CLH report

Proposal for Harmonised Classification and Labelling

Based on Regulation (EC) No 1272/2008 (CLP Regulation), Annex VI, Part 2

Substance Name:

Sodium hypochlorite, solution ... % Cl active

EC Number: 231-668-3

CAS Number: 7681-52-9

Index Number: 017-011-00-1

Contact details for dossier submitter:

RIVM/VSP, Bureau REACH

PO Box 1, 3720 BA Bilthoven. The Netherlands

bureau-reach@rivm.nl

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Part A.

1 PROPOSAL FOR HARMONISED CLASSIFICATION AND LABELLING

1.1 Substance

Table 1: Substance identity

Substance name:	Sodium hypochlorite, solution % Cl active
EC number:	231-668-3
CAS number:	7681-52-9
Annex VI Index number:	017-011-00-1
Degree of purity:	Maximum 25% w/w
Impurities:	Maximum 0.8% (w/w) sodium chlorate

1.2 Harmonised classification and labelling proposal

Table 2: The current Annex VI entry and the proposed harmonised classification

	CLP Regulation
Current entry in Annex VI, CLP	Skin Corr. 1B H314
Regulation	Aquatic Acute 1 H400
Current proposal for consideration by	Aquatic Acute 1 H400
RAC	Aquatic Chronic 1 H410
	Acute M-factor 100
	Chronic M-factor 10
Resulting harmonised classification	Skin Corr. 1B H314
(future entry in Annex VI, CLP	Aquatic Acute 1 H400
Regulation	Aquatic Chronic 1 H410
	Acute M-factor 100
	Chronic M-factor 10

1.3 Proposed harmonised classification and labelling based on CLP Regulation

Table 3: Proposed classification according to the CLP Regulation

CLP Annex I ref	Hazard class	Proposed classification	Proposed SCLs and/or M- factors	Current classification 1)	Reason for no classification ²⁾
2.1.	Explosives				Not reviewed
2.2.	Flammable gases				Not reviewed
2.3.	Flammable aerosols				Not reviewed
2.4.	Oxidising gases				Not reviewed
2.5.	Gases under pressure				Not reviewed
2.6.	Flammable liquids				Not reviewed
2.7.	Flammable solids				Not reviewed
2.8.	Self-reactive substances and mixtures				Not reviewed
2.9.	Pyrophoric liquids				Not reviewed
2.10.	Pyrophoric solids				Not reviewed
2.11.	Self-heating substances and mixtures				Not reviewed
2.12.	Substances and mixtures which in contact with water emit flammable gases				Not reviewed
2.13.	Oxidising liquids				Not reviewed
2.14.	Oxidising solids				Not reviewed
2.15.	Organic peroxides				Not reviewed
2.16.	Substance and mixtures corrosive to metals				Not reviewed
3.1.	Acute toxicity - oral				Not reviewed
	Acute toxicity - dermal				Not reviewed
	Acute toxicity - inhalation				Not reviewed
3.2.	Skin corrosion / irritation			Skin Corr. 1B	Not reviewed
3.3.	Serious eye damage / eye irritation				Not reviewed
3.4.	Respiratory sensitisation				Not reviewed
3.4.	Skin sensitisation				Not reviewed
3.5.	Germ cell mutagenicity				Not reviewed
3.6	Carcinogenicity				Not reviewed
3.7.	Reproductive toxicity				Not reviewed
3.8.	Specific target organ toxicity -single exposure				Not reviewed
3.9.	Specific target organ toxicity				Not reviewed

CLP	Hazard class	Proposed	Proposed SCLs	Current	Reason for no
Annex I ref		classification	and/or M- factors	classification 1)	classification 2)
rei	- repeated exposure		lactors		
3.10.	Aspiration hazard				Not reviewed
4.1.	Hazardous to the aquatic environment	Aquatic Acute 1 (H400) Aquatic Chronic 1 (H410)	Acute M-factor 100 Chronic M-factor 10	Aquatic Acute 1 (H400)	
5.1.	Hazardous to the ozone layer				Not reviewed

¹⁾ Including specific concentration limits (SCLs) and M-factors

<u>Labelling:</u> <u>Signal word:</u> Danger

Pictogram: GHS05, GHS09

Hazard statements: H314, Causes severe skin burns and eye damage

H410, Very toxic to aquatic life with long lasting effects

EUH031, Contact with acids liberates toxic gas

Proposed notes assigned to an entry:

Note B is assigned to the current entry in Annex VI. No additional notes are proposed.

2 BACKGROUND TO THE CLH PROPOSAL

2.1 History of the previous classification and labelling

Sodium hypochlorite was notified as an existing active substance and assessed in accordance to Directive 91/414/EEC concerning the placing of plant protection products on the market, with a view to the possible inclusion of the substance into Annex I to the directive (Draft Assessment Report, May 2008, RMS the Netherlands).

Sodium hypochlorite was discussed at the Commission working group on the classification and labelling in December 1998 and added to Annex I of Directive 67/548/EEC in the 29th ATP with classification C; R34, R31, N; R50.

Sodium hypochlorite is currently listed (entry 017-011-00-1) in Annex VI of Regulation EC no. 1272/2008 with the same classification as was listed in the 29th ATP to Directive 67/548/EEC.

Sodium hypochlorite as a substance has been assessed extensively in the past (RAR, DAR and CAR, although that the CAR has not yet been finalised). The studies that already have been assessed and agreed upon at the EU level have not been reassessed, but have been summarized in the current harmonized classification and labelling dossier. New data which is provided in the REACH registration dossier has been assessed and summarized in more detail.

2.2 Short summary of the scientific justification for the CLH proposal

Sodium hypochlorite is currently listed in Annex VI to the CLP as acutely hazardous to the aquatic environment. However, no harmonised M-factor is listed in Annex VI. Furthermore, the currently

²⁾ Data lacking, inconclusive, or conclusive but not sufficient for classification

available data suggest that sodium hypochlorite needs to be classified as Aquatic Chronic Cat 1 based on the criteria of the 2nd ATP to the CLP (Regulation 286/2011).

In this dossier, a chronic aquatic classification and M-factors for acute and chronic toxicity are proposed.

The physical hazards and human health hazards have not been evaluated, this dossier does not propose any changes to the classification of physical hazards or human health hazards.

2.3 Current harmonised classification and labelling

2.3.1 Current classification and labelling in Annex VI, Table 3.1 in the CLP Regulation

Table 4: Current classification and labelling in Annex VI, Table 3.1 in the CLP Regulation

Classif	ication		Labelling	Specific	Notes		
Hazard Class and Category Code(s)	Hazard Statement Code(s)	Hazard Statement Code(s)	Supplementary Hazard Statement Code(s)	Pictograms, Signal Word Code(s)	Concentration limits, M- Factors		
Skin Corr. 1B	H314	H314	EUH031	GHS09 GHS05		Note B	
Aquatic Acute 1	H400	H400		Dgr			

2.3.2 Current classification and labelling in Annex VI, Table 3.2 in the CLP Regulation

Table 5: Current classification and labelling in Annex VI, Table 3.2 in the CLP Regulation

Classification	Labelling
C; R34	C; N
R31	R: 31-34-50
N; R50	S: (1/2-)28-45-50-61

2.4 Current self-classification and labelling

2.4.1 Current self-classification and labelling based on the CLP Regulation criteria

Table 6 shows the notifications made to the CLP Inventory for sodium hypochlorite as of 13-11-2014.

Table 6: Notifications made to the CLP Inventory for sodium hypochlorite

Classification		Labelling			Specific Concentration		
Hazard Class and Category Code(s)	Hazard Statement Code(s)	Hazard Statement Code(s)	Supplementary Hazard Statement Code(s)	Pictograms Signal Word Code(s)	limits, M- Factors	Notes	Number of Notifiers
Ox. Gas	H270		EUH031	GHS09		Note B	355
Skin Corr. 1B	H314	H314	EUHUSI	GHS05		Note D	333

Classification		Labelling			Specific Concentration		
Hazard Class and Category Code(s)	Hazard Statement Code(s)	Hazard Statement Code(s)	Supplementary Hazard Statement Code(s)	Pictograms Signal Word Code(s)	limits, M- Factors	Notes	Number of Notifiers
Eye Dam. 1	H318	H318		GHS03			
Aquatic Acute 1	H400	H400		Dgr			
		H272					
Skin Corr. 1B	H314	H314	EUH031	GHS09 GHS05		Note B	324
Aquatic Acute 1	H400	H400	Dgr		Note B	324	
Skin Corr. 1B	H314	H314	E111021	GHS09		N. C. D.	205
Aquatic Acute 1	H400	H400	EUH031	GHS05 Dgr		Note B	295
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318	H318		GHS07			
STOT SE 3	H335 (not available)	H335		GHS09 GHS05 Dgr	M=10		93
Aquatic Acute 1	H400	H400					
Aquatic Chronic 1	H410	H410					
Met. Corr. 1	H290	H290		GHS09 GHS05 Dgr	M=10		
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318		EUH031				78
Aquatic Acute 1	H400	H400					
Aquatic Chronic 2	H411	H411					
Met. Corr. 1	H290	H290			GHS05 M=10		
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318			CHEOZ			
STOT SE 3	H335 (Respiratory tra) (inhalation)	H335	EUH031	GHS07 GHS09 GHS05 Dgr			78
Aquatic Acute 1	H400	H400					
Aquatic Chronic 1	H410	H410					
Skin Irrit. 2	H315	H315					
Eye Irrit. 2	H319	H319		GHS07 GHS09	M=10		78
Aquatic Acute 1	H400	H400		Wng	IVI-1U		70
Aquatic Chronic 2	H411	H411					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314		GHS07			
Eye Dam. 1	H318		EUH031	GHS09	M(Chronic)=1		78
STOT SE 3	H335 (Respiratory tra) (inhalation)	H335		GHS05 Dgr	M=10		

