

Safety Data Sheet

according to 1907/2006/EC, Article 31

Printing date 05.01.2017

Version number 1

Revision: 05.01.2017

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifier

Trade name: Citric Acid Anhydrous

CAS number:

77-92-9

EC number:

201-069-1

REACH registration number: 01-2119457026-42-0020

1.2 Relevant identified uses of the substance or mixture and uses advised against

Application of the substance / the preparation:

Intermediate

Formulation

Detergents and cleaning products

Agricultural applications

Personal care products

Paper industry

Construction products

Polymers and plastics

Oil industry

Textile industry

Paints and coatings

Photography products

Laboratory reagents

Water treatment

Treatment of metal surfaces

Medical devices

1.3 Details of the supplier of the safety data sheet

Manufacturer/Supplier:

RZBC (JUXIAN) CO., LTD.

NO. 209, LAIYANG ROAD (WEST SIDE OF NORTH CHENGYANG ROAD),

JUXIAN ECONOMIC DEVELOPMENT ZONE, RIZHAO CITY, SHANDONG PROVINCE CHINA

Tel: 0086 633 2163576

Fax: 0086 633 2163500

E-mail: sales@rzbc.com

Further information obtainable from:

B-Lands Consulting

WTC, 5 Place Robert Schuman, BP 1516

38025 Grenoble, FRANCE

Tel: +33 476 295 869

Fax: +33 476 295 870

Email: clients@reachteam.eu

www.reachteam.eu

1.4 Emergency telephone number(s):

NHS Direct: 111 (England and Scotland), 0845 46 47 (Wales).

National Poisons Information Service (NPIS): 0344 892 0111 (healthcare professionals only).

Ireland - National Poisons Information Centre: 01 837 9964 or 01 809 2566 (healthcare professionals only).

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008

Eye Irrit. 2 H319 Causes serious eye irritation.

2.2 Label elements

Labelling according to Regulation (EC) No 1272/2008:

The substance is classified and labelled according to the CLP regulation.

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Trade name: Citric Acid Anhydrous**Hazard pictograms:**

GHS07

Signal word: Warning**Hazard statements:**

H319 Causes serious eye irritation.

Precautionary statements:

P264 Wash thoroughly after handling.

P280 Wear protective gloves/protective clothing/eye protection/face protection.

P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P337+P313 If eye irritation persists: Get medical advice/attention.

2.3 Other hazards**Results of PBT and vPvB assessment****PBT:** No PBT.**vPvB:** No vPvB.**SECTION 3: Composition/information on ingredients****3.1 Substances****CAS Number. Description.**

77-92-9 Citric Acid Anhydrous

Identification number(s)**EC number:** 201-069-1**SECTION 4: First aid measures****4.1 Description of first aid measures****After inhalation:** Move patient to fresh air, if symptoms persist consult a doctor.**After skin contact:** If skin irritation continues, consult a doctor.**After eye contact:**

Rinse opened eye for several minutes under running water. If symptoms persist, consult a doctor.

After swallowing:

Rinse out mouth and then drink plenty of water.

Do not induce vomiting; call for medical help immediately.

4.2 Most important symptoms and effects, both acute and delayed

Serious eye damage/eye irritation: Eye Irrit. 2

4.3 Indication of any immediate medical attention and special treatment needed

No further relevant information available.

SECTION 5: Firefighting measures**5.1 Extinguishing media****Suitable extinguishing agents:**CO₂, powder or water spray. Fight larger fires with water spray or alcohol resistant foam.**5.2 Special hazards arising from the substance or mixture**Carbon dioxide (CO₂)

Carbon monoxide (CO)

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Trade name: Citric Acid Anhydrous**5.3 Advice for firefighters****Protective equipment:**

Wear fully protective suit.

Wear self-contained respiratory protective device.

SECTION 6: Accidental release measures**6.1 Personal precautions, protective equipment and emergency procedures**

Use personal protective equipment.

Ensure adequate ventilation.

Wear eye protection. Avoid contact with skin and eyes.

6.2 Environmental precautions

Do not allow to enter sewers/ surface or ground water.

No special measures required.

Prevent further leakage or spillage if safe to do so.

6.3 Methods and material for containment and cleaning up

Send for recovery or disposal in suitable receptacles.

Retrieve the product by mechanical means.

Dispose contaminated material as waste according to item 13.

Pick up and transfer to properly labelled containers. After cleaning, flush away traces with water.

6.4 Reference to other sections

See Section 7 for information on safe handling.

See Section 8 for information on personal protection equipment.

See Section 13 for disposal information.

SECTION 7: Handling and storage**7.1 Precautions for safe handling**

Avoid breathing vapours.

Do not get in eyes, on skin, or on clothing.

Use only in well ventilated areas.

Provide suction extractors if dust is formed.

Do not inhale dust / smoke / mist.

Information about fire - and explosion protection: No special measures required.**7.2 Conditions for safe storage, including any incompatibilities****Requirements to be met by storerooms and receptacles:**

Store in a cool and dry place.

Provide ventilation for receptacles.

Store only in the original receptacle.

Information about storage in one common storage facility: Store away from oxidising agents.**Further information about storage conditions:** Keep container tightly sealed.**7.3 Specific end use(s):** No further relevant information available.**SECTION 8: Exposure controls/personal protection****8.1 Control parameters****Ingredients with limit values that require monitoring at the workplace:** Not required.**PNECs**

PNEC	0.44 mg/L (Water (Freshwater))
	0.044 mg/L (Water (Marine Water))
	>1000 mg/L (Sewage Treatment Plant (STP))
PNEC	3.46 mg/kg sedim. dw (Sediment (Marine Water))
	34.6 mg/kg sedim. dw (Sediment (Freshwater))

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PNEC	33.1 mg/kg soil dw (Soil)
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Additional information: The lists valid during the making were used as basis.

8.2 Exposure controls

Personal protective equipment

General protective and hygienic measures:

Do not eat, drink, smoke or sniff while working.
 Keep away from foodstuffs, beverages and feed.
 Immediately remove all soiled and contaminated clothing
 Wash hands before breaks and at the end of work.
 Avoid contact with the eyes.
 Avoid contact with the eyes and skin.

Respiratory protection: Suitable respiratory protective device recommended.

Protection of hands:

The glove material has to be impermeable and resistant to the product/ the substance/ the preparation.
 Due to missing tests no recommendation to the glove material can be given for the product/the preparation/ the chemical mixture.
 Select the glove material based on a consideration of the penetration times, rates of diffusion and the degradation.

Material of gloves:

Rubber, PVC or neoprene gloves recommended.
 The selection of the suitable gloves does not only depend on the material, but also on further marks of quality and varies from manufacturer to manufacturer.

Penetration time of glove material:

The determined penetration times according to EN 374 part III are not performed under practical conditions. Therefore a maximum wearing time, which corresponds to 50% of the penetration time, is recommended.
 The exact break through time must be determined by the manufacturer of the protective gloves.

Eye protection:



Tightly sealed goggles (EN 166).

Body protection: Protective work clothing.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

General Information

Appearance:

Form: Solid.
Crystalline

Colour: White.

Odour: Odourless.

Odour threshold: Not determined.

pH-value (100 g/l) : 1.7

Melting point/Melting range: 153 °C

Boiling point/Boiling range: Decomposes before boiling

Flash point: Not applicable.

Flammability (solid, gaseous): Product is not flammable.

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Ignition temperature:	Not applicable.
Decomposition temperature:	Not determined.
Danger of explosion:	Product does not present an explosion hazard.
Explosion limits:	
Lower:	Not determined.
Upper:	Not determined.
Oxidising properties	None.
Vapour pressure at 25 °C:	2.21*10 ⁻⁶ Pa
Density:	Not determined.
Relative density at 20 °C	1.665
Vapour density	Not applicable.
Evaporation rate	Not applicable.
Solubility in / Miscibility with	
Water at 20 °C:	590 g/l
Alcohols:	Partly soluble.
Partition coefficient (n-octanol/water):	-0.2 to -1.8 log POW
Viscosity:	
Dynamic:	Not applicable.
Kinematic:	Not applicable.
9.2 Other information	No further relevant information available.

SECTION 10: Stability and reactivity

10.1 Reactivity No data available.

10.2 Chemical stability

Thermal decomposition / conditions to be avoided:

Stable up to melting point.

Keep away from heat and direct sunlight.

10.3 Possibility of hazardous reactions Reacts with alkali (lyes).

10.4 Conditions to avoid Strong oxidizing agents.

10.5 Incompatible materials

Protect from moisture.

Avoid strong oxidants, strong alkalis and strong acids.

Sodium nitrite, potassium nitrite

10.6 Hazardous decomposition products

Carbon dioxide

Carbon monoxide

SECTION 11: Toxicological information

11.1 Information on toxicological effects

Acute toxicity Based on available data, the classification criteria are not met.

LD/LC50 values:

Oral	LD50	5400 mg/Kg bw (Mouse) (OECD 401)
Dermal	LD50	>2000 mg/Kg bw (Rat) (OECD 402)

Primary irritant effect:

Skin corrosion/irritation: Based on available data, the classification criteria are not met.

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Trade name: Citric Acid Anhydrous**Serious eye damage/irritation:**

Causes serious eye irritation.

Respiratory or skin sensitisation: Based on available data, the classification criteria are not met.**CMR effects (carcinogenicity, mutagenicity and toxicity for reproduction):****Germ cell mutagenicity:** Based on available data, the classification criteria are not met.**Carcinogenicity:** Based on available data, the classification criteria are not met.**Reproductive toxicity:** Based on available data, the classification criteria are not met.**STOT-single exposure:** Based on available data, the classification criteria are not met.**STOT-repeated exposure:** Based on available data, the classification criteria are not met.**Aspiration hazard:** Based on available data, the classification criteria are not met.**SECTION 12: Ecological information****12.1 Toxicity****Aquatic toxicity:**

LC50/48h 440 mg/L (Fish) (OECD 203)

NOEC 425 mg/L (Algae)

LC50/24h 1535 mg/L (Daphnia Magna)

12.2 Persistence and degradability Easily biodegradable**12.3 Bioaccumulative potential** Does not accumulate in organisms.**12.4 Mobility in soil** pKa: 3.13, 4.76 and 6.4 at 25 °C**Additional environmental information:****General notes:**

Water hazard class 1 (German Regulation) (Self-assessment): slightly hazardous for water
 Do not allow undiluted product or large quantities of it to reach ground water, water course or sewage system.

12.5 Results of PBT and vPvB assessment**PBT:** No PBT.**vPvB:** No vPvB.**12.6 Other adverse effects** No further relevant information available.**SECTION 13: Disposal considerations****13.1 Waste treatment methods****Recommendation:** Do not allow product to reach sewage system.**Uncleaned packaging:****Recommendation:**

Disposal must be made according to official regulations.

Packaging that may not be cleansed must be disposed of in the same manner as the product.

SECTION 14: Transport information**14.1 UN Number****ADR, ADN, IMDG, IATA** Not applicable.**14.2 UN proper shipping name****ADR, ADN, IMDG, IATA** Not applicable.**14.3 Transport hazard class(es)****ADR, ADN, IMDG, IATA**
Class Not applicable.**14.4 Packing group****ADR, IMDG, IATA** Not applicable.

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Trade name: Citric Acid Anhydrous**14.5 Environmental hazards****Marine pollutant:** No**14.6 Special precautions for user** Not applicable.**14.7 Transport in bulk according to Annex II of MARPOL 73/78 and the IBC Code** Not applicable.**SECTION 15: Regulatory information****15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture**

This safety data sheet complies with the requirements of Regulation (EC) No. 1907/2006.

15.2 Chemical safety assessment A Chemical Safety Assessment has been carried out.**SECTION 16: Other information**

This information is based on our present knowledge. However, this shall not constitute a guarantee for any specific product features and shall not establish a legally valid contractual relationship.

Abbreviations and acronyms:

ADR: Accord européen sur le transport des marchandises dangereuses par Route (European Agreement concerning the International Carriage of Dangerous Goods by Road)

IMDG: International Maritime Code for Dangerous Goods

IATA: International Air Transport Association

GHS: Globally Harmonised System of Classification and Labelling of Chemicals

EINECS: European Inventory of Existing Commercial Chemical Substances

CAS: Chemical Abstracts Service (division of the American Chemical Society)

PNEC: Predicted No-Effect Concentration (REACH)

LC50: Lethal concentration, 50 percent

LD50: Lethal dose, 50 percent

Eye Irrit. 2: Serious eye damage/eye irritation – Category 2

Annexes I. Exposure scenarios

M1 – Manufacturing

IU1 – Industrial use as chemical intermediate

IU2 – Formulation into preparations at industrial site

IU3 – Industrial, professional and consumer use in personal care

IU4 – Industrial, professional and consumer use in cleaning products

IU5 – Industrial use in production of paper

IU6 – Industrial, professional and consumer use in construction products

IU7 – Industrial use in production of polymers and plastics

IU8 – Industrial use in the oil industry

IU9 – Industrial use in the textile industry

IU10 – Industrial, professional and consumer use in paints and coatings

IU11 – Professional and consumer use in photography

IU12 – Industrial use in laboratory reagents

IU13 – Industrial use in water treatment

IU14 – Industrial use in treatment of metal surfaces

IU15 – Industrial, professional and consumer use in agricultural applications

IU16 – Industrial and consumer use in medical devices

9.1 ES1: Production of citric acid

9.1.1 Exposure scenario

9.1.1.1 Description of activities and processes covered in the exposure scenario

Citric acid production is largely by microbiological fermentation of molasses and sugar solutions. Extraction from lemon juice or chemical synthesis is possible but rarely used. Dilute citric acid from filtered fermentation broths is precipitated as practically insoluble calcium citrate by addition of calcium hydroxide. The calcium citrate is then reacted with sulfuric acid to form citric acid and calcium sulphate.

In a typical process for the production of citrate salts, citric acid is dissolved in deionised water. Addition of a source of the other ion results in conversion of citric acid to its salt. The salt is separated by evaporation and centrifugation, then dried, sieved and bagged.

A generic approach to production is used, based on a maximum site size of 10,000 tonnes per year. Such a site can produce citric acid or its salts. Only the tonnage destined for REACH-relevant applications is considered; material manufactured for uses that are exempt from REACH, such as food and pharmaceuticals, are not included.

Manufacture takes place at industrial sites in batch or continuous processes with limited opportunities for exposure (PROCS 1, 2, 3, 4). Loading/unloading operations at dedicated facilities (PROC8b) are also covered by the scenario.

9.1.1.2 Operational conditions related to frequency, duration and amount of use

Table 9.3: Duration, frequency and amount

Information type	Data field	Explanation
Used amount of substance per day	30 tonnes	
Duration of exposure per day at workplace [for one worker]	>4 hours (all PROCs)	REACH default used as a worst-case; actual exposure times may be significantly less.
Frequency of exposure at workplace [for one worker]	Once per day	
Annual amount used per site	10,000 tonnes	
Emission days per site	350	

9.1.1.3 Operational conditions and risk management measures related to product characteristics

There is a risk of dust explosion, particularly for fine powder grades. Therefore, build-up of dust is avoided and precautionary measures against electrostatic discharge are taken. LEV and respiratory protection are used in areas where workers may come into contact with dust.

Table 9.4: Characteristics of the substance or preparation

Information type	Data field	Explanation
Physical state	Solid. Various powder and crystalline grades are available.	
Risk management measures related to the design of product	Precautions against dust explosion and irritation caused by dust inhalation.	See text

9.1.1.4 **Operational conditions related to available dilution capacity and characteristics of exposed humans**

Table 9.5: Operational conditions related to respiration and skin contact

Information type	Data field	Explanation
Respiration volume under conditions of use	10 m ³ /d	Default for workers, light activity
Area of skin contact with the substance under conditions of use	240 cm ² 480 cm ² 240 cm ² 480 cm ² 480 cm ²	ECETOC TRA default: PROC 1: palm of one hand PROC 2: palms of both hands PROC 3: palm of one hand PROC4: palms of both hands PROC8b: palms of both hands
Body weight	70 kg	Default

Environmental surroundings characteristics

Dilution factor: 40 (default for large industrial site).

9.1.1.5 **Other operational conditions of use**

No measured data are available for releases of citric acid to air and waste water for the generic production site. Releases are therefore estimated on the basis of other information.

Releases to air

Due to the very low vapour pressure of the key intermediates and of citric acid itself, losses to air are considered to be zero.

