Appendix A. Supporting Information

This appendix provides additional methodological information supporting the Life Cycle Assessment presented in the main manuscript. The material includes: (i) the preliminary screening used to justify the exclusion of minor processes from the system boundaries; (ii) detailed descriptions of the chlorine dioxide production routes evaluated in the study; (iii) the modelling approach adopted to represent sodium chlorite production in the life-cycle inventory; (iv) foreground inventory data for the production systems considered; (v) sensitivity analysis results addressing key modelling assumptions; and (vi) alternative allocation scenarios for co-product generation.

These materials are provided to improve transparency and reproducibility of the modelling approach and to allow independent evaluation of the assumptions underlying the comparative environmental assessment.

A1. Preliminary Screening of Excluded Processes

Process residue treatment was excluded from the main analysis following preliminary screening showing contributions below 2% of total environmental impacts. According to ISO 14044 (§4.2.3.3.2), processes contributing less than approximately 2% to overall impacts may be excluded without significantly affecting results.

Table A1 Preliminary screening of excluded processes.

Process	Contribution to GWP	Justification for exclusion
Wastewater treatment	0.8%	Dilute aqueous streams with low organic load
Solid waste disposal	0.4%	Minimal solid residues generated
Air emission treatment	0.6%	Scrubber systems with low energy demand
Total excluded	1.8%	Below ISO cut-off threshold

A2. Detailed Process Descriptions

The following sections summarize the main industrial production routes for chlorine dioxide considered in this study. Reaction schemes and operating conditions are simplified representations based on technical literature and are intended to support interpretation of the life-cycle inventory model rather than provide detailed process design information.

A2.1 Chlorate-Based Production Routes (M1–M5)

M1 – Methanol Reduction Process (R8)

Reaction:

$6\ NaClO_3 + CH_3OH + 6\ H_2SO_4 \rightarrow 6\ ClO_2 + 6\ NaHSO_4 + CO_2 + 5\ H_2O$

Typical conditions:

- Conversion efficiency: 95–98%
- Temperature: 60–70 °C
- Pressure: 150–200 mbar
- Highly acidic medium

M2 – Hydrogen Peroxide Reduction

Reaction:

$2\ NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2\ ClO_2 + Na_2SO_4 + O_2 + 2\ H_2O$

Typical conditions:

- Conversion efficiency: 95–97%
- Temperature: 50–60 °C
- Atmospheric pressure

M3 – Hydrochloric Acid Reduction

Reaction:
$5\ NaClO_3 + 4\ HCl \rightarrow 4\ ClO_2 + Cl_2 + 5\ NaCl + 2\ H_2O$
Typical conditions:

- Conversion efficiency: 92–95%
- Temperature: 40–50 °C

M4 – Sulfur Dioxide Reduction (Mathieson Process)
Reaction:
$2\ NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2\ ClO_2 + 2\ NaHSO_4$
Typical conditions:

- Conversion efficiency: 90–94%
- Temperature: 40–60 °C

M5 – Sodium Chloride Co-Feed Process
Reaction:
$2\ NaClO_3 + 2\ NaCl + 2\ H_2SO_4 \rightarrow 2\ ClO_2 + Cl_2 + 2\ Na_2SO_4 + 2\ H_2O$
Typical conditions:

- Conversion efficiency: 93–96%
- Temperature: 50–65 °C

A2.2 Chlorite-Based Production Routes (M6–M10)
M6 – Hydrochloric Acid Activation
$5\ NaClO_2 + 4\ HCl \rightarrow 4\ ClO_2 + 5\ NaCl + 2\ H_2O$
Typical conditions:

- Conversion efficiency: 95–98%
- Temperature: 20–40 °C

M7 – Sulfuric Acid Activation
$5\ NaClO_2 + 2\ H_2SO_4 \rightarrow 4\ ClO_2 + 2\ Na_2SO_4 + NaCl + 2\ H_2O$
Typical conditions:

- Conversion efficiency: 94–97%

M8 – Chlorine Activation
$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$
Typical conditions:

- Conversion efficiency: 96–99%

M9 – Electrochemical Oxidation
Anodic reaction:
$ClO_2^- \rightarrow ClO_2 + e^-$
Cathodic reaction:
$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$
Typical conditions:

- Conversion efficiency: 85–92%
- Current density: 50–200 mA cm^{-2}

M10 – Phosphoric Acid Activation
$5\ NaClO_2 + 2\ H_3PO_4 \rightarrow 4\ ClO_2 + Na_3PO_4 + Na_2HPO_4 + 2\ H_2O$
Typical conditions:

- Conversion efficiency: 90–95%

A3. Sodium Chlorite Proxy Modelling

Because sodium chlorite is not available as a dedicated dataset in the ecoinvent database, its production was approximated through a proxy inventory derived from industrial production chemistry.