Classification		Labelling			Specific Concentration		
Hazard Class and Category Code(s)	Hazard Statement Code(s)	Hazard Statement Code(s)	Supplementary Hazard Statement Code(s)	Pictograms Signal Word Code(s)	limits, M- Factors	Notes	Number of Notifiers
Aquatic Acute 1	H400						
Aquatic Chronic 1	H410	H410					
Skin Irrit. 2	H315	H315					
Eye Dam. 1	H318	H318		GHS09	M=10		78
Aquatic Acute 1	H400	H400		GHS05 Dgr	NI-10		76
Aquatic Chronic 2	H411	H411					
Aquatic Chronic 3	H412	H412					78
Skin Irrit. 2	H315	H315					
Eye Irrit. 2	H319	H319	-	GHS07 Wng			78
Aquatic Chronic 3	H412	H412	-	,,,,,,			
Skin Corr. 1B	H314	H314		GHS09			
Aquatic Acute 1	H400	H400	-	GHS05			62
Skin Corr. 1B	H314	H314		CHGOO			
Aquatic Acute 1	H400		EUH031	GHS09 GHS05			47
		H410	Dgr				
Skin Corr. 1B	H314	H314		Dgr			
		H400	EUH031				45
		H318					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314		GHS07			
STOT SE 1	H335 (not specified)	H335	EUH031	GHS09 GHS05 Dgr			45
Aquatic Acute 1	H400	H400	=				
Skin Corr. 1B	H314	H314		GHS05 Dgr			37
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314	=				
Eye Dam. 1	H318				M 10		24
STOT SE 3	H335 (respiratory sys)	H335		Dgr	M=10		34
Aquatic Acute 1	H400	H400					
Met. Corr. 1	H290			CHSOO			
Skin Corr. 1B	H314	H314	EUH031 GHS09 GHS05		Note B	32	
Aquatic Acute 1	H400	H400		Dgr			
Skin Corr. 1B	H314	H314	ELHIO21	GHS09			20
Aquatic Acute 1	H400	H400	EUH031	GHS05 Dgr			29

Classification		Labelling			Specific Concentration		
Hazard Class and Category Code(s)	Hazard Statement Code(s)	Hazard Statement Code(s)	Supplementary Hazard Statement Code(s)	Pictograms Signal Word Code(s)	limits, M- Factors	Notes	Number of Notifiers
		H314	EUH031	Dgr	M=10		24
		H400	E011031	Dgi	IVI-10		24
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318		EUH031	GHS07 GHS09			
STOT SE 3	H335 (Respiratory Sys) (Inhalation)	H335		GHS09 GHS05 Dgr		Note B	22
Aquatic Acute 1	H400	H400					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314	GHS07				
STOT SE 3	H335 (lungs)	H335	EUH031	GHS09 GHS05 Dgr			18
Aquatic Acute 1	H400	H400					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314		GHS07 GHS09 GHS05 Dgr			
STOT SE 3	H335 (not specified)	H335	EUH031		M=10		17
Aquatic Acute 1	H400	H400					
Skin Corr. 1B	H314	H314		GHS07			
Eye Irrit. 2	H319	H319		GHS09 GHS05			4
Aquatic Acute 1	H400	H400		Dgr			
Skin Corr. 1B	H314	H314 (H314)		GHS09		Note D	4
Aquatic Acute 1	H400	H400 (H400)		GHS05 Dgr		Note B	4
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318	H318		GHS07			
STOT SE 3	H335 (Respiratory tra) (Inhalation)	H335	EUH031	GHS09 GHS05 Dgr	M=10		4
Aquatic Acute 1	H400	H400					
		H318	GHS09 EUH031 GHS05	CHSOO			
		H314		M=10		4	
		H400		Dgr			
Met. Corr. 1	H290			GHS07			
Skin Corr. 1B	H314	H314	EUH031	GHS09 GHS05	M=10	Note B	2
Eye Dam. 1	H318			Dgr			

Classification		Labelling			Specific Concentration limits, M- Factors		
Hazard Class and Category Code(s)	Hazard Statement Code(s)	Hazard Statement Code(s)	Supplementary Hazard Statement Code(s)	Pictograms Signal Word Code(s)	nmits, M- Factors	Notes	Number of Notifiers
STOT SE 3	H335 (data lacking)						
Aquatic Acute 1	H400	H400					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314		GHS07			
Eye Dam. 1	H318		EUH031	GHS09 GHS05	M=10	Note B	2
STOT SE 3	H335 (unknown)	Н335		Dgr			
Aquatic Acute 1	H400	H400					
Skin Corr. 1B	H314	H314	ELHIO21	GHS09	W 1	N. S	
Aquatic Acute 1	H400	H400	EUH031	GHS05 Dgr	M=1	Note B	2
Skin Corr. 1B	H314	H314	ELHIO21	GHS09		N · D	2
Aquatic Acute 1	H400	H400	EUH031	GHS05 Dgr		Note B	2
Skin Corr. 1A	H314	H314 (EUH031 Contact)	EUH031	GHS09 GHS05			2
Eye Dam. 1	H318		EUHOSI	Dgr			2
Aquatic Acute 1	H400	H400					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318			GHS07 GHS09			
STOT SE 3	H335 (respiratory sys) (inhalation)	H335	EUH031	GHS05 Dgr			1
Aquatic Acute 1	H400	H400					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318	H318		GHS07 GHS09			
STOT SE 3	H335 (respiratory sys) (inhalation)	H335	EUH031	GHS05 Dgr	M=10	Note B	1
Aquatic Acute 1	H400	H400					
Aquatic Acute 1	H400			GHS09			1
		H314		GHS05 Dgr			1
Skin Corr. 1B	H314			Dor			1
Aquatic Acute 1	H400			Dgr			1
Met. Corr. 1	H290	H290		GHS07			
Skin Corr. 1B	H314	H314	EUH031	GHS09 GHS05	M=10	Note B	1
Eye Dam. 1	H318	H318		Dgr			

Classification		Labelling			Specific Concentration		
Hazard Class and Category Code(s)	Hazard Statement Code(s)	Hazard Statement Code(s)	Supplementary Hazard Statement Code(s)	Pictograms Signal Word Code(s)	limits, M- Factors	Notes	Number of Notifiers
STOT SE 3	H335 (respiratory voi)	H335					
Aquatic Acute 1	H400	H400					
Skin Corr. 1A	H314	H314					
Aquatic Acute 1	H400	H400		GHS09			
		H290	EUH031	GHS05 Dgr		Note B	1
		H318					
Skin Corr. 1B	H314	H314 (C>=5%)	EUH031	GHS09 GHS05			1
Aquatic Acute 1	H400	H400		Dgr			
Skin Corr. 1B	H314	H314	EUH031	GHS05 Dgr	Skin Corr. 1B: C: ≥ 5%		1
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314		GHS07			
STOT SE 3	H335 (not available)	H335	EUH031	GHS09 GHS05 Dgr		Note B	1
Aquatic Acute 1	H400	H400					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318			GHS07			
STOT SE 3	H335 (respiratory tra) (inhalation)	Н335	ЕUН031	GHS09 GHS05 Dgr	M=10	Note B	1
Aquatic Acute 1	H400	H400					
Met. Corr. 1	H290	H290					
Skin Corr. 1B	H314	H314					
Eye Dam. 1	H318		E111021	GHS07 GHS09	W 10	N. D	
STOT SE 3	H335 (respiratory tra)	H335	EUH031	GHS05 Dgr	M=10	Note B	1
Aquatic Acute 1	H400	H400					
Skin Corr. 1B	H314	H314					
Aquatic Acute 1	H400	H400		GHS07 GHS09		., -	
		H335	EUH031	GHS05 Dgr		Note B	1
		H290		25.			
Skin Corr. 1B	H314	H314					
Aquatic Acute 1	H400		EUH031	GHS05 Dgr		Note B	1
		H290		- 8-			

3 JUSTIFICATION THAT ACTION IS NEEDED AT COMMUNITY LEVEL

Sodium hypochlorite is an active substance in the meaning of Directive 91/414/EEC and therefore subject to harmonised classification and labelling (CLP, article 36.2).

Part B.

SCIENTIFIC EVALUATION OF THE DATA

1 IDENTITY OF THE SUBSTANCE

1.1 Name and other identifiers of the substance

Table 7: Substance identity

EC number:	231-668-3
EC name:	Sodium hypochlorite, solution % Cl active
CAS number (EC inventory):	7681-52-9
CAS number:	7681-52-9
CAS name:	Sodium hypochlorite
IUPAC name:	Sodium hypochlorite
CA index name:	Hypochlorous acid, sodium salt (1:1)
CLP Annex VI Index number:	017-011-00-1
Molecular formula:	ClONa
Molecular weight range:	74.4 g/mol

Structural formula: Na⁺ClO⁻

1.2 <u>Composition of the substance</u>

Table 8: Constituents (non-confidential information)

Constituent	Typical concentration	Concentration range	Remarks	
Sodium hypochlorite	12-14 % (w/w) as active or available chlorine	< 24 % (w/w) as active or available chlorine	Sodium hypochlorite, solution % Cl active is produced as an aqueous solution (EU RAR)	

See Annex for confidential information.