Releases to waste water

The key production stage is the precipitation of calcium citrate. This substance is of low solubility, although a small quantity of citric acid could remain dissolved, a fraction of 0.0001, or 2.86 kg/d over 350 days.

There could be losses during handling and packaging processes, but when around 30 tonnes per day are handled these processes are highly automated. It can be anticipated that occasional spillages can occur due to small levels of leakage, amounting to at most 1 kg per day passing to aqueous waste.

The total passing to aqueous waste water is 3.86 kg/d.

Table 9.6: Technical fate of substance and losses from process/use to waste, waste water and air

Information type	Data field	Explanation
Fraction of applied amount lost from process/use to waste gas	0 kg/kg	See text
Fraction of applied amount lost from process/use to waste water	0.0001 kg/kg	See text

9.1.1.6 Risk management measures

Table 9.7 summarises the risk management measures in place during production of citric acid. Processes take place under controlled conditions with opportunities for manual handling minimised. Good working practices such as minimisation of splashes and spills, avoidance of contact with the substance or contaminated objects, regular cleaning of equipment and work area, good personal hygiene, staff training and management/supervision are in place.

Table 9.7: Risk management measures for industrial site

Information type	Data field	Explanation
Containment and local exhaust ventilation		
Containment plus good work practice required	Yes	
Local exhaust ventilation required plus good work practise	Yes	Typical practice of chemical industry. Not applicable for PROC1.
Personal protective equipment (PPE)		
Skin protection	Protective gloves	
Eye protection	Safety glasses	
Respiratory protection	Dust mask. In case of open handling of larger quantities or accidental release: particle mask or respirator with independent air supply	
Clothing	Working clothing worn.	
Other risk management measures related to workers		
N/A		
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water	Yes	Neutralisation
Resulting fraction of initially applied amount in waste water released from site to the external		On-site biological waste treatment is expected to remove a high proportion of citric acid, as the

Information type	Data field	Explanation
sewage system		substance is highly biodegradable.
Air emission abatement	No measured data	
Resulting fraction of applied amount in waste gas released to environment	No measured data	
Onsite waste treatment	No measured data	Secondary biological treatment
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste gas treatment.	No measured data	
Municipal or other type of external waste water treatment	None	None
Effluent (of the waste water treatment plant) discharge rate	1×10^7 l/d	Default for a large industrial site
Recovery of sludge for agriculture or horticulture	Yes	Dried sludge may be sold as an approved agricultural fertiliser

9.1.1.7 Waste related measures

Solid wastes may be disposed of via landfill or incineration, or are recycled outside of the process. Dried sludge from on-site waste water treatment plants may be sold as approved agricultural fertiliser.

Details of the treatment of aqueous waste vary at different sites but as a minimum, wastes are neutralised and the effluent treated in on- or off-site secondary biological treatment plants prior to discharge.

Waste gases are not generated.

9.1.2 Exposure estimation

9.1.2.1 Workers exposure

9.1.2.1.1 Acute/Short term exposure

Workers at the production site are routinely involved with the same tasks, therefore it is more appropriate to consider long-term exposure, and short-term exposure is not quantified.

9.1.2.1.2 Long-term exposure

Table 9.9 gives a summary of the long-term exposure values for PROCs 1, 2, 3, 4 and 8b, based on the ECETOC TRA model. Defaults for duration of exposure (>4 hours) and use of LEV (no for PROC 1, yes for PROCs 2, 3, 4, 8b) have been used. It has been assumed that respiratory protection is not used; where this is not the case, actual exposure may be much lower. Durations of exposure may also be less than 4 hours and in this case the following modifications factors can be applied: 0.6 for 1-4 hours, 0.2 for 15 mins to 1 hour, 0.1 for <15 mins.

Inhalation exposure

Based on the vapour pressure (negligibly low) and physical state (aqueous solution), aqueous formulations of citrates fall into the ‘minimal’ availability band (ECETOC 2009), and the potential for exposure is minimal to low (ECETOC 2009). Inhalation exposure for aqueous products is expected to be negligible as citric acid and its salts are extremely involatile with vapour pressures $<10^{-5}$ Pa and negligibly small Henry’s Law constants, indicating there is no potential for exposure via vapour.

The exceptions are where there is a possibility for inhalatory exposure via spray mists. In addition, use of dusty powder forms of citric acid and citrate salts may result in inhalation exposure.

Citric acid is a solid and during production, it may be handled in solid form. Citric acid is available in a range of particle size grades, from granular to fine powders. Therefore, a worst case scenario is that the substances are very dusty. This is defined as ‘high fugacity’ in the ECETOC TRA worker model. This is considered as worst case scenario for workers exposure.

Dermal exposure

Dermal uptake of citrate is expected to be minimal as it is extremely hydrophilic with a very low octanol-water partition coefficient (-1.8 to -0.12). The USEPA DERMWIN model allows for uptake from aqueous solution to be calculated on the basis of a proportion of the worst-case calculated by ECETOC TRA. This approach is indicated in the ECETOC (2004).

A worst-case estimate for the uptake fraction from aqueous solution has been calculated as 0.006 (see Section 5.1); actual uptake is expected to be much less. The dermal exposure estimated using ECETOC TRA and presented in Table 9.8 may be multiplied by this factor to obtain a worst-case estimate of the dermal exposure. Dermal uptake of solid citrates is expected to be negligible and is not considered.

Table 9.8: Dermal exposure estimates (based on ECETOC TRA model)

Exposure scenario	Process category	Description	LEV present?	Dermal exposure?	Predicted exposure ($\mu\text{g}/\text{cm}^2/\text{day}$)	Exposed skin surface area (cm^2)	Dermal exposure ($\text{mg}/\text{kg}/\text{day}$) ^a
Industrial use	PROC1	Use in closed process, no likelihood of exposure	No ^b	Yes	100	240	0.3
	PROC2	Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	Yes	Yes	20	480	0.14
	PROC3	Use in closed batch process (synthesis or formulation)	Yes	Yes	10	240	0.03
	PROC4	Use in batch and other process (synthesis) where opportunity for exposure arises	Yes	Yes	100	480	0.69
	PROC8b	Transfer from/to large vessels (dedicated)	Yes	Yes	100	480	0.69

a) Calculated assuming a default bodyweight of 70 kg for worker. b) In the ECETOC TRA model, LEV is not considered relevant for PROC1.

Table 9.9: Inhalation exposure estimates (based on ECETOC TRA model)

Exposure scenario	Process category	Description	LEV present?	LEV efficiency	Predicted exposure (ppm)	Predicted exposure (mg/m ³) ^c	Inhalation exposure (mg/kg/day) ^d
Industrial use	PROC1	Use in closed process, no likelihood of exposure	No ^b	-	0.001	0.01	0.001
	PROC2	Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	Yes	90%	0.01	0.1	0.01
	PROC3	Use in closed batch process (synthesis or formulation)	Yes	90%	0.01	0.1	0.01
	PROC4	Use in batch and other process (synthesis) where opportunity for exposure arises	Yes	90%	0.31	2.5	0.36
	PROC8b	Transfer from/to large vessels(dedicated)	Yes	95%	0.16	1.25	0.18

b) In the ECETOC TRA model, LEV is not considered relevant for PROC1. c) Results are calculated as mg/m³ for solids and ppm for non-solids d) Calculated assuming a default bodyweight of 70 kg for workers and a default respiratory volume of 10 m³, light activity, for an 8 hour work shift

Table 9.10: Summary of long-term exposure concentration to workers

Routes of exposure	Concentrations	Justification
Dermal local exposure (in $\mu\text{g}/\text{cm}^2$)	0.6	ECETOC TRA prediction for PROC8b, multiplied by an uptake factor of 0.006.
Dermal systemic exposure (in mg/kg bw/d)	0.004	ECETOC TRA prediction for PROC8b, multiplied by an uptake factor of 0.006.
Inhalation exposure (in mg/m^3)/8h workday	2.5	ECETOC TRA prediction for PROC8b
Inhalation exposure (in $\text{mg}/\text{kg}/\text{d}$)/8h workday	0.36	ECETOC TRA prediction for PROC8b

9.1.2.2 Consumer exposure

Consumer exposure is not applicable to chemical manufacturing.

9.1.2.3 Indirect exposure of humans via the environment (oral)

Exposure of humans to citric acid via the environment is not significant, as the substance is readily biodegradable.

9.1.2.3.1 Environmental exposure

9.1.2.3.2 Environmental releases

Predicted environmental release estimates have been used for releases during production. No measured data are available for the concentration of citric acid in any environmental compartment. The releases have been estimated using the exposure scenario for production (section 9.1.1.2 and 9.1.1.6) and Predicted Environmental Concentrations have been determined using EUSES 2.1.1. The EUSES program implements the environmental exposure models described in REACH Technical Guidance Chapter R16. Default model parameters have been used unless stated below.

The basis of local and regional production tonnages is to consider the sizes of the largest sites in the EU relative to the total tonnage as follows:

Production volume in EU: 100 000 tonnes

Regional tonnage: 10 000 tonnes

Fraction of main local source: 1

Local tonnage: 29 tonnes per day

Number of days: 350

The contribution of local releases to the regional concentration has been considered using the appropriate calculation in EUSES 2.1.1.

Table 9.11 shows the Predicted Environmental Concentrations. Due to the ready-biodegradability of citric acid it has not been considered necessary to define a PEC in STP.

The low log K_{ow} and ready biodegradability indicate that bioaccumulation is not a concern for citric acid. Therefore, the assessment of secondary poisoning is not considered.

Table 9.11: Summary of Predicted Exposure Concentrations

	PEC	unit
AIR		
Annual average local PEC in air (total)	3.50×10^{-16}	[mg m ⁻³]
WATER, SEDIMENT		
Local PEC in surface water during emission episode (dissolved)	0.0153	[mg l ⁻¹]
Annual average local PEC in surface water (dissolved)	0.0153	[mg l ⁻¹]
Local PEC in fresh-water sediment during emission episode	0.261	[mg kg ww ⁻¹]
Local PEC in seawater during emission episode (dissolved)	1.80×10^{-3}	[mg l ⁻¹]
Annual average local PEC in seawater (dissolved)	1.78×10^{-3}	[mg l ⁻¹]
Local PEC in marine sediment during emission episode	0.0307	[mg kg ww ⁻¹]
SOIL, GROUNDWATER		
Local PEC in agric. soil (total) averaged over 30 days	0.0227	[mg kg ww ⁻¹]
Local PEC in agric. soil (total) averaged over 180 days	7.43×10^{-3}	[mg kg ww ⁻¹]
Local PEC in grassland (total) averaged over 180 days	2.97×10^{-3}	[mg kg ww ⁻¹]
Local PEC in pore water of agricultural soil	1.12×10^{-4}	[mg l ⁻¹]
Local PEC in pore water of grassland	4.48×10^{-5}	[mg l ⁻¹]
Local PEC in groundwater under agricultural soil	1.12×10^{-4}	[mg l ⁻¹]

The EUSES model uses the Simple Treat sewage treatment model to predict the fate of a substance in the STP, based on the physicochemical and biodegradation properties. For citric acid, SimpleTreat predicts the following:

1.4 % to water:

0 % to air:

2.2 % to sludge:

96.4 % degraded.

The biodegradation rates used in the SIMPLETREAT model have been set up to be ten times faster than the default value for a readily degradable substance as a realistic way of modelling the substance being an essential metabolite.

Sludge from WWTPs may be spread on agricultural soil.

The dilution factor of 900 and 1000 (in the receiving water) have been applied for fresh water and marine water respectively, as there is no information on specific hydrodynamic conditions.

9.2 ES2: Use of citric acid as a chemical intermediate

9.2.1 Exposure scenario

9.2.1.1 Description of activities and processes covered in the exposure scenario

This scenario covers the use of citric acid as a chemical intermediate in the synthesis of other chemicals, such as citrate salts and esters. Only use at downstream user sites is considered here; intermediate use at producer sites is covered by ES1.

Chemical synthesis takes place at industrial sites in batch or continuous processes with limited opportunities for exposure (PROCS 1, 2, 3, 4). Loading/unloading operations at dedicated facilities (PROC8b) are also covered by the scenario.

9.2.1.2 Operational conditions related to frequency, duration and amount of use

Table 9.12: Duration, frequency and amount

Information type	Data field	Explanation
Used amount of substance per day	10,000 kg/d	Generic information
Duration of exposure per day at workplace [for one worker]	>4 hours (all PROCs)	REACH default used as a worst case; actually exposure times may be significantly less
Frequency of exposure at workplace [for one worker]	Once per day	In situations where the duration of exposure is lower, frequency of exposure may be higher
Annual amount used per site	3,000 tpa	Generic information
Emission days per site	300 d/y	REACH default number of days for high volumes

9.2.1.3 Operational conditions and risk management measures related to product characteristics

There is a risk of dust explosion, particularly for fine powder grades. Therefore, build-up of dust is avoided and precautionary measures against electrostatic discharge are taken. LEV and respiratory protection are used in areas where workers may come into contact with dust.

Table 9.13: Characteristics of the substance or preparation

Information type	Data field	Explanation
Physical state	Solid. Various powder and crystalline grades are available.	
Risk management measures related to the design of product	Precautions against dust explosion and irritation caused by dust inhalation.	See text

9.2.1.4 **Operational conditions related to available dilution capacity and characteristics of exposed humans**

Table 9.14: Operational conditions related to respiration and skin contact

Information type	Data field	Explanation
Respiration volume under conditions of use	10 m ³ /d	Default for workers, light activity
Area of skin contact with the substance under conditions of use	240 cm ²	ECETOC TRA default:
	480 cm ²	PROC1: palm of one hand
	240 cm ²	PROC2: palms of both hands
	480 cm ²	PROC3: palm of one hand
	480 cm ²	PROC4: palms of both hands
	480 cm ²	PROC8b: palms of both hands
Body weight	70 kg	Default

Environmental surroundings characteristics

Dilution factor: 40 (default for large industrial site).

9.2.1.5 **Other operational conditions of use**

No measured data are available for releases to air and waste water during the processing of citric acid as an intermediate. Releases are therefore estimated on the basis of information in the public domain.

Releases to air

Due to the very low vapour pressure of the key intermediates and of citric acid itself, losses to air are considered to be zero.

Releases to water

The REACH ERC 6A (Industrial use of intermediate) release default estimates to waste water is 2%.

The default TGD (TGD ESD part IV) release rate from processing of synthetic intermediate is 0.7% by weight for a wet process and 0% for a dry (water-free) process. Processing of citric acid is a wet-process. On-site waste water treatment at the plant (e.g. activated carbon, precipitation and so on) is already included in the emission factors.

The default loss of 70 kg/d (EU TGD 0.7% default) from the processing of 30 t/d of citric acid is not considered to be realistic. Realistic losses to waste water from the processing of citric acid at a typical industrial site are expected to come from:

- Substance washout from ventilation systems
- Minor routine spillages

- Occasional equipment loss/leakages

Given that a solid is precipitated efficiently it is considered that 7 kg/d is a more realistic estimate.

Citric acid is highly degradable and on-site waste water treatment is expected to mean that little of the substance is released to the wider environment.

It can be assumed that this process will be taking place at a large industrial site with waste water passing to a larger-than-default WWTP with a flow rate of 10,000 m³/day.

Table 9.15: Technical fate of substance and losses from process/use to waste, waste water and air

Information type	Data field	Explanation
Fraction of applied amount lost from process/use to waste gas	0 kg/kg	See text
Fraction of applied amount lost from process/use to waste water	0.007 kg/kg	See text

1.4.3.1 Risk management measures

Table 9.16 summarises the risk management measures in place during use of citric acid as a chemical intermediate. Process take place under controlled conditions with opportunities for manual handling minimised. Good working practices such as minimisation of splashes and spills, avoidance of contact with the substance or contaminated objects, regular cleaning of equipment and work area, good personal hygiene, staff training and management/supervision are in place.