A3.1 Industrial Production Pathway

Step 1 – absorption of chlorine dioxide:

$2\ ClO_2 + 2\ NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$

Step 2 – chlorate reduction:

$NaClO_3 + H_2O_2 \rightarrow NaClO_2 + O_2 + H_2O$

A3.2 Proxy Mass Balance

Table A2 Proxy inventory inputs for sodium chlorite production.

Input	Amount per kg $NaClO_2$
Sodium chlorate	1.18 kg
Hydrogen peroxide	0.15 kg
Sodium hydroxide	0.35 kg
Electricity	0.80 kWh
Process water	2.5 kg

A3.3 Energy Balance

Table A3 Estimated energy requirements.

Process stage	Energy (kWh/kg $NaClO_2$)
ClO_2 generation	0.35
Absorption and reaction	0.15
Crystallization	0.20
Drying	0.10
Total	0.80

A3.4 Proxy Bias Assessment

The proxy approach may underestimate environmental impacts due to simplified modelling assumptions, including omission of mother liquor recycling, simplified crystallization modelling, and the use of average electricity mixes. Overall bias is estimated between −5% and −15%, resulting in a conservative estimate for chlorite-based methods.

A4. Foreground Life Cycle Inventory

Table A4 Foreground inventory for chlorate-based production routes.

Flow	Unit	M1	M2	M3	M4	M5
Sodium chlorate	kg	1.58	1.62	1.65	1.68	1.60
Methanol	kg	0.08	–	–	–	–
Hydrogen peroxide	kg	–	0.25	–	–	–
Hydrochloric acid	kg	–	–	0.85	–	–
Sulfur dioxide	kg	–	–	–	0.52	–
Sulfuric acid	kg	1.45	1.42	–	0.75	0.95
Electricity	kWh	0.35	0.40	0.30	0.45	0.38

Table A5 Foreground inventory for chlorite-based production routes.

Flow	Unit	M6	M7	M8	M9	M10
Sodium chlorite	kg	1.42	1.45	1.38	1.52	1.48
Hydrochloric acid	kg	0.65	–	–	–	–

Sulfuric acid	kg	–	0.58	–	–	–
Chlorine	kg	–	–	0.42	–	–
Phosphoric acid	kg	–	–	–	–	0.72
Electricity	kWh	0.25	0.28	0.22	2.85	0.30

A5. Sensitivity Analysis

Table A6 Sensitivity of Global Warming Potential to sodium chlorite proxy assumption.

Method	Baseline	−30%	−20%	−10%	+10%	+20%	+30%
M6	4.15	3.43	3.67	3.91	4.39	4.63	4.87
M7	4.08	3.38	3.61	3.85	4.31	4.54	4.78
M8	3.92	3.28	3.49	3.71	4.13	4.35	4.56
M9	3.86	3.25	3.45	3.66	4.06	4.26	4.47
M10	4.25	3.52	3.76	4.01	4.49	4.73	4.98

Ranking stability: M9 < M8 under baseline and +10% scenarios.

Equivalence occurs near +15%, and M8 becomes marginally preferable beyond +20%.

Table A7 Electricity carbon intensity thresholds for electrochemical production.

Comparison	Breakeven (kg CO_2/kWh)	95% CI
M9 vs M8	0.35	0.31–0.39
M9 vs M7	0.28	0.24–0.32
M9 vs M1	0.52	0.46–0.58
M9 vs M3	0.65	0.58–0.72

A6. Co-Product Allocation Scenarios

Table A8 System expansion credits applied.

Method	Co-product	Credit (kg CO_2-eq/kg ClO_2)
M1	Na_2SO_4	−0.15
M2	Na_2SO_4 + O_2	−0.83
M3	NaCl + Cl_2	−0.42
M8	NaCl	−0.08
M9	NaOH + H_2	−0.44