tow by the *Abeille Liberté* on 31 January, bound for the port of Le Havre. On 1st February, in the course of towing, the vessel sank. The wreck lies in international waters, on the continental shelf of the United Kingdom, in the French exclusive economic zone and the French pollution response zone.

The Manche Plan, a bilateral Franco-British plan for mutual assistance in rescue and pollution response, was activated on 1st February.

On 7 February, experts from *Cedre*, CEPPOL, LASEM and Ifremer, who were monitoring surveillance operations above the chemical tanker, in partnership with Météo France, were gathered together to form an expert committee in view of the upcoming wreck treatment operation which was to be implemented by the shipowner. They were to work in close collaboration with the British MCA experts.

Emergency response

The tanks of the *Ece* contained the cargo of phosphoric acid as well as oil:

Phosphoric acid (10,000 t)
IFO 180 (70 t)
Diesel (20 t)
Lubricating oil (40 t)

The *Abeille Liberté* used 5 m^3 of dispersant, on a surface oil slick, necessary due to the density of the pollution.

The main questions which arose from the beginning were in relation to the products transported by the chemical tanker which had already been spilt through the breach in the hull.

The expert committee set up was to define and advise on actions and equipment to be implemented, i.e. to decide whether the cargo should be pumped out or if release could be an acceptable option.

Risk assessment

The conclusion of the analysis conducted by *Cedre* in relation to the phosphoric acid transported by the *Ece* was as follows: this acid does not represent a risk for the environment except in cases of high concentrations. The product does not accumulate along the food chain.
A fishing ban was imposed within a radius of one nautical mile (1.852 km) around the tanker.

Behaviour in the environment

As of the day following the incident, trials were undertaken in *Cedre*'s laboratory in order to characterise the behaviour of the acid when in contact with water according to natural agitation.

Results of the analysis of this acid:

- immediately after the acid comes into contact with seawater, a small volume of phosphoric acid forms a plume (acid cloud which is rapidly diluted).
- because its density is higher than that of seawater, the majority of the acid will remain trapped at the bottom of the container, and its dilution kinetics will be very slow.
- the dilution of residual acid (quantity of acid trapped at the bottom of the container) may be effectively accelerated by mixing, with assistance, for example, from an injection of water.
- the main impact of a phosphoric acid spill is the significant decrease in pH at the spill location and in the surrounding area; the extent of this decrease depends on the environmental conditions, such as natural agitation, the quantity of water available and the weather.

Risks of eutrophication of the environment due to phosphates
Phosphates are not toxic for marine organisms. They are nutrients for aquatic organisms, but can, in excess, lead to eutrophication phenomena. However, simulations carried out by Ifremer, UGMM (department of the Royal Belgian Institute of Natural Sciences) and the University of Southampton showed that the release of the entire cargo over a short period of time would not lead to a eutrophication phenomenon, due to the rapid dilution in the Channel.

Risks due to impurities

- Trace metals: according to tests conducted by LASEM on a sample of phosphoric acid of the same quality as that of the *Ece*'s cargo, the metals are trace metals and should not reach dangerous concentrations for larvae or crustaceans. The release of these dozens of kilos of metals becomes insignificant in relation to the concentrations of metals brought by rivers, which represent dozens of tonnes.
- Radioactivity: the normal concentration of uranium in seawater is to the order of 3 µg/l. In the event of a release of the entire cargo over 10 days, according to modelling carried out by Ifremer, a local, temporary increase of 0.1 µg/l of uranium (3.3% increase) would be observed. Thus, the uranium concentration in seawater would rise to 3.1 µg/l for around 30 days, before falling back down rapidly to the normal concentration. The level of radioactivity of the cargo does not classify it as a radioactive substance. Finally, the radioactivity of granitic soil is 8,000 Bq/kg, while that of the acid is 4,400 Bq/kg.

Securing the wreck

Pumping out the oil

The response option chosen involved pumping out the oil (IFO 180 and lubricating oil), which was all located in the stern section of the vessel. Around forty tonnes were pumped out of the technically accessible tanks. The main bunker tanks were empty at the time of the incident.

The chemical tanker

The UK Hydrographic Office, in charge of mapping the area, reported that the hull of the *Ece* did not represent a danger for navigation. The wreck therefore remained as it was, without any particular response effort. The chemical tanker is separated from the surface by a water depth of 45 metres. The presence of the *Ece* will be indicated on nautical charts.

Releasing the acid

The impact study conducted by the French and British experts showed that a controlled and programmed release of the phosphoric acid was a possibility, in order to prevent any harmful impact. The release was to be conducted in the marine environment, using a remote controlled robot to open the access panels to each of the six tanks. The simulations and laboratory trials conducted by *Cedre* and Ifremer showed that the impact due to the acid would be restricted to a distance of a few hundred metres around the hull and that after a few days all measurable traces would have disappeared.

A few weeks after the controlled release

The surveillance of the area and the scientific monitoring of the water quality continued at an appropriate rate. The last measurements in the area around the *Ece* were within the range of the average natural concentration of phosphates, which is around 0.05 mg/L with normal fluctuations of up to 0.1 mg/L, thus allowing the ban on fishing and nautical activities in the area to be lifted.

Examples of spills

(BARPI database)

Phosphoric acid spill in MUGRON (France, 06/05/2005)

A trailer containing 3,000 litres of liquid fertiliser, towed by a farm tractor, overturned on a hill. An exclusion zone was set up and the emergency services carried out reconnaissance, equipped with SCBA masks. Around 1,000 litres of fertiliser made from phosphoric acid were spilt into the rainwater drainage system. A hairdressers and a house were evacuated (four people) and the traffic was interrupted on the D3 road in both directions. The emergency services spread sorbents and the damaged trailer was evacuated.

Phosphoric acid spill in LAKELAND (USA, 29/09/2004)

A fertiliser production facility released 15,000 m^3 of acidic water into the environment. The use of phosphogypsum in the production of phosphate fertiliser produces gypsum and phosphoric acid, leading to the production of triple superphosphate. The incident occurred the weekend after hurricane Jeanne hit the area, during which more than 30 cm of rain battered down on the plant. The water level was already high in the process water network after the severe weather conditions due to hurricanes Charley and Frances. The rain therefore caused the process water to overflow, carrying a small quantity of phosphoric acid from the gypsum stack towards the plant. The overflow then spilled into the adjacent basin containing the storm water and into former phosphate mines located around the site. The acidic water ran into the trenches and wells of the former mine site. The employees built dams and attempted to contain the pollution in this area in order to neutralise it before it hit Peace River. Samples taken within an area of 4 km around the plant did not show significant concentrations of acid. A Florida Department of Environmental Protection manager declared that the pollution had been contained and that any impact on the environment had been prevented. The authorities however feared that the acidic effluents had travelled along a drainage pipe from the mine that had not been sealed off. Investigations lasting one to two months were necessary to determine whether the environment had been polluted. This was the second incident in a month involving this company. Three months earlier, in Riverview, 265,000 m^3 of acidic water had been released into Archie Creek Canal, Hillsborough Bay, when a berm on a phosphogypsum stack failed. The operators had to ensure that rain run-off from the gypsum stacks carrying phosphoric acid was contained. The government environmental organisation considered reinforcing the management of gypsum stacks and rain run-off.

Onland spill at BLOIS (France, 20/07/2004)

Eight hundred litres of phosphoric acid from a 1,000 litre container were spilt on the ground. The spill was covered with sand and sorbents.