Table 9.16: Risk management measures for industrial site

Information type	Data field	Explanation
Containment and local exhaust ventilation		
Containment plus good work practice required	Yes	
Local exhaust ventilation required plus good work practise	Yes	Typical practice of chemical industry. Not applicable for PROC1.
Personal protective equipment (PPE)		
Skin protection	Protective gloves	
Eye protection	Safety glasses	
Respiratory protection	Dust mask. In case of open handling of larger quantities or accidental release: particle mask or respirator with independent air supply	
Clothing	Working clothing worn.	
Other risk management measures related to workers		

Information type	Data field	Explanation
N/A		
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water	Yes	Neutralisation
Resulting fraction of initially applied amount in waste water released from site to the external sewage system		On-site biological waste treatment is expected to remove a high proportion of citric acid, as the substance is highly biodegradable.
Air emission abatement	No measured data	
Resulting fraction of applied amount in waste gas released to environment	No measured data	
Onsite waste treatment	No measured data	Secondary biological treatment
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste gas treatment.	No measured data	
Municipal or other type of external waste water treatment	None	None
Effluent (of the waste water treatment plant) discharge rate	1x 10 ⁷ l/d	Default for a large industrial site
Recovery of sludge for agriculture or horticulture	Yes	Dried sludge may be sold as an approved agricultural fertiliser

9.2.1.6 Waste related measures

Solid wastes may be disposed of via landfill or incineration, or are recycled outside of the process. Dried sludge from on-site waste water treatment plants may be sold as approved agricultural fertiliser.

Details of the treatment of aqueous waste vary at different sites but as a minimum, wastes are neutralised and the effluent treated in on- or off-site secondary biological treatment plants prior to discharge.

Waste gases are not generated.

9.2.2 Exposure estimation

9.2.2.1 Workers exposure

9.2.2.1.1 Acute/Short term exposure

Workers at the production site are routinely involved with the same tasks, therefore it is more appropriate to consider long-term exposure, and short-term exposure is not quantified.

9.2.2.1.2 Long-term exposure

Table 9.17 gives a summary of the long-term exposure values for PROCs 1, 2, 3, 4 and 8b, based on the ECETOC TRA model. Defaults for duration of exposure (>4 hours) and use of LEV (no for PROC 1, yes for PROCs 2, 3, 4, 8b) have been used. As a worst case, it has been assumed that respiratory protection is not used; where this is not the case, actual exposure may be much lower. Durations of exposure may also be less than 4 hours and in this case the following modification factors can be applied: 0.6 for 1-4 hours, 0.2 for 15 mins to 1 hour, 0.1 for <15 mins.

Inhalation exposure

Based on the vapour pressure (negligibly low) and physical state (aqueous solution), aqueous formulations of citrates fall into the 'minimal' availability band (ECETOC 2009), and the potential for exposure is minimal to low (ECETOC 2009). Inhalation exposure for aqueous products is expected to be negligible as citric acid and its salts are extremely involatile with vapour pressures $<10^{-5}$ Pa and negligibly small Henry's Law constants, indicating there is no potential for exposure via vapour.

The exceptions are where there is a possibility for inhalatory exposure via spray mists. In addition, use of dusty powder forms of citric acid and citrate salts may result in inhalation exposure.

Citric acid is a solid and during use as an intermediate, it may be handled in solid form. Citric acid is available in a range of particle size grades, from granular to fine powders. Therefore, a worst case scenario is that the substances are very dusty. This is defined as 'high fugacity' in the ECETOC TRA worker model. This is considered as worst case scenario for workers exposure.

Dermal exposure

Dermal uptake of citrate is expected to be minimal as it is extremely hydrophilic with a very low octanol-water partition coefficient (-1.8 to -0.12). The USEPA DERMWIN model allows for uptake from aqueous solution to be calculated on the basis of a proportion of the worst-case calculated by ECETOC TRA. This approach is indicated in the ECETOC (2004).

A worst-case estimate for the uptake fraction from aqueous solution has been calculated as 0.006 (see Section 5.1); actual uptake is expected to be much less. The dermal exposure estimated using ECETOC TRA and presented in Table 9.17 may be multiplied by this factor to obtain a worst-case estimate of the dermal exposure. Dermal uptake of solid citrates is expected to be negligible and is not considered.

Table 9.17: Dermal exposure estimates (based on ECETOC TRA model)

Exposure scenario	Process category	Description	LEV present?	Dermal exposure?	Predicted exposure ($\mu\text{g}/\text{cm}^2/\text{day}$)	Exposed skin surface area (cm^2)	Dermal exposure ($\text{mg}/\text{kg}/\text{day}$) ^a
Industrial use	PROC1	Use in closed process, no likelihood of exposure	No ^b	Yes	100	240	0.3
	PROC2	Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	Yes	Yes	20	480	0.14
	PROC3	Use in closed batch process (synthesis or formulation)	Yes	Yes	10	240	0.03
	PROC4	Use in batch and other process (synthesis) where opportunity for exposure arises	Yes	Yes	100	480	0.69
	PROC8b	Transfer from/to large vessels (dedicated)	Yes	Yes	100	480	0.69

a) Calculated assuming a default bodyweight of 70 kg for worker

b) In the ECETOC TRA model, LEV is not considered relevant for PROC1.

Table 9.18: Inhalation exposure estimates (based on ECETOC TRA model)

Exposure scenario	Process category	Description	LEV present?	LEV efficiency	Predicted exposure (ppm)	Predicted exposure (mg/m ³) ^c	Inhalation exposure (mg/kg/day) ^d
Industrial use	PROC1	Use in closed process, no likelihood of exposure	No ^b	-	0.001	0.01	0.001
	PROC2	Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	Yes	90%	0.01	0.1	0.01
	PROC3	Use in closed batch process (synthesis or formulation)	Yes	90%	0.01	0.1	0.01
	PROC4	Use in batch and other process (synthesis) where opportunity for exposure arises	Yes	90%	0.31	2.5	0.36
	PROC8b	Transfer from/to large vessels(dedicated)	Yes	95%	0.16	1.25	0.18

b) In the ECETOC TRA model, LEV is not considered relevant for PROC1.

c) Results are calculated as mg/m³ for solids and ppm for non-solids

d) Calculated assuming a default bodyweight of 70 kg for workers and a default respiratory volume of 10 m³, light activity, for an 8 hour work shift

Table 9.19: Summary of long-term exposure concentration to workers

Routes of exposure	Concentrations	Justification
Dermal local exposure (in $\mu\text{g}/\text{cm}^2$)	0.6	ECETOC TRA prediction for PROC8b, multiplied by an uptake factor of 0.006.
Dermal systemic exposure (in mg/kg bw/d)	0.004	ECETOC TRA prediction for PROC8b, multiplied by an uptake factor of 0.006.
Inhalation exposure (in mg/m^3)/8h workday	2.5	ECETOC TRA prediction for PROC8b
Inhalation exposure (in $\text{mg}/\text{kg}/\text{d}$)/8h workday	0.36	ECETOC TRA prediction for PROC8b

9.2.2.2 Consumer exposure

Consumer exposure is not applicable to use of citric acid as an intermediate.

9.2.2.3 Indirect exposure of humans via the environment (oral)

There is no significant exposure of humans to citric acid via the environment, as the substance is readily biodegradable.

9.2.2.4 Environmental exposure

9.2.2.4.1 Environmental releases

Predicted environmental release estimates have been used for releases during intermediate use. The releases have been estimated using the exposure scenario for intermediate use (section 9.2.1.2 and 9.2.1.6) and Predicted Environmental Concentrations have been determined using EUSES 2.1.1. The EUSES program implements the environmental exposure models described in REACH Technical Guidance Chapter R16. Default model parameters have been used with the following exceptions:

Dilution factor: 40 (large industrial site).

WWTP flow rate: $10,000 \text{ m}^3/\text{d}$ (large industrial site).

The basis of local and regional production tonnages is to consider the sizes of the largest sites in the EU relative to the total tonnage as follows:

Application volume in EU: 12000 tonnes

Regional tonnage: 3000 tonnes

Fraction of main local source: 1

Local tonnage: 10 tonnes per day

Number of days: 300

Table 9.20 shows the Predicted Environmental Concentrations. Due to the ready-biodegradability of citric acid it has not been considered necessary to define a PEC in STP. The low log K_{ow} and ready biodegradability indicate that bioaccumulation is not a concern for citric acid. Therefore, the assessment of secondary poisoning is not considered.

Table 9.20: Summary of Predicted Exposure Concentrations

	PEC	unit
AIR		
Annual average local PEC in air (total)	5.45×10^{-16}	[mg m ⁻³]
WATER, SEDIMENT		
Local PEC in surface water during emission episode (dissolved)	0.0154	[mg l ⁻¹]
Annual average local PEC in surface water (dissolved)	0.0154	[mg l ⁻¹]
Local PEC in fresh-water sediment during emission episode	0.263	[mg kg ww ⁻¹]
Local PEC in seawater during emission episode (dissolved)	0.0084	[mg l ⁻¹]
Annual average local PEC in seawater (dissolved)	0.00716	[mg l ⁻¹]
Local PEC in marine sediment during emission episode	0.144	[mg kg ww ⁻¹]
SOIL, GROUNDWATER		
Local PEC in agric. soil (total) averaged over 30 days	0.0411	[mg kg ww ⁻¹]
Local PEC in agric. soil (total) averaged over 180 days	0.0135	[mg kg ww ⁻¹]
Local PEC in grassland (total) averaged over 180 days	0.00539	[mg kg ww ⁻¹]
Local PEC in pore water of agricultural soil	0.000203	[mg l ⁻¹]
Local PEC in pore water of grassland	0.0000813	[mg l ⁻¹]
Local PEC in groundwater under agricultural soil	0.000203	[mg l ⁻¹]

No measured data are available for the concentration of citric acid in sewage treatment plants (STP). The concentration has been estimated using a waste water treatment plant flow rate of 10000 m³/d and a dilution factor of 40 (Section 9.2.1.6) in EUSES 2.1.1.

The EUSES model uses the Simple Treat sewage treatment model to predict the fate of a substance in the STP, based on the physicochemical and biodegradation properties. For citric acid, SimpleTreat predicts the following:

12.7 % to water:

6×10^{-11} % to air:

0.017 % to sludge:

87.3 % degraded.

Sludge from WWTPs may be spread on agricultural soil.

The dilution factor of 40 and 100 (in the receiving water) have been applied for fresh water and marine water respectively, as there is no information on specific hydrodynamic conditions. No measured data are available for the concentration of citric acid due to its use as a chemical intermediate in the aquatic pelagic compartment.

9.3 ES3: Formulation of citric acid into preparations

9.3.1 Exposure scenario

The primary uses of citric acid are described in the exposure scenarios 2-17. However, formulation is a general process needed in many industries and Exposure Scenario 3 covers the major uses in addition to the possibility of minor uses which require an industrial formulation stage.

The formulation of cleaning products is the largest application and can be taken as the worst case for the environmental exposure assessment, and this ES is expressed in terms of cleaning products but is applicable more generally.

9.3.1.1 Description of activities and processes covered in the exposure scenario

The following processes have been identified as being associated with formulation of citric acid. Other processes may also be used but the processes listed are considered to include the worst-case scenarios.

PROC1: Use in closed process, no likelihood of exposure

PROC2: Use in closed, continuous process with occasional controlled exposure

PROC3: Use in closed batch process (synthesis or formulation)

PROC4: Use in batch and other process (synthesis) where opportunity for exposure arises

PROC5: Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact); Industrial setting.

PROC7: Industrial spraying

PROC8: Transfer of substance or preparation from/to vessels/large containers; Industrial setting. This may be at non-dedicated (PROC8a) or dedicated (PROC8b) facilities depending on the situation, and may relate to both neat substance and preparations.

PROC9: Transfer of substance or of preparation into small containers (dedicated filling line, including weighing); Industrial setting.

PROC13: Treatment of articles by dipping and pouring

PROC14: Production of preparations or articles by tableting, compression, extrusion, pelletisation

PROC15: Use of laboratory reagents in small scale laboratories

PROC19: Hand-mixing with intimate contact (only PPE available)

Operational conditions related to frequency, duration and amount of use

Table 9.21: Duration, frequency and amount

Information type	Data field	Explanation
Used amount of substance per day	6000 tonnes	
Duration of exposure per day at workplace [for one worker]	>4 hours (all PROCs)	For some applications/setting exposure times may be significantly less
Frequency of exposure at workplace [for one worker]	Once per day	For some applications/settings with shorter duration exposures, multiple exposures may occur in a single day
Annual amount used per site	20 tonnes	
Emission days per site	300 days	

9.3.1.2 Operational conditions and risk management measures related to product characteristics

There is a risk of dust explosion, particularly for fine powder grades. Therefore, build-up of dust is avoided and precautionary measures against electrostatic discharge are taken. LEV and respiratory protection are used in areas where workers may come into contact with dust.

Table 9.22: Characteristics of the substance or preparation

Information type	Data field	Explanation
Physical state	Solid. Various powder and crystalline grades are available. The substance may also be handled as part of, usually aqueous-based, formulations.	
Risk management measures related to the design of product	Precautions against dust explosion and irritation caused by dust inhalation.	See text

9.3.1.3 Operational conditions related to available dilution capacity and characteristics of exposed humans

Table 9.23: Operational conditions related to respiration and skin contact

Information type	Data field	Explanation
Respiration volume under conditions of use	10 m ³ /d	Default worker respiration rate for light activity

Information type	Data field	Explanation
Area of skin contact with the substance under conditions of use	240 cm ² 480 cm ² 960 cm ² 1500 cm ² 1980 cm ²	ECETOC TRA default: PROC1, 13, 15: palm of 1 hand PROC2, 4, 5, 8b, 9, 13 and 14: palms of both hands PROC8a: 2 hands PROC7: 2 hands, forearms PROC19: 2 hands
Body weight	10 m ³ /d	Default worker respiration rate for light activity

Environmental surroundings characteristics

Dilution factor: 40 (default for large industrial site).

9.3.1.4 Other operational conditions of use

The citrates used in the formulation of products are generally solids which may be mixed with other solids or dissolved in aqueous solution. There is some potential for airborne release of citric acid (or citrate) particulates on charging (transfer, dosing) to the process equipment used, especially if containment is not good. However, the most likely release will be to waste water *via* clean out or spillage.

Tables 9.32 and 9.33 show the default emission factors from the EU TGD (EU TDG Parts II and IV, EC 2003a,b) and REACH Environmental Release Categories (ERC), for emissions to water and air respectively, during the formulation of personal care (based on cosmetics) products.

Table 9.24: Releases to waste water for formulation

Source	REACH ERC2	TGD Part IV Table 2 , Table A 2#
Fraction to waste water	0.02	0.0009

Table 9.25: Releases to air for formulation

Source	REACH ERC2	TGD Part IV Table 2 , Table A 2# (Formulation of liquid products)	TGD Part IV Table 2 , Table A 2# (Formulation of others/unknown products)
Fraction to air	0.025	0.00002	0.0002

The B Tables presented in the EU TGD (EC, 2003c) show the number of emission days for the formulation of personal care products at a tonnage of 1000 tpa and above as 300 days (EU TGD Table B2.3), while the REACH guidance for exposure estimation (R16) specifies 100 days for 100 – 2000 tpa and 300 days for greater than 2000 tpa of formulated products.

Detergents manufacturing facilities either treat effluents in on-site waste water treatment plants followed by discharge to sewers, or discharge effluents directly to the municipal waste water treatment system. Most facilities, however, discharge gaseous emissions directly to the atmosphere, with a few incorporating filtration. Therefore the values from the TGD are considered to be a realistic worst-case, especially given the low volatility of citric acid.

Taking the HERA figure of *approx.* 100 000 tpa [HERA, 2005] for total use of citrates in detergents, and realistic values of 10% formulated in a single region, and 60% of that at a single location, gives a volume of 6,000 tpa citrates formulated at a single location.

For this generic site, the daily loss rate to waste water is
 $6000 \text{ t} \times 1000 \text{ kg/t} \times 0.0009 / 300 \text{ d} = 18 \text{ kg/d}$.

The tonnage to be covered is now 150 000 tpa, but the site size is retained. The loss rate is considered to be a reasonable worst case for a large site. At smaller formulation sites the amount handled per day would be lower and the controls could be less, but overall rates per day would be similar.

Table 9.26: Technical fate of substance and losses from process/use to waste, waste water and air.

Information type	Data field	Explanation
Fraction of applied amount lost from process/use to waste gas	0.0025	See text
Fraction of applied amount lost from process/use to waste water	0.0005	See text

9.3.1.5 Risk management measures

Table 9.27: Risk management measures for industrial site .