Current Annex VI entry:

Table 3.1: Skin Corr. 1B (H314), Aquatic Acute 1 (H400)

Table 3.2: C; R34, R31, N; R50

Table 9: Impurities

Impurity	Typical concentration	Concentration range	Remarks
Sodium chlorate		< 0.7 % (w/w)	EU-RAR

See Annex for confidential information.

Only impurities which are classified as hazardous to the aquatic environment are shown in the table. Sodium chlorate is classified in CLP Annex VI as Aquatic Chronic 2 (H411). However, it is present in quantities that will not affect the classification of the sodium hypochlorite solution.

Table 10: Additives

Additive	Function	Typical concentration	Concentration range	Remarks
Water	Stabiliser		<76 %	
Sodium hydroxide	Stabiliser			Sodium hydroxide is left as excess in the hypochlorite solution in order to stabilize the pH value at about 12 and decrease the rate of decomposition. (EU RAR)

See Annex for confidential information.

1.2.1 Composition of test material

1.3 Physico-chemical properties

Table 11: Summary of physico - chemical properties.

Property	Value	Reference	Comment (e.g. measured or estimated)		
State of the substance at 20°C	Liquid	EU-RAR	In aqueous solution		
and 101,3 kPa		REACH registration	Sodium hypochlorite is a yellow, limpid liquid with a chlorinated odour		
Melting/freezing point	-20 to -30°C	EU-RAR			
	-28.9°C	REACH registration	Measured (24.3% available chlorine)		
Boiling point	96 to 120°C	EU-RAR			
	≥60.4°C	REACH registration	Measured (24.3% available chlorine)		
Relative density	1.23 g/cm³ at 25°C	EU-RAR	15% (w/w) active chlorine solution		
	1.3 g/cm ³	DAR, REACH registration	Measured (24.3% available chlorine)		
Vapour pressure	17.4 - 20 hPa at 20°C	EU-RAR, DAR	Sodium hypchlorite, solution%		
	Ca. 25 hPa at 20°C	REACH registration	Cl is an aqueous solution of an inorganic salt		
Surface tension	82.4 mN/M at 20°C	REACH registration	(24.3% available chlorine) No surface tension properties		
Water solubility	Miscible [29.3 g/100 g (0 °C) in water]	EU-RAR	(Merck, 2001)		
Partition coefficient n- octanol/water	Not applicable	EU-RAR			
Flash point	Not applicable	EU-RAR			
	>111°C	REACH registration	Measured		
Flammability	Not applicable	EU-RAR			
Explosive properties	Not explosive	EU-RAR	Anhydrous sodium hypochlorite is very explosive		
Self-ignition temperature	Not applicable	EU-RAR			
Oxidising properties	Strong oxidizing agent but is not oxidizing when tested using methods A17 (solids) or A21 (liquids)	EU-RAR, DAR			
Granulometry	Not applicable	EU-RAR			
Stability in organic solvents and identity of relevant degradation products	No information				
Dissociation constant	In solution the sodium hypochlorite is in equilibrium with chlorine and hypochlorous acid. The equilibrium is temperature and pH dependent. Hypochlorous acid has a	DAR	(WHO, 2000)		

Property	Value	Reference	Comment (e.g. measured or estimated)
	pKa of 7.5 (at 25°C)		
Viscosity	0.956 to 1.110 mPa.s (at 25° C) for 0.5-5% NaClO solution	DAR	Measured

2 MANUFACTURE AND USES

2.1 Manufacture

Sodium hypochlorite is manufactured by the absorption of chlorine in ca. 21% caustic soda solution. The chlorine and the caustic soda are made by electrolysis of brine, and the chlorine is added as gas or liquid.

2.2 Identified uses

Sodium hypochlorite is used mainly in chemical synthesis, for cleaning, disinfection and sanitation in household, for municipal water and sewage disinfection and for bleaching.

3 CLASSIFICATION FOR PHYSICO-CHEMICAL PROPERTIES

No changes are proposed to the classification of physical hazards of sodium hypochlorite.

4 HUMAN HEALTH HAZARD ASSESSMENT

No changes are proposed to the human health classifications of sodium hypochlorite.

5 ENVIRONMENTAL HAZARD ASSESSMENT

Data from the European Risk Assessment Report (RAR), the plant protection product Draft Assessment Report (DAR) and the REACH Registration Dossiers were included in this CLH report for sodium hypochlorite, solution ... % Cl active. The Competent Authority Report (CAR) for sodium hypochlorite as biocide was not finalised at the time of writing the CLH report.

Studies considered valid in the RAR and DAR (reliability score of 1 or 2) have been included in this report. Studies from the REACH registration (reliability score of 1 or 2), which were not included in the RAR and DAR were assessed for their reliability and also included in this report. Based on the behaviour of sodium hypochlorite in water, studies in which no analytical monitoring was performed were considered not sufficient reliable. In case of conflicting assignment of reliability score between the RAR, DAR and REACH registration dossier, the validity of the study was reassessed by examination of the robust study summaries.

Different terms are used to describe the concentration of sodium hypochlorite solutions. The terms are not consequently used in the literature. The EU-RAR and DAR use the following terminology:

- <u>Available chlorine</u> measures the concentration of the three species HOCl, OCl⁻ and Cl₂. In practice, only HOCl and OCl⁻ are usually present because chlorine (Cl₂) is formed only at pH < 4;
- <u>Active chlorine</u> measures the concentration of HOCl and Cl_2 . In practice, this usually includes only HOCl because chlorine (Cl_2) is formed only at pH < 4;
- HOCl or OCl⁻ are mostly used in cases in which one of the two species was predominant because of the pH value of the tested solution;
- Combined chlorine or Bound chlorine measures chlorine bound to amines (chloramines).

In freshwater, measured concentrations are usually expressed as Free Available Chlorine (FAC) or Total Residual Chlorine (TRC); the latter encompasses free plus combined chlorine (i.e. TRC is FAC plus combined chlorine). In chlorinated salt water, what is measured is generally called Total Residual Oxidant (TRO) including free chlorine and bromine, or Chlorine Produced Oxidant (CPO) that encompasses free and combined chlorine and bromine species.

In many aquatic toxicity studies, the results are expressed in terms other than active chlorine, such as TRC. The FAC content in TRC varies. Depending on the composition of the test media, (a part of the) FAC is bounded to amines resulting in combined chlorine. Therefore it is not possible to determine the actual active chlorine content in total residue chlorine. For classification purposes, it is assumed that TRC equals the FAC content. As the entry for sodium hypochlorite in Annex VI gives the concentration as % active chlorine, the assumption that TRC is equal to the FAC may possibly lead to an underestimation of the toxicity of sodium hypochlorite solutions.

As the results of the aquatic toxicity studies are given as mg/l active chlorine, it is necessary to convert those results to mg/l NaOCl in order to compare the results with the CLP criteria. The following assumptions and equations have been used for converting mg/L active chlorine species to mg/L NaOCl, and then back to % Cl active.

- $[Cl_2]$ to [NaOCl]: 1.05 x Cl_2 = NaOCl
- $[Cl_2]$ and HOCl: $0.74 \times Cl_2 = HOCl$
- HOCl and NaCl: 1.43 x HOCl = NaCl
- HOCl and Cl_2 : 1.35 x HOCl = Cl_2
- NaOCl and HOCl: 0.70 x NaOCl = HOCl
- NaOCl and Cl₂: 0.95 x NaOCl = Cl₂

5.1 Degradation

5.1.1 Stability

Speciation forms in water

Sodium hypochlorite, solution ... % Cl active exists in water as Na⁺ and chlorine species. There are three species of chlorine in equilibrium in water: gaseous chlorine (Cl₂), HOCl (also a gas at room temperature and pressure), and ClO. An example of the distribution between them as a function of pH is shown in Figure 1 that is a reproduction of figure 2.1 from the EU-RAR. At pH values above 4.0, chlorine (Cl₂) does not exist (DAR, EU-RAR).

Figure 1.

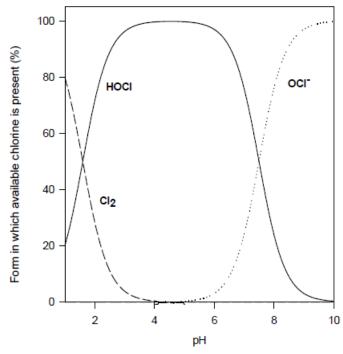


Figure 2.1. Calculated variation in composition of a chlorine solution with degree of acidity or alkalinity for 0.1 M Cl₂ in water at standard temperature and pressure (The data in this figure are based on general chemistry handbooks).

