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Environmental performance of industrial chlorine dioxide production methods: A life cycle assessment

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ABSTRACT

Chlorine dioxide (ClO_2) has emerged as a widely used disinfectant in water treatment due to its broad-spectrum antimicrobial efficacy and reduced formation of halogenated disinfection by-products compared with conventional chlorination. Despite its increasing adoption, the environmental sustainability of different ClO_2 production routes remains insufficiently quantified. Most previous life cycle assessment (LCA) studies treat chlorine dioxide generation as a single aggregated process, without distinguishing among alternative synthesis pathways. This study bridged this gap through a comparative LCA of ten industrial ClO_2 production methods. An attributional LCA framework was applied using inventory data from the ecoinvent v3.8 database. Environmental impacts were evaluated across six categories—Global Warming Potential, freshwater ecotoxicity, human toxicity, water consumption, acidification, and eutrophication—using the EF 3.0, TRACI 2.1, and USEtox impact assessment methods. The functional unit was defined as 1 kg of ClO_2 produced under the cradle-to-gate system boundaries. Sensitivity analyses were conducted to address sodium chlorite proxy assumptions, electricity grid carbon intensity, and co-product allocation scenarios. Results indicate substantial variation in environmental performance across production routes. Global Warming Potential ranged from 3.86 to 5.20 kg CO_2-eq per kg ClO_2, representing a 35% difference between the lowest and highest impact methods. Electrochemical production and the Cl_2 + $NaClO_2$ route exhibited the lowest overall climate impacts, whereas hydrochloric-acid-based methods showed higher toxicity indicators. Contribution analysis revealed that precursor production dominates environmental burdens, accounting for 85–97% of total GWP. Sensitivity analysis identified a critical electricity carbon-intensity threshold of approximately 0.35 kg CO_2 kWh^{-1}, below which electrochemical production becomes environmentally advantageous. These findings demonstrate that environmental performance varies significantly across synthesis routes and that electrochemical chlorine dioxide production represents a conditionally sustainable option depending on regional energy infrastructure. The results provide quantitative benchmarks to support technology selection by water utilities and regulators.

Keywords: life cycle assessment, chlorine dioxide, water treatment, disinfection, environmental impact, sustainability.

INTRODUCTION

Waterborne pathogens remain a significant global health burden, causing approximately 485,000 diarrhoeal deaths annually and necessitating effective chemical disinfection for public health protection (World Health Organization, 2023; Gagnon et al., 2005). Chlorination has served as the primary disinfection strategy for over a century; however, the reaction of chlorine with natural organic matter generates potentially carcinogenic disinfection by-products (DBPs), including trihalomethanes and haloacetic acids (Richardson et al., 2007; Li and Mitch, 2018). This toxicological concern has prompted extensive research into alternative disinfectants capable of achieving microbial inactivation while minimizing harmful by-product formation (Hua

and Reckhow, 2007; von Gunten, 2003). ClO_2 has emerged as a versatile disinfectant, finding application in drinking water treatment, pulp and paper bleaching, food sanitation, and medical sterilization (Gordon, 2001; Casini et al., 2014). As a dissolved gas with water solubility approximately five times greater than molecular chlorine (~8 g/L at 25 °C), ClO_2 acts as a selective oxidant through single-electron transfer, rather than electrophilic halogenation (Ogata, 2007; Noszticzius et al., 2013). This mechanistic distinction enables preferential oxidation of electron-rich microbial proteins, achieving rapid inactivation kinetics while avoiding the chlorine substitution reactions responsible for organohalide formation (Ison et al., 2006; Stewart et al., 2008). The operational advantages of chlorine dioxide are well documented in scientific literature. ClO_2 maintains consistent biocidal activity across a broad pH range (4–10), unlike hypochlorous acid, the efficacy of which diminishes substantially above pH 7.5 (Taylor et al., 2000; Gordon and Rosenblatt, 2005). In the waters containing ammonia and organic nitrogen, ClO_2 does not form chloramines, avoiding the taste, odor, and reduced disinfection capacity associated with combined chlorine residuals (van Wijk et al., 1998). Superior biofilm penetration has been demonstrated compared to free chlorine, attributable to its uncharged molecular structure that facilitates diffusion through extracellular polymeric matrices (Vaid et al., 2010; Simpson, 1995). Potent virucidal activity has been reported, with 4-log reductions achieved at concentrations below 1 mg/L for enteric viruses (Xue et al., 2013; Totaro et al., 2021). The primary driver for ClO_2 adoption in drinking water applications is the substantial reduction in organic DBP formation. Comparative studies have demonstrated 70–90% lower trihalomethane and haloacetic acid concentrations when ClO_2 is employed as the primary disinfectant (Chang et al., 2000; Werner et al., 2016). However, ClO_2 generates inorganic by-products, primarily chlorite (ClO_2^-) through reduction and chlorate (ClO_3^-) through disproportionation reactions (Sorlini et al., 2014; Gómez-Lavín and Irabien, 2019). Both species pose toxicological concerns: chlorite affects erythrocyte membrane integrity and induces oxidative hemolysis, while chlorate inhibits thyroidal iodine uptake with potential developmental implications (U.S. Environmental Protection Agency, 2000; Bercz et al., 1982). Regulatory limits reflect these risks: the World Health Organization recommends 0.7 mg/L for chlorite, the U.S. Environmental Protection Agency mandates a Maximum Contaminant Level of 1.0 mg/L, and the European Union Drinking Water Directive imposes 0.25 mg/L for the sum of chlorite and chlorate (World Health Organization, 2005; European Union, 2020). The instability of chlorine dioxide precludes storage and transport, necessitating on-site generation through chemical or electrochemical synthesis (Knapp and Battisti, 2001). Industrial production proceeds via two principal precursor routes. The chlorate-based methods employ reducing agents including methanol, sulfur dioxide, hydrogen peroxide, or hydrochloric acid under acidic conditions; the methanol-based R8 process achieves conversion efficiencies exceeding 95% and dominates large-scale pulp bleaching applications (Burke et al., 1993; Ni and Wang, 1997). Chlorite-based methods, generally preferred for drinking water treatment due to simpler equipment requirements and smaller production scales, include acid activation, molecular chlorine reaction, and electrochemical oxidation (Monteiro et al., 2021; Pillai et al., 2009). Each synthesis pathway entails distinct precursor requirements, energy inputs, and by-product profiles that influence both operational costs and environmental footprints. Life cycle assessment (LCA) provides a standardized framework for quantifying environmental impacts across the full life cycle of products and processes, as codified in ISO 14040 and ISO 14044 (ISO, 2006a, 2006b). Within water treatment, LCA methodologies have been applied to compare disinfection processes (Corominas et al., 2013), evaluate DBP reduction strategies (Mo et al., 2018), and assess chlorine versus ozone versus ultraviolet treatment alternatives (Jachimowski and Nitkiewicz, 2019; Busse et al., 2022). However, systematic LCA of chlorine dioxide production methods remains notably absent from the scientific literature. Existing studies either omit ClO_2 entirely or treat production as an aggregated black box without distinguishing among synthesis routes (Tak and Kumar, 2017; Lindmark et al., 2022). This knowledge gap has practical implications for technology selection. Water utilities and regulators currently lack quantitative environmental data to make informed decisions among production alternatives, defaulting instead to economic and operational considerations. As sustainability criteria increasingly influence infrastructure investment and regulatory frameworks, method-specific environmental