Information type	Data field	Explanation
Containment and local exhaust ventilation		
Containment plus good work practice required	Yes	General good hygiene and housekeeping
Local exhaust ventilation required plus good work practise	Yes	Typical practice of chemical industry.
Personal protective equipment (PPE)		
Skin protection	Protective gloves	
Eye protection	Safety glasses	
Clothing	Working clothing worn.	
Other risk management measures related to workers		

Information type	Data field	Explanation
N/A		
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water	Yes	Removal of solids in settling tanks
Resulting fraction of initially applied amount in waste water released from site to the external sewage system	No measured data	
Air emission abatement	No measured data	
Resulting fraction of applied amount in waste gas released to environment	No measured data	See text
Onsite waste treatment	No	Worst-case assumption as no specific information available.
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste gas treatment.	No measured data	
Municipal or other type of external waste water treatment	Yes	Typical practise in the chemical industry
Effluent (of the waste water treatment plant) discharge rate	$1 * 10^7$ L/d	Default for a large industrial site.
Recovery of sludge for agriculture or horticulture	Yes	Worst-case assumption as no specific information available.

9.3.1.6 Waste related measures

Solid wastes may be disposed of via landfill or incineration, or are recycled outside of the process. Dried sludge from on-site waste water treatment plants may be spread on agricultural land.

Details of the treatment of aqueous waste vary at different sites but as a minimum, wastes are neutralised and the effluent treated in on- or off-site secondary biological treatment plants prior to discharge.

Waste gases are not generated.

9.3.2 Exposure estimation

9.3.2.1 Workers exposure

9.3.2.1.1 Acute/Short term exposure

Workers in industrial settings are routinely involved with the same tasks, therefore it is more appropriate to consider long-term exposure, and short-term exposure is not quantified.

9.3.2.1.2 Long-term exposure

Table 9.28 gives a summary of the long-term exposure values for PROCs 1, 2, 3, 4, 5, 7, 8a, 8b, 9, 13, 14, 15, 19, based on the ECETOC TRA model. Defaults for duration of exposure (>4 hours) and use of LEV (no for PROC 1, yes for all other PROCs) have been used. It has been assumed that respiratory protection is not used; where this is not the case, actual exposure may be much lower. Durations of exposure may also be less than 4 hours and in this case the following modification factors can be applied: 0.6 for 1-4 hours, 0.2 for 15 mins to 1 hour, 0.1 for <15 mins. The concentration in the formulation is assumed to be >25%; reductions in the exposures may be applied for formulations with a lower percentage citrate (*0.6 for 5-25%, *0.2 for 1-5% and *0.1 for <1%).

Inhalation exposure

Based on the vapour pressure (negligibly low) and physical state (aqueous solution), aqueous formulations of citrates fall into the 'minimal' availability band (ECETOC 2009), and the potential for exposure is minimal to low (ECETOC 2009). Inhalation exposure for aqueous products is expected to be negligible as citric acid and its salts are extremely involatile with vapour pressures $<10^{-5}$ Pa and negligibly small Henry's Law constants, indicating there is no potential for exposure via vapour.

The exceptions are where there is a possibility for inhalatory exposure via spray mists. In addition, use of dusty powder forms of citric acid and citrate salts may result in inhalation exposure.

The substances may be handled as a solid during some stages of the formulation process. The citrates are available in a range of different grades, from fine powders to granular material. Therefore, for most PROCs the substance is considered as a solid with high fugacity as this represents a worst cases scenario. The exception is PROCs 13 (Treatment of articles by dipping and pouring) and 19 (Hand-mixing with intimate contact) which are only expected to take place with already formulated product; the fugacity is assumed to be low.

Dermal exposure

Dermal uptake of citrate is expected to be minimal as it is extremely hydrophilic with a very low octanol-water partition coefficient (-1.8 to -0.12). The USEPA DERMWIN model allows for uptake from aqueous solution to be calculated on the basis of a proportion of the worst-case calculated by ECETOC TRA. This approach is indicated in the ECETOC (2004).

A worst-case estimate for the uptake fraction from aqueous solution has been calculated as 0.006 (see Section 5.1); actual uptake is expected to be much less. The dermal exposure estimated using ECETOC TRA and presented in Table 9.7 may be multiplied by this factor to obtain a worst-case estimate of the dermal exposure. Dermal uptake of solid citrates is expected to be negligible and is not considered.

Table 9.28: Dermal exposure estimates (based on ECETOC TRA model) for formulation

Life cycle stage	Process category	Description	Fugacity	LEV present?	Dermal exposure?	Predicted exposure ($\mu\text{g}/\text{cm}^2/\text{day}$)	Exposed skin surface area (cm^2)	Dermal exposure ($\text{mg}/\text{kg}/\text{day}$) ^a
Industrial use	PROC1	Use in closed process, no likelihood of exposure	High	No ^b	Yes	100	240	0.34
Industrial use	PROC2	Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	High	Yes	Yes	20	480	0.14
Industrial use	PROC3	Use in closed batch process (synthesis or formulation)	High	Yes	Yes	10	240	0.034
Industrial use	PROC4	Use in batch and other process (synthesis) where opportunity for exposure arises	High	Yes	Yes	100	480	0.69
Industrial use	PROC5	Mixing or blending in batch processes (multistage and/or significant contact)	High	Yes	Yes	200	480	1.37
Industrial use	PROC7	Industrial spraying	High	Yes	Yes	200	1500	4.29
Industrial use	PROC8 a	Transfer from/to large vessels (non-dedicated).	High	Yes	Yes	100	960	1.37
Industrial use	PROC8 b	Transfer from/to large vessels (dedicated)	High	Yes	Yes	100	480	0.69
Industrial use	PROC9	Transfer to small containers	High	Yes	Yes	100	480	0.69
Industrial use	PROC13	Treatment of articles by dipping and pouring	Low	Yes	Yes	100	480	0.69
Industrial use	PROC14	Production of preparations or articles by tableting, compression, extrusion, pelletisation	High	Yes	Yes	50	480	0.34

Life cycle stage	Process category	Description	Fugacity	LEV present?	Dermal exposure?	Predicted exposure ($\mu\text{g}/\text{cm}^2/\text{day}$)	Exposed skin surface area (cm^2)	Dermal exposure ($\text{mg}/\text{kg}/\text{day}$) ^a
Industrial use	PROC15	Use of laboratory reagents in small scale laboratories	High	Yes	Yes	10	240	0.034
Industrial use	PROC19	Hand-mixing with intimate contact (only PPE available)	Low	Yes	Yes	500	1980	14.1

(a) Calculated assuming a default bodyweight of 70 kg for workers

Table 9.29: Inhalation exposure estimates (based on ECETOC TRA model) for formulation

Life cycle stage	Process category	Description	Fugacity	LEV present?	LEV efficiency	Predicted exposure (ppm)	Predicted exposure (mg/m^3) ^b	Inhalation exposure ($\text{mg}/\text{kg}/\text{day}$) ^c
Industrial use	PROC1	Use in closed process, no likelihood of exposure	High	No ^b	n/a	0.0013	0.01	0.0014
Industrial use	PROC2	Use in closed, continuous process with occasional controlled exposure (e.g. sampling)	High	Yes	90%	0.0125	0.1	0.014
Industrial use	PROC3	Use in closed batch process (synthesis or formulation)	High	Yes	90%	0.0125	0.1	0.014
Industrial use	PROC4	Use in batch and other process (synthesis) where opportunity for exposure arises	High	Yes	90%	0.31	2.5	0.36
Industrial use	PROC5	Mixing or blending in batch processes (multistage and/or significant contact)	High	Yes	90%	0.31	2.5	0.36
Industrial use	PROC7	Industrial spraying	High	Yes	90%	1.25	10	1.43
Industrial use	PROC8a	Transfer from/to large vessels (non-dedicated)	High	Yes	90%	0.63	5	0.71

Life cycle stage	Process category	Description	Fugacity	LEV present?	LEV efficiency	Predicted exposure (ppm)	Predicted exposure (mg/m ³) ^b	Inhalation exposure (mg/kg/day) ^c
Industrial use	PROC8b	Transfer from/to large vessels (dedicated)	High	Yes	90%	0.31	2.5	0.36
Industrial use	PROC9	Transfer to small containers	High	Yes	90%	0.25	2	0.29
Industrial use	PROC13	Treatment of articles by dipping and pouring	Low	Yes	90%	0.0013	0.01	0.0014
Industrial use	PROC14	Production of preparations or articles by tableting, compression, extrusion, pelletisation	High	Yes	90%	0.13	1	0.14
Industrial use	PROC15	Use of laboratory reagents in small scale laboratories	High	Yes	90%	0.063	0.5	0.071
Industrial use	PROC19	Hand-mixing with intimate contact (only PPE available)	Low	Yes	90%	0.0063	0.05	0.0071

b) Results are calculated as mg/m³ for solids and ppm for non-solids

c) Calculated assuming a default bodyweight of 70 kg for workers and a default respiratory volume of 10 m³, light activity, for an 8 hour work shift

Table 9.30: Summary of long-term exposure concentration to workers

Routes of exposure	Concentrations	Justification
Dermal local exposure (in $\mu\text{g}/\text{cm}^2$)	3	ECETOC TRA prediction for PROC19, multiplied by an uptake factor of 0.006.
Dermal systemic exposure (in $\text{mg}/\text{kg bw}/\text{d}$)	0.08	ECETOC TRA prediction for PROC19, multiplied by an uptake factor of 0.006.
Inhalation exposure (in mg/m^3)/8h workday	10	ECETOC TRA prediction for PROC7
Inhalation exposure (in $\text{mg}/\text{kg}/\text{d}$)/8h workday	1.43	ECETOC TRA prediction for PROC7

9.3.2.2 Consumer exposure

There is no consumer exposure associated with industrial formulation.

9.3.2.3 Indirect exposure of humans via the environment (oral)

There is no exposure of humans to the substance via the environment.

9.3.2.4 Environmental exposure

9.3.2.4.1 Environmental releases

Predicted environmental release estimates have been used for releases during formulation. The releases have been estimated using the exposure scenario for formulation (section 9.3.1.2 and 9.3.1.6) and Predicted Environmental Concentrations have been determined using EUSES 2.1.1.

The EUSES program implements the environmental exposure models described in REACH Technical Guidance Chapter R16. Default model parameters have been used with the following exceptions:

Dilution factor: 40 (large industrial site).

WWTP flow rate: 10,000 m^3/d (large industrial site).

The basis of local and regional tonnages is to consider the sizes of the largest sites in the EU relative to the total tonnage as follows:

Application volume in EU: 150000 tonnes

Regional tonnage: 15000 tonnes

Fraction of main local source: 0.4

Local tonnage: 2 tonnes per day

Number of days: 300

The contribution of local releases to the regional concentration has been considered using the appropriate calculation in EUSES 2.1.1.

Table 9.31 shows the Predicted Environmental Concentrations. Due to the ready-biodegradability of citric acid it has not been considered necessary to define a PEC in STP. The low log K_{ow} and ready biodegradability indicate that bioaccumulation is not a concern for citric acid. Therefore, the assessment of secondary poisoning is not considered.

Table 9.31: Summary of Predicted Exposure Concentrations

	PEC	unit
AIR		
Annual average local PEC in air (total)	1.4×10^{-15}	[mg.m ⁻³]
WATER, SEDIMENT		
Local PEC in surface water during emission episode (dissolved)	0.0158	[mg l ⁻¹]
Annual average local PEC in surface water (dissolved)	0.0157	[mg l ⁻¹]
Local PEC in fresh-water sediment during emission episode	0.27	[mg kg wwt ⁻¹]
Local PEC in seawater during emission episode (dissolved)	0.0194	[mg l ⁻¹]
Annual average local PEC in seawater (dissolved)	0.0162	[mg l ⁻¹]
Local PEC in marine sediment during emission episode	0.331	[mg kg wwt ⁻¹]
SOIL, GROUNDWATER		
Local PEC in agric. soil (total) averaged over 30 days	0.106	[mg kg wwt ⁻¹]
Local PEC in agric. soil (total) averaged over 180 days	0.347	[mg kg wwt ⁻¹]
Local PEC in grassland (total) averaged over 180 days	0.0139	[mg kg wwt ⁻¹]
Local PEC in pore water of agricultural soil	5.23×10^{-4}	[mg l ⁻¹]
Local PEC in pore water of grassland	2.09×10^{-4}	[mg l ⁻¹]
Local PEC in groundwater under agricultural soil	5.23×10^{-4}	[mg l ⁻¹]

No measured data are available for the concentration of citric acid in sewage treatment plants (STP). The concentration has been estimated using a waste water treatment plant flow rate of 10,000 m³/d (Section 9.3.1.6) in EUSES 2.1.1.

The EUSES model uses the Simple Treat sewage treatment model to predict the fate of a substance in the STP, based on the physicochemical and biodegradation properties. For citric acid, SimpleTreat predicts the following:

12.7 % to water:

$6 * 10^{-11}$ % to air:

0.017 % to sludge:

87.3 % degraded.

Sludge from WWTPs may be spread on agricultural soil.

Estimated local exposure concentrations for freshwater and marine water have been based on the exposure scenario for production (Sections 9.1.1.2 and 9.1.1.6) and EUSES 2.1.1 model output. The dilution factor of 10 (in the receiving water) has been applied. No measured data are available for the concentration of citric acid in the aquatic pelagic compartment.

9.4 ES4: Personal care use

Personal care use is treated as exempt from REACH in respect of human health. Formulation is covered by ES3.

Citric acid and its salts are used in a wide range of personal care products, including:

- Shampoos and conditioners
- Astringent lotions
- Bubble baths
- Creams and lotions
- Facial cleaners
- Feminine hygiene products
- Permanent wave neutraliser
- Propellants for aerosol-type dispensers
- Toothpastes
- Mouth rinses
- Body wash/cleanser
- Hair colour and bleaching
- Moisturisers
- Hand soaps
- Nail polish
- Anti-aging products

In these products, citrates act as clarifying agents, water softeners, buffers, foam boosters and stabilizers, complexing agents (for example to stabilize the formulation by chelating metal ions and preventing discoloration and decomposition).

9.4.1 Exposure scenario

9.4.1.1 Other operational conditions of use

The EU TGD A-Table A4.1 gives the releases of cosmetics to air and wastewater as 0 and 100% respectively. This seems reasonable, given that citrates are non-volatile and highly water soluble. It is also in agreement with Colipa's assessment of the fate of non-volatile components of cosmetics (Colipa 2008).

The TGD defaults and REACH environmental release category (ERC8a) assume that if a substance is used widely across the EU, the fraction of the production volume used in the standard EU Region is 10%. For cosmetics, the fraction of the main local source ($f_{\text{mainsource}}$) is 0.0005 (HERA, 2005, page 27). This is equivalent to saying that use in a region is evenly distributed. The number of days of use is 365 per year. Therefore, for 7500 tpa of citric acid in personal care products used widely across the EU, the estimated release of citric acid to a particular default-sized local waste water treatment plant is at most:

$$7\,500\,000 \text{ kg/y} \times 0.1 \times 0.0005 / 365 \text{ d/y} = 1.03 \text{ kg/d}$$

Table 9.32: Technical fate of substance and losses from process/use to waste, waste water and air.

Information type	Data field	Explanation
Fraction of applied amount lost from process/use to waste gas	0 kg/kg	See text
Fraction of applied amount lost from process/use to waste water	1 kg/kg	See text

9.4.1.2 Risk management measures

No risk management measures are possible for personal care use in respect of the environment.