Dockside spill in the port of LE TREPORT (France, 28/07/2003)

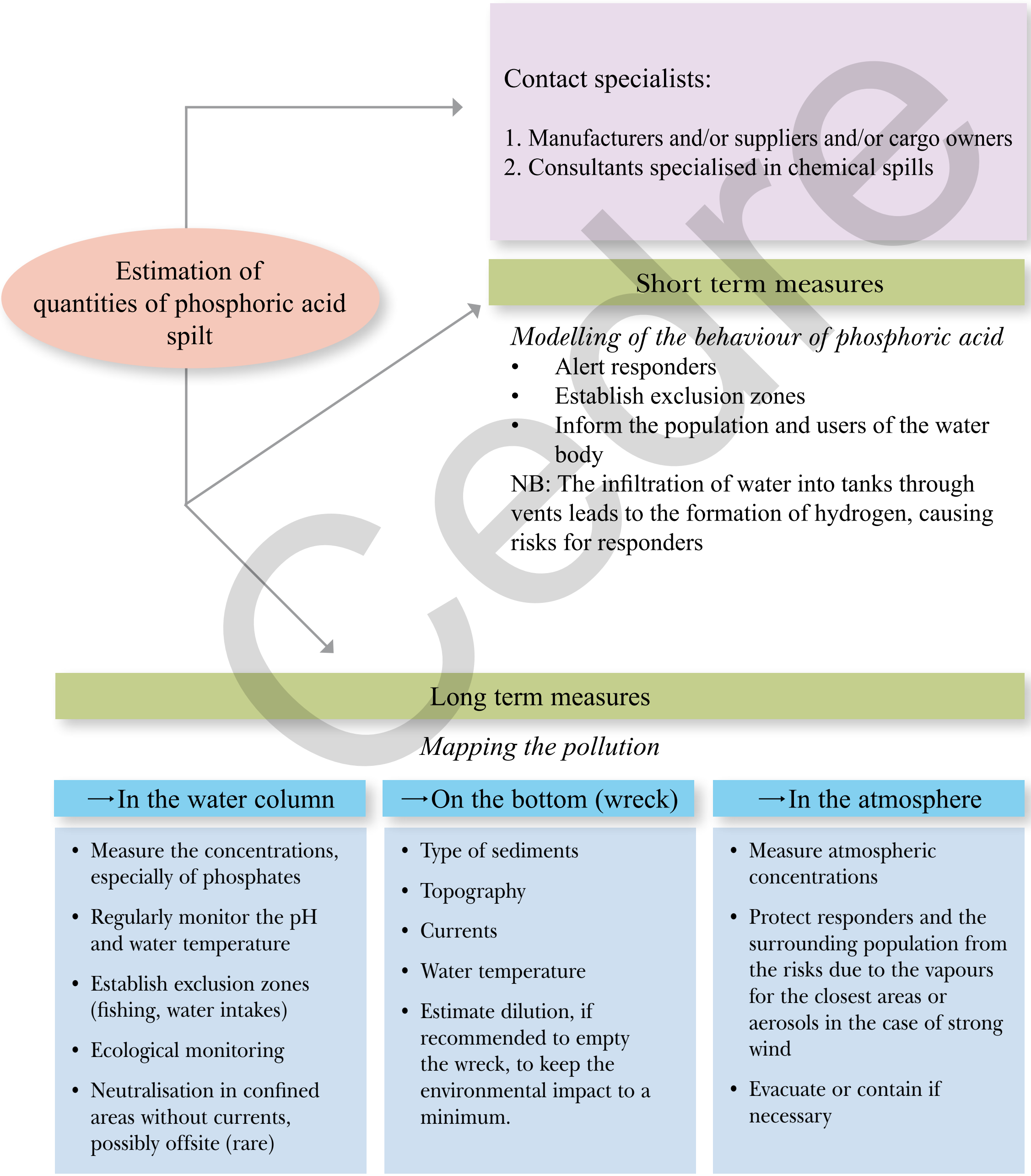
A leak of 75% concentrated phosphoric acid occurred on a pipeline in a fertiliser production plant. Two hundred litres were spilt on the dockside and partly in the harbour basin. The traffic on the dockside was interrupted. The leak was stopped and the acid was neutralised by the plant personnel using sodium carbonate on the ground and sodium carbonate, natural phosphate and potassium chlorate in the water. The measurements taken showed water pollution in the harbour basin over a distance of 200 metres. The pH was 9 on the surface and 7 in the depths.

Spill in a canal in OTTMARSHEIM (France, 20/02/1993)

A wrong manoeuvre during a maintenance operation (not closing a valve) led to a spill lasting 5 hours of 30 tonnes of phosphoric acid into the Grand Canal of Alsace, affluent of the Rhine. The phosphoric acid was diluted in 60,000 m³ of cooling effluents before being dispersed in the waterway. No impact on the environment was reported.

Response recommendations

Diagram showing response actions in the event of a spill



Estimation of quantities of phosphoric acid spilt

Contact specialists:

1. Manufacturers and/or suppliers and/or cargo owners
2. Consultants specialised in chemical spills

Short term measures

Modelling of the behaviour of phosphoric acid

- Alert responders
- Establish exclusion zones
- Inform the population and users of the water body

NB: The infiltration of water into tanks through vents leads to the formation of hydrogen, causing risks for responders

Long term measures

Mapping the pollution

→In the water column

- Measure the concentrations, especially of phosphates
- Regularly monitor the pH and water temperature
- Establish exclusion zones (fishing, water intakes)
- Ecological monitoring
- Neutralisation in confined areas without currents, possibly offsite (rare)

→On the bottom (wreck)

- Type of sediments
- Topography
- Currents
- Water temperature
- Estimate dilution, if recommended to empty the wreck, to keep the environmental impact to a minimum.

→In the atmosphere

- Measure atmospheric concentrations
- Protect responders and the surrounding population from the risks due to the vapours for the closest areas or aerosols in the case of strong wind
- Evacuate or contain if necessary

Is response possible? (CEFIC, 2005; CANUTEC, 2008)

If an incident occurs (vessel, truck, stockpile...), as an immediate prevention measure, set up an exclusion zone with a minimum radius of 50 metres for a liquid and 25 metres for a solid, around the location of the spill or leak.

Response may be envisaged if the following precautions are taken:

- phosphoric acid may come into contact with water: either directly in the sea or any other water body which would rapidly dilute the acid concentrations and restrict the heat release, either in transport tanks or storage tanks. The reaction may be dangerous if the acid is very concentrated. This exothermic reaction may cause projections of liquid (water and acid mixture). Phosphoric acid, in the presence of heat or humidity/water, may react with the steel of a hull or a tank and give off hydrogen. When heated, the acid will produce corrosive and irritating fumes.
- the accident area must be approached from upwind, equipped with Personal Protective Equipment (PPE). The number of responders in the risk area should be kept to a minimum.
- set up a water spray if there is a risk of hydrogen production.
- in theory, the action of phosphoric acid could be neutralised in shallow waters and in limited quantities using bicarbonate of soda. According to tests conducted by *Cedre*, the acid dissolves slowly if there is no agitation and spreads across the bottom in shallow waters.

Emergency measures in the event of a leak or spill (CEFIC, 2005; CANUTEC, 2008)

Ban access to the spill location and prohibit the use of polluted waters. Display signs marked “CORROSIVE”.

- Use breathing apparatus and facial protection and wear a hazmat suit.
- Stop or reduce water flow if doing so is not dangerous.
- Avoid all direct contact with the product and do not inhale vapours.
- Use fireproof equipment.

Emergency measures in the case of a tank fire (CEFIC, 2005; CANUTEC, 2008)

Cool the containers/tanks by spraying with water.

- Beat down gases/fumes/dust by spraying with water.
- Do not use a solid water stream to extinguish the fire.
- Eliminate all sources of sparks or ignition. Do not smoke.
- Ensure that no water leaks into the containers of acid.
- The fire extinguishers which can be used will depend on the products involved in the fire. In certain cases, the use of foam compounds can be considered, or for small fires, use carbon dioxide or chemical powder.

If only water is available, use it in the form of a mist.

Response techniques

Response

(FICHE RÉFLEXE D'INTERVENTION ANTIPOLLUTION "PRODUITS DANS LA COLONNE D'EAU ET SUR LE FOND : LIQUIDES SOLUBLES ET COULANTS", FICHE GUIDE N°3 : "LUTTE EN MILIEU AQUATIQUE", FICHES STRATÉGIES ET MOYENS N°4, 5, 8, 9,13. CEDRE, 2004)

On land

It is essential to intervene as rapidly as possible in order to prevent any polluted water from reaching a sewer system or a waterway. The technique involves containing the acid spill with dams made of earth, sand or other materials or by deflecting it towards an impermeable surface.