characterization becomes essential for evidence-based decision-making. The present study addresses this gap through a comprehensive comparative LCA of ten industrial ClO_2 production methods. The objectives are: (i) to quantify environmental impacts across climate change, ecotoxicity, human toxicity, water consumption, acidification, and eutrophication categories; (ii) to identify environmental hotspots through contribution analysis; (iii) to conduct sensitivity analyses addressing key methodological uncertainties; and (iv) to provide technology selection guidance based on electricity grid carbon intensity.

MATERIALS AND METHODS

The study followed ISO 14040:2006 and ISO 14044:2006 requirements (ISO, 2006a, 2006b), employing an attributional LCA framework. Inventory modeling adhered to attributional principles, utilizing average rather than marginal data and applying the cut-off allocation approach implemented in the ecoinvent system model (Wernet et al., 2016). The interpretation phase incorporated decision-support elements, including threshold analysis and technology selection guidelines, aligning with the ILCD Handbook Situation B framework for meso-level decision support (European Commission–JRC, 2010). The functional unit was defined as 1 kg of ClO_2 produced at an industrial scale, enabling direct comparison across synthesis routes with varying precursor requirements and reaction stoichiometries. System boundaries followed a cradle-to-gate approach encompassing: (a) extraction and processing of raw materials; (b) production of chemical precursors; (c) energy generation for electricity supply; and (d) ClO_2 synthesis operations. Excluded from the analysis were: downstream distribution and application of ClO_2, treatment and disposal of process residues (contributing <2% of total impacts based on preliminary screening), capital equipment manufacturing, and facility construction (see Appendix A1 for screening details).

Production methods evaluated

Ten ClO_2 production routes were selected for analysis based on industrial relevance and availability of process data (Knapp and Battisti, 2001; Burke et al., 1993; Ni and Wang, 1997; Monteiro et al., 2021; Pillai et al., 2009). Five methods employ sodium chlorate as precursor: methanol reduction (R8 process), sulfur dioxide reduction (Mathieson process), hydrogen peroxide reduction, hydrochloric acid reduction, and the sodium chloride co-feed process (R2). Five methods employ sodium chlorite: hydrochloric acid activation, molecular chlorine activation, electrochemical oxidation, CO_2 activation, and phosphoric acid activation. Table 1 summarizes the principal characteristics and reaction stoichiometry of each method. Detailed process descriptions and reaction conditions are provided in Appendix A2.

Life cycle inventory

Life cycle inventory (LCI) data were sourced from the ecoinvent v3.8 database (November 2024 release), implementing the cut-off system model (Wernet et al., 2016). European regional data (RER) were prioritized where available, while global averages (GLO) were employed for chemicals without regional differentiation. Stoichiometric inputs were calculated from balanced

Table 1. Chlorine dioxide production methods evaluated in this study

Method	Precursor	Reaction	Efficiency (%)
R8 (Methanol)	$NaClO_3$	$NaClO_3 + CH_3OH + H_2SO_4 \rightarrow ClO_2 + CO_2 + Na_2SO_4$	>95
Mathieson (SO_2)	$NaClO_3$	$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4$	90–95
H_2O_2 reduction	$NaClO_3$	$2NaClO_3 + H_2O_2 + H_2SO_4 \rightarrow 2ClO_2 + O_2 + Na_2SO_4$	85–92
HCl + $NaClO_3$	$NaClO_3$	$5\ NaClO_3 + 4\ HCl \rightarrow 4\ ClO_2 + Cl_2 + 5\ NaCl + 2\ H_2O$	80–85
R2 (NaCl co-feed)	$NaClO_3$	$NaClO_3 + NaCl + H_2SO_4 \rightarrow ClO_2 + ½Cl_2 + Na_2SO_4$	90–95
HCl + $NaClO_2$	$NaClO_2$	$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$	>95
Cl_2 + $NaClO_2$	$NaClO_2$	$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$	>95
Electrochemical	$NaClO_2$	$NaClO_2 \rightarrow ClO_2 + e^-$ (anodic oxidation)	85–95
CO_2 + $NaClO_2$	$NaClO_2$	$5NaClO_2 + 4CO_2 + 2H_2O \rightarrow 4ClO_2 + 4NaHCO_3 + NaCl$	85–90
H_3PO_4 + $NaClO_2$	$NaClO_2$	$5NaClO_2 + 4H_3PO_4 \rightarrow 4ClO_2 + 4NaH_2PO_4 + NaCl$	85–90

reaction equations, with conversion efficiencies derived from technical literature (Knapp and Battisti, 2001; Burke et al., 1993; Ni and Wang, 1997; Monteiro et al., 2021; Pillai et al., 2009). Table 2 presents the unit process data for key precursors as extracted from the ecoinvent database.