Sodium hypochlorite decay is second order with respect to NaOCl concentration. The second order rate law predicts that diluting the NaOCl by a factor of 2 should decrease the rate of NaOCl decay by a factor of 4. However, actual decay data for sodium hypochlorite solutions shows that a factor of 2 decrease in the NaOCl concentration results in an approximate factor of 5 decrease in the rate of decay. This is because of the effect of the decay rate by the decrease in the total ionic concentration of the solution. Since the dilution of a sodium hypochlorite solution not only decreases the NaOCl concentration but also decreases the concentration of all the ions in the solution (TCI, 2006, pamphlet 96; DAR).

In concentrated sodium hypochlorite solutions, the content of available chlorine decreases because NaClO tends to disproportionate to chloride and chlorate ions. The reaction is:

$$3 \text{ NaClO} \rightarrow 2 \text{ NaCl} + \text{NaClO}_3$$
 $K_{eq} = 10^{27}$

It is the result of two reactions: a slow one with formation of chlorite and a fast one with formation of chlorate by reaction between chlorite and hypochlorite.

The first reaction (that produces chlorite) controls the reaction rate producing chlorate. The formation rate of chlorate, at room temperature and pH = 11, is very slow. The process is dependent on the time, temperature, impurities, pH and concentration of the sodium hypochlorite solution. Also light can decompose hypochlorite solutions.

Time dependence

At constant temperature the inverse of the active product concentration is a linear function of the time. A solution dosed at 150 g/l available chlorine which is kept away from sunlight and at constant 15°C, loses 1/6 of its concentration within less than 3 months. In diluted hypochlorite solutions the losses are minor.

pH dependence

Hypochlorite should not be added to an unbuffered medium, because at low pH, the following secondary reactions could occur:

In acid media under pH 4, hypochlorite will be transformed to gaseous chlorine $HOCl + H+ + Cl^{-} \rightarrow Cl_2 + H_2O$

Between pH 4 and 11, both ClO⁻ and HOCl are present with the latter being much more active. Degradation of HOCl is more rapid than the degradation of ClO-.

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if pH <6, the main reaction is: 2HOCl \rightarrow 2HCl + O_2 if pH >6, the main reaction is: 3NaClO \rightarrow NaClO_3 + 2 NaCl
```

Hypochlorous acid (HClO) is very unstable and it suddenly decomposes with formation of oxygen: $2 \text{ HOCl} \rightarrow 2 \text{ HCl} + O_2$

Dependence upon impurities

Sodium hypochlorite can decompose to oxygen according to the following reaction: $2 \text{ NaClO} \rightarrow 2 \text{ NaCl} + \text{O}_2$

The decomposition reaction is a bimolecular one and requires activation energy of 113.3 kJ/mol (26.6 kcal/mol). Although it is slower than the chlorate formation reaction, it is catalysed by trace amounts of metallic impurities. The strongest decomposition catalysts to oxygen are: Co, Ni and Cu; whereas Fe and Mn are weaker catalysts. Salts such as sodium chloride, sodium carbonate and sodium chlorate have only a very low influence on reaction rate within the range of concentration where they are normally present. Sodium hydroxide does not influence the reaction rate if its concentration is greater than 10^{-3} M (0.04 g/l).

Temperature dependence

The influence of temperature is very high. The decomposition rate doubles if the temperature increases by $\sim 5.5^{\circ}$ C. If temperature is more than 35°C, the decomposition reactions are very rapid: $3\text{NaClO} \rightarrow \text{NaClO}_3 + 2\text{NaCl}$

In every case, the temperature of the solution must be below 55°C in order to prevent a sudden decomposition of the hypochlorite. The more stable solutions are those of low hypochlorite concentration, with a pH of 11 and low iron, copper, and nickel content, stored in the dark at low temperature.

In water containing organic matter and impurities, sodium hypochlorite may also react to form chloramines (R-NHCl, R-NCl₂ or NCl₃), monochlorophenols, chloroacetaldehydes, chloroacetonitriles and chloroacetic acids and chloroform (CHCl₃) (EU-RAR). In natural waters free chlorine is very rapidly and totally transformed to combined chlorine (EU-RAR).

Stability in water

The REACH registration dossier contains the following (confidential) information on the half-life of sodium hypochlorite solutions at different temperatures:

Table 12

10% available chlorine	Temperature (°C)	Half-life (days)
	15	800
	25	220
	60	3.5
	100	0.079
5% available chlorine	15	5000
	25	790
	60	13.5
	100	0.25

From Table 12 it can be concluded that under environmental relevant temperature hydrolysis is not a significant transformation route for sodium hypochlorite. Sodium hypochlorite solutions in pure water and at lower concentration levels are stable, when stored in the dark and at low temperature.

Phototransformation in water

A photolysis study carried out in a non-guideline study (Nowell and Hoigne, 1992) is available for sodium hypochlorite. When exposed as a horizontal water layer to solar irradiation of 1.05 kW/m², the photolysis half-life of sodium hypochlorite solution is 12 min at pH 8 (OCI⁻), 37 min at pH 7 and 60 min at pH 5 (HOCl).

Sodium hypochlorite solutions are very sensitive to light. Direct sunlight may cause rearrangement and decomposition resulting in the formation of chlorate and oxygen (EU-RAR).

Phototransformation in air

The photochemical and oxidative decomposition of hypochlorous acid in air was calculated according to Atkinson (Görg and Glöckner, 2007). The reaction rate constant KOH is $0.14x10^{-12}$ cm³molecule⁻¹sec⁻¹. The DT50 for hypochlorous acid was estimated to be 114.6 days (24 hour day), corresponding to 2750 hours, using the reaction rate constant KOH. As hypochlorous acid contains no olefinic carbon-carbon and acetylenic triple bonds, it is not supposed to react with ozone.

5.1.2 Biodegradation

Sodium hypochlorite is an inorganic compound. Therefore, biodegradation studies such as the OECD301 screening tests and water/sediment studies are not relevant for sodium hypochlorite.

5.1.3 Summary and discussion of degradation

No biodegradation or water sediment studies were performed for sodium hypochlorite. Since sodium hypochlorite is an inorganic compound, these studies are not considered relevant in the degradation assessment. According to CLP Annex I section 4.1.2.10.1, for metals and inorganic compounds, the concept of degradability as applied to organic compounds has limited or no meaning. Still it has to be considered for sodium hypochlorite for the derivation of an M-factor for chronic aquatic toxicity.

The degradability of sodium hypochlorite solutions is subject of discussion. Under specific conditions sodium hypochlorite solutions are quite stable, while in aquatic test systems the test substance concentrations drop quite instantly after the beginning of the test. Below the reasoning is listed in favor or against the conclusion that sodium hypochlorite solutions can be considered rapidly degradable.

In favor:

Sodium hypochlorite, solution ... % Cl active exists in water as Na⁺ and chlorine species. In water, three chlorine species are in equilibrium: Cl₂, HOCl and ClO⁻. The fraction of each species depends on pH, temperature and chlorine species concentration. At pH above 4, Cl₂ does not exist; Cl₂ is therefore considered to make negligible contribution to the fate and toxicity of sodium hypochlorite under environmentally relevant conditions. Between pH 4 and 11, both ClO⁻ and HOCl are present. The decomposition of hypochlorite and hypochlorous acid is complex and dependent on concentration, pH, temperature and the presence of impurities. Degradation products that can be formed are Cl₂ (chlorine), sodium chloride (NaCl), sodium chlorite (NaClO₂), sodium chlorate (NaOCl₃) and oxygen (O₂), as well as chloramines and chloroform.

Sodium hypochlorite is very sensitive to photolysis. The photolysis half-life of sodium hypochlorite solution is 12 min at pH 8, 37 min at pH 7 and 60 min at pH 5 when exposed as a horizontal water layer to solar irradiation of 1.05 kW/m². Chlorate and oxygen are formed as photolysis products.

In natural waters free chlorine is very rapidly and totally transformed to combined chlorine (EU-RAR). The reactivity and degradation is illustrated by the fact that it is very hard in the aquatic toxicity tests to maintain the test substance concentrations stable, the only way of doing so is to make use of a flow-through test system.

Against:

The CLP Guidance v4.0 uses the term degradation in the following way: "Generally expressed in terms of biotic or abiotic degradation of organic substances (or transformation of inorganic substances)." Furthermore, section 4.1.2.9.4 of CLP Annex I states that "The criteria used reflect the fact that environmental degradation may be biotic or abiotic. Hydrolysis can be considered if the hydrolysis products do not fulfil the criteria for classification as hazardous to the aquatic environment."

In case of sodium hypochlorite, the reaction products of transformation in natural environment are at least partially unknown because of oxidation and carbon or nitrogen chlorination processes and depend on many factors, among which temperature and pH.

The degradation products chlorine and sodium chlorate have a harmonized classification as hazardous to the aquatic environment; chlorine is classified as Aquatic Acute 1 (with an M-factor of 100) and sodium chlorate is classified as Aquatic Chronic 2.

Hypochlorite solutions (kept away from sunlight) and at constant 15°C are relatively stable (rate of hydrolysis is low). Especially at low concentration levels the losses are minor.

Although that sodium hypochlorite is susceptible for photolysis, "the Guidance on the Application of the CLP criteria" in Annex II.2.3.9 states that "The actual degree of photochemical degradation in the aquatic environment depends on local conditions e.g. water depth, suspended solids, turbidity as well as seasonal influences, and the hazard of the degradation products is usually not known. Probably only seldom will enough information be available for a thorough evaluation based on photochemical degradation".

Conclusion:

The discussion if the inorganic compound sodium hypochlorite can be considered rapidly degradable is complex. Given the fact that hypochlorite solutions (kept away from sunlight and stored at low temperature) are stable and that some degradation products are also hazardous to the environment it is stated that sodium hypochlorite cannot considered being rapidly degradable for classification purposes.

5.2 Environmental distribution

5.2.1 Adsorption/Desorption

No K_{oc} value was determined for sodium hypochlorite.

5.2.2 Volatilisation

Sodium hypochlorite has negligible volatility whilst hypochlorous acid has low volatility. The equilibrium concentration of hypochlorous acid vapour in the gaseous phase above a solution depends upon the solution pH, as expected from the fact that hypochlorous acid is more volatile than the hypochlorite anion (DAR volume B8).

The volatility of the species of available chlorine in water and of three main species of combined chlorine have been studied by Holzwarth et al (1984), Blatchley et al (1992), published the Henry's constant of HOCl. These references expressed this information with different units and using different forms of Henry's law. Currently Henry's law constant is expressed in atm. and is the ratio between partial pressure in the air divided by a mole fraction in water. The figure given by Blatchley is expressed in atm and is 0.06 atm. The figures calculated by Holzwarth are without unit and expressed in mole fraction in the air divided by mole fraction in the water (for HOCl at pH 5.5 and at a temperature of 20°C, 0.076). These two expressions of Henry's law constant are not very easy to interpret. It is proposed to use a figure without unit expressing mg/l in air divided by mg/l in water. After correction of Holzwarth figures in this new unit (1 mole of air weighing 28 g and 1 mole of water 18 g; 1 m³ of air weighing 1.2 kg and 1 litre of water weighing 1 kg), new figures of a Henry's coefficient for the different products at a temperature of 20°C are proposed:

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\begin{array}{lll} \text{ClO}^{\text{-}} & \text{pH} = 8.5 & \text{H} = 0.07 \text{x} 10^{\text{-}4} \\ \text{HOCl} & \text{pH} = 5.5 & \text{H} = 0.4 \text{x} 10^{\text{-}4} \\ \text{NH}_2 \text{Cl} & \text{pH} = 9 & \text{H} = 2.4 \text{x} 10^{\text{-}4} \\ \text{NHCl}_2 & \text{pH} = 6.4 & \text{H} = 8 \text{x} 10^{\text{-}4} \\ \text{NCl}_3 & \text{pH} = 1.8 & \text{H} = 2300 \text{x} 10^{\text{-}4} \end{array}
```