In inland waters

As phosphoric acid is highly soluble in water, it is difficult to respond to a spill in water. Where possible, deflect polluted waters immediately after the spill for subsequent storage and treatment. If the polluted water cannot be deflected, a possible response option is to promote dilution. Dilution may occur naturally (for instance in the case of a small stream flowing into a larger river with a faster flow). The pH of the aquatic environment, the phosphate concentration and the temperature must be monitored in the case of an acid spill.

In shallow waters without current

Water intakes must be closed off and the evolution of the pH, phosphate concentration and water temperature regularly monitored. The polluted water mass may be pumped off for treatment in an appropriate treatment plant. Accumulation of the acid can also be prevented by promoting dilution (agitation of the water mass using fire hoses for instance).

At sea

It is important to stop the leak and the flow into the aquatic environment if this is possible and not dangerous. The role of natural dilution must be taken into account in the case of a spill at sea, as well as the buffering capacity of seawater in the event of an acid spill. The environment must be monitored by regularly measuring the pH and temperature. Be careful of spray in the air, due to mixtures of acid and water. In adverse weather conditions, acid aerosols can be transported over long distances by the wind.

NB: Except in a few rare cases (e.g. small harbour basins with no current), it is impossible to recover the polluted water.

If the polluted water is even partially recovered by pumping, it may be neutralised. This involves bringing the pH of the polluted water mass back as close as possible to its usual value. This can be carried out using two different methods: either by natural dilution in a large water mass (spill at sea) or by adding a neutralising agent such as bicarbonate of soda ($NaHCO_3$). This second possibility can only be conducted for small or moderate volumes of pollution due to the quantity of agent needed (2 to 3 times the mass of the product spilt). The agent is added using a fire hose or by directly applying it from the container.

Finally, it is useful for responders to understand the behaviour of phosphoric acid in the water column. This behaviour can be modelled using the CHEMMAP model for the simulation of chemical spills (see C2).

Transshipment

- Phosphoric acid must be unloaded from tanks with extreme caution. Provide storage tanks for the acid or possible acid and water mixture, as well as pumps made of 316 stainless steel, chromium alloy cast iron or coated steel (butyl or equivalent).
- Approach the spill location from upwind and keep the wind behind you throughout response, paying particular attention to any projections of liquid, equipped with breathing apparatus and hazmat suits.
- If hydrogen is formed, the tanks can be emptied by pumping, using an inert gas such as nitrogen. It is essential to inert tanks before pumping.

Choosing Personal Protective Equipment (PPE)

Ensure maximum protection in the case of high or unknown concentrations of phosphoric acid in the atmosphere

Choosing breathing apparatus (CCHST, 1998)

As an indication, in Canada:

- **Up to 25 mg/m³**: supplied-air respirator (SAR), operated in continuous flow mode.
- **Up to 50 mg/m³**: Full-face piece respirator with high-efficiency particulate filter(s); or full-face piece SCBA; or full-face piece SAR.
- **Up to 1,000 mg/m³**: Positive pressure, full-face piece SAR.
- **Concentrations over IDLH (>1,000 mg/m³)**: Positive pressure, full-face piece SCBA; or positive pressure, full-face piece SAR with an auxiliary positive pressure SCBA.

For unknown concentrations:

- **Escape**: Full-face piece respirator with high-efficiency particulate filter(s); or escape-type SCBA.

In France for example, priority is given to the use of inner or outer SCBA (self-contained breathing apparatus). If there is a possibility of acid vapours, inner SCBA is recommended.

Choosing protective clothing

(CCHST, 1998)

In most cases, it is necessary to wear a hazmat suit as well as chemical safety goggles. A face shield, chemical resistant gloves, coveralls, boots and/or other resistant protective clothing may also be necessary. A shower and/or eye-wash fountain must be readily available in the immediate work area.

Recommended gloves: Linear low density polyethylene (LLDPE). A degradation test was not carried out for this chemical. Nevertheless, given the results obtained through the degradation tests for similar compounds, the degradation rating should be good or excellent. The permeation time is greater than 480. The permeability is excellent, with a permeation rate of 0 to ½ drop per hour passing through the glove.

Recommendations for use in the event of a spill (FINGAS M., 2000)

- Open-circuit, pressure demand self-contained breathing apparatus (SCBA) gives the best safety protection. Their protection factor is around 10,000 (e.g. ELV = 0.7 ppm, protection up to 7,000 ppm of phosphoric acid in ambient air temperatures).
- Use SCBA to face a spill situation involving unknown quantities.
- An air-purifying respirator can be used in a stable situation where the concentration of acid does not reach the IDLH value and is unlikely to increase.
- Warning: certain facial features such as a scar, a narrow face shape or facial hair may lead to poor adjustment of the mask and impair the level of protection.
- In warm weather: excessive perspiration reduces the effectiveness of the watertight seal between the mask and the skin.
- In cold weather: ice may form on the regulator and the mask may steam up.
- Warning: ordinary glasses cannot be worn under the mask; special lens holders

exist. However contact lenses can now be used, as new contact lenses allow for gas exchange and thus do not dry out or stick to the eyeball.

- Mask adjustment tests are recommended for new users and regular fit testing for other users.

Measures to take after using PPE in a spill situation (FINGAS M., 2000)

- Decontaminate boots after response. A foot bath and mild detergent can be used. Do not forget to treat the contaminated water.
- Decontaminate gloves separately from boots in a bucket with a mild detergent.
- Only reuse protective suits if they have been cleaned.

Permeation times through different materials (CCHST, 1998)

- Recommended (permeation resistance over 8 hours): butyl rubber, natural rubber, neoprene, nitrile rubber, polyethylene, polyvinyl chloride, Viton, Saranex.
- Not recommended (permeation resistance less than 1 hour): Polyvinyl alcohol (PVA)

Measuring devices and waste treatment

Methods of detection and measurement in water

pH meter, thermometer.

Methods of detection and measurement in air (INRS, 1997)

- Sampling by bubbling through an alkaline solution or pumping through a cellulose membrane, followed by colorimetric determination of a molybdenum blue complex.
- Sampling using a tube containing silica gel, dosage by ion chromatography after desorption with an eluent.
- Sampling using PVC air sampling filters (aerosols) used in conjunction with cellulose filters impregnated with sodium carbonate (gaseous pollutants), dosage by ion chromatography.

All these methods take into account all the phosphate ions.

Further information

Glossary

Acceptable Daily Dose (ADD)

For humans this dose is the quantity of a substance that can be ingested by an organism per day for its entire lifetime without presenting a health hazard for the organism in question.

Acute Exposure Guideline Levels (AEGLs)

Defined by the National Research Council's Committee on Toxicology (USA), AEGLs are three levels above which the general population may experience certain effects. These three AEGLs are given for five exposure times: 10, 30 min, 1, 4 and 8 hours.

AEGL 1: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non sensory effects. However, the effects are transient and reversible when exposure ceases.

AEGL 2: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

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.

Aerosol

A mass of solid or liquid particles in suspension in a gaseous environment.

Bioaccumulation

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

Bioamplification

Retention of a substance in the tissue at increasingly higher concentrations the higher one goes in the food chain.

Bioconcentration

Retention of a substance in the tissue of an organism to the extent that the content of the substance in the tissue exceeds that found in nature at one point in the lifetime of the organism.

Bioconcentration factor (BCF)

The relationship between the concentration of the chemical compound in the living organism and the concentration in the environment (water/air/ground). This factor is used to determine the bioaccumulation.

Biotransformation

Biological transformation of substances in a living organism via enzymatic processes.

Boiling Liquid Expanding Vapour Explosion (BLEVE)

A violent vapour explosion of a liquid that is significantly above its usual boiling point at atmospheric pressure after a tank has burst.

Boiling point (measured at a pressure of 1 atmosphere)

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.