9.4.1.3 Environmental exposure

9.4.1.3.1 Environmental releases

Predicted Environmental Concentrations have been determined using EUSES 2.1.1. The EUSES program implements the environmental exposure models described in REACH Technical Guidance Chapter R16. Default model parameters have been used with the following exceptions:

The basis of local and regional production tonnages is to consider the sizes of the largest sites in the EU relative to the total tonnage as follows:

Production volume in EU: 7,500,000 tonnes

Regional tonnage: 750,000 tonnes

Fraction of main local source: 0.0005

Local tonnage: 1.03 tonnes per day

Number of days: 365

The contribution of local releases to the regional concentration has been considered using the appropriate calculation in EUSES 2.1.1. Table 9.33 shows the Predicted Environmental Concentrations. Due to the ready-biodegradability of citric acid it has not been considered necessary to define a PEC. The low log K_{ow} and ready biodegradability indicate that bioaccumulation is not a concern for citric acid. Therefore, the assessment of secondary poisoning is not considered further

Table 9.33: Summary of Predicted Exposure Concentrations

	PEC	unit
AIR		

	PEC	unit
Annual average local PEC in air (total)	5.45×10^{-16}	[mg.m ⁻³]
WATER, SEDIMENT		
Local PEC in surface water during emission episode (dissolved)	1.59×10^{-2}	[mg l ⁻¹]
Annual average local PEC in surface water (dissolved)	1.59×10^{-2}	[mg l ⁻¹]
Local PEC in fresh-water sediment during emission episode	2.71×10^{-1}	[mg kg wwt ⁻¹]
Local PEC in seawater during emission episode (dissolved)	1.48×10^{-3}	[mg l ⁻¹]
Annual average local PEC in seawater (dissolved)	1.48×10^{-3}	[mg l ⁻¹]
Local PEC in marine sediment during emission episode	2.53×10^{-2}	[mg kg wwt ⁻¹]
SOIL, GROUNDWATER		
Local PEC in agric. soil (total) averaged over 30 days	3.02×10^{-2}	[mg kg wwt ⁻¹]
Local PEC in agric. soil (total) averaged over 180 days	9.89×10^{-3}	[mg kg wwt ⁻¹]
Local PEC in grassland (total) averaged over 180 days	3.95×10^{-3}	[mg kg wwt ⁻¹]
Local PEC in pore water of agricultural soil	1.49×10^{-4}	[mg l ⁻¹]
Local PEC in pore water of grassland	5.97×10^{-5}	[mg l ⁻¹]
Local PEC in groundwater under agricultural soil	1.49×10^{-4}	[mg l ⁻¹]

The EUSES model uses the Simple Treat sewage treatment model to predict the fate of a substance in the STP, based on the physicochemical and biodegradation properties. For citric acid, SimpleTreat predicts the following:

12.6 % to water:

0.112 % to air:

0.0154 % to sludge:

87.3 % degraded.

Sludge from WWTPs may be spread on agricultural soil.

The dilution factor of 900 and 1000 (in the receiving water) have been applied for fresh water and marine water respectively, as there is no information on specific hydrodynamic conditions.

There is no direct release to the terrestrial compartment on a local scale as biosludge from on-site waste water treatment is disposed of via incineration or landfill. However, due to use of municipal WWTP by some EU production sites, spreading of sludge on agricultural soil is included as a reasonable worst case.

9.5 ES5: Use of citric acid in cleaning products

9.5.1 Exposure scenario

Following the REACH descriptor system, the following product types are covered by this generic scenario:

- Washing and cleaning products (PC35): Detergents, fabric washing, dish cleaning and surface cleaning products;
- Automotive care products (PC06).

As some products combine the task of cleaning and polishing, making it difficult to make a clear distinction between types of products, the following product type may also be relevant:

- Polishes and Wax Blends (PC31).

9.5.1.1 Description of activities and processes covered in the exposure scenario

This scenario covers the use of citric acid as an ingredient in detergent, cleaning and other household products used in industrial, professional and consumer settings. Formulation of citric acid into such products is covered by ES3.

The generic EU tonnage is considered to be 100 000 tonnes per year.

Industrial use

Activities during industrial use of cleaning and maintenance products are usually characterised by a frequency of once in 5 days for cleaning or laundry products; and 480 times in 1 day for vehicle cleaning products (e.g. aeroplane and train cleaners) [AISE, 2009]. While industrial cleaning products are used indoors, without local exhaust ventilation; vehicle cleaning products are used outdoors. The relevant PROCs for the activities considered for workers exposure are:

PROC2: Use in closed, continuous process with occasional controlled exposure.

PROC4: Use in batch and other process (synthesis) where opportunity for exposure arises.

PROC7: Industrial spraying

PROC8: Transfer of substance or preparation from/to vessels/large containers; Industrial setting. This may be at non-dedicated (PROC8a) or dedicated (PROC8b) facilities depending on the situation, and may relate to both neat substance and preparations.

PROC9: Transfer of substance of preparation into small containers (dedicated filling line, including weighing); Industrial setting.

PROC10: Roller application or brushing. This describes activities such as application of surface cleaning products using wet wipes, use of polishes and vehicle cleaning products

PROC13: Treatment of articles by dipping and pouring

PROCs 7, 8, 9, 10 and 13 are quantified as these are considered to cover the worst-case for exposures.

No modifying factors have been taken into account for the initial assessment, other than presence or absence of Local Exhaust Ventilation. Possible refinements that would lower that actual exposure include modification for concentration in preparations and modification for duration of exposure.

The substances are solid but are mostly used in an aqueous-based solution. Therefore, fugacity is low, except where aerosol mists may be generated (PROC7).

Professional use

Activities during professional use of cleaning and maintenance products vary depending on the application. Duration of 15 minutes per application and 30 minutes per application appears to be worse case scenarios for laundry and vehicle cleaning products respectively [AISE, 2009]). The relevant PROCs for the activities considered for workers exposure are:

PROC1: Use in closed process, no likelihood of exposure

PROC4: Use in batch and other process (synthesis) where opportunity for exposure arises

PROC8a: Transfer of substance or preparation from/to vessels/large containers at a non-dedicated facility.

PROC9: Transfer of substance of preparation into small containers (dedicated filling line, including weighing); Industrial setting.

PROC10: Roller application or brushing. This describes activities such as application of surface cleaning products using wet wipes, use of polishes and vehicle cleaning products

PROC11: Non-industrial spraying

PROC13: Treatment of articles by dipping and pouring

PROC19: Hand-mixing with intimate contact and only PPE available

PROCs 8a, 9, 10, 11, and 19 are quantified as these are considered to be the most common and represent the worst-case for exposures.

No modifying factors have been taken into account for the initial assessment, other than presence or absence of Local Exhaust Ventilation. Possible refinements that would lower that actual exposure include modification for concentration in preparations and modification for

duration of exposure. Duration of exposure of 15 minutes – 1 hour gives a modification factor of 0.2.

The substances are solid but are mostly used in an aqueous-based solution. Therefore, fugacity is low, except where the product is an aerosol or spray (PROC11).

Consumer use

Processes carried out during consumer use of detergent and cleaning products containing citric acid are expected to be similar to those outlined above for professional use. Professional use is considered to represent a worst-case for exposure because durations and frequencies of exposure will be greater.

9.5.1.2 Operational conditions related to frequency, duration and amount of use

Table 9.34: Duration, frequency and amount

Information type	Data field	Explanation
Used amount of substance per day	200,000 kg/d	Generic information
Duration of exposure per day at workplace [for one worker]	>4 hours (all PROCs)	For some applications/setting exposure times may be significantly less
Frequency of exposure at workplace [for one worker]	Once per day	For some applications/settings with shorter duration exposures, multiple exposures may occur in a single day
Annual amount used per site	10 kg/d	0.00005 (10% in region, plus 0.0005 fraction of main local source from HERA)
Emission days per site	365 d/y	Default for ERC8

9.5.1.3 Operational conditions and risk management measures related to product characteristics

Citric acid used in cleaning and detergent applications is part of a preparation. Products may be liquids, pastes, creams, or aerosols; the concentration of citrate used in these applications varies. The HERA risk assessment for household cleaning products gives the following figures:

- laundry detergents 0-10%
- fabric conditioners <1%
- surface cleaners 0-30%
- laundry additives 0-55%
- machine/hand dishwashing detergents 0-45%
- toilet cleaners 0-7%.

Table 9.35: Characteristics of the substance or preparation

Information type	Data field	Explanation
Physical state	Part of a preparation; may be	

	liquid or solid.	
Risk management measures related to the design of product	The pH of liquid formulations is controlled. Solid products are granular and thus exposure to dust is not expected.	

9.5.1.4 **Operational conditions related to available dilution capacity and characteristics of exposed humans**

Table 9.36: Operational conditions related to respiration and skin contact

Information type	Data field	Explanation
Respiration volume under conditions of use	10 m ³ /d	Default for workers, light activity
Area of skin contact with the substance under conditions of use	480 cm ² 1500 cm ² 960 cm ² 480 cm ² 480 cm ² 960 cm ² 1500 cm ² 480 cm ² 1980 cm ²	ECETOC TRA default: PROC5: PROC7: PROC8a: PROC8b: PROC9 PROC10 PROC11 PROC13 PROC19
Body weight	70 kg	Default for workers

Table 9.37: Operational conditions related to respiration, skin contact and ingestion for the general public

Information type	Data field	Explanation
Skin contact area	960 cm ²	ConsExpo default
Mouth contact area	-	Not applicable – no oral exposure
Respiration volume under conditions of use	26 m ³	Default: Light activity 26 m ³ /24 h
Room size and ventilation rate	20m ³ ₁ ; exchange per hour 0.6 h ⁻¹	ConsExpo defaults
Body weight	65 kg	Default adult bodyweight

Environmental surroundings characteristics

Dilution factor: 10 (default).

9.5.1.5 Other operational conditions of use

No measured data are available for releases to air and waste water during the use of citric acid in cleaning products. Releases are therefore estimated on the basis of information in the public domain.

Citric acid and citrates are used in a variety of cleaning products but generally in aqueous solution. The most likely release route will, therefore, be to waste water *via* rinsing to drain in-use, spillage, clean out or discharge of cleaning baths or liquors. Indeed, releases to waste water can be assumed to be 100%, since all the citric acid/citrate will eventually be washed to drain. This may be an overestimate since it does not allow for any of the substance to be either released to air (extremely unlikely) during the process or to adsorb to a surface on drying or to a cleaning implement (*e.g.*, cloth) which may be landfilled.

The release of citrates from use in cleaning products in industrial, professional and consumer use can be estimated. The TGD defaults and REACH environmental release category (ERC8a) assume that if a substance is used widely across the EU, the fraction of the production volume used in the standard EU Region is 10%. For cleaning products, the fraction of the regional tonnage discharging to a particular waste water treatment plant can be estimated as 0.0005 (HERA, 2005). The number of days of use is 365 per year. Therefore, for 100,000 tpa of citric acid in cleaning products used widely across the EU, the estimated release of citrates to a particular default-sized local waste water treatment plant is at most:

$$100,000,000 \text{ kg/y} \times 0.1 \times 0.0005 / 365 \text{ d/y} = 13.7 \text{ kg/d}$$

= (Amount of citrates used in cleaning products per year x fraction to water x fraction in the region x fraction of main local source) / number of days per year

The research carried out by the HERA project was thorough and accepted by the EU authorities as valid.

Table 9.38: Technical fate of substance and losses from process/use to waste, waste water and air

Information type	Data field	Explanation
Fraction of applied amount lost from process/use to waste gas	0 kg/kg	See text
Fraction of applied amount lost from process/use to waste water	1 kg/kg	See text

9.5.1.6 Risk management measures

Table 9.39 summarises the risk management measures in place during use of citric acid at industrial sites.

Table 9.39: Risk management measures for industrial site

Information type	Data field	Explanation
Containment and local exhaust ventilation		

Information type	Data field	Explanation
Containment plus good work practice required	Yes	General good hygiene and housekeeping
Local exhaust ventilation required plus good work practise	No	
Personal protective equipment (PPE)		
Skin protection	Protective gloves	
Eye protection	Safety glasses	
Clothing	Working clothing worn.	
Other risk management measures related to workers		
N/A		
Risk management measures related to environmental emissions from industrial sites		
Onsite pre-treatment of waste water	Yes	Neutralisation
Resulting fraction of initially applied amount in waste water released from site to the external sewage system		On-site biological waste treatment is expected to remove a high proportion of citric acid, as the substance is highly biodegradable.
Air emission abatement	No measured data	
Resulting fraction of applied amount in waste gas released to environment	No measured data	
Onsite waste treatment	No measured data	Secondary biological treatment
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste gas treatment.	No measured data	
Municipal or other type of external waste water treatment	None	None
Effluent (of the waste water treatment plant) discharge rate	2000000 l/d	Default for a standard WWTP
Recovery of sludge for agriculture or horticulture	Yes	Dried sludge may be sold as an approved agricultural fertiliser

9.5.1.7 Waste related measures

At industrial sites, solid wastes may be disposed of via landfill or incineration, or are recycled outside of the process. Dried sludge from on-site waste water treatment plants may be sold as approved agricultural fertiliser. Details of the treatment of aqueous waste vary at different sites but as a minimum, wastes are neutralised and the effluent treated in on- or off-site secondary biological treatment plants prior to discharge. Waste gases are not generated.

In consumer and professional use, waste water passes to municipal WWTPs. Sludge may be spread on agricultural land.

9.5.2 Exposure estimation

9.5.2.1 Workers exposure – industrial settings

9.5.2.1.1 Acute/Short term exposure

Workers in industrial settings are routinely involved with the same tasks, therefore it is more appropriate to consider long-term exposure, and short-term exposure is not quantified.

9.5.2.1.2 Long-term exposure

Table 9.40 and 9.41 give a summary of the long-term exposure values for PROCs 7, 8 and 9, based on the ECETOC TRA model. The default for duration of exposure (>4 hours) has been used and it has been assumed that LEV and respiratory protection are not present. The exception to this is PROC7 (industrial spraying) where it is assumed that LEV is present.

Where the worst-case defaults do not apply, actual exposure may be much lower. In particular, actual durations of exposure may be much less than 4 hours; in this case the following modification factors can be applied: 0.6 for 1-4 hours, 0.2 for 15 mins to 1 hour, 0.1 for <15 mins. The concentration in the formulation is assumed to be >25%; reductions in the exposures may be applied for formulations with a lower percentage citrate: *0.6 for 5-25%, *0.2 for 1-5% and *0.1 for <1%.

Inhalation exposure

Based on the vapour pressure (negligibly low) and physical state (aqueous solution), aqueous formulations of citrates fall into the 'minimal' availability band (ECETOC 2009), and the potential for exposure is minimal to low (ECETOC 2009). Inhalation exposure for aqueous products is expected to be negligible as citric acid and its salts are extremely involatile with vapour pressures 10^{-5} Pa and negligibly small Henry's Law constants, indicating there is no potential for exposure via vapour.

The exceptions are where there is a possibility for inhalatory exposure via spray mists. In addition, use of dusty powder forms of citric acid and citrate salts may result in inhalation exposure.

The substances are solid but are mostly used in an aqueous-based solution. Therefore, fugacity is low, except where aerosol mists may be formed (PROC7).

Dermal exposure

Dermal uptake of citrate is expected to be minimal as it is extremely hydrophilic with a very low octanol-water partition coefficient (-1.8 to -0.12). The USEPA DERMWIN model allows for uptake from aqueous solution to be calculated on the basis of a proportion of the worst-case calculated by ECETOC TRA. This approach is indicated in the ECETOC (2004).

A worst-case estimate for the uptake fraction from aqueous solution has been calculated as 0.006 (see Section 5.1); actual uptake may be much less. The dermal exposures estimated using ECETOC TRA and presented in Table 9.40 may be multiplied by this factor to obtain a

worst-case estimate of the dermal exposure. Dermal uptake of solid citrates is expected to be negligible and is not considered.

Table 9.40 Dermal exposure estimates (based on ECETOC TRA model) for cleaning and maintenance

Life cycle stage	Process category	Description	Fugacity	LEV present?	Dermal exposure?	Predicted exposure ($\mu\text{g}/\text{cm}^2/\text{day}$)	Exposed skin surface area (cm^2)	Dermal exposure ($\text{mg}/\text{kg}/\text{day}$) ^a
Industrial use	PROC8a	Transfer from/to large vessels (non-dedicated)	Low	No	Yes	1000	960	13.7
Industrial use	PROC8b	Transfer from/to large vessels(dedicated)	Low	No	Yes	1000	480	6.9
Industrial use	PROC9	Transfer to small containers	Low	No	Yes	1000	480	6.9
Industrial use	PROC7	Industrial spraying	High	Yes	Yes	100	1500	2.14
Industrial use	PROC10	Roller application or brushing	Low	No	Yes	2000	960	27.4
Industrial use	PROC13	Dipping or pouring	Low	No	Yes	2000	480	13.7

(a) Calculated assuming a default bodyweight of 70 kg for workers

Table 9.41 Inhalation exposure estimates (based on ECETOC TRA model) for cleaning and maintenance products

Life cycle stage	Process category	Description	Fugacity	LEV present?	LEV efficiency	Predicted exposure (ppm)	Predicted exposure (mg/m^3) ^b	Inhalation exposure ($\text{mg}/\text{kg}/\text{day}$) ^c
Industrial use	PROC8a	Transfer from/to large vessels (non-dedicated)	Low	No	n/a	0.063	0.5	0.07
Industrial use	PROC8b	Transfer from/to large vessels (dedicated)	Low	No	n/a	0.012	0.1	0.014
Industrial use	PROC9	Transfer to small containers	Low	No	n/a	0.012	0.1	0.01
Industrial use	PROC7	Spraying in industrial settings and applications	High	Yes	95%	0.63	5	0.71
Industrial use	PROC10	Roller application or brushing	Low	No	n/a	0.063	0.5	0.07
Industrial use	PROC13	Dipping or pouring	Low	No	n/a	0.012	0.1	0.014

b) Results are calculated as mg/m^3 for solids and ppm for non-solids

c) Calculated assuming a default bodyweight of 70 kg for workers and a default respiratory volume of 10 m^3 , light activity, for an 8 hour work shift

Table 9.42: Summary of long-term exposure concentration to workers

Routes of exposure	Concentrations	Justification
Dermal local exposure (in $\mu\text{g}/\text{cm}^2$)	12	ECETOC TRA prediction for PROC10; multiplied by a dermal uptake factor of 0.006.
Dermal systemic exposure (in mg/kg bw/d)	0.16	ECETOC TRA prediction for PROC10; multiplied by a dermal uptake factor of 0.006.
Inhalation exposure (in mg/m^3)/8h workday	5	ECETOC TRA prediction for PROC7
Inhalation exposure (in $\text{mg}/\text{kg}/\text{d}$)/8h workday	0.71	ECETOC TRA prediction for PROC7

9.5.2.2 Consumer/professional exposure

9.5.2.2.1 Acute/Short term exposure

It is expected that both workers and consumers will make use of cleaning products on a routine basis. Therefore, only long-term exposure is discussed. This is considered to cover the worst-case for professional and consumer exposure.