The volatility of NCl_3 is about one thousand times the volatility of the 3 other compounds. The ClO^- Henry's coefficient is about five times lower than the coefficient of HOCl. At $40^{\circ}C$ and pH = 1.8 the Henry's coefficient for NCl_3 is 0.6, very close to the maximum possible figure which is 1. These figures make clear that NCl_3 is completely extracted by stripping and that ClO^- is extremely difficult to extract (EU-RAR).

5.2.3 Distribution modelling

Not available.

5.3 Aquatic Bioaccumulation

Sodium hypochlorite is an inorganic substance. No log Kow value can be determined for sodium hypochlorite.

No bioaccumulation studies have been performed for sodium hypochlorite. Based on the environmental fate and behaviour of the substance, bioaccumulation in the aquatic ecosystem is not expected.

5.4 Aquatic toxicity

Source of studies

Sodium hypochlorite aquatic toxicity studies have been extensively assessed in the past (RAR, DAR and CAR, although that the CAR has not yet been finalised). The studies that already have been assessed and agreed upon at the EU level have not been reassessed, but have been summarized in Table 13. New data which is provided in the REACH registration dossier has been assessed in more detail.

Studies with critical effect data (also those which are considered invalid or not sufficient reliable to take into account for risk assessment and classification purposes, according to the registrant) have also been included in Table 13. Studies with results expressed in only nominal test substance concentrations in combination with static test conditions, have been left out. In addition, many studies in the REACH registration dossier have been assigned a Klimisch score of 2, but are considered not valid in the RAR and DAR and are left out of Table 13.

Explanation with regard to relevant and reliable studies used for C&L

A large number of aquatic toxicity studies have been carried out for sodium hypochlorite and the related substance calcium hypochlorite, both in fresh water as in salt or brackish water. However, most of the studies are considered not reliable, for example due to lack of analytical monitoring and use of nominal concentrations to express the results, or give information that cannot directly be used to derive a classification. Table 13 contains a summary of all relevant and reliable studies from the information sources used. In the table it is indicated if the study has been assigned to be a key study or if it is used as supportive evidence. If sufficient information was available for sodium hypochlorite, then results from studies conducted with calcium hypochlorite were not included in the assessment. For the long term toxicity study on invertebrate (21-d study on *Epioblasma capsaerformis*), calcium hypochlorite is used due to the fact that this study is the only long-term invertebrate toxicity study available for fresh water. The use of the data on calcium hypochlorite as an alternative is justified by the fact that both substances are hypochlorite salts with comparable water solubility (ClONa; 29.3 g/ 100g and ClOCa; 21 g/l).

Furthermore, short study summaries have been included for the key studies with the lowest effect results for both acute and chronic toxicity for all three trophic levels (copied from the EU-RAR if available). Finally, a more extensive study summary have been included for a new *Ceriodaphnia dubia* and algae study which are included in the REACH registration dossier for sodium hypochlorite.

It should be noted that different Klimisch scores have been assigned to identical study data in the RAR, DAR and registration dossier. As a rule of thumb the reliability scores (notes a and b) from the previous assessment reports are leading. For some studies no Klimisch score has been derived in the previous assessments, but have been assigned to be supportive data. Also these studies have not been re-assessed.

Table 13: Summary of relevant information on aquatic toxicity (**bold faced** values indicate key study data, in addition, data which are considered supportive are in *italics*)

Species	Criterion	Result [µg/L]	Result [µg NaOCl/L]	Reliability	Reference	
Fish						
FRESH WATER – SHORT-TERM						

Species	Criterion	Result [µg/L]	Result [µg NaOCl/L]	Reliability	Reference
beeles	Criterion	60 (TRC)*	63 (TRC)*	s ^{ab} /2 ^c	Bass et al (1977),
Salmo gairdneri	96h LC50	30 (FAC)*	32 (FAC)*	3 /2	Heath (1978) ^{abc}
Samo garraneri	7011 EC30	64 (TRC)*	67 (TRC)*	s ^{ab} /2 ^c	Bass et al (1977),
Ictalurus punctatus	96h LC50	32 (FAC)*	34 (FAC)*	3 /2	Heath (1978) ^{abc}
Salmo gairdneri (juveniles)	24h LC50	430*	452*	s ^{ab} /2 ^c	Brooks and Seegert
sumo guiraneri (javennes)	2 111 EC50	130	132	3 72	(1977) ^{abc}
Onchorhyncus kisutch	48h LC50	1260-2410*	1323-2531*	s ^{ab} /2 ^c	Seegert and Brooks
Alosa pseudoharengus					$(1978)^{abc}$
Notropis hudsonius					
Osmerus mordax					
Pimephales promelas	96h LC50	80 (TRC)*	84 (TRC)*	s ^{ab} /3 ^c	Wilde et al
1		>40 (FAC)*	>42 (FAC)*		$(1983a,b)^{abc}$
Cyprinus carpio	48h LC50	260*	273*	s	Tsai et al (1990) ^{ab}
Gambusia affinis	48h LC50	610*	641*	s	Tsai et al (1990) ^{ab}
Gambusia affinis	48h LC50	840*	882*	s	Mattice et al
					$(1981)^{ab}$
Menidia menidia	96h LC50	37 (TRC)	39 (TRC)	s ^{ab} /3 ^c	Roberts et al
					$(1975)^{abc}$
BRACKISH & SEA WATER	- SHORT-TERM	1			,
Leiostomus xanthurus	96h LC50	90 (TRC & FAC)	95 (TRC & FAC)	1 ^{ab} /2 ^c	Bellanca and Bailey
					$(1977)^{abc}$
Oncorhynchus kisutch	96h LC50	32 (TRO)	34 (TRO)	$2^{a}/s^{b}$	Thatcher (1978) ^{ab}
Gasterosteous aculeatus	96h LC50	167 (TRO)	175 (TRO)	$2^{a}/s^{b}$	Thatcher (1978) ^{ab}
Morone saxatilis	48h LC50	8 (TRC)	8.4 (TRC)	s ^{ab} /2 ^c	Middaugh et al
					$(1977)^{abc}$
FRESH WATER – LONG-TE	ERM				
Ictalarus punctatus	134d NOEC	5 (TRC)	5.3 (TRC)	S	Hermanutz et al
	134d LOEC	53 (TRC)	56 (TRC)		$(1990)^{ab}$
		350 (available	368 (available	s/2°	Soivo, Nukinen and
Oncorhynchus mykiss	48h LC50	chlorine)	chlorine)		Tuurala (1988) ^c
BRACKISH & SEA WATER	– LONG-TERM				
Menidia peninsulae	28d NOEC	40 (TRC)	42 (TRC)	1	Goodman et al
					$(1983)^{ab}$
Invertebrates					
FRESH WATER – SHORT-T	ERM				
Ceriodapnia dubia	24h LC50	5 (FAC)	5.3 (FAC)	2 ^{ab} /4 ^c	Taylor (1993) ^{abc}
Ceriodapnia dubia	48h EC50	<25.8 (active	<27.1 (active	1	Gallagher, Lezotte
1		chlorine, mean	chlorine, mean		and Krueger
		measured)	measured)		$(2011)^{c}$
Daphnia magna	48h EC50	<49 (active	<51 (active	1	Gallagher, Lezotte
		chlorine, mean	chlorine, mean		and Krueger
		measured)	measured)		(2009) ^c
Baetis harrisoni	48h LC50	5 & 6 (TRC)	5.3 & 6.3 (TRC	2 /4 ^c	Williams et al
	96h LC50	4.1 & 4.8 (TRC)	4.3 & 5 (TRC)		(2003) ^c
BRACKISH & SEA WATER	- SHORT-TERM	1			
Pandalus goniurus	96h LC50	90 (TRC)	95 (TRC)	2 ^{ac} /s ^b	Thatcher (1978) ^{abc}
Brachionus plicatilis	48h LC50	10-820*	10.5-861*	S	Capuzzo et al
Acartia tonsa	48h LC50	180*	189*	s	$(1976, 1979a,b)^{ab}$
Crassostrea virginica	48h LC50	80-120*	84-126*	s	
(larvae)					
Crassostrea virginica	96h EC50,	23 (TRC)	24 (TRC)	S	Roberts et al
(juveniles)	shell				$(1975)^{ab}$
	1	ĺ			
	deposition				
Crassostrea virginica	deposition 48h EC50	26 (TRC, CaOCl)	27 (TRC)	2	Roberts and
Crassostrea virginica (larvae)	•	26 (TRC, CaOCl)	27 (TRC)	2	Roberts and Gleeson (1978) ^{ab}
	•	26 (TRC, CaOCl) 29 (TRC, CaOCl)	27 (TRC) 30 (TRC)	2 2	