Buffering capacity

Capacity of a solution to absorb a certain quantity of acid or base without causing a significant variation in pH. In the marine environment, the buffering capacity is due to the dihydrogenocarbonate/carbonate balance.

Combustion rate

Rate at which an object subjected to fire will burn entirely.

Critical point

Point at which the temperature and pressure at which the intensive properties of a liquid and vapour (density, calorific value...) are equal. It represents the highest temperature (critical temperature) and pressure (critical pressure) at which a gas phase and a liquid phase of a given compound can coexist.

Critical pressure

Maximum pressure for which the distinction can be made between a gas and a liquid.

Critical temperature
Temperature at which, when boiling, there is no longer any clear cut transition between the liquid and the gas state.

Daily exposure dose
Dose (internal or external) of a substance in an organism compared to the weight of the individual and the number of days of exposure (in the case of a non carcinogenic substance) and the number of days lived by the organism (for a carcinogenic substance).

Decomposition products
Products stemming from chemical or thermal disintegration of a substance.

Dermatitis
Inflammation of the skin

Diffusion coefficient in air (and in water)
A constant that describes the movement of a substance in the gas phase (or liquid phase) in response to a concentration differential in the gas phase (or liquid phase).

Effective concentration 50 (EC_{50})
Concentration causing a given effect (mortality, growth inhibition...) for 50% of the population under consideration during a given period of time.

Emergency Response Planning Guidelines (ERPG)
The American International Health Alliance (AIHA) set three maximum concentrations in 1988 below which a category of effects is not expected for an exposure duration of one hour, in a bid to protect the general public.
ERPG1: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly identifiable odour.
ERPG2: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to protect themselves.
ERPG3: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.

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.

Foam
The foam layer absorbs most of the vapours, physically eliminates vapours and isolates the chemical from sunlight and ambient air which reduces the amount of heat and subsequent vaporisation.

Henry's law constant
Value indicating a substance's volatility.

Immediately Dangerous to Life or Health (IDLH)
Level below which a worker can escape to safety in thirty minutes in the event of sudden exposure to a dangerous atmosphere, without respiratory protection and without impairing his ability to escape.

Irreversible effect threshold (IET)
Concentration, for a stated exposure duration, above which irreversible effects can occur in the exposed population.

Lethal effect threshold (LET)
Concentration, for a stated exposure duration, above which mortality can be observed in the exposed population.

Lower Explosive Limit (LEL)
Minimum airborne concentration above which vapours ignite.

Lowest Observed Effect Concentration (LOEC)
Lowest concentration at which an effect is observed.

Marine pollutant
Substance, object or matter likely to cause serious damage to the marine environment when spilled.

Maximum Allowable Relief Valve Setting (MARVS)
Indicates the maximum admissible calibration of pressure relief valves of a cargo tank.

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 (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 during a given time period.

Melting point
Temperature at which solid and liquid state coexist. The melting point is a constant for a pure substance and is usually calculated at standard atmospheric pressure (one atmosphere).

Minimum Risk Level (MRL)
This level is an estimate of daily human exposure to a chemical which probably has no appreciable risk of non-carcinogenic noxious effect on health for a specific exposure duration.

Miscible
Matter that mixes readily with water

MITI test
Test used to determine how easily a product breaks down in the aqueous phase (aerobic conditions).

Narcotic
A product which induces sleep or stupor and has a numbing effect.

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.

No Observed Effect Concentration (NOEC)
Concentration of a substance measured during chronic toxicity tests for which no effect is observed, meaning that the substance presents no chronic toxicity below this concentration.

No Observed Effect Level (NOEL)
The highest dose of a substance that causes no distinct changes as compared with those observed in control animals.

Olfactory threshold
Minimum air or waterborne concentration to which the human nose is sensitive.

Partition coefficient for organic carbon and water (Koc)
(for organic substances)
Ratio of the amount of compound absorbed per unit mass of organic carbon in the soil or in a sediment and the concentration of the same compound in a water solution in a state of equilibrium.

Photo-oxidation
Oxidation of a chemical compound caused by exposure to light energy.

pKa
The term pKa is the cologorithm of Ka, the acid dissociation constant to distinguish acids and bases.
Ka = ([base] x [H3O+])/[acid]
pH = pKa + log [base]/[acid]

Polymerisation
This term describes the chemical reaction generally associated with the production of plastics. Fundamentally, the individual molecules of a chemical (liquid or gas) react together to form a long chain. These chains can be used for many applications.

Protective equipment
This refers to the respiratory or physical protection of a human being. Protection levels have been defined, including both protective clothing and breathing apparatus as accepted by response authorities such as the USCG, NIOSH and the EPA (US).
Level A: an SCBA (self contained breathing apparatus/respirator) and fully air and chemical-tight suit (that resists permeation).
Level B: an SCBA and a suit that protects against liquid spray (splash proof).
Level C: a full face mask or goggles and a suit that protects responders against chemicals (splash proof).
Level D: overalls without a respirator.

Rate of evaporation or volatility (ether = 1)
The rate of evaporation expresses the number of times that a product takes to evaporate as compared with a control substance of an equal volume (ether for instance). This rate varies with the nature of the product and the temperature.

Regression speed
Speed at which a burning liquid slick reduces in thickness. For a given liquid, this speed is constant regardless of the slick surface (slick diameter greater than 2 metres). Regression speed allows the total duration of a fire to be estimated if no attempt is made to extinguish it.
e.g. a 1,000 mm thick slick, where the regression speed is 10 mm/minute
→ duration of fire = 1000/10 = 100 minutes.

Relative density
Ratio of the mass 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, vapour is heavier than air and will tend to stay near ground level and spread.

Self-ignition temperature
Minimal 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 eliminated when handling flammable products or responding to an emergency in risky areas (use explosion proof pumps and VHF walky-talkies).

Surface roughness
Length of a transfer area between the atmospheric layer and a contact surface. This will depend on the average size of the roughness of the contact and atmospheric parameters near the water surface. When the sea is calm it is of the order of 0.02 to 0.06 cm.

Surface tension
A constant that expresses the force owing to molecular interaction exerted at the surface of a liquid when it comes into contact with another surface (liquid or solid) and that affects surface dispersion.

Temporary Emergency Exposure Limits (TEEL)
Exposure times when there is no ERPG.
TEEL 0 is the threshold concentration below which a large part of the population will experience no effect on health. TEEL 1 is equivalent to ERPG1, TEEL 2 is equivalent to ERPG2 and TEEL 3 is equivalent to ERPG3.

Threshold Limit Value (TLV)
Average limit value (weighted as a function of time) that people can be exposed to regularly at work 8 hours a day, 5 days a week without experiencing noxious effects. This value was defined and determined by ACGIH.
TLV-STEL: Mean weighted 15 minutes concentration that must never be exceeded at any time during the day.
TLV-TWA: Mean weighted values for an 8 hour period per day and 40 hours a week.
TLV-ceiling Ceiling values never to be exceeded not even for an instant.

Unconfined Vapour Cloud Explosion (UVCE)
Explosion of a gas cloud or slick of combustible vapours in an unconfined environment.