Sodium chlorite proxy modeling

A methodological limitation of this study is the representation of sodium chlorite in the life cycle inventory. The ecoinvent database does not include sodium chlorite as a discrete unit process, reflecting broader data availability challenges for specialty chemicals with limited production volumes and proprietary manufacturing processes. Industrial sodium chlorite production proceeds through controlled reduction of sodium chlorate via two principal synthetic routes (Qi et al., 2020; Deshwal and Lee, 2004). Route A employs hydrogen peroxide as reducing agent: $NaClO_3 + H_2O_2 \rightarrow NaClO_2 + ½O_2 + H_2O$. Route B utilizes sulfur dioxide in alkaline medium: $NaClO_3 + SO_2 + NaOH \rightarrow NaClO_2 + NaHSO_4$. Based on stoichiometric analysis and literature energy consumption data (Qi et al., 2020; Nouryon, 2021), the additional processing burden is estimated to add 8–25% to the baseline sodium chlorate inventory, with the range reflecting route selection and process efficiency. The mass and energy balances supporting this estimate are detailed in Appendix A3. The lower bound corresponds to hydrogen peroxide reduction at optimal conversion efficiency, whereas the upper bound reflects sulfur dioxide reduction with additional purification requirements. Given this uncertainty, sodium chlorate inventory data were employed as baseline proxy. To propagate this limitation explicitly, sensitivity analysis was conducted applying multiplicative adjustments of +10%, +20%, and +30% to all sodium chlorite-dependent inventory flows. It should be emphasized that this limitation is epistemic, rather than merely parametric: the proxy approach cannot fully capture process-specific emissions, energy integration, or waste treatment configurations that may differ substantially between chlorate and chlorite manufacturing. Consequently, chlorite-based results should be regarded as indicative estimates suitable for comparative screening, pending primary data collection from chlorite producers.

Impact assessment methods

Three complementary life cycle impact assessment (LCIA) methods were applied: (1) EF 3.0 EN15804, the European Commission Environmental Footprint method (Fazio et al., 2018); (2) TRACI 2.1, the U.S. EPA Tool for Reduction and Assessment of Chemicals (Bare, 2011); and (3) USEtox 2.1, the UNEP/SETAC consensus model for toxicity characterization (Rosenbaum et al., 2008). The use of multiple LCIA methods was intended to improve the robustness and enable cross-method comparison of environmental impacts. Six impact categories were evaluated: Global Warming Potential (GWP100, kg CO_2-eq), Freshwater Ecotoxicity (CTUe), Human Toxicity—carcinogenic and non-carcinogenic (CTUh), Water Consumption (m^3 world-eq following the AWARE methodology; Boulay et al., 2018), Acidification Potential (mol H^+-eq), and Eutrophication Potential (kg P-eq). Data quality was evaluated using a pedigree matrix approach (Weidema and Wesnæs, 1996), scoring each inventory component on a 1 (excellent) to 5 (poor) scale for reliability, completeness,

Table 2. Life cycle inventory data for precursor chemicals (per kg, ecoinvent v3.8)

Chemical	GWP (kg CO_2-eq)	Water (m^3)	Electricity (kWh)	Acidification (mol H^+-eq)	Region
Sodium chlorate	2.18	8.42	2.41	0.0156	RER
Sodium chlorite*	2.18–2.73	8.42–10.95	2.41–3.13	0.0156–0.020	RER
Chlorine (Cl_2)	1.14	3.21	0.89	0.0089	RER
Hydrochloric acid	0.88	2.15	0.42	0.0234	RER
Sulfuric acid	0.12	0.85	0.18	0.0312	RER
Hydrogen peroxide	1.23	4.56	1.12	0.0078	RER
Methanol	0.74	1.89	0.35	0.0045	GLO
Phosphoric acid	1.45	3.78	0.67	0.0198	GLO

Note: * Estimated range based on proxy modeling (see Appendix A3).

temporal correlation, geographical correlation, and technological correlation dimensions. The ecoinvent-sourced data received scores of 1–2, whereas the literature-derived values received scores of 2–3. The sodium chlorite proxy assumption received a score of 4–5, representing the primary uncertainty source addressed through sensitivity analysis.

RESULTS

Table 3 presents the complete LCIA results for all ten ClO_2 production methods evaluated in this study. The ratios between the highest and lowest impacts ranged from 1.35 (global warming potential, GWP) to 6.58 (human toxicity, non-carcinogenic). GWP values ranged from 3.86 kg CO_2-eq kg^{-1} ClO_2 for the electrochemical method to 5.20 kg CO_2-eq kg^{-1} ClO_2 for the HCl + $NaClO_3$ process, representing a 35% difference between the lowest and highest impact routes. The sodium chlorate-based methods showed GWP values between 4.28 and 5.20 kg CO_2-eq kg^{-1} ClO_2, compared with 3.86–4.95 kg CO_2-eq kg^{-1} ClO_2 for chlorite-based alternatives.

Human toxicity (non-carcinogenic) exhibited the greatest inter-method variation. The HCl-based processes showed impacts of 3.72×10^{-7} CTUh (HCl + $NaClO_3$) and 2.20×10^{-7} CTUh (HCl + $NaClO_2$), compared with 6.32×10^{-8} CTUh for the electrochemical method.

Water consumption ranged from 7.89 m^3 kg^{-1} ClO_2 for the Cl_2 + $NaClO_2$ route to 17.17 m^3 kg^{-1} ClO_2 for the electrochemical method. Despite favorable performance in several other impact categories, the electrochemical route exhibited the highest water consumption.