			Result [µg					
Species	Criterion	Result [µg/L]	NaOCl/L]	Reliability	Reference			
FRESH WATER – LONG-TE		resure [µg/L]	THE CHE	remanity	Hererence			
Epioblasma capsaerformis	21 d NOEC	10 (TRC,	10.5 (TRC	2	Valenti et al (2006) ^c			
		nominal, CaOCl)	nominal, CaOCl)					
BRACKISH & SEA WATER	BRACKISH & SEA WATER – LONG-TERM							
Crassostrea virginica	15d NOEC,	7 (TRO)	7.4 (TRO)	$2^{a}/s^{b}$	Liden et al (1980) ^{ab}			
	shell							
	deposition							
Rangia cuneata	15d NOEC	62 (TRO)	65 (TRO)					
Algae								
FRESH WATER – SHORT-T	ERM							
Pseudokirchneriella	24h EC50 _r	<23.3 (FAC)	<24.5 (FAC)	1	Liedtke (2013) ^d			
subcapitata								
FRESH WATER – LONG-TE	ERM							
Pseudokirchneriella	24h LOEC _r	<10.8 (FAC)	<11.3 (FAC)	1	Liedtke (2013) ^d			
subcapitata	24h LOEC _b	<10.8 (FAC)	<11.3 (FAC)					
Myriophyllum spicatum	96h NOEC	20 (TRC,	21 (TRC,	2	Watkins and			
		measured)	measured)		Hammerschlag			
					(1984) ^a			
Peryphytic community	7d NOEC _b	3 (FAC)	3.2 (FAC)	2	Cairns et al (1990) ^{ab}			
Protozoan species	28d NOEC	2.1 (FAC)	2.2 (FAC)	S	Pratt et al (1988) ^a			
Zooplankton (density)	24d NOEC	1.5 (FAC)*	1.6 (FAC)*	S	Pratt et al (1988) ^a			
BRACKISH & SEA WATER	– LONG-TERM							
Phytoplankton	21d EC50 _b	1-10 (TRC)*	1.1-10.5 (TRC)*	S	Sanders et al			
					(1981) ^{ab}			
Plankton	1y NOEC _b	<10 (TRC)	10.5 (TRC)	S	Erickson and Foulk			
					$(1980)^{a}$			

Remark: Klimisch scores (1-4) or s: supportive data

5.4.1 Fish

5.4.1.1 Short-term toxicity to fish

Study 1

Thatcher (1978) conducted many laboratory flow-through bioassays on 8 species of estuarine and marine fish, belonging to different families including salmonidae, clupeidae and percidae. Since the main purpose of the study was to investigate the impact of chlorinated effluents from power plants, fish were simultaneously exposed to sodium hypochlorite and to a 5°C thermal stress. The 96h LC50 ranged from 0.032 mg/l (as TRO), for the most sensitive species (*Oncorhynchus kisutch*), to 0.167 mg/l (*Gasterosteous aculeatus*). These data were considered relevant for the assessment because heat is usually associated to chlorine in power plants effluents, but they were rated 2 because the authors report that in a previous study the addition of thermal stress resulted in a toxicity higher than chlorine alone and, moreover, LC50 was calculated pooling data from different tests.

Study 2

FAC = free available chlorine, TRC = total residue chlorine, TRO = total residue oxidant. * No continuous exposure.

^a As summarized in the European Commission. Risk Assessment Report Sodium hypochlorite. Prepared by Italy, November 2007.

^b As summarized in the European Commission. Draft Assessment Report Sodium hypochlorite. Prepared by the Netherlands, May, 2008.

^c As summarized in the REACH registration for sodium hypochlorite, accessed on November 2014

^d Provided by the industry but not yet included in the REACH registration dossier (November 2014)

Middaugh et al. (1977) tested the toxicity of chlorinated brackish pond water to early-life stages of *Morone saxatilis* in a flow-through test. No indication on test guideline or GLP is reported. Only data relative to eggs hatchability could be retrieved. A rough estimate of the 48h LC50 = $8 \mu g/L$ TRC was calculated using the authors' raw data relative to percentages of hatched eggs per test concentration. This data can be used as indicative information of eggs sensitivity (EU-RAR).

5.4.1.2 Long-term toxicity to fish

Study 1

Goodman et al. (1983) developed a method for testing the early-life stages of *Menidia peninsulae*, an estuarine fish of the Atherinidae family. They carried out a 28d test starting with 36h old eggs, under flow through conditions using natural seawater diluted with freshwater to a 20‰ salinity, and measured the effects of sodium hypochlorite on eggs survival and fry survival and growth. Fry were the most sensitive stage. The authors calculated a NOEC (fry survival) = 0.04 mg CPO/l (CPO is to be considered analogous to TRC measured by other authors in saline waters), concentration at which only 5% of fish died. At this concentration no sublethal effects were evident (EU-RAR).

Study 2

The long-term toxicity to four standard fish species has been investigated by Hermanutz et al. (1990) in two field studies under flow-through conditions, lasting up to 134 days. Test guideline and GLP are not indicated. In the first study, 3 chlorine concentrations were tested with one or two replicate fish pools; in the second study, only two concentrations with no replicates were tested. In all experiments, no effect on survival was observed in any species up to 183 μ g/L TRC. In the first experiment, a concentration-effect relationship, although partial, was observed only for the growth endpoint in channel catfish. At the highest concentration tested (52 and 183 μ g/L), the mean weight decreased by 25% and 34%, respectively, whereas at the immediately lower concentration (5 μ g/L) it was equal to that of the control group. In the second experiment, growth reduction in the same species was observed only at 62 μ g/L (37% reduction) but no effect at 53 μ g/L. The experiment was not conducted under standard conditions, no statistical analysis of data was carried out by the authors to identify the NOEC or LOEC, and raw data do not allow the estimation of any endpoint useful for the assessment. Therefore we cannot derive any valid endpoint, but considering that 25% effect is biologically significant we can consider the NOEC for growth 5 μ g/L and use it as an indication of the long term toxicity (EU-RAR).

5.4.2 Aquatic invertebrates

5.4.2.1 Short-term toxicity to aquatic invertebrates

Study 1

The key aquatic toxicity study in the EU RAR is the study of Taylor (1993). In this study, the acute toxicity of various forms of free and combined chlorine to *Ceriodaphnia dubia* were tested in a standard 24h toxicity tests, carried out under static and flow through conditions. No test guideline was followed and no GLP statement was given. Sodium hypochlorite was tested at pH 7 for HOCl (70% HOCl and 30% OCl) and pH 8 for OCl (80% OCl and 20% HOCl). The toxicity tests were performed at 25°C, with 10 neonate (< 24h old) *Ceriodaphnia dubia*.

In static tests the decay of free chlorine was very rapid (1 minute and 7 hours in tests with or without food, respectively) and the results were not considered valid.

Flow-through tests (without food) were carried out to maintain a constant concentration over the exposure time. Only the results of the flow-through test can be used for classification. The 24h LC50 values from this test were found to be 5 and 6 μ g/L for HOCl and OCl⁻, respectively.

These data were judged valid with restriction (rated 2) because the test concentrations were calculated from measured chlorine concentration of the stock solution and dilution ratios, the number of concentrations/replicates are not specified, the performance of the controls not mentioned, and the 24h LC50s determined by graphical interpolation (EU-RAR).