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

ACGIH	American Conference of Governmental Industrial Hygienists
ADD	Acceptable Daily Dose
ADNR	European Agreement concerning International Carriage of Dangerous Goods on the Rhine river
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
AEGLs	Acute Exposure Guideline Levels
AFFF	Aqueous Film-Forming Foam
AFSSA	French National Agency for Food Safety
AIHA	American International Health Alliance
ALOHA	Areal Locations of Hazardous Atmospheres
ATSDR	Agency for Toxic Substances and Disease Registry
AUV	Autonomous Underwater Vehicle
BCF	Bio Concentration Factor
BLEVE	Boiling Liquid Expanding Vapour Explosion
BOD	Biochemical Oxygen Demand
CAS	Chemical Abstracts Service
CEA	French Atomic Energy Commission
CEDRE	Centre of Documentation, Research and Experimentation on Accidental Water Pollution
CEFIC	European Chemical Industry Council
CHRIS	Chemical Hazards Response Information System
COD	Chemical Oxygen Demand
CSST	French Occupational Health and Safety Commission
CSTEE	French Scientific Committee on Toxicity, Ecotoxicity and the Environment
DDASS	French Departmental Health and Social Action Directorate
DDE	French Departmental Equipment Directorate
DIPPR	Design Institute for Physical Properties
DRASS	French Regional Department of Health and Social Affairs
DRIRE	French Regional Directorates for Industry, Research and Environment
EC	Effective Concentration
ECB	European Chemicals Bureau
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
EFMA	European Fertilizer Manufacturers Association
EINECS	European Inventory of Existing Chemical Substances
ELV	Exposure Limit Value
EPA	Environmental Protection Agency
ERPG	Emergency Response Planning Guidelines
ETC	Environmental Technology Centre
FID	Flame Ionisation Detector
GPC	Gas Phase Chromatography
GPN	Grande Paroisse Nitrogen
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IATA	International Air Transport Association
IBC	International Bulk chemical Code
ICSC	International Chemical Safety Cards
IDLH	Immediately Dangerous to Life or Health
IFREMER	French Research Institute for Exploitation of the Sea
IGC	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk

IMDG	International Maritime Dangerous Goods
IMO	International Maritime Organization
INCHEM	International Chemical industries, Inc.
INERIS	French National Institute for Industrial Environment and Risks
INRS	French National Research and Safety Institute for occupational risk prevention
IPCS	International Programme on Chemical Safety
IPSN	French Institute for Nuclear Safety and Protection
IUCLID	International Uniform Chemical Information Database
LC	Lethal Concentration
LEL	Lower Explosive Limit
LET	Lethal Effect Threshold
LLDPE	Linear Low Density PolyEthylene
LOEC	Lowest Observed Effect Concentration
MARPOL	Marine Pollution
MARVS	Maximum Allowable Relief Valve Setting
MCA	Maritime and Coastguard Agency
MEEDDAT	Ministère de l’Écologie, de l'Énergie, du Développement durable et de l’Aménagement du Territoire
MEV	Mean Exposure Value
MFAG	Medical First Aid Guide
MP	Marine Pollutant
MRL	Minimum Risk Level
MSDS	Safety Data Sheet
MUC	Maximum Use Concentrations
NIOSH	National Institute for Occupational Safety and Health
NM	Nautical mile
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observed Effect Concentration
OECD	Organisation for Economic Co-operation and Development
OELV	Occupational Exposure Limit Value
PEC	Predicted Effect Concentration
PID	Photo Ionisation Detector
PNEC	Predicted No-Effect Concentration
PPE	Personal Protective Equipment
ppm	Parts per million
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
PVDF	Polyvinylidene fluoride
REMPEC	Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea
ROV	Remote Operated Vehicle
SAR	Supplied Air Respirator
SCBA	Self-Contained Breathing Apparatus
SEBC	Standard European Behaviour Classification system of chemicals spilled into the sea
SIDS	Screening Information Data Set
SINOE	Système d’Information et d’Observation de l’Environnement
SIW	Special Industrial Waste
TEEL	Temporary Exposure Limits
TGD	Technical Guidance Document
TLV-ceiling	Threshold Limit Values – Ceiling

TLV-STEL	Threshold Limit Values - Short Term Exposure Limit
TLV-TWA	Threshold Limit Values - Time Weighted Average
TNO	Netherlands Organisation for Applied Scientific Research
TRANSAID	Agreement between UIC (French Chemical Industry Association) & the French Government
TROCS	Transport of Chemical Substances - database created by REMPEC
UEL	Upper Explosive Limit
UIISC	French Unit of Instruction and Intervention on Civil Security
US EPA	United States Environmental Protection Agency
UVCE	Unconfined Vapour Cloud Explosion
VCM	Vinyl chloride monomer
VHF	Very High Frequency
v/v	Volume to volume
WHO	World Health Organisation

Useful websites

Bonn Agreement, European Classification System
Available at http://www.bonnagreement.org

Cedre (Centre of Documentation, Research and Experimentation on Accidental Water Pollution)
Available at http://www.cedre.fr

CEFIC (European Chemical Industry Council)
Available at http://www.ericards.net

CHRIS (Chemical Hazards Response Information System)
Available at http://www.chrismanual.com/findform.htm

CSST (Commission de la Santé et de la Sécurité du Travail)
Available at http://www.reptox.csst.qc.ca

ECB (European Chemicals Bureau)
Available at http://ecb.jrc.it

EFMA (European Fertilizer Manufacturers Association)
Available at http://www.efma.org

GPN
Available at http://www.gpn.fr

HSDB (Hazardous Substances DataBank)
Available at http://toxnet.nlm.nih.gov

ICSC (International Chemical Safety Cards)
Available at http://www.cdc.gov/niosh/ipcs/nicstart.html

IFA (International Fertilizer Industry Association)
Available at http://www.fertilizer.org

INRS (Institut National de Recherche et de Sécurité)
Available at http://www.inrs.fr

NIOSH (National Institute for Occupational Safety and Health)
Available at http://www.cdc.gov/niosh

NPI (National Pollutant Inventory)
Available at http://www.npi.gov.au

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ANNEXES

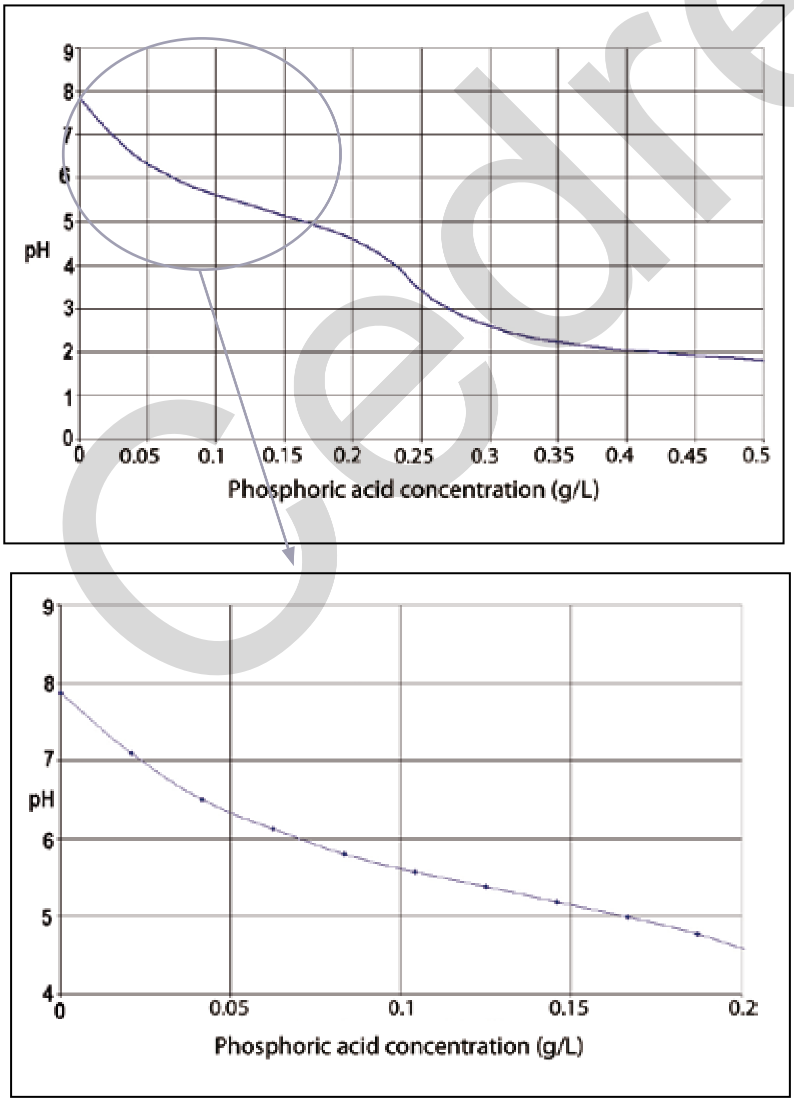
- Annex 1: pH graphs
- Annex 2: Summary and additional physical and toxicological data
- Annex 3: Fax format data card
- Annex 4: Classification of noxious liquid substances