Freshwater ecotoxicity ranged from 9.6 CTUe (electrochemical) to 18.9 CTUe (HCl + $NaClO_3$), with chlorite-based methods generally showing lower values (9.6–16.7 CTUe) compared with chlorate-based alternatives (12.4–18.9 CTUe). The acidification potential followed a similar pattern, ranging from 0.022 mol H^+-eq (electrochemical) to 0.056 mol H^+-eq (HCl + $NaClO_3$). The eutrophication potential showed the smallest relative variation among impact categories, ranging from 0.0008 kg P-eq (electrochemical) to 0.0019 kg P-eq (HCl + $NaClO_3$).

Contribution analysis revealed that precursor production dominates environmental impacts across all methods and impact categories. For global warming potential (GWP), sodium chlorate or sodium chlorite production contributed between 85% and 97% of total impacts. Direct synthesis operations (mixing, reaction, and gas handling) accounted for only 2–8% of total impacts, with the remaining contributions attributable to auxiliary chemicals and process utilities.

For the chlorate-based production routes, the sodium chlorate manufacture accounted for 78–85% of total GWP, while sulfuric acid production contributed 8–12% and direct energy consumption represented 3–6%. For the chlorite-based methods employing the proxy inventory, sodium chlorite production contributed 82–91% of total GWP, with activation chemicals (HCl, Cl_2, H_3PO_4) contributing an additional 4–12%, depending on the specific synthesis route.

The electrochemical route exhibited a distinct contribution structure. Direct electricity consumption represented approximately 45% of total GWP under the baseline European grid carbon intensity (0.42 kg CO_2 kWh^{-1}), while precursor production accounted for the remaining 55%.

Table 3. Life cycle impact assessment results per kg ClO_2 produced

Method	GWP (kg CO_2-eq)	Ecotox. (CTUe)	Human tox. (CTUh)	Water (m^3)	Acid. (mol H^+)	Eutroph. (kg P)
R8 (Methanol)	4.28	12.4	8.91×10^{-8}	10.23	0.031	0.0012
Mathieson (SO_2)	4.52	14.8	1.02×10^{-7}	11.45	0.042	0.0015
H_2O_2 reduction	4.65	13.2	9.45×10^{-8}	12.34	0.028	0.0011
HCl + $NaClO_3$	5.20	18.9	3.72×10^{-7}	9.87	0.056	0.0019
R2 (NaCl)	4.45	15.6	1.15×10^{-7}	10.89	0.038	0.0014
HCl + $NaClO_2$	4.95	16.7	2.20×10^{-7}	9.12	0.048	0.0017
Cl_2 + $NaClO_2$	3.92	10.8	7.15×10^{-8}	7.89	0.024	0.0009
Electrochemical	3.86	9.6	6.32×10^{-8}	17.17	0.022	0.0008
CO_2 + $NaClO_2$	4.12	11.5	8.23×10^{-8}	9.45	0.026	0.0010
H_3PO_4 + $NaClO_2$	4.38	12.9	9.12×10^{-8}	10.12	0.033	0.0013

Table 4 presents the GWP results across the sensitivity range applied to the sodium chlorite inventory. Multiplicative adjustment factors of +10%, +20%, and +30% were applied to all $NaClO_2$-dependent inventory flows for chlorite-based production routes. Extended sensitivity results covering the full ±30% range are reported in Appendix A5.

Across all sensitivity scenarios tested, the ranking of chlorite-based production routes remained stable. The electrochemical method (M9) exhibited the lowest GWP under baseline conditions and at the +10% adjustment level. The Cl_2 + $NaClO_2$ route (M8) became equivalent at approximately +15% adjustment and marginally preferable beyond +20%. The crossover point between M9 and M8 occurred at approximately +17% inventory adjustment, corresponding to a $NaClO_2$ GWP of 3.85 kg CO_2-eq kg^{-1} compared with the baseline proxy value of 3.28 kg CO_2-eq kg^{-1}.

GWP for the electrochemical route was evaluated across electricity carbon intensities ranging from 0.01 kg CO_2 kWh^{-1} (fully renewable electricity) to 0.90 kg CO_2 kWh^{-1} (coal-intensive systems). Break-even thresholds for all method comparisons, including 95% confidence intervals, are reported in Appendix A5.

At an electricity carbon intensity of 0.35 kg CO_2 kWh^{-1}, the GWP of the electrochemical method equals that of the Cl_2 + $NaClO_2$ route (3.92 kg CO_2-eq kg^{-1} ClO_2). At 0.65 kg CO_2 kWh^{-1}, the electrochemical route reaches 5.3 kg CO_2-eq kg^{-1} ClO_2.

System expansion credits were applied to the methods generating valuable co-products, including Na_2SO_4 (0.42 kg CO_2-eq kg^{-1}), O_2 (0.89 kg CO_2-eq kg^{-1}), and Cl_2 (1.23 kg CO_2-eq kg^{-1}). Details of the allocation procedure are provided in Appendix A6. This relationship is illustrated in Figure 1, which shows the sensitivity of electrochemical chlorine dioxide production to the carbon intensity of the electricity grid, relative to conventional synthesis routes.

The electrochemical method retained the lowest GWP under all allocation scenarios tested. Environmental impacts were further interpreted using CT values (concentration × contact time) corresponding to 99% (2-log) pathogen inactivation at pH 6–7 and 20 °C (U.S. Environmental Protection Agency, 1991; Ruffell et al., 2000). For bacterial and viral inactivation, chlorine dioxide generally requires CT values approximately 10–20 times higher than molecular chlorine. In contrast, for chlorine-resistant protozoa, such as *Giardia* and *Cryptosporidium*, ClO_2 can achieve equivalent inactivation at CT values 4–90 times lower than chlorine.

It is important to clarify that the CT-normalized comparison presented here does not represent a change in the functional unit, which remains defined as 1 kg of ClO_2 produced throughout this study. Instead, CT normalization is used as a post-hoc interpretative tool to contextualize production-phase environmental impacts relative to disinfection efficacy during application. This approach allows exploration of functional trade-offs without modifying the underlying LCA model structure. A similar conceptual framework is often applied in energy system LCAs, where production impacts are related to service-delivery metrics, such as energy output or conversion efficiency.