9.5.2.2.2 Long-term exposure

Table 9.40 and 9.41 give a summary of the long-term exposure values for PROCs 8a, 9, 10, 11 and 19, based on the ECETOC TRA model. The default for duration of exposure (>4 hours) has been used and it has been assumed that LEV and respiratory protection are not present. Where this is not the case, actual exposure may be much lower. In particular, actual durations of exposure may be much less than 4 hours; in this case the following modification factors can be applied: 0.6 for 1-4 hours, 0.2 for 15 mins to 1 hour, 0.1 for <15 mins. The concentration in the formulation is assumed to be >25%; reductions in the exposures may be applied for formulations with a lower percentage citrate: *0.6 for 5-25%, *0.2 for 1-5% and *0.1 for <1%.

Inhalation exposure

Based on the vapour pressure (negligibly low) and physical state (aqueous solution), aqueous formulations of citrates fall into the 'minimal' availability band (ECETOC 2009), and the potential for exposure is minimal to low (ECETOC 2009). Inhalation exposure for aqueous products is expected to be negligible as citric acid and its salts are extremely involatile with vapour pressures $<10^{-5}$ Pa and negligibly small Henry's Law constants, indicating there is no potential for exposure via vapour.

The exceptions are where there is a possibility for inhalatory exposure via spray mists. In addition, use of dusty powder forms of citric acid and citrate salts may result in inhalation exposure.

The citrates are solid but are mostly used in an aqueous-based solution in cleaning applications. Formation of aerosol mists is not expected in consumer or professional applications. Consumer products in wide-spread use which are solids are granular and, therefore, significant exposure to dusts is not expected. The substances are considered to be low fugacity for all calculations.

Dermal exposure

Dermal uptake of citrate is expected to be minimal as it is extremely hydrophilic with a very low octanol-water partition coefficient (-1.8 to -0.12). The USEPA DERMWIN model allows for uptake from aqueous solution to be calculated on the basis of a proportion of the worst-case calculated by ECETOC TRA. This approach is indicated in the ECETOC (2004).

A worst-case estimate for the uptake fraction from aqueous solution has been calculated as 0.006 (see Section 5.1); actual uptake is expected to be much less. The dermal exposure estimated using ECETOC TRA and presented in Table 9.43 may be multiplied by this factor to obtain a worst-case estimate of the dermal exposure. Dermal uptake of solid citrates is expected to be negligible and is not considered.

The highest exposure in Table 9.43 is predicted to be associated with PROC19, intimate hand-mixing. The dermal exposure after correction for uptake fraction is $141 * 0.006 = 0.8$ mg/kg/d. However, the duration of exposure for this type of process is expected to be considerably lower than the default >4 h on which the estimate is based. Duration of exposure of 1 h over the course of a day is considered to be a realistic worst-case, therefore, the corrected exposure is 0.16 mg/kg/d.

The second highest predicted exposure in Table 9.43 is associated with PROC11, non-industrial spraying. It is possible that this type of process could have a longer duration of exposure; therefore, no duration of exposure modification is applied. The estimated exposure after correction for uptake fraction is $107 * 0.006 = 0.6$ mg/kg/d.

Table 9.43 Dermal exposure estimates (based on ECETOC TRA model) for cleaning and maintenance

Life cycle stage	Process category	Description	Fugacity	LEV present?	Dermal exposure?	Predicted exposure ($\mu\text{g}/\text{cm}^2/\text{day}$)	Exposed skin surface area (cm^2)	Dermal exposure ($\text{mg}/\text{kg}/\text{day}$) ^a
Professional use	PROC8a	Transfer from/to large vessels (non-dedicated)	Low	No	Yes	1000	960	13.7
Professional use	PROC9	Transfer to small containers	Low	No	Yes	1000	480	6.86
Professional use	PROC10	Roller application or brushing	Low	No	Yes	2000	960	27.4
Professional use	PROC11	Non-industrial spraying	Low	No	Yes	5000	1500	107
Professional use	PROC19	Intimate hand mixing	Low	No	Yes	5000	1980	141

(a) Calculated assuming a default bodyweight of 70 kg for workers

Table 9.44 Inhalation exposure estimates (based on ECETOC TRA model) for cleaning and maintenance products

Life cycle stage	Process category	Description	Fugacity	LEV present?	LEV efficiency	Predicted exposure (ppm)	Predicted exposure (mg/m^3) ^b	Inhalation exposure ($\text{mg}/\text{kg}/\text{day}$) ^c
Professional use	PROC8a	Transfer from/to large vessels (non-dedicated)	Low	No	N/A	0.06	0.5	0.07
Professional use	PROC9	Transfer to small containers	Low	No	N/A	0.06	0.5	0.07
Professional use	PROC10	Roller application or brushing	Low	No	N/A	0.06	0.5	0.07
Professional use	PROC11	Non-industrial spraying	Low	No	N/A	0.125	1	0.14
Professional use	PROC19	Intimate hand mixing	Low	No	N/A	0.06	0.5	0.07

b) Results are calculated as mg/m^3 for solids and ppm for non-solids

c) Calculated assuming a default bodyweight of 70 kg for workers and a default respiratory volume of 10 m^3 , light activity, for an 8 hour work shift

Table 9.45: Summary of long-term exposure concentration to workers

Routes of exposure	Concentrations	Justification
Dermal local exposure (in $\mu\text{g}/\text{cm}^2$)	30	ECETOC TRA prediction for PROC11, multiplied by an uptake factor of 0.006
Dermal systemic exposure (in mg/kg bw/d)	0.6	ECETOC TRA prediction for PROC11, multiplied by an uptake factor of 0.006
Inhalation exposure (in mg/m^3)/8h workday	1	ECETOC TRA prediction for PROC
Inhalation exposure (in $\text{mg}/\text{kg}/\text{d}$)/8h workday	0.14	ECETOC TRA prediction for PROC

9.5.2.3 Environmental exposure

9.5.2.3.1 Environmental releases

For the purposes of estimating releases to the environment, industrial, professional and consumer uses are equivalent and are covered together in the following sections. Predicted environmental release estimates have been used for releases resulting from use of cleaning products containing citric acid. The releases have been estimated using the exposure scenario for this use (section 9.4.1.2 and 9.4.1.6) and Predicted Environmental Concentrations have been determined using EUSES 2.1.1. The EUSES program implements the environmental exposure models described in REACH Technical Guidance Chapter R16. Default model parameters have been used.

The basis of local and regional production tonnages is to consider the sizes of the largest sites in the EU relative to the total tonnage as follows:

Application volume in EU: 100 000 tonnes

Regional tonnage: 10 000 tonnes

Fraction of main local source: 0.0005

Number of days: 365 (consistent with the default)

The contribution of local releases to the regional concentration has been considered using the appropriate calculation in EUSES 2.1.1.

Table 9.46 shows the Predicted Environmental Concentrations. Due to the ready-biodegradability of citric acid it has not been considered necessary to define a PEC in STP. The low $\log K_{ow}$ and ready biodegradability indicate that bioaccumulation is not a concern for citric acid. Therefore, the assessment of secondary poisoning is not considered.

Table 9.46: Summary of Predicted Exposure Concentrations

	PEC	unit
AIR		
Annual average local PEC in air (total)	1.30×10^{-15}	[mg.m ⁻³]
WATER, SEDIMENT		
Local PEC in surface water during emission episode (dissolved)	2.48×10^{-2}	[mg l ⁻¹]
Annual average local PEC in surface water (dissolved)	2.48×10^{-2}	[mg l ⁻¹]
Local PEC in fresh-water sediment during emission episode	4.23×10^{-1}	[mg kg wwt ⁻¹]
Local PEC in seawater during emission episode (dissolved)	2.37×10^{-3}	[mg l ⁻¹]
Annual average local PEC in seawater (dissolved)	2.37×10^{-3}	[mg l ⁻¹]
Local PEC in marine sediment during emission episode	4.05×10^{-2}	[mg kg wwt ⁻¹]
SOIL, GROUNDWATER		
Local PEC in agric. soil (total) averaged over 30 days	4.02×10^{-1}	[mg kg wwt ⁻¹]
Local PEC in agric. soil (total) averaged over 180 days	1.32×10^{-1}	[mg kg wwt ⁻¹]
Local PEC in grassland (total) averaged over 180 days	5.27×10^{-2}	[mg kg wwt ⁻¹]
Local PEC in pore water of agricultural soil	1.99×10^{-3}	[mg l ⁻¹]
Local PEC in pore water of grassland	7.95×10^{-4}	[mg l ⁻¹]
Local PEC in groundwater under agricultural soil	1.99×10^{-3}	[mg l ⁻¹]

No definitive measured data are available for the concentration of citric acid in sewage treatment plants (STP). A source to which reliability could not be assigned gives a concentration of citrate in raw sewage of up to 10 mg/l (OECD SIDS). This concentration will arise from both natural and man-made sources of citrate.

The concentration in sewage treatment plants due to use of cleaning products containing citric acid has been estimated using a default waste water treatment plant flow rate of 2000 m³/d and a dilution factor of 10 (Section 9.2.1.6) in EUSES 2.1.1.

The EUSES model uses the Simple Treat sewage treatment model to predict the fate of a substance in the STP, based on the physicochemical and biodegradation properties. For citric acid, SimpleTreat predicts the following:

12.7 % to water:

6×10^{-11} % to air:

0.017 % to sludge:

87.3 % degraded.

Sludge from WWTPs may be spread on agricultural soil.

The percentage degraded is the default for a readily biodegradable substance; actual degradation of citric acid may be higher.

An alternative approach to calculating the concentration in sewage sludge was used by HERA in their risk assessment of citric acid and salts in household cleaning products. 20% of the total production tonnage of 500,000 tonnes per annum was assumed to be used in wide dispersive technical applications (the bulk of the tonnage being used in the food and pharmaceutical industries). Based on a population figure of *approx.* 470 million people and a per capita water consumption of 200 l/day, a raw waste water concentration of 2.9 mg/l was calculated (HERA 2005).

For the present risk assessment, the EUSES value of 5.1 mg/l is used to represent a worst-case, although it is likely to be very conservative.

Estimated local exposure concentrations for freshwater and marine water have been based on the exposure scenario for production (Sections 9.1.1.2 and 9.1.1.6) and EUSES 2.1.1 model output. The default dilution factors of 10 and 100 (in the receiving water) have been applied for fresh water and marine water respectively, as there is no information on specific hydrodynamic conditions.

Measured background concentrations in surface waters range from <0.04 to 0.2 mg/l in river water and 0.025-0.145 mg/l in Atlantic coast seawater (OECD SIDS). These concentrations will result from both man-made and natural sources. The measured data provides a useful comparison with the predicted levels but are not considered sufficiently robust for use in the risk characterisation. In addition, it is not possible to separate the contributions from different sources. Therefore, the estimated PECs are used in the remainder of the exposure assessment. Exposure concentrations in soil and groundwater are estimated (on a regional basis) based on EUSES 2.1.1. No measured data on concentrations due to this use are available. Sewage sludge from waste water treatment plants may be spread on agricultural soil.

The Predicted Exposure Concentration (PEC) of citric acid in the atmosphere is estimated based on EUSES 2.1.1. No measured data are available.

9.6 ES6: Use in paper

Following the REACH descriptor system, the following product type is covered by this generic scenario: Paper and board dye, finishing and impregnation products: including bleaches and other processing aids (PC26).

Citric acid is used in the cleaning of papermaking machines and to prevent build up of deposits. It is added to the pulp slurry prior to bleaching to control paper staining by sequestering metal ions. Cleaning applications are covered under another exposure scenario; this document covers use of citrate as a processing aid in the paper-making industry.

This generic scenario makes use of the following documents:

- OECD Emission Scenario Documents on Kraft, Non-Integrated and Recovered Pulp Mills.

This covers the use of citrate as a process aid in the paper-making industry. It is possible that a small amount of citrate is incorporated into the finished paper products. However, it is considered that the amount of citrate that ends up in articles and could be released (resulting in consumer exposure) is likely to be negligible.

The amount of citric acid believed to be used in this application is at most 1000 tpa. The industrial use per site is unknown. However, a default approach would be to consider 10 paper mills in a single region, operating over 300 days per year. The substance is not mixed into pulp, but is applied to machinery. A loss of 2% is a realistic maximum.

This gives a daily release of

$$100 \text{ t} \times 1000 \text{ kg/t} \times 0.02 / 300 \text{ d} = 6.7 \text{ kg/d}$$

For the environment, the amounts passing to waste are very likely to be less than those from the ES 1-5. Therefore there is no need to complete an exposure assessment at a local scale with full details of PEC values etc.

However, a regional release of 67 kg/d to waste water will be added to the model.

For human health worker exposure at paper mills will be to aqueous formulations for which no hazard has been identified. In addition, relevant exposures have been calculated for life cycle stages with higher exposures. Therefore no attempt at quantification will be made nor is needed.

9.7 ES7: Use in construction

Following the REACH descriptor system, the following product types are covered by this generic scenario: PC10 (Building and construction preparations not covered elsewhere).

The following substances are used in construction materials: citric acid and trisodium citrate. Citrates can be used to retard the setting rate of cement and reduce the amount of water needed. They may therefore be added to concrete, mortar, plaster and render formulations. The concentration in these products is generally low (<1%).

This document provides an environmental generic exposure scenario for substances used in construction materials. This generic scenario makes use of the following documents:

- EU Technical Guidance Document (TGD) emission scenario document.
- REACH Technical Guidance.

The amount of citric acid believed to be used in this application is at most 1500 tpa. The industrial use per site is unknown, but should be considered as a widely dispersed use. In the worst case a release of the entire tonnage to the region could be included, *i.e.* 1500 tpa. Of this, part will be released to industrial soil (90%) and part to waste water (10%).

A regional release of $150 \times 1000/365 = 411$ kg/d to waste water will be added to the model, and 3699 kg/d to industrial soil will be included.

For human health worker exposure at construction sites will be to aqueous formulations for which no hazard has been identified. In addition, relevant exposures have been calculated for life cycle stages with higher exposures. Therefore no attempt at quantification will be made nor is needed.

9.8 Use in polymers and plastics

Following the REACH descriptor system [ECHA, 2009], the sectors of use (SU) covered by this generic scenario are:

SU11 (Manufacture of rubber products) and

SU12 (Manufacture of plastics products, including compounding and conversion).

Applications encompass the following product categories (PC):

PC32: Polymer Preparations and Compounds.

Polyolefin foams are used for a variety of applications such as automotive, construction, food packaging, sport and leisure, and many other industrial and consumer uses. They usually have a high strength to weight ratio and are manufactured in a variety of processes and in low density (25 - 250 kg/m³) or high density (250 - 700 kg/m³) versions, or even in densities as low as 16 kg/m³ for polystyrene. All current extrusion processes involve the following steps: melting, mixing with blowing agents, cooling of melt, expansion and degassing/aging. The steps in this process can be realized in different configurations of equipment, *e.g.*, with long single-screw extruders, twin-screw extruders, or tandem extruder lines.