ANNEX 1: PH GRAPHS

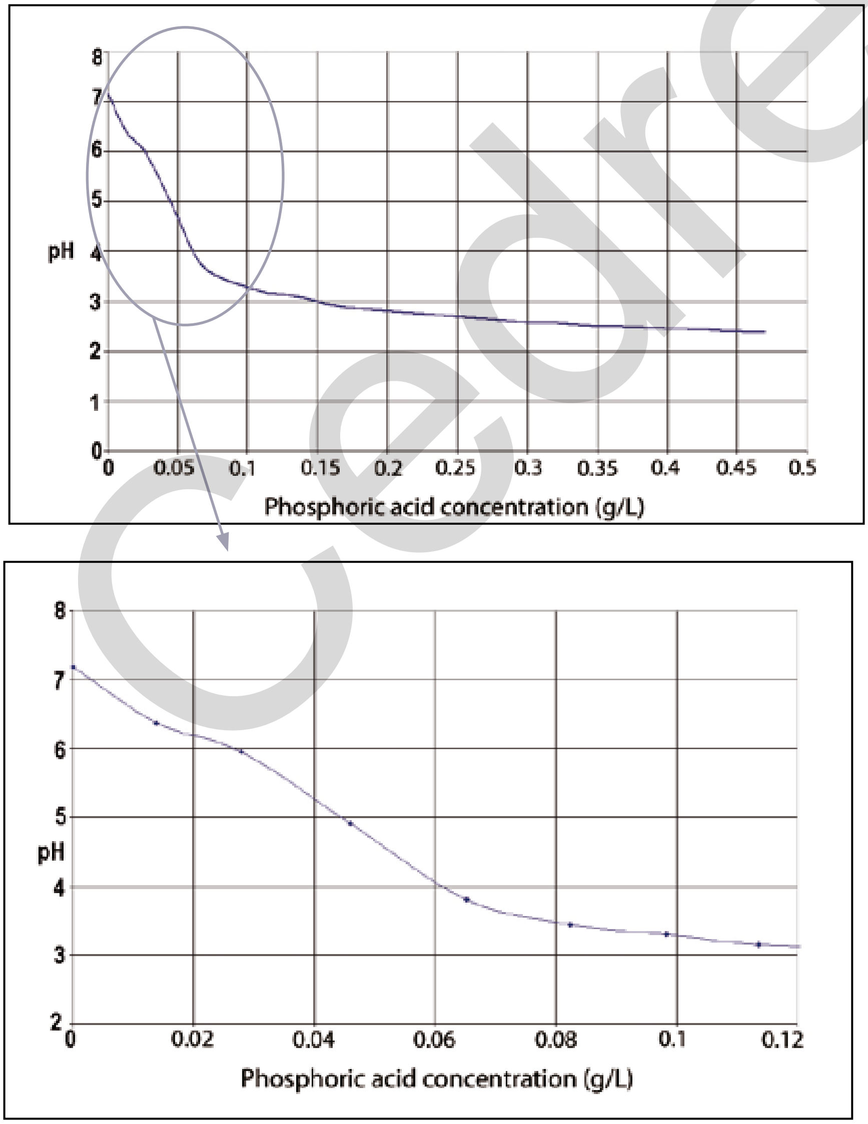
pH values in the aquatic environment according to the concentration of phosphoric acid in the water.

(Experiments conducted by *Cedre* with phosphoric acid in a 72% solution and a quantity of one litre of water)

- Seawater



- Fresh water


pH
8
7
6
5
4
3
2
1
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
Phosphoric acid concentration (g/L)
pH
8
7
6
5
4
3
2
0
0.02
0.04
0.06
0.08
0.1
0.12
Phosphoric acid concentration (g/L)

ANNEX 2: SUMMARY AND ADDITIONAL PHYSICAL AND TOXICOLOGICAL DATA

Classification

CAS n°: 7664-38-2
EC n° (EINECS): 231-633-2
UN n°: 1805
INDEX n°: 015-011-00-6
Class: 8

Physical data

Pure phosphoric acid (solid)	
Molecular mass	
98 g/mol	INRS, 1997
Key temperatures	
Boiling point: 260°C	NPI, 2004; INRS, 1997
Melting point: 42.4°C	NPI, 2004; INRS, 1997; ECB, 2000
Density	
Vapour density: 3.4	NPI, 2004
Relative density: 1.864 to 25°C	INRS, 1997
Vapour pressure/tension	
4 Pa at 20°C	
16 Pa at 40°C	
177 Pa at 80°C	INRS, 1997
487 Pa at 100°C	
Phosphoric acid in a 75% solution	
Physical state: liquid	
Key temperatures	
Boiling point: 133°C	ECB, 2000; EFMA, 1996
Melting point (freezing point): - 17.5°C	EFMA, 1996; CSST, 2006; ECB, 2000
Critical temperature: N/A	
Density	
Relative density (water = 1): 1.57 to 25°C	ECB, 2000; CSST, 2006; DEKKER, 1968
Vapour density (air = 1): 3.4	approximate value: few references available
Solubility	
Solubility in seawater: 100% (totally miscible)	
Solubility in fresh water: 100% (totally miscible)	
Vapour pressure/tension (20°C)	
267 Pa (75%)	EFMA, 1996
290 Pa (85%)	CSST, 2006
Other properties	
pKa: pKa1 = 2.15	
pKa2 = 7.09	HSDB, 2005
pKa3 = 12.32	
Viscosity at 20°C: 24 cPo (75%)	DEKKER, 1968
Olfactory threshold in air: odourless	
pH < 1	EFMA, 1996

Toxicological data

Concentrated solutions of phosphoric acid result in severe lesions of the tissues with which they come into contact, while diluted solutions of phosphoric acid are only moderately irritating. The intensity and nature of the lesions caused will depend on the concentration of the acid and the duration of exposure.

Threshold toxicological values

Occupational exposure values

MEV (France)/OELV 8 hours: 1 mg/m^3	code du travail, arrêté du 30 juin 2004
MEV (France)/OELV short term: 2 mg/m^3	code du travail, arrêté du 30 juin 2004
TLV-TWA (ACGIH): 1 mg/m^3	EFMA, 1996; ICSC, 2000

Risk management values for the population (ICSC, 2000)

IDLH:	1,000 mg/m^3	NIOSH, 2005
TLV STEL (ACGIH):	3 mg/m^3	EFMA, 1996
TEEL 0:	1 mg/m^3	
TEEL 1 (ERPG 1):	3 mg/m^3	US DEPARTMENT OF ENERGY'S CHEMICAL SAFETY PROGRAM, 2005
TEEL 2 (ERPG 2):	5 mg/m^3	
TEEL 3 (ERPG 3):	500 mg/m^3	

Specific effects

Carcinogenic effects: not classed as carcinogenic by ACGIH
Genotoxicity: not considered as genotoxic
Mutagenic effects: classed as non-mutagenic

General toxicity

Acute human toxicity

- by inhalation: causes severe irritation of the upper respiratory tract, accompanied by a cough, burns, breathing difficulties and a risk of coma. Can cause irritation liable to trigger pulmonary congestion by chemicals and pulmonary oedema.
- by ingestion: causes acute pain, nausea, vomiting and diarrhoea. There is also a risk of haemorrhage of the digestive tract, which may lead to corrosion and permanent destruction of the tissues of the oesophagus and digestive tract.
- by skin contact: all contact with the liquid is corrosive and causes severe burns, redness and ulceration.
- by eye contact: risk of irreversible corneal lesions. Contact with this chemical is corrosive for the eyes and causes severe burns.

Chronic human toxicity

Prolonged inhalation can cause inflammation of the respiratory tract and pulmonary lesions. Prolonged or repeated skin contact can cause dermatitis. Prolonged or repeated contact with the eyes can cause conjunctivitis.