DISCUSSION

The results demonstrated that the environmental performance of chlorine dioxide production depends strongly on the synthesis route, with differences that cannot be captured by treating ClO_2 generation as a single aggregated process. The observed 35% variation in GWP and up to 6.6-fold differences in human toxicity indicate that method-specific assessment is essential for meaningful environmental evaluation. This finding contrasts with the previous LCA studies that employed generic ClO_2 emission factors without

Table 4. GWP sensitivity to sodium chlorite proxy assumptions (kg CO_2-eq/kg ClO_2)

Method	Baseline	+10%	+20%	+30%
$HCl + NaClO_2$	4.95	5.15	5.35	5.55
$Cl_2 + NaClO_2$	3.92	4.12	4.32	4.52
Electrochemical	3.86	4.06	4.26	4.46
$CO_2 + NaClO_2$	4.12	4.32	4.52	4.72
$H_3PO_4 + NaClO_2$	4.38	4.58	4.78	4.98

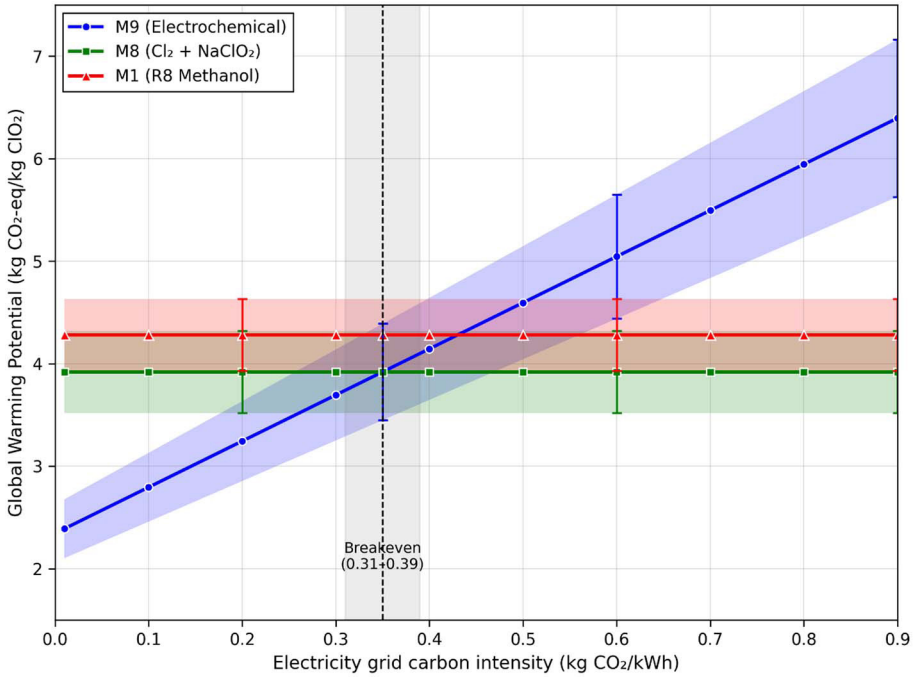

Figure 1. Global warming potential (GWP) of chlorine dioxide production as a function of electricity grid carbon intensity for the electrochemical method (M9) compared with Cl_2 + $NaClO_2$ (M8) and R8 methanol (M1). Shaded bands indicate uncertainty ranges, and the gray vertical band shows the breakeven threshold (0.31–0.39 kg CO_2 kWh^{-1})

differentiation among production routes (Tak and Kumar, 2017; Lindmark et al., 2022).

Chlorite-based routes generally exhibited lower climate impacts than chlorate-based processes. This difference is primarily attributable to the high electricity demand associated with sodium chlorate electrolysis. Industrial sodium chlorate production requires approximately 2.4 MWh per tonne (O'Brien et al., 2005), and this energy-intensive upstream process dominates the environmental footprint of chlorate-based ClO_2 synthesis. This result is consistent with broader literature on electrochemical commodity chemical production, where electricity consumption represents the primary environmental leverage point (Pillai et al., 2009).

The elevated human toxicity impacts observed for HCl-based processes reflect the USEtox characterization factors associated with chlorinated intermediate emissions and hydrochloric acid production (Rosenbaum et al., 2008). Although absolute toxicity values are subject to significant uncertainty, the order-of-magnitude differences between HCl-based and electrochemical methods provide robust directional guidance for technology selection in applications where human health impacts represent priority concerns.

A key contribution of this study is the explicit treatment of methodological uncertainty. The absence of sodium chlorite as a discrete process in the ecoinvent database represents a known limitation for specialty chemical LCAs (Wernet et al., 2016). However, sensitivity analysis demonstrated that inventory adjustments up to +25% do not alter relative rankings among production routes, and order-of-magnitude toxicity differences are preserved even at +30% adjustment. Similarly, alternative co-product allocation approaches using system expansion did not change the relative performance hierarchy. These findings indicate that comparative conclusions reflect intrinsic technological differences rather than modeling artifacts.

The electricity grid threshold analysis reveals the contextual nature of environmental performance. The electrochemical route exhibits the lowest impacts only under low-carbon electricity supply, with a critical threshold at approximately 0.35 kg CO_2 kWh^{-1}. Below this value—typical of electricity systems dominated by renewable or nuclear energy (e.g., Scandinavia, France, Switzerland, Quebec)—electrochemical production represents the environmentally preferable option. Above this threshold, particularly in coal-dominated systems, its climate impact rapidly exceeds

conventional alternatives. This behavior supports classification of electrochemical ClO_2 production as a conditionally low-carbon technology, whose environmental viability depends more on external energy-system characteristics than intrinsic process efficiency. This finding aligns with broader literature on electrified chemical processes (Monteiro et al., 2021).

The CT-normalized interpretation further contextualizes the production-phase results by considering disinfection efficacy against different pathogen classes. While chlorine maintains functional advantages for bacterial and viral targets, ClO_2 demonstrates superior efficacy against chlorine-resistant protozoa such as *Giardia* and *Cryptosporidium* (U.S. Environmental Protection Agency, 1991; Ruffell et al., 2000). In source waters where protozoan contamination represents the dominant risk, ClO_2 may therefore provide favorable functional environmental performance despite somewhat higher production-phase impacts. These results highlight that optimal technology selection requires integration of production-phase environmental impacts with application-specific disinfection performance.