The choice of chemical or physical blowing agents depends on the foam density to be reached (*e.g.* the foam application) and influences the necessary foaming equipment and the costs of the foamed materials. High-density thermoplastic foams based on, *e.g.*, polypropylene or polystyrene, may be produced using blowing agents which decompose to generate gas which is soluble in the melt but which is released as the pressure is reduced (*e.g.*, by passing through a dye) to produce a foam. The foaming process is complex but involves bubble nucleation followed by bubble growth.

One example of a commercially used chemical foaming agent is based on citric acid (or monosodium citrate) in combination with sodium carbonate or (sodium bicarbonate) in a weight ratio of between about 1:1 and about 5:1 respectively [US 5,302,455]. The citric acid/sodium bicarbonate system decomposes at 160 – 210°C to release 120 cm³/g of CO₂. [Karger-Kocsis, 1999; Brydson, 1999; Holmberg, 2002]

Both citric acid (or citrate salt) and (bi)carbonate may be surface-treated with, for example, a fatty acid ester to make them compatible with the polyolefin. A concentrated master batch of the formulated foaming agent in polymer at loading levels of from about 5% to about 50% actives may then be prepared. The master batch is added to the polymer melt which is to be foamed such that the blowing agents are at 0.1 to 2.0% active levels in the final formulation [US 5,302,455 and refs. therein].

By-products of this reaction are mono-, di-, and/or trisodium citrate, in combination with other sodium salts, which will still be present within the foamed polymer. These residues are typically present at around 50 wt.% of the initial foaming agent formulation, which is equivalent to <1 wt.% of the total foamed polymer in most cases [RAPRA, 2004].

9.8.1 Exposure scenario

There is some potential for airborne release of citric acid (or citrate) particulates in preparing the mix of ingredients and on charging (transfer, dosing) to the extruder or other process equipment used, especially if containment is not good. Ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) is assumed to go to solid waste from the plastics processing site [OECD 2004].

The OECD Plastics Additives ESD gives the following figures for loss from raw materials handling for powders of particle size <40 µm (losses for smaller particle sizes are smaller):

$F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$ to solid waste/water

$F_{\text{handling, air}} = 0\%$

$F_{\text{handling, waste}} = 1.0\%$ to solid waste as residue in bags

Losses for compounding for powders of particle size <40 µm are as follows:

$F_{\text{compounding, water}} = 0.05\%$

$F_{\text{compounding, air}} = 0\%$

Losses from conversion, service life and disposal for chemical blowing agents are considered to be zero as the additive is destroyed during the conversion process.

Thus, for 200 tpa of citrates used in plastics applications, assumed to be used at 10 sites across Europe, the local losses to water air and solid waste are:

The REACH defaults for ERC6d are for the production on 300 days per year if the tonnage of the product is >5000 tpa [ECHA, 2009]. Citrate is present at <1% in plastics applications (see Section 2.1.1), therefore, the total production volume is *approx.* 100,000 tpa. Therefore, the maximum daily releases are as follows:

Water: $20 \text{ t} \times 1000 \text{ kg/t} \times (0.0065) / 300 = 0.43 \text{ kg/d}$

Air: 0

For the environment, the amounts passing to waste are very likely to be less than those from the ES 1-5. Therefore there is no need to complete an exposure assessment at a local scale with full details of PEC values etc.

However, a regional release of 0.35 kg/d to waste water will be added to the model, and similarly 3.18 kg/d to the continental scale.

For human health worker exposure at construction sites will be to aqueous formulations for which no hazard has been identified. In addition, relevant exposures have been calculated for life cycle stages with higher exposures. Therefore no attempt at quantification will be made nor is needed.

9.9 ES9: Use in the oil industry

Following the REACH descriptor system [ECHA, 2009], the sectors of use (SU) covered by this generic scenario are:

SU2a Mining (without offshore industries)

SU2b (Offshore industries)

Applications encompass the following product categories (PC):

PC20: Products such as ph-regulators, flocculants, precipitants, neutralization agents, other unspecific

In the oil industry, citric acid is often used for oil-well acidizing to prevent the formation of insoluble gels of iron hydroxide [APAC]. Oil well acidizing is the term used for the application of hot hydrochloric acid (200-300°F; 93-149°C) to remove tough wellbore scale [McGraw-Hill].

Oxidation reactions, which occur in wells injected with HCl, cause formation of insoluble iron hydroxide gels [APAC]. The pumping operations are thus interrupted by these gels, and hence, citric acid is added to complex the iron, thus preventing gel formation [APAC].

Oil producing well formations can become plugged with acid soluble minerals and restrict fluid flow and reduce oil production [Gewanter, Herman L. et al]. Production can be increased by forcing acid down the well formations to dissolve the minerals [Gewanter, Herman L. et al]. The acids readily dissolve the iron and iron containing compounds from the well casing and the formation [Gewanter, Herman L. et al]. However, water and carbonates will neutralize the acid in the formation, which allows for the re-precipitation of the iron to ferric hydroxide above a pH of 2.2. [Gewanter, Herman L. et al]. Certain chemicals must be added at this point to maintain it in a soluble state [Gewanter, Herman L. et al].

Control of the re-precipitation of iron and the pH, as the acid is spent, can be achieved by the sequestration by organic chelants and the reduction to soluble ferrous iron [Gewanter, Herman L. et al]. Citric acid is a useful organic chelant and is used for this purpose [Gewanter, Herman L. et al]. Other chelants may include gluconic acid, the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA), and the trisodium salt of nitrilotriacetic acid (NTA) [Gewanter, Herman L. et al].

This is a widely dispersed use but in the worst case it can be envisaged that the entire tonnage could pass to surface marine water. This equates to

$100 \text{ t} \times 1000 \text{ kg/t} / 365 = 274 \text{ kg/d}$ to the regional surface water

$900 \text{ t} \times 1000 \text{ kg/t} / 365 = 2740 \text{ kg/d}$ to the continental surface water

For human health worker exposure at oil production sites will be to aqueous formulations for which no hazard has been identified. In addition, relevant exposures have been calculated for life cycle stages with higher exposures. Therefore no attempt at quantification will be made nor is needed.

9.10 Use in textiles

Following the REACH descriptor system [ECHA, 2009], the sectors of use (SU) covered by this generic scenario are:

SU5 (Manufacture of textiles, leather, fur) and

SU10 (Formulation [mixing] of preparations and/or re-packaging).

Applications encompass the following product categories (PC):

PC20: Products such as pH-regulators, flocculants, precipitants, neutralization agents;

PC23: Leather tanning, dye, finishing, impregnation and care products; and

PC34: Textile dyes, finishing and impregnating products.

The OECD Emission Scenario Document on the Textile Finishing Industry [OECD, 2004A] describes the textile industry as “one of the largest and most complicated industrial chains in manufacturing industry”. The industry is dominated by small and medium-sized companies, working in three main sectors: clothing, home furnishings and industrial.

Activity in the textile finishing industry is distributed across the EU, but (within the EU-15) the dominant Member State is Italy, accounting for around 36% of production, followed by German (*approx.* 13%), France (*approx.* 12%), the UK and Spain (*approx.* 10% each). The overall market for textiles, including yarn production and carpets, is also dominated by Italy, with around a 30% market share (EC, 2002). Similarly, for leather, the most important producer and transformer in Europe is Italy (84% of all companies), followed by Spain [OECD, 2004B].

Within the textile and leather finishing industries, citric acid and related salts may be used in a wide variety of applications. However, these uses may be summarized (albeit with some overlap) as being based on either acidity (and pH regulation) or ability to complex metal ions. Examples of applications where these are important are:

- Curing catalyst for treatments such as easy-care resins
- Acidification of flame-retardant treating baths
- Sequestering of alkaline earth or transition metal ions to prevent interference in dyeing and other processes.

Potential exposure to humans and especially the environment is dependent on the intended function of the substance, as well as the substrates and processes used. Functional finishing

agents and other chemically reactive substances are intended to be consumed during use, therefore the amount released is related to efficiency of the process. On the other hand, non-reacting substances (e.g. processing aids) are not consumed and will ultimately be lost to air or waste water, depending on their function and physicochemical properties. In virtually all cases, it is expected that citric acid or citrate salts, as process aids, will be lost to waste water. The annual tonnage of 300 t is considered to be used at 40% in the region. The largest site is estimated to use around 6 tpa. If all passed to waste water this is:

$$6 \text{ t} \times 1000 \text{ kg/t} / 300 = 20 \text{ kg/d.}$$

For human health worker exposure at textile production sites will be to aqueous formulations for which no hazard has been identified. In addition, relevant exposures have been calculated for life cycle stages with higher exposures. Therefore no attempt at quantification will be made nor is needed.

9.10.1 Exposure scenario

9.10.1.1 Other operational conditions of use

No measured data are available for releases of citric acid to air and waste water from textile production sites. Releases are therefore estimated on the basis of information in the public domain.

Releases to air

As the citrates are solids with high water solubility, losses to air are considered to be negligible.

Releases to waste water

Citric acid and citrates are used in textile and leather treatment in aqueous solution. The most likely release route will be to waste water *via* spillage, clean out and discharge of spent treatment baths and liquors recovered in handling fabrics after treatment. Indeed, releases to waste water can be assumed to be 100%, since all the citric acid/citrate may be washed to drain.

Table 9.47: Technical fate of substance and losses from process/use to waste, waste water and air

Information type	Data field	Explanation
Fraction of applied amount lost from process/use to waste gas	0 kg/kg	See text
Fraction of applied amount lost from process/use to waste water	1 kg/kg	See text

9.10.1.2 Risk management measures

Table 9.48 summarises the risk management measures in place during production of citric acid.

Table 9.48: Risk management measures for industrial site

Information type	Data field	Explanation
Onsite pre-treatment of waste water	Yes	Neutralisation
Resulting fraction of initially applied amount in waste water released from site to the external sewage system		On-site biological waste treatment (where present) is expected to remove a high proportion of citric acid, as the substance is highly biodegradable. However, on-site biological waste treatment is not assumed as it is not known that this is always present.
Air emission abatement	No measured data	
Resulting fraction of applied amount in waste gas released to environment	No waste gases	
Onsite waste treatment	No measured data	Secondary biological treatment may be present but this is not assumed in the scenario
Fraction of initially applied amount sent to external waste treatment. This is the sum of direct losses from processes to waste, and the residues from onsite waste water and waste gas treatment.	No measured data	
Municipal or other type of external waste water treatment	None	None
Effluent (of the waste water treatment plant) discharge rate	2000000 l/d	Default for a standard WWTP
Recovery of sludge for agriculture or horticulture	Yes	

9.10.1.3 Waste related measures

At industrial sites, solid wastes may be disposed of via landfill or incineration, or are recycled outside of the process. Dried sludge from on-site waste water treatment plants may be sold as approved agricultural fertiliser. Details of the treatment of aqueous waste vary at different sites but as a minimum, wastes are neutralised and the effluent treated in on- or off-site secondary biological treatment plants prior to discharge. Waste gases are not generated.

In consumer and professional use, waste water passes to municipal WWTPs. Sludge may be spread on agricultural land.

9.10.2 Exposure estimation

9.10.2.1 Environmental exposure

9.10.2.1.1 Environmental releases

Predicted environmental release estimates have been used for releases during production. The releases have been estimated using the exposure scenario for use in textiles (section 9.1.1.2

and 9.1.1.6) and Predicted Environmental Concentrations have been determined using EUSES 2.1.1. The EUSES program implements the environmental exposure models described in REACH Technical Guidance Chapter R16. Default model parameters have been used with the following exceptions:

The basis of local and regional production tonnages is to consider the sizes of the largest sites in the EU relative to the total tonnage as follows:

Production volume in EU: 300 tonnes

Regional tonnage: 120 tonnes

Fraction of main local source: 0.05

Local tonnage: 0.02 tonnes per day

Number of days: 300

The contribution of local releases to the regional concentration has been considered using the appropriate calculation in EUSES 2.1.1.

Table 9.49 shows the Predicted Environmental Concentrations. Due to the ready-biodegradability of citric acid it has not been considered necessary to define a PEC in STP. The low log K_{ow} and ready biodegradability indicate that bioaccumulation is not a concern for citric acid. Therefore, the assessment of secondary poisoning is not considered.

Table 9.49: Summary of Predicted Exposure Concentrations

	PEC	unit
AIR		
Annual average local PEC in air (total)	1.56×10^{-15}	[mg.m ⁻³]
WATER, SEDIMENT		
Local PEC in surface water during emission episode (dissolved)	2.92×10^{-2}	[mg l ⁻¹]
Annual average local PEC in surface water (dissolved)	2.67×10^{-2}	[mg l ⁻¹]
Local PEC in fresh-water sediment during emission episode	4.98×10^{-1}	[mg kg wwt ⁻¹]
Local PEC in seawater during emission episode (dissolved)	1.01×10^{-1}	[mg l ⁻¹]
Annual average local PEC in seawater (dissolved)	8.35×10^{-2}	[mg l ⁻¹]
Local PEC in marine sediment during emission episode	1.73	[mg kg wwt ⁻¹]
SOIL, GROUNDWATER		
Local PEC in agric. soil (total) averaged over 30 days	5.87×10^{-1}	[mg kg wwt ⁻¹]
Local PEC in agric. soil (total) averaged over 180 days	1.93×10^{-1}	[mg kg wwt ⁻¹]
Local PEC in grassland (total) averaged over 180 days	7.70×10^{-2}	[mg kg wwt ⁻¹]
Local PEC in pore water of agricultural soil	2.91×10^{-3}	[mg l ⁻¹]
Local PEC in pore water of grassland	1.16×10^{-3}	[mg l ⁻¹]
Local PEC in groundwater under agricultural soil	2.91×10^{-3}	[mg l ⁻¹]

9.10.2.1.2 **Exposure concentration in sewage treatment plants (STP)**

No measured data are available for the concentration of citric acid in sewage treatment plants (STP). The concentration of the citrate has been estimated using EUSES 2.1.1. The EUSES model uses the Simple Treat sewage treatment model to predict the fate of a substance in the STP, based on the physicochemical and biodegradation properties. For citric acid, SimpleTreat predicts the following:

12.6 % to water:

0.112 % to air:

0.0154 % to sludge:

87.3 % degraded.

Sludge from WWTPs may be spread on agricultural soil.

Estimated local exposure concentrations for freshwater and marine water have been based on the exposure scenario for production (Sections 9.1.1.2 and 9.1.1.6) and EUSES 2.1.1 model output.

Estimated predicted exposure concentrations in freshwater and marine sediment are based on EUSES 2.1.1. No measured data are available.

Exposure concentrations in soil and groundwater are estimated (on a regional basis) based on EUSES 2.1.1. No measured data are available.

The Predicted Exposure Concentration (PEC) of citric acid in the atmosphere is estimated based on EUSES 2.1.1. No measured data are available.

9.11 ES11: Use in paints and coatings

Following the REACH descriptor system [ECHA, 2009], one sector of use (SU) covered by this generic scenario is:

SU10: (Formulation [mixing] of preparations and/or re-packaging).

However, use of paints and coatings is ubiquitous, encompassing several SUs, *e.g.*:

SU3: Industrial Manufacturing (all);

SU17: General manufacturing, *e.g.* machinery, equipment, vehicles, other transport equipment;

SU18: Manufacture of furniture;

SU19: Building and construction work;

SU21: Private households (= general public = consumers);

SU22: Public domain (administration, education, entertainment, services, craftsmen).

Applications covered by this generic scenario encompass the following product categories (PC):

PC9: Coatings and Paints, Fillers, Putties, Thinners.

The term “coatings” as used here describes any material that can be applied to a surface as a thin continuous, layer (film). This includes paints, lacquers or varnishes. Such coatings are used in a wide range of application to protect surfaces from corrosion and other environmental effects, provide decorative effects and improve inherent performance properties. Film formation can be a physical process, where solvents evaporate from solutions or melted substances solidify, or a chemical process involving reactions between reactive groups in binders [OECD, 2007].

The application of a coating to a surface can be by manual use of brush/roller, spraying systems, and dip or roll coating systems [OECD, 2007]. The type and constituent composition of the coating product are based on the substrate, intended use, service environment and the desired role of coating. Decorative coatings cover the use of paints applied to buildings, their trim and fittings and for decorative and protective purposes by both professionals and the general public. All decorative coatings are supplied as liquid materials [OECD, 2007].