Ecotoxicological data

Acute ecotoxicity (ECB, 2000)

Fish (*Lepomis macrochirus*)	LC_{50} (96 h)	=	pH between 3.25 and 3.0
Fish (*Gambusia affinis*)	LC_{50} (96 h)	=	pH between 3.5 and 3
Crustacean (*Daphnia magna*)	EC_{50} (12 h)	=	pH 4.6
Crustacean (*Daphnia pulex*)	EC_{50} (12 h)	=	pH 4.1
Crustacean (*Gammarus pulex*)	LC_{50} (12 h)	=	pH 3.4
Aquatic bacteria	EC_{50} = pH 2.55	=	270 mg/L

Chronic ecotoxicity

Recommended maximum limit of total phosphorus in order to prevent unwanted development of algae: 0.1 mg/L

Additional remarks

Increased acidity of the environment can lead to sublethal effects on fish such as interrupted reproduction, altered growth rate or skeletal malformations. Increased acidity can also be directly toxic for fish. A pH of less than 3 causes the coagulation of gill mucus, which can result in anoxia or breathing difficulties. For a higher pH, fish mortality is due to a decrease in chloride ions and sodium ions, as well as an increase in hydrogen ions in the blood. However, the toxicity can also be due to anions as well as to an increase in the acidity of the environment. A comparative study showed that phosphoric acid is the most toxic for fish, while nitric and hydrochloric acid are moderately toxic and phosphoric acid the least toxic. The different toxicities of these acids can be caused by anions produced during acid dissociation, however further investigation would be needed to come to a definitive conclusion.

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PNEC (Predicted No-Effect Concentration):

No PNEC was able to be calculated as the buffering capacity, the pH and its fluctuation are very specific to the ecosystem in question. To estimate the effect of a phosphoric acid spill, the change in pH of the water must be calculated or measured. **Variation by one pH unit can affect flora and fauna**. The average pH of water can vary in seawater from 8 to 8.4 (stable pH with high buffering capacity) and in fresh water from 6 to 7.5.

Examples of pH in natural waters

Bay of Brest	Fos-sur-mer	Fresh water
8	7.95	6 - 7.5

ANNEX 3: FAX FORMAT DATA CARD

Phosphoric acid

Orthophosphoric acid, white phosphoric acid, o-phosphoric acid, green acid.

H_3PO_4

CAS n°: 7664-38-2
EC n° (EINECS): 231-633-2
INDEX N°: 015-011-00-6
Phosphoric acid in solution
UN n°: 1805
Class: 8
Solid phosphoric acid
UN n°: 3453
Class: 8

First aid information

The corrosive action of phosphoric acid can appear after a certain delay: **it is important to take immediate action.** Immediately remove all soiled or spotted clothes, including shoes.

Intoxication by inhalation

- Immediately move the affected person into the fresh air and away from the contaminated area.
- Where necessary, give artificial respiration.
- Immediately obtain medical care.

Skin contact

- Remove contaminated clothing.
- Rinse the skin with plenty of water for at least 15 minutes or have a shower.
- Immediately obtain medical care.

Eye contact

- Rinse the eyes with plenty of water for at least 15 minutes (if possible remove contact lenses).
- Immediately obtain medical care and consult an eye specialist.

Intoxication by ingestion

- If the person is fully conscious, rinse out their mouth with water.
- Give the person plenty to drink.
- Do not induce vomiting.
- Immediately obtain medical care.

Physical data

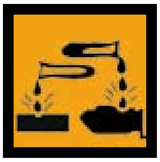
Pure phosphoric acid (solid)

Molecular mass:	98 g/mol
Key temperatures:	
Boiling point:	260°C
Melting point:	42.4°C
Density	
Vapour density:	3.4
Relative density:	1.864 at 25°C
Vapour pressure/tension	4 Pa at 20°C 16 Pa at 40°C 177 Pa at 80°C 487 Pa at 100°C

Phosphoric acid in a 75% solution

Key temperatures	
Boiling point:	133°C
Melting point (freezing point):	- 17.5°C
Critical temperature:	N/A
Density	
Relative density (water = 1):	1.57 at 25°C
Vapour density (air = 1):	3.4
Solubility	
Solubility in seawater: 100% (totally miscible)	
Solubility in fresh water: 100% (totally miscible)	
Vapour pressure/tension (20°C)	267 Pa (75%) 290 Pa (85%)
Other properties	
pKa:	pKa1 = 2.15 pKa2 = 7.09 pKa3 = 12.32
Viscosity at 20°C:	24 cPo (75%)
Olfactory threshold in air	odourless
pH	< 1

EU classification:



C: corrosive

R34:	Causes burns.
S1/2:	Keep locked up and out of the reach of children.
S26:	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S45:	In case of accident or if you feel unwell, seek medical advice immediately (show label where possible).

September 2008

Toxicological data

Concentrated solutions of phosphoric acid result in severe lesions of the tissues with which they come into contact, while diluted solutions of phosphoric acid are only moderately irritating. The intensity and nature of the lesions caused will depend on the concentration of the acid and the duration of exposure.

Threshold toxicological values

Occupational exposure values:
MEV (France)/OELV 8 hours: 1 mg/m^3
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TEEL 1 (ERPG 1): 3 mg/m^3
TEEL 2 (ERPG 2): 5 mg/m^3
TEEL 3 (ERPG 3): 500 mg/m^3

Chronic human toxicity

Prolonged inhalation can cause inflammation of the respiratory tract and pulmonary lesions. Prolonged or repeated skin contact can cause dermatitis. Prolonged or repeated contact with the eyes can cause conjunctivitis.

Specific effects

Carcinogenic effects: not classed as carcinogenic by ACGIH
Genotoxicity: not considered as genotoxic
Mutagenic effects: classed as non-mutagenic

Acute human toxicity

By inhalation: causes severe irritation of the upper respiratory tract, accompanied by a cough, burns, breathing difficulties and a risk of coma. Can cause irritation liable to trigger pulmonary congestion by chemicals and pulmonary oedema.

By ingestion: causes acute pain, nausea, vomiting and diarrhoea. There is also a risk of haemorrhage of the digestive tract, which may lead to corrosion and permanent destruction of the tissues of the oesophagus and digestive tract.

By skin contact: all contact with the liquid is corrosive and causes severe burns, redness and ulceration.

By eye contact: risk of irreversible corneal lesions. Contact with this chemical is corrosive for the eyes and causes severe burns.

Ecotoxicological data

Acute ecotoxicity

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Fish (*Gambusia affinis*)	LC_{50} (96h) = pH between 3.5 and 3
Crustacean (*Daphnia magna*)	EC_{50} (12h) = pH 4.6
Crustacean (*Daphnia pulex*)	EC_{50} (12h) = pH 4.1
Crustacean (*Gammarus pulex*)	LC_{50} (12 h) = pH 3.4
Aquatic bacteria	EC_{50} = 270 mg/L = pH 2.55

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Increased acidity of the environment can lead to sublethal effects on fish such as interrupted reproduction, altered growth rate or skeletal malformations. Increased acidity can also be directly toxic for fish. A pH of less than 3 causes the coagulation of gill mucus, which can result in anoxia or breathing difficulties. For a higher pH, fish mortality is due to a decrease in chloride ions and sodium ions, as well as an increase in hydrogen ions in the blood. However, the toxicity can also be due to anions as well as to an increase in the acidity of the environment. A comparative study showed that phosphoric acid is the most toxic for fish, while nitric and hydrochloric acid are moderately toxic and phosphoric acid the least toxic. The different toxicities of these acids can be caused by anions produced during acid dissociation, however further investigation would be needed to come to a definitive conclusion.

Persistence in the environment

The risk presented by phosphoric acid for the environment is due to hydronium ions (pH effect). The effect of phosphoric acid therefore depends on the buffering capacity of the aquatic or terrestrial ecosystem. A pH of less than 5.5 is harmful for aquatic life. The effect of this ion is naturally reduced by dilution and in seawater by a buffering effect.