The dominance of precursor production in overall impacts (85–97% of GWP) indicates that upstream decarbonization of sodium chlorate and chlorite supply chains represents the most effective leverage point for sustainability improvement. Incremental efficiency gains in synthesis operations are unlikely to offset the environmental influence of precursor production pathways.

From a decision-making perspective, the results suggest that no single production method can be universally recommended. Technology selection should account for regional electricity composition, water scarcity constraints, regulatory requirements regarding inorganic by-products, and the pathogen profiles relevant to specific water sources. Several limitations warrant acknowledgment. The sodium chlorite proxy assumption introduces systematic uncertainty affecting all chlorite-based methods; although sensitivity analysis confirms ranking stability, the underlying limitation is epistemic rather than purely quantitative. Toxicity indicators also carry greater uncertainty than climate metrics due to variability in characterization factors and simplified emission modeling. In addition, the present cradle-to-gate system boundaries exclude downstream disinfection by-product formation, which may influence overall environmental performance in real water treatment systems. Future research should therefore extend the assessment to cradle-to-use system boundaries incorporating regional water quality parameters and DBP formation dynamics.

CONCLUSIONS

This study provides the first systematic comparative life cycle assessment of industrial chlorine dioxide production methods. Environmental impacts vary substantially across the ten synthesis routes evaluated. Electrochemical and Cl_2 + NaClO_2 processes exhibit the lowest climate impacts under favorable energy conditions, whereas HCl-based processes show elevated toxicity indicators.

Precursor production dominates environmental footprints, contributing 85–97% of total GWP and identifying upstream supply-chain decarbonization as the most effective sustainability leverage point. Sensitivity analyses confirm that comparative rankings are robust to key methodological uncertainties, including sodium chlorite inventory assumptions and co-product allocation choices.

A critical electricity carbon-intensity threshold of approximately 0.35 kg CO_2 kWh^{-1} determines the environmental viability of electrochemical ClO_2 production. Below this threshold, the electrochemical route represents the lowest-impact option, whereas above it, conventional chemical routes may exhibit lower climate impacts. Electrochemical chlorine dioxide production can therefore be characterized as a conditionally sustainable technology whose environmental performance depends on regional energy infrastructure.

The result for chlorite-based routes (M6–M10) should be interpreted as screening-level estimates due to the use of proxy inventory data. Development of sodium chlorite-specific life-cycle inventories through primary data collection from manufacturers represents an important priority for future research.

Further work should also extend the assessment to cradle-to-use system boundaries, incorporating disinfection by-product formation during water treatment. Integration of regional energy mixes, water-scarcity indicators, and multi-criteria decision frameworks combining environmental, economic, and operational considerations would enhance the practical applicability of these results for water utilities and regulators.

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REFERENCES

1. World Health Organization. (2023). *Drinking-water: Key facts*. https://www.who.int/news-room/fact-sheets/detail/drinking-water
2. Gagnon, G. A., Rand, J. L., O'Leary, K. C., Rygel, A. C., Chauret, C., Andrews, R. C. (2005). Disinfectant efficacy of chlorite and chlorine dioxide in drinking water biofilms. *Water Research*, *39*(9), 1809–1817. https://doi.org/10.1016/j.watres.2005.02.004
3. Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., DeMarini, D. M. (2007). Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research/Reviews in Mutation Research*, *636*(1–3), 178–242. https://doi.org/10.1016/j.mrrev.2007.09.001
4. Li, X.-F., Mitch, W. A. (2018). Drinking water disinfection byproducts (DBPs) and human health effects: Multidisciplinary challenges and opportunities. *Environmental Science & Technology*, *52*(4), 1681–1689. https://doi.org/10.1021/acs.est.7b05440
5. Hua, G., Reckhow, D. A. (2007). Comparison of disinfection byproduct formation from chlorine and alternative disinfectants. *Water Research*, *41*(8), 1667–1678. https://doi.org/10.1016/j.watres.2007.01.032
6. von Gunten, U. (2003). Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Research*, *37*(7), 1469–1487. https://doi.org/10.1016/S0043-1354(02)00458-X
7. Gordon, G. (2001). Is all chlorine dioxide created equal? *Journal AWWA*, *93*(1), 163–174. https://doi.org/10.1002/j.1551-8833.2001.tb09186.x
8. Casini, B., Buzzigoli, A., Cristina, M. L., Spagnolo, A. M., Del Giudice, P., Brusaferro, S., Poscia, A., Moscato, U., Valentini, P., Baggiani, A., Privitera, G. (2014). Long-term effects of hospital water network disinfection on Legionella and other waterborne bacteria. *Infection Control & Hospital Epidemiology*, *35*(3), 293–299. https://doi.org/10.1086/675280
9. Ogata, N. (2007). Denaturation of protein by chlorine dioxide: Oxidative modification of tryptophan and tyrosine residues. *Biochemistry*, *46*(17), 4898–4911. https://doi.org/10.1021/bi061827u
10. Noszticzius, Z., Wittmann, M., Kály-Kullai, K., Beregvári, Z., Kiss, I., Rosivall, L., Szegedi, J. (2013). Chlorine dioxide is a size-selective antimicrobial agent. *PLOS ONE*, *8*(11), e79157. https://doi.org/10.1371/journal.pone.0079157
11. Ison, A., Odeh, I. N., Margerum, D. W. (2006). Kinetics and mechanisms of chlorine dioxide and chlorite oxidations of cysteine and glutathione. *Inorganic Chemistry*, *45*(22), 8768–8775. https://doi.org/10.1021/ic0609554
12. Stewart, D. J., Napolitano, M. J., Bakhmutova-Albert, E. V., Margerum, D. W. (2008). Kinetics and mechanisms of chlorine dioxide oxidation of tryptophan. *Inorganic Chemistry*, *47*(5), 1639–1647. https://doi.org/10.1021/ic701761p
13. Taylor, R. H., Falkinham, J. O., Norton, C. D., LeChevallier, M. W. (2000). Chlorine, chloramine, chlorine dioxide, and ozone susceptibility of *Mycobacterium avium*. *Applied and Environmental Microbiology*, *66*(4), 1702–1705. https://doi.org/10.1128/AEM.66.4.1702-1705.2000
14. Gordon, G., Rosenblatt, A. A. (2005). Chlorine dioxide: The current state of the art. *Ozone: Science & Engineering*, *27*(3), 203–207. https://doi.org/10.1080/01919510590945741
15. van Wijk, D. J., Kroon, S. G. M., Garttener-Arends, I. C. M. (1998). Toxicity of chlorate and chlorite to selected species of algae, bacteria, and fungi. *Ecotoxicology and Environmental Safety*, *40*(3), 206–211. https://doi.org/10.1006/eesa.1998.1685
16. Vaid, R., Linton, R. H., Morgan, M. T. (2010). Comparison of inactivation of *Listeria monocytogenes* within a biofilm matrix using chlorine dioxide gas, aqueous chlorine dioxide and sodium hypochlorite treatments. *Food Microbiology*, *27*(8), 979–984. https://doi.org/10.1016/j.fm.2010.05.024
17. Simpson, G. D. (1995). Biofilm: Removal and prevention with chlorine dioxide. *Proceedings of the Third International Symposium on Chlorine Dioxide*.
18. Xue, B., Jin, M., Yang, D., Guo, X., Chen, Z., Shen, Z., Wang, X., Qiu, Z., Wang, J., Li, J., Li, J. (2013). Effects of chlorine and chlorine dioxide on human rotavirus infectivity and genome stability. *Water Research*, *47*(10), 3329–3338. https://doi.org/10.1016/j.watres.2013.03.025
19. Totaro, M., Badalucco, F., Costa, A. L., Giorgi, S., Valentini, P., Baggiani, A. (2021). Effectiveness of disinfection with chlorine dioxide on respiratory transmitted, enteric, and bloodborne viruses: A narrative synthesis. *Pathogens*, *10*(8), 1017. https://doi.org/10.3390/pathogens10081017
20. Chang, C. Y., Hsieh, Y. H., Hsu, S. S., Hu, P. Y., Wang, K. H. (2000). The formation of disinfection