The industry rated the study reliability as 4 (invalid). The reasoning provided is:

This article lacks description of several important features of the experiment, which means that this set of data cannot be used with confidence. For example:

- there is no information on the tested material: "Stock solutions containing about 20 mg/L of NH₂Cl, NHCl₂, or sodium hypochlorite were prepared and then diluted with DMW to make the various test solutions" (rk: DMW is 20% v/v degassed Perrier© in deionized water; hardness or other characteristics not provided);
- there is little information on the analytical measurements: "Measurements of free chlorine, NH₂Cl, and NHCl₂ concentrations were made with a Wallace & Tiernan (Atlanta, GA) amperometric titrator, using the procedures recommended in the instruction manual". It is stated that the detection limit of the titrator is 0.01 mg/L (no indication of whether this refers to total available chlorine, free available chlorine or even test material is given). Given the characteristics of this method and its precision in the low level range targeted here, it would have been of prime importance to get information on limit of quantification and confidence intervals. Below 0.01 mg/L, concentrations are calculated from dilution factors of the stock solutions;
- there is no indication on sample treatment: i.e. number of analytical measurements between 0 and 24 hours, and, most importantly, time between sampling and titration. A significant decay can happen in this period and result in measured concentrations that are lower than those to which the animals are actually exposed;
- it is not indicated if the concentrations mentioned are initial measured, mean of initial and final, or nominal ones. Separate stability experiments described in the same article, performed without animals, show different rates of decay according to conditions, but no information is given on stability during the flow-through exposure of animals itself;
- there is no data on test design: number of tested concentrations, range of concentrations, separation factors in the flow-through experiments, number of animals, number of replicates, lighting conditions (which plays an important role in stability);
- in contrast to the requirements of the standard OECD TG 202, exposure duration was only 24 hours instead of 48 hours.

Since no reassessment is made and the study is assigned in the EU-RAR as key-study for classification, the study is still considered as key-study despite of the shortcomings reported by industry.

Study 2

The REACH registration dossier for sodium hypochlorite contains a more recent study of the acute toxicity of sodium hypochlorite to *Ceriodaphnia dubia*. Gallagher (2011) performed an acute toxicity test with *Ceriodaphnia dubia* according to OECD guideline 202. Neonate (< 24 h old)

Ceriodaphnia dubia were exposed to sodium hypochlorite (active chlorine content 14.5%) in concentrations of 0, 25, 50, 100, 200 and 400 µg active chlorine/L. Exposure duration was 48 hours under flow-through conditions, number of immobilised animals was determined after 3.5, 24 and 48 h. The test was performed at 25°C, pH 8.1.

Water samples were taken one day prior to the start and at the start and end of test. Analysis for chlorine by HPLC with UV detection (210 nm) after derivatisation with o-tolidine in methanol under acidic conditions (method recovery 113%, LOQ: 10 µg active Cl/L).

Measured concentrations of active chlorine in samples one day prior to the start ranged from < LOQ (for the lowest concentration) to 48% of nominal. Mean measured concentrations of active chlorine during the test ranged from < LOQ to 56% of nominal. Mean measured concentrations were: 25.8, 55.7, 106, and 181 μ g active Cl/L for 50, 100, 200, and 400 μ g active Cl/L, respectively.

After 48h, all but one daphnid in the control, and all daphnids in the 25 μg active Cl/L group were normal whereas all daphnids in the 50, 100, 200 μg active Cl/L groups were immobile. This suggests a steep dose-response curve. At 100 and 200 μg active Cl/L some daphnids could not be observed due to their small size. The measured concentrations were lower than 80% of nominal. Given the uncertainty in average actual measured concentrations the conclusion that the 48h EC50 <25.8 μg active Cl/L (since the 48h EC100 equals to 25.8 μg active Cl/L) seems appropriate.

Study 3

Williams et al. (2003) performed experiments (not according to established test guidelines and no GLP statement given) to determine acute chlorine tolerance of *Baetis harrisoni* (ephemeroptera) from two rivers in KwaZulu-Natal, SouthAfrica. Via a flow through artificial streams the mortality after 24, 48 and 96 hours was determined at test substance concentrations of 0, 4, 8 and 12 μ g/L TRC for the Umbilo River and at 0, 4, 6, 8, 12 and 16 μ g/L TRC for Westville Stream. All test substance concentrations, including the controls were at least tested in triplicate, the test substance concentrations of the Umbilo were tested with 6 replicates. Per artificial stream 35 to 90 nymphs of the mayfly were added. The experiment was started after 48h of acclimatization and after removal of the dead nymphs. Chlorine levels were determined continuously. The 48h LC50 and 96h LC50 values were 5 and 4.1 μ g/L TRC for Westville Stream and 6.5 and 4.8 μ g/L TRC for the Umbilo River, respectively. Since natural waters are used in a non-standardised test-system, the study has been rated 2. This study is assigned as key-study for classification. In the registration dossier the reliability of the study was scored 4 (not assignable).

5.4.2.2 Long-term toxicity to aquatic invertebrates

Study 1

In the scientific literature, three studies investigating the long-term toxicity of sodium hypochlorite have been found. In a field study on chlorinated condenser cooling effluents using mollusk bivalves (Liden et al., 1980), the survival of oysters (*Crassostrea virginica*) and clams (*Rangia cuneata*) maintained at three TRO concentrations for 15 days was not affected at concentration as high as 62 μ g/L, while oyster mean shell deposition was significantly reduced in the treated animals. The field study has not been performed according to established test guidelines and no GLP statement given. At the lowest test concentration (14 μ g/L) a 14% reduction in shell deposition was observed, so that following TGD the NOEC can be estimated as LOEC/2, i.e. 7 μ g/L (7.4 μ g Na OCl/L). This data is

rated 2 because it was obtained from a non-standard test (EU-RAR). This study is assigned as key-study for classification.

Study 2

Valenti et al. (2006) performed 21-d bioassays with two-month-old *Epioblasma capsaeformis* (oyster mussel) and three-, six-, and 12-month old *Villosa iris* (rainbow mussel) juveniles (not according to established test guidelines and no GLP statement given). Calcium hypochlorite was used as test substance, with seven (including control) test substance concentrations varying from 5 to 250 μ g/L TRC for the two- and three-month-old mussels and 10-500 μ g/L TRC for the older mussels. TRC was measured twice a day, FRC and CRC at the start of the experiment and weekly thereafter. The 120L test medium was composed of 50% tap water and 50% (v/v) natural water from the Sinking Creek (USA). Per concentration 20 mussels were tested. Significant declines in growth (80%) and survival (50%) were observed in the 21-d test with *E. capsaeformis* at 20 μ g TRC/L. Lowest-observed-adverse-effects concentrations in bioassays with juvenile *V. iris* were higher (30–60 μ g TRC/L) but showed a significant trend of declining toxicity with increased age. The NOEC with respect to growth was found to be the test substance concentration of 10 μ g TRC/L (growth at this test substance concentration was reduced with 6%). Since natural waters are used in a non-standardised test-system, the study has been rated 2.

5.4.3 Algae and aquatic plants

5.4.3.1 Short-term toxicity to algae and aquatic plants

No reliable EC50 values could be determined for sodium hypochlorite for algae or aquatic plants in the past. Therefore the industry was asked to perform an algae study. Liedtke (2013) performed a standard acute aquatic toxicity test (OECD 201) on the algae *Pseudokirchneriella subcapitata*. For a standard algae test a flow-through test system cannot be applied, consequently available chlorine levels drop quite instantly after the beginning of the test. In the lowest nominal test substance concentration of 125 μ g FAC/L the initial measured concentration is determined to be below the level of quantification (LOQ) of 10.8 μ g FAC/L. After 24 hours only for the highest nominal test substance concentration of 2 mg/l FAC/L, some active chlorine could be detected. In all other test substance concentrations the levels are below the LOQ. After 24 hours the inhibition of the growth rate for the initial measured concentration of 23.3 μ g FAC/L is 60%. After 24 hours the measured concentration by the authors of this study, than the geometric mean measured concentration equals to 11 μ g FAC/L. It can be concluded that the 24h EC50_r is <23.3 μ g FAC/L.

5.4.3.2 Long-term toxicity to algae and aquatic plants

Study 1

The study of Liedtke (2013) showed fast decreasing test substance concentrations. The initial measured concentration for lowest test substance concentration was at the start already below the LOQ of 10.8 μ g FAC/L. Still after 24 hours for the lowest test substance concentration a 9.3% inhibition in growth rate was observed. In terms of biomass the inhibition was even higher (17.3%). The lowest test substance concentration (<10.8 μ g FAC/L) can therefore be considered to be an LOEC.

Study 2

Cairns et al. (1990) used a laboratory multispecies microcosm to study the chronic effects of chlorine (alone or together with ammonia) to naturally derived periphytic communities exposed for 7 days to sodium hypochlorite in a flow-through system (not according to established test guidelines and no GLP statement given). Sodium hypochlorite concentration was expressed as TRC; FAC accounted for $73 \pm 19.9\%$. Chlorine was tested at nominal concentration of 6 and 60 µg TRC/L. Mean measure TRC were $6.3 \pm 3.9 \,\mu\text{g/L}$ and $56.6 \pm 24.5 \,\mu\text{g/L}$ in the low and high treatment respectively. The reduction in protozoa species richness was statistically significant (LOEC) at 6 µg TRC/L, while for a reduction of 20%, considered biologically significant, a concentration of 2.7 µg TRC/L was calculated. At 6 µg/L the composition of protozoa communities (number of taxa) changed significantly; since the effect was about 10% we can calculate for this endpoint a NOEC (LOEC/2) = 3 µg TRC/L. The results from this study are interesting because protozoa represent a group with a great diversity in physiology and function; data were judged reliable and relevant but rated 2 because a non-standard test system was used. Non-taxonomic responses were also measured. In vivo fluorescence, used as an index of algal biomass, was significantly reduced (22%) at 6 µg TRC/L (the lowest tested concentration). This data can be used to calculate a NOEC = $3 \mu g$ TRC/L as an indication of long-term toxicity to algae (EU-RAR).