Risks for the environment

A high concentration of phosphoric acid in the water will increase the acidity of the water, which can be harmful for aquatic life.

In seawater, some types of algae can survive at a pH of 6, but cannot endure a decrease in pH to less than 5.5.

Fresh water fish cannot survive at a pH of less than 4.5. Marine organisms generally cannot endure significant variations in pH.

Breakdown

The acidity of the water due to phosphoric acid may be rapidly reduced by the minerals present, and the phosphates will be consumed as nutritive salts.

Bioaccumulation

Phosphoric acid is a substance which does not bioaccumulate along the food chain.

Indirect pollution

Although the phosphate ions formed by the dissociation of phosphoric acid are nutritive salts for aquatic organisms, concentrations of over 0.1mg/L of inorganic phosphorus can act as fertilisers for macroscopic or microscopic algae, causing objectionable effects in areas of low aeration or semi-closed areas (decrease in oxygen content). Phosphoric acid is an acid which cause the release of the metal ions contained in the mud or sediments present at the base of the water column (case for lakes and ports).

Partition coefficient for octanol and water (Log Kow): 0.31.

Particular risks

Danger

- Heating the recipient provokes an increase in pressure with a risk of shattering.
- Release of corrosive and irritating vapours in the case of fire.
- Possibility of metals being attacked and hydrogen being produced, possibly forming an explosive mixture with air.
- The vapours are invisible and heavier than air. They spread out across the ground and can infiltrate sewer systems and basements.

Stability and reactivity

- Stable at room temperature and in normal conditions of use.
- Phosphoric acid is a corrosive substance (effect varies according to the concentration). It attacks most metals (in particular iron, zinc and aluminium). Its corrosivity increases with the temperature and when the acid contains impurities such as fluorine and chlorine products (technical grade phosphoric acid).
- Phosphoric acid reacts energetically with bases and violently with nitrates, chlorates and calcium carbide, causing fire and explosion.
- Due to heat action, phosphoric acid undergoes dehydration from 160°C and becomes pyrophosphoric acid. At over 300°C, it turns into metaphosphoric acid then polyphosphoric acid.
- Dangerous products of decomposition: at over 200 to 300°C, phosphoric acid, due to heat action, breaks down, giving off corrosive vapours and toxic gases (phosphorus oxides).
- Upon contact with sulphides, cyanides, carbonates, fluorides and phosphides, phosphoric acid solutions can produce highly toxic and flammable gases.
- Phosphoric acid solutions can react with chemicals such as aldehydes, amines, amides, alcohols and glycols. Phosphoric acid in solution can accelerate the violent polymerisation of certain compounds such as epoxides and accelerate the breakdown of unstable compounds such as nitrate compounds.
- Solid or very concentrated phosphoric acid: hygroscopic product which absorbs water from damp air.

Transportation

UN n°: 1805

Land transportation:

RID (rail) /ADR (road)

- Proper shipping name: liquid phosphoric acid
- Danger n°: 80
- Class: 8
- Packaging group: III
- Classification code: C1 (liquid inorganic acid)
- Danger labels: 8
- Tunnel restriction code: E

Transportation via inland waterways

ADN/ADNR

- Class: 8
- Classification code: C1 (liquid inorganic acid)
- Packaging group: III
- Danger labels: 8
- Tunnel restriction code: E

Maritime transport: IMDG

- Class or division: 8
- Packaging group: III
- Marine pollutant (MP): No
- Danger labels: 8

Air transport: IATA

- Class or division: 8
- Subsidiary risk: -
- Packaging group: III
- Hazard label: corrosive

Handling

The recommendations relating to storage areas are applicable to areas where phosphoric acid or its aqueous solutions are handled.

- Inform personnel of the risks presented by the product, precautions to be respected and measures to be taken in the event of a spill.
- Avoid inhalation of vapours and aerosols when the product is being heated. Wherever possible, carry out industrial operations in closed apparatus. In all cases, capture emissions at their source. Provide nearby respiratory protective apparatus and protective equipment suitable for short periods of work, of an exceptional nature, or for emergency response.
- Avoid contact of the product with the skin and eyes. Provide personnel with protective clothing, boots, gloves and safety goggles. Keep equipment in good condition and clean after use.
- Provide safety showers and eye fountains systematically in workplaces where the product is handled.
- When transferring, diluting, dissolving etc. the product, be sure to prevent localised overheating, projections of liquid and vapour emissions. Never prime a siphon using the mouth, rather use specially designed equipment for this purpose.
- Never conduct operations on or in tanks containing or having contained phosphoric acid or its aqueous solutions without taking the necessary precautions.
- Do not release phosphoric acid solutions into the sewer system. Discharge may only be disposed of after neutralisation by alkaline agents and dilution.
- Dilute the product immediately in plenty of water in the event of a leak or small spill. If the quantities spilt are significant, evacuate the personnel and only leave trained and equipped response teams to conduct response.
- Store waste in specially designed receptacles and tanks. To dispose of this waste, dilute and neutralise it at appropriate facilities. When the quantities needing destroyed are significant, dispose of them according to the conditions set out by the regulations (processing by a specialised company or centre).

Storage

- Store phosphoric acid in a cool, well ventilated place, out of direct sunlight and away from all sources of heat or ignition and products liable to react with it.
- Keep away from all metal or metal object liable to react when in contact with phosphoric acid to give off hydrogen.
- Store on impermeable ground in the form of a retention tank so that in the event of a spill the solutions do not spread outside the storage facility.
- Containers should be tightly closed and clearly labelled. Relabel in the event of damage to packaging.
- Provide protective equipment nearby and outside of the storage facility, in particular self contained breathing apparatus, a high flow water supply, safety showers and eye fountains, in case of accident.

Use

Eliminate all sources of ignition at metal tank openings. Phosphoric acid is non-flammable, however its corrosive action on many metals can result in the release and accumulation of hydrogen.

Incompatible products

A violent reaction can be generated upon contact with metals, strong bases and with nitrates, chlorates and calcium carbides. Phosphoric acid can also react with aldehydes, amines, alcohols, glycols, cyanides, ketones, phenols, esters, sulphides and halogenated organic substances.

Recommended packaging materials

Commercial phosphoric acid solutions are generally stored in stainless steel containers (type 316) or containers lined with an acid resistant coating (coated steel: ebonite, natural rubber, butyl, neoprene), or in containers made of polyethylene, polyester or glass fibre reinforced PVC. Glass can also be used for small quantities; in this case cylinders can be protected by a more resistant, suitably adjusted metal envelope.

ANNEX 4: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Dangerous goods

Regulations governing the carriage in bulk of hazardous liquid substances (MARPOL Annex II) provide valuable indications on the hazards that such substances can produce during transportation.

Noxious liquid substances are divided into 4 categories (X, Y, Z and OS) starting with the most dangerous substances (MARPOL X) and ending with the least dangerous ones (MARPOL OS).

The MARPOL classification system is based on risk assessment profiles for chemicals transported in bulk by sea, as defined by a GESAMP working group (Group of Experts on the Scientific Aspects of Marine Pollution).

Revised MARPOL Annex II (IMO, 2005)

The revised Annex II Regulations for the control of pollution by noxious liquid substances in bulk was adopted in October 2004. It includes a new four-category categorization system for noxious and liquid substances. The revised annex entered into force on 1 January 2007.

The new categories are:

Category X: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a major hazard to either marine resources or human health and, therefore, justify the prohibition of the discharge into the marine environment;

Category Y: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a hazard to either marine resources or human health or cause harm to amenities or other legitimate uses of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment;

Category Z: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a minor hazard to either marine resources or human health and therefore justify less stringent restrictions on the quality and quantity of the discharge into the marine environment; and

Other Substances: Substances which have been evaluated and found to fall outside Category X, Y or Z because they are considered to present no harm to marine resources, human health, amenities or other legitimate uses of the sea when discharged into the sea from tank cleaning of deballasting operations.

The revision of this annex is based on the modification of other classifications such as the GESAMP classification and led to consequential amendments to the IBC Code.