by-products in water treated with chlorine dioxide. *Journal of Hazardous Materials*, *79*(1–2), 89–102. https://doi.org/10.1016/S0304-3894(00)00184-9

21. Werner, D., Valdivia-Garcia, M., Weir, P., Haffey, M. (2016). Trihalomethanes formation in point of use surface water disinfection with chlorine or chlorine dioxide tablets. *Water and Environment Journal*, *30*(3–4), 271–277. https://doi.org/10.1111/wej.12209
22. Sorlini, S., Gialdini, F., Biasibetti, M., Collivignarelli, C. (2014). Influence of drinking water treatments on chlorine dioxide consumption and chlorite/chlorate formation. *Water Research*, *54*, 44–52. https://doi.org/10.1016/j.watres.2014.01.038
23. Gómez-Lavín, S., Irabien, A. (2019). Formation of chlorate and perchlorate during electrochemical production of chlorine dioxide using sodium chlorite. *Chemosphere*, *230*, 460–468. https://doi.org/10.1016/j.chemosphere.2019.05.089
24. U.S. Environmental Protection Agency. (2000). *Toxicological review of chlorine dioxide and chlorite* (EPA/635/R-00/007). https://cfpub.epa.gov/ncea/iris/iris_documents/documents/toxreviews/0496tr.pdf
25. Bercz, J. P., Jones, L., Garner, L., Murray, D., Ludwig, D. A., Boston, J. (1982). Subchronic toxicity of chlorine dioxide and related compounds in drinking water in the nonhuman primate. *Environmental Health Perspectives*, *46*, 47–55. https://doi.org/10.1289/ehp.824647
26. World Health Organization. (2005). *Chlorite and chlorate in drinking-water: Background document for development of WHO guidelines for drinking-water quality*. WHO Press.
27. European Union. (2020). Directive (EU) 2020/2184 of the European Parliament and of the Council on the quality of water intended for human consumption. *Official Journal of the European Union*, L 435, 1–62.
28. Knapp, J. E., Battisti, D. L. (2001). Chlorine dioxide. In S. S. Block (Ed.), *Disinfection, sterilization and preservation* (5th ed., pp. 215–228). Lippincott Williams & Wilkins.
29. Burke, M., Tenney, J., Indu, B., Mehrotra, A. K., Smith, J. P. (1993). Kinetics of hydrogen peroxide–chlorate reaction in the formation of chlorine dioxide. *Industrial & Engineering Chemistry Research*, *32*(7), 1449–1456. https://doi.org/10.1021/ie00019a018
30. Ni, Y., Wang, X. (1997). Mechanism and kinetics of chlorine dioxide reaction with hydrogen peroxide under acidic conditions. *The Canadian Journal of Chemical Engineering*, *75*(1), 31–36. https://doi.org/10.1002/cjce.5450750107
31. Monteiro, M. K. S., Monteiro, M. M. S., de Melo Henrique, A. M., da Silva, D. R., Martínez-Huitle, C. A., dos Santos, E. V. (2021). A review on the electrochemical production of chlorine dioxide from chlorates and hydrogen peroxide. *Current Opinion in Electrochemistry*, *27*, 100685. https://doi.org/10.1016/j.coelec.2020.100685
32. Pillai, K. C., Kwon, T. O., Park, B. B., Moon, I. S. (2009). Studies on process parameters for chlorine dioxide production using IrO2 anode in an un-divided electrochemical cell. *Journal of Hazardous Materials*, *164*(2–3), 812–819. https://doi.org/10.1016/j.jhazmat.2008.08.090
33. International Organization for Standardization. (2006). *ISO 14040:2006 Environmental management—Life cycle assessment—Principles and framework*. ISO.
34. International Organization for Standardization. (2006). *ISO 14044:2006 Environmental management—Life cycle assessment—Requirements and guidelines*. ISO.
35. Corominas, L., Foley, J., Guest, J. S., Hospido, A., Larsen, H. F., Morera, S., Shaw, A. (2013). Life cycle assessment applied to wastewater treatment: State of the art. *Water Research*, *47*(15), 5480–5492. https://doi.org/10.1016/j.watres.2013.06.049
36. Mo, W., Cornejo, P. K., Malley, J. P., Lester, Y., Apul, D. S. (2018). Life cycle environmental and economic implications of small drinking water system upgrades to reduce disinfection byproducts. *Water Research*, *143*, 155–164. https://doi.org/10.1016/j.watres.2018.06.047
37. Jachimowski, A., Nitkiewicz, T. (2019). Comparative analysis of selected water disinfection technologies with the use of life cycle assessment. *Archives of Environmental Protection*, *45*(1), 3–10. https://doi.org/10.24425/aep.2019.128635
38. Busse, M. M., Hawes, J. K., Blatchley, E. R. (2022). Comparative life cycle assessment of water disinfection processes applicable in low-income settings. *Environmental Science & Technology*, *56*(23), 16336–16346. https://doi.org/10.1021/acs.est.2c02393
39. Tak, S., Kumar, A. (2017). Chlorination disinfection by-products and comparative cost analysis of chlorination and UV disinfection in sewage treatment plants: Indian scenario. *Environmental Science and Pollution Research*, *24*(30), 26269–26278. https://doi.org/10.1007/s11356-017-0568-z
40. Lindmark, M., Cherukumilli, K., Crider, Y. S., Marcenac, P., Lozier, M., Raj, S., Pickering, A. J. (2022). Passive in-line chlorination for drinking water disinfection: A critical review. *Environmental Science & Technology*, *56*(13), 9164–9181. https://doi.org/10.1021/acs.est.1c08580
41. Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., Weidema, B. (2016). The ecoinvent database version 3 (part I): Overview and methodology. *The International Journal of Life Cycle Assessment*, *21*(9), 1218–1230. https://doi.org/10.1007/s11367-016-1087-8