Study 3

Another study on the microbial community was carried out in outdoor enclosures by the same researchers (Pratt et al., 1988; (not according to established test guidelines and no GLP statement given). Each enclosure consisted of a 130L polyethylene bag containing lake water and littoral sediment, which provided immigrating pelagic and benthic microorganisms for the colonization of the artificial substrates added. In the enclosures chlorine was introduced as a daily pulse, and decay curves were used to estimate the average chlorine concentration over a 24h period. The substrates were examined once a week for protozoan species and algal genera. At the end of the exposure period (day 24) the water was sampled for zooplankton enumeration (filtered with a Wisconsin plankton net n. 10) and substrates were sampled for non-taxonomic measures (chlorophyll a, total protein, alkaline phosphatase activity) and microscopic examination.

In the 24d field test, both taxonomic and non-taxonomic parameters showed lower sensitivity than in the laboratory test, likely due to differences in test design (water, source of species and, most important, method or chlorine application). The authors comment that "Possibly the timing of dosing could have maintained communities in a constant state of recovery and therefore made them appear less sensitive to chlorine stress". At 79 μ g TRC/L, neither chlorophyll a nor the number of algal genera was reduced (NOEC). Protozoan species number was not significantly reduced at the lower test concentration, i.e. NOEC = 24 μ g TRC/L. The most sensitive endpoint was the zooplankton density (24d NOEC = 1.5 μ g TRC/L). Anyhow, the authors report only the number of zooplankton/ml of water without providing any other information about the effects on taxonomic composition of zooplankton community, so that it is not possible to draw any conclusion about the eventual elimination of taxa from the system. Also the potential for system recovery was not evaluated. In this study FAC concentration accounted for 100% of the measured TRC so that the above endpoint can be expressed also as μ g FAC/L.

Because of the uncertainty associated to the most sensitive endpoint and likely underestimation of toxicity due to the pulse dosing system, the results of this test should be interpreted with caution. This conclusion is supported by the comparison of the long term zooplankton NOEC from this test (24d NOEC = $1.5 \mu g$ FAC(or TRC)/L) with the laboratory short-term toxicity to daphnia (24h LC50 = $5 \mu g$ FAC/L) which suggests that a continuous long term exposure of $1.5 \mu g$ FAC/L might

dramatically affect daphnia populations. For these reasons data from this study are not considered valid for the assessment, but have been used in the final discussion as supportive information (rated s) (EU-RAR).

5.5 Comparison with criteria for environmental hazards (sections 5.1 - 5.4)

As the entry for sodium hypochlorite in Annex VI gives the concentration as % active chlorine, the assumption that TRC is equal to the FAC may possibly lead to an underestimation of the toxicity of sodium hypochlorite solutions. In Table 13 approximately half of the key-study data is reported as TRC.

The lowest acute aquatic toxicity values for sodium hypochlorite are:

- a (supportive) 48-hour LC50 value of 8.4 μg sodium hypochlorite per litre for *Morone* saxatilis
- a 24-hour LC50 of 5.3 µg sodium hypochlorite per litre for *Ceriodaphnia dubia*
- a 48-hour LC50 of 5.3 µg sodium hypochlorite per litre for *Baetis harrisoni*
- a 24-hour EC50_r of <24.5 μg sodium hypochlorite per litre for *Pseudokirchneriella* subcapitata

Most of the studies are not standardized or have at least some short-comings compared to the standard test protocol. Therefore a weight of evidence approach is applied for this data leading to the conclusion that the lowest and most critical 50% effect concentrations are between 1 and 10 μ g per litre.

The lowest chronic aquatic toxicity values for sodium hypochlorite are:

- a (supportive) 134-day NOEC of 5.3 μg sodium hypochlorite per litre for *Ictalarus* punctatus
- a 15-day NOEC (shell deposition) of 7.4 μg sodium hypochlorite per litre for *Crassostrea virginica*
- a (supportive) 7-day NOEC (biomass) of 3.2 μg sodium hypochlorite per litre for the peryphytic community
- a (supportive) 24-day NOEC (density) of 1.6 μg sodium hypochlorite per litre for zooplankton

Most of the studies are not standardized or have at least some short-comings compared to the standard test protocol. Therefore a weight of evidence approach is applied for this data leading to the conclusion that the lowest no observed effect concentrations are between 1 and 10 μ g per litre.

The discussion if the inorganic compound sodium hypochlorite can be considered rapidly degradable is complex. Given the fact that hypochlorite solutions (kept away from sunlight and stored at low temperature) are stable and that some degradation products are also hazardous to the environment it is stated that sodium hypochlorite cannot considered being rapidly degradable for classification purposes.

Sodium hypochlorite is not expected to bioaccumulate.

5.6 Conclusions on classification and labelling for environmental hazards (sections 5.1 – 5.4)

Aquatic acute toxicity

Acute toxicity data are available for all three trophic levels. The lowest $L(E)C_{50}$ obtained in acute aquatic toxicity studies is 5.3 μ g NaOCl/L, for the invertebrates *Ceriodapnia dubia* and *Baetis harrsoni*. This value is below the classification threshold value of 1 mg/L. Based on this information, sodium hypochlorite fulfils the criteria for classification with Aquatic Acute 1. Based on a weight of evidence approach, it can be concluded that the lowest LC50 values are between 0.001 and 0.01 mg/L. Therefore an acute M-factor of 100 is assigned to sodium hypochlorite.

Aquatic chronic toxicity

Chronic toxicity data are available for all trophic levels. The lowest chronic NOEC value for sodium hypochlorite is < 1 mg/L (15d NOEC of 7.4 μg NaOCl/L for *Crassostrea virginica* (shell deposition) besides the supportive data). Sodium hypochlorite is considered not rapidly degradable in the environment.

Based on this information, sodium hypochlorite fulfils the criteria for classification as Aquatic Chronic Category 1. Based on a weight of evidence approach it can be concluded that the lowest NOEC values are between 0.001 and 0.01 mg/L. Since the substance is considered non-rapidly degradable, a chronic M-factor of 10 is assigned to sodium hypochlorite.

6 OTHER INFORMATION

No other relevant information available.

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8 ANNEXES

Adapted from Annex 4 in the EU RAR

ACTIVE/AVAILABLE CHLORINE AND HYPOCHLORITE

The active chlorine content of a chlorinated substance (in g/kg) is the amount of pure (100%) chlorine (in g) that has the same oxidizing power as one kg of the substance.

Example: 1 kg of a sodium hypochlorite solution containing 12.5% of active chlorine (125 g/kg) has the same oxidizing power as 125 g of pure chlorine.

The oxidizing power of a substance characterizes the number of electrons exchanged during reaction of this substance. While transforming in chloride ions (Cl⁻), 1 molecule of the following substances exchanges.

- Chlorine (Cl₂) : 2 electrons
- Hypochlorite ion (ClO) or hypochlorous acid (HClO): 2 electrons
- -> 1 mole of pure NaClO (74.5 g) has the same oxidizing power as 1 mole of chlorine (71 g)

Example: The active chlorine content of a sodium hypochlorite solution containing 15 % (150 g/kg) of NaClO is : 150 * 71 / 74.5 = 143 g act. Cl_2 / kg

Two terms are used for defining the concentration of bleach in the lay-man literature and the market:

Active chlorine is by definition the amount of pure (100%) chlorine, in aqueous solution, which has the same oxidizing power as a unit quantity of that substance. In other words, the oxidizing properties of a substance are compared with chlorine and expressed as such. In practice, this corresponds to $Cl_2 + HOCl$ (active chlorine). However, it is often used for available chlorine which is the sum of $Cl_2 + HOCl + ClO$ (available chlorine). Both active and available chlorine are expressed as equivalent content of Cl_2 (molecular weight: 71g).

Sodium hypochlorite is the word used to give the concentration of bleach in North America. The molecular weight of NaOCl is 74.5 g. Since the molecular weights of Cl₂ and NaOCl are slightly different, the way of expressing the concentration is slightly different. However, the difference is small; the active chlorine equivalent content is:

- for chlorine Cl₂:100 % (by definition)
- for sodium hypochlorite NaOCl : 95 % (by calculation: 71/74.5 = 0.95)

In the case of sodium hypochlorite, there are small difference in figures expressed in active chlorine or in weight of substance (i.e.% act. $Cl_2 = \%$ weight).

What is measured in environmental media like surface fresh water is generally expressed as free available chlorine (FAC) or total residual chlorine (TRC) which encompass free and combined chlorine (like chloramines). In saltwater what is measured is generally called total residual oxidant (TRO) including free chlorine and bromine or chlorine produced oxidant (CPO) which encompasses free and combined chlorine and bromine species.