Titanium dioxide (TiO₂) is the most important inorganic pigment in terms of quantity. The world production in 2000 amounted to nearly 4 million tonnes per year. Titanium dioxide white inorganic pigments are used primarily in the production of paints, printing inks, paper and plastic products. Titanium dioxide is of outstanding importance as a white pigment because of its scattering properties, its chemical stability, and lack of toxicity [BREF, 2007].

The following application should be taken as representative rather than the sole example of where and why citric acid or citrates may be used within the coatings industry.

In the paint industry citric acid and citrate salts are used to retard the settling of titanium dioxide, the most common pigment used in paints and other coatings [APAC, 2009]. Thus, shipping of titanium dioxide as an aqueous slurry has advantages in handling and storage space *versus* shipping as a fine solid. Although titanium dioxide particles will initially disperse in water, they separate rapidly and in a short time will form a hard-packed sediment which is virtually impossible to re-disperse. The presence of ions such as calcium or iron causes flocculation which exacerbates the problem. In the early 1970s, it was discovered that addition of 0.04 – 0.4% citric acid or tartaric acid or their simple salts (sodium, potassium, ammonium) substantially retarded the settling and packing of titanium dioxide particles in aqueous dispersions [US 3,663,284].

At least a portion of the citric acid added to aid shipment of the pigment is likely to still be present during formulation of the paint. Indeed, it is possible that further additions are made to allow re-dispersion of pigment in the final paint formulation.

9.11.1 Exposure scenario

Formulation

A paint factory formulating 10000 tpa of formulated paint could need around $10000 \times 0.001 = 10$ tpa of citric acid. Paint formulation is a widespread activity and this estimate is consistent with a total market size of 300 tpa.

It is taken that the regional tonnage is 40 tpa.

Assuming a worst case of 2% handling loss this is a local release of 200 kg per year. Such a wastage rate is less than for scenarios considered earlier and there is no need to calculate local exposures. The releases will be added as regional and continental losses to waste water:

$$\text{Regional} = 200 \times (40/10) / 365 = 2.2 \text{ kg/d}$$

$$\text{Continental} = 2.2 \times (260/40) = 14.3 \text{ kg/d}$$

Use

The coating process used by both professionals and consumers is typically by brush or roller application. For releases to waste water during consumer use, the OECD Emission Scenario Document for coatings assumes that an estimated 1% of the volatile fraction of the coating will be lost as brush residues and then end up in the sewer. The same fraction (1%) of the volatile fraction is assumed to be lost during professional use, but this is properly disposed and does not end up in the sewer [OECD, 2007].

Therefore the amount of citric acid in the application passing to waste is estimated to be widely dispersed:

Regional wastewater:

$$0.1 \times 300 \text{ tpa} \times 1000 \text{ kg/t} \times 0.01 / 365 = 0.82 \text{ kg/d}$$

Continental wastewater:

$$0.9 \times 300 \text{ tpa} \times 1000 \text{ kg/t} \times 0.01 / 365 = 7.40 \text{ kg/d}$$

Therefore, for simplicity, for this application area, the totals are:

Regional wastewater:

$$2.2 + 0.82 = 3.0 \text{ kg/d}$$

Continental wastewater:

$$14.3 + 7.4 = 21.7 \text{ kg/d}$$

For human health worker exposure at paint production sites will be to aqueous formulations for which no hazard has been identified. In addition, relevant exposures have been calculated for life cycle stages with higher exposures. Therefore no attempt at quantification will be made nor is needed.

9.12 ES12: Use in photography

Following the REACH descriptor system [ECHA, 2009] the following sectors of use are covered by this scenario:

SU21 Professional uses

SU22 Consumer uses

The relevant product category is PC30: Photochemicals.

Citric acid is one of a range of complexing agents used in photography to control the effects of calcium and magnesium hardness, and to keep iron soluble in solution as part of redox processes.

Due to the rapid growth of digital photography, use of chemicals in film processing is now limited almost entirely to a small number of professional providers. The chemicals used are collected by photochemical companies in order to recover silver and disposal to drain does not take place.

Citrate may also be used as a stop bath in professional or consumer settings as part of the process for the manual development of photographic film. Releases to the environment from this application are insignificant compared to those from considered in other exposure scenarios (cleaning products for example).

Therefore this scenario need not be considered further in respect of the environment.

For human health, the processes applied during both professional and consumer uses are:

PROC 9 Transfer of substance or preparation into small containers (dedicated filling line, including weighing)

PROC 5 Mixing or blending in batch processes for formulation of preparations and articles (multistage and/or significant contact)

PROC 13 Treatment of articles by dipping and pouring

9.13 Use as a laboratory reagent

Following the REACH descriptor system [ECHA, 2009] the following sector of use is covered by this scenario: SU3 Industrial uses

The relevant product category is PC21 Laboratory chemicals

Citric acid may be used at low levels within laboratories. Exposures will take place but under highly controlled conditions. Therefore this scenario need not be considered further for human health or the environment.

9.14 Use in water treatment

This scenario covers use in smaller-scale circulating water treatment in industrial settings, which typically use high substance concentration at low discharges and would usually have a waste water treatment plant (WWTP) in place. The degradability of citric acid in power station cooling systems makes it not suitable for such purposes.

The tonnage of 1000 tpa is an estimate.

REACH Guidance R.12 describes Sectors of use, Product Categories generic Environmental Release Categories (ERCs) that can be linked to the lifecycle and use pattern of substances. The REACH descriptors relevant to the use of citrates in water treatment products are as follows:

Sectors of use:

Main user groups:

SU3: Industrial manufacturing (all)

End user groups:

SU10: Formulation of preparations

Chemical product category:

PC20: Products such as pH-regulators, flocculants, precipitants, neutralisation agents, other unspecified

PC37: Water treatment chemicals

Environmental release categories

ERC2: Formulation of preparations

ERC4: Industrial use of processing aids

9.14.1 Exposure scenario

Industrial cooling systems can be categorized by their design and by using water as coolants. The exchange of heat between process medium and coolant is enhanced by heat exchangers. From the heat exchangers the coolant transports the heat into the environment.

Usage of water treatments containing citrates would be continuous for the correct functioning of the cooling water system. Re-loading may be needed more or less frequently, for open and closed cooling water systems respectively, to refresh the system.

The worst-case for the local environment is to assume treatment of a large industrial plant, open cooling system, which requires the use of large volumes of a high concentration product on a continuous basis and involves the direct release of blow down effluent to the river or receiving water.

In **open recirculating systems**, alkaline conditions (pH of 8-9), in combination with organic complexing agents are effective against corrosion and scaling. Most currently used corrosion programmes are based on phosphates, and zinc is added if water conditions require this.

Typical concentrations of scale control agents (polyphosphates, phosphonates, polyacrylates, copolymers and ter-polymers) range from 2 to 20 mg/l, as active compound. Hardness stabilisers prevent the formation of crystals and are used in recirculating systems, but rarely or never in once-through systems. Citrates may be used to enhance the performance of the other additives.

In most downstream uses treatment chemicals are applied in water-based processes. The final concentration in the water used in scale inhibition is typically from less than 1 to 10 ppm. Depending on the exact nature of the process, the complexing agents may remain present in the aqueous effluent and the discharge streams. These streams will be treated on the user's site, discharged to sewer systems or discharged to waterways (wide dispersive use).

Given the low volatility and the high water solubility of the substances, direct releases to air and soil can be considered negligible.

The OECD Emission Scenario Document for Water Treatment discusses scenarios that are relevant for open cooling systems. It refers to the possibility of loss of treated cooling water from the system through process of drift (the spray (plume) produced from the top of an evaporative cooling tower); windage (physical loss of water from a cooling tower caused by draught of air or wind); or bleed/purge/blowdown (water deliberately removed from a cooling system to control the concentration factor of dissolved solids). Depending on the type of drift and mist elimination equipment fitted, these losses may be small. For the UK, a loss of 0.01% of the recirculation rate in the system is suggested. Given the chemical properties of citrates, it can be assumed that the entire release is via water and not volatilised. It is assumed that traps on the site will collect the majority of the windage loss. In the UK approximately half of the bleed/purge discharges are to sewer and the remainder are to estuaries or to sea (though these would be treated before discharge). Blow down losses can be considered to be on a continuous basis. Overall, it is assumed that citrates released to waste water for treatment equivalent to that associated with a municipal WWTP. Many installations will be situated next to much larger rivers than the default size.

In the UK, the capacity of 50% of installed base cooling towers is in the range of 22.7 m³ and 227 m³ (OECD, 2004). The water circulation rate of a typical open cooling system (with capacity of 100 m³), for an industrial plant, is assumed to be 350 m³/h (3.5 times the capacity). The blowdown of open cooling systems is related to the rate of evaporation (1% of the circulation rate) and the concentration cycle, which is the ratio (typically 3) of the maximum concentration of dissolved solids in the recirculating water to the concentration in the make up water (OECD, 2004).

For the purpose of this calculation, a scaling inhibitor product with an active content of citrate at 25% is assumed.

Therefore, for a blowdown of 1.75 m³/h from an open cooling system; the estimated release of citrates to water is

$$0.25 \times 20 \text{ mg/l} \times 1.75 \text{ m}^3/\text{h} \times 1000 \text{ l/m}^3 \times 24 \text{ h/d} \times 10^{-6} \text{ kg/mg}$$
$$= 0.44 \text{ kg/day.}$$

This is lower than ES considered above and there is therefore no need to develop the scenario further.

In the nature of the use it must be assumed that all the citric acid used in water treatment could pass to waste water. Therefore:

Regional wastewater:

$$0.1 \times 1000 \text{ tpa} \times 1000 \text{ kg/t} / 365 = 274 \text{ kg/d}$$

Continental wastewater:

$$0.9 \times 1000 \text{ tpa} \times 1000 \text{ kg/t} \times /365 = 2470 \text{ kg/d}$$

For human health worker exposure at industrial sites will be to aqueous formulations for which no hazard has been identified. In addition, relevant exposures have been calculated for life cycle stages with higher exposures. Therefore no attempt at quantification will be made nor is needed.

9.15 ES15: Use in metal surface treatment

Citric acid may be used as a complexing agent during metal surface treatment operations. This includes cleaning, brightening and passivation of fabricated stainless steel components, and other metal components, cleaning of circuit boards prior to soldering, and metal cleaning or chemical polishing for the surface treatment of aluminium, copper and other metals. The following applications should be taken as representative rather than the sole example of where and why citric acid or citrates may be used in the treatment of metal surfaces. Some industries using citric acid include fasteners, medical devices, semi-conductors, automotive and aerospace.

Passivation: Citric acid may be used in stainless steel passivation to remove iron from the surface of the stainless steel and prevent later corrosion. After thorough cleaning, the stainless steel part is immersed in a passivating acid bath. Any one of three approaches can be used: nitric acid passivation, nitric acid with sodium dichromate passivation and citric acid passivation. Which approach to use depends on the grade of stainless steel and prescribed acceptance criteria. When citric acid passivation is used, typical solutions range from 4 to 10% citric acid by weight.

Electroless plating: Plating describes the coating of surfaces with metals, either through an electrolysis or electroless plating processes. Electroless plating is also known as ‘autocatalytic’ plating; deposition of the metal starts on metal nuclei such as palladium and continues autocatalytically. Electroless plating is favoured over electrolysis for most component production (EA 2009).

There are usually three stages in the electroless plating process: de-smearing, activation and electroless copper plating. The plating solution has a copper content of 2 – 5 g/l, with sodium hydroxide (15 – 20 g/l), complexing agents (10 – 15 g/l) or tartrates (5 – 10 g/l) and reducing agents, such as formaldehyde (3 – 5 g/l). The process solution lifetime is limited by the build-up of reaction products and is proportional to the rate of throughput of components (EA 2009). Citrate may be used as a complexing agent.

Electroless plating involves the large-scale use of water in both providing the medium for the process itself and for the subsequent rinsing and washing of components. There is a degree of recycling of rinse water through use to top-up the plating tanks, but there is ultimately loss through carry-over on components. Spent fluids can only be topped up a limited number of times before the media needs replacing. Water-soluble waste is discharged in waste water for basic on-site treatment (settling and pH adjustment) before discharge to municipal treatment works, controlled by local discharge consent agreements (EA 2009).

The use of citrate in metal-surface treatment is estimated as *approx.* 1000 tpa. Therefore, environmental releases are not dissimilar to those discussed in the cleaning scenario (ES5) but on a much smaller scale. Therefore, it is not considered necessary to further assess environmental exposure.

For workers, exposures are not expected to be greater than those discussed in other industrial use scenarios. The basic risk management measures discussed for these scenarios are considered sufficient to ensure safe use. Human health exposure is not discussed further.

9.16 ES16: Use in agriculture

Following the REACH descriptor system, the following product types are covered by this generic scenario: PC12 Fertilizers and PC22 Lawn and Garden Preparations, including fertilizers.

Citrate complexes of iron, copper, magnesium, manganese and zinc are used to correct soil deficiencies of these minerals because they are soluble in water at normal soil pH. The soluble citrate complex promotes the transfer of the metal nutrient into the plant's root or leaf system. The biodegradability of citric acid is important for this application (APAC 2009).

One common method for making fertilisers involves dissolving metal sulfates in water and citric acid followed by neutralization with ammonia. This process may be carried out in an industrial setting as part of the formulation of solid or liquid fertilisers/plant feeds. In this case, citric acid is an intermediate and it is the metal-citrate or ammonium citrate that must be considered for the professional or consumer use of fertilisers/plant feeds. Magnesium citrate may be used in this context. Alternatively, mixing of fertilisers may take place on farms. In this case, exposure may be to solid or liquid citric acid or metal-citrate (including sodium citrate).

Citrates may also be present as dispersant/scale inhibiting agents, i.e. adjuvants in the preparation. Evidence from other applications in which citrate is acting as a scale control agent/dispersant suggests that citrate may be present at very low levels in the formulation, perhaps *approx.* 1-20 ppm.

In any of the above cases, marketed products may be solid (granules or pellets) or solution. Processes used may include transfer, loading, mixing, rolling/brushing and spraying. Plant feeds containing citrates may also be used in professional or consumer settings. The products may be liquids or granules and may be sprayed or poured.

Citrates may also be used in plant protection products and in animal feed; however, these applications fall outside the scope of REACH.

The amount of citric acid believed to be used in this application is at most 1500 tpa. The use per site is unknown, but this should be considered as a widely dispersed use. In the worst case a release of the entire tonnage to the region could be included, *i.e.* 1500 tpa. Of this, part will be released to agricultural soil (90%) and part to waste water (10%).

A regional release of $150 \times 1000/365 = 411$ kg/d to waste water will be added to the model, and 3699 kg/d to soil will be included.

For human health worker exposure will be to aqueous formulations for which no hazard has been identified. In addition, relevant exposures have been calculated for life cycle stages with higher exposures. Therefore no attempt at quantification will be made nor is needed.

9.17 Use in medical devices

Citrates may be used in medical devices, for example, citrate is added to human blood to prevent coagulation. The whole blood collection process is a closed process as sterility must be maintained. Procedures are carried out by trained personnel in a controlled environment. Therefore, exposures from this use are expected to be minimal and the scenario is not considered further for human health or the environment.

9.18 Regional exposure concentrations

Table 9.50 shows the predicted regional exposure concentrations calculated from the sum of the regional PECs for each exposure scenario. Bioaccumulation is not of concern for this substance, so regional concentrations in the food chain are not assessed.

Table 9.50: Regional exposure concentrations

	Predicted regional Exposure Concentrations		Measured regional exposure concentrations		Explanation / source of measured data
	value	unit	value	unit	
Freshwater	1.52×10^{-2}	mg/l	No data		The value represents the sum of the regional PECs calculated by EUSES 2.1.1
Marine water	1.41×10^{-3}	mg/l	No data		The value represents the sum of the regional PECs calculated by EUSES 2.1.1
Freshwater sediments	3.32×10^{-1}	mg/kg d.w.	No data		The value represents the sum of the regional PECs calculated by EUSES 2.1.1
Marine sediments	2.60×10^{-2}	mg/l	No data		The value represents the sum of the regional PECs calculated by EUSES 2.1.1
Agricultural soil	3.19×10^{-3}	mg/kg wwt	No data		The value represents the sum of the regional PECs calculated by EUSES 2.1.1
Grassland	7.47×10^{-12}	mg/kg wwt	No data		The value represents the sum of the regional PECs calculated by EUSES 2.1.1
Air	1.24×10^{-19}	(mg/m^3)	No data		The value represents the sum of the regional PECs calculated by EUSES 2.1.1