42. European Commission–Joint Research Centre. (2010). *ILCD handbook: General guide for life cycle assessment—Detailed guidance* (EUR 24708 EN). Publications Office of the European Union. https://doi.org/10.2788/38479
43. Qi, M., Yi, T., Mo, Q., Fan, Y., Ji, H. (2020). Preparation of high-purity chlorine dioxide by combined reduction. *Chemical Engineering & Technology*, *43*(9), 1850–1858. https://doi.org/10.1002/ceat.202000121
44. Deshwal, B. R., Lee, H. K. (2004). Kinetics and mechanism of chloride-based chlorine dioxide generation process from acidic sodium chlorate. *Journal of Hazardous Materials*, *108*(3), 173–182. https://doi.org/10.1016/j.jhazmat.2003.12.006
45. Nouryon. (2021). *Chlorine dioxide technologies: Best available techniques for ClO_2 production* [Technical report].
46. Fazio, R., Castellani, A., Sala, S., Schau, E., Zampori, L., Diaconu, E. (2018). *Supporting information to the characterisation factors of EF LCIA methods* (EUR 28888 EN). Publications Office of the European Union.
47. Bare, J. (2011). TRACI 2.0: The tool for the reduction and assessment of chemical and other environmental impacts 2.0. *Clean Technologies and Environmental Policy*, *13*(5), 687–696. https://doi.org/10.1007/s10098-010-0338-9
48. Rosenbaum, R. K., Bachmann, T. M., Gold, L. S., Huijbregts, M. A. J., Jolliet, O., Juraske, R., Koehler, A., Larsen, H. F., MacLeod, M., Margni, M., McKone, T. E., Payet, J., Schuhmacher, M., van de Meent, D., Hauschild, M. Z. (2008). USEtox—The UNEP-SETAC toxicity model: Recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *The International Journal of Life Cycle Assessment*, *13*(7), 532–546. https://doi.org/10.1007/s11367-008-0038-4
49. Boulay, A.-M., Bare, J., Benini, L., Berger, M., Lathuillière, M. J., Manzardo, A., Margni, M., Motoshita, M., Núñez, M., Pastor, A. V., Ridoutt, B., Oki, T., Worbe, S., Pfister, S. (2018). The WULCA consensus characterization model for water scarcity footprints: Assessing impacts of water consumption based on available water remaining (AWARE). *The International Journal of Life Cycle Assessment*, *23*(2), 368–378. https://doi.org/10.1007/s11367-017-1333-8
50. Weidema, B. P., Wesnæs, M. S. (1996). Data quality management for life cycle inventories—An example of using data quality indicators. *Journal of Cleaner Production*, *4*(3–4), 167–174. https://doi.org/10.1016/S0959-6526(96)00043-1
51. U.S. Environmental Protection Agency. (1991). *Guidance manual for compliance with the filtration and disinfection requirements for public water systems using surface water sources*. EPA.
52. Ruffell, K. M., Rennecker, J. L., Mariñas, B. J. (2000). Inactivation of *Cryptosporidium parvum* oocysts with chlorine dioxide. *Water Research*, *34*(3), 868–876. https://doi.org/10.1016/S0043-1354(99)00230-X
53. O'Brien, T. F., Bommaraju, T. V., Hine, F. (2005). *Handbook of chlor-alkali technology*. Springer. https://doi.org/10.1007/b113786
54. Schiffer, Z. J., Manthiram, K. (2017). Electrification and decarbonization of the chemical industry. *Joule*, *1*(1), 10–14. https://doi.org/10.1016/j.joule.2017.07.008
55. De Luna, P., Hahn, C., Higgins, D., Jaffer, S. A., Jaramillo, T. F., Sargent, E. H. (2019). What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science*, *364*(6438), eaav3506. https://doi.org/10.1126/science.aav3506