**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY**
**WASHINGTON, D.C. 20460**

**OFFICE OF PREVENTION,**
**PESTICIDES AND**
**TOXIC SUBSTANCES**

**Chemical**: Sodium Chlorate
**PC Code:** 073301
**DP Barcode:** D303884

## MEMORANDUM

**DATE:** January 31, 2005

**SUBJECT:** Sodium Chlorate (CAS Reg. No. 7775-09-9)
Reregistration (Terrestrial Food/Feed and Non-food/Non-feed Uses)
Reregistration Case 4049
Ecological Risk Assessment

**FROM:** Brian Anderson, Biologist
Silvia Termes, Chemist
Environmental Risk Branch 3
and
James Hetrick, Chemist
Environmental Risk Branch 1
Environmental Fate and Effects Division (7507C)

**THRU:** Dan Rieder, Branch Chief
Environmental Risk Branch 3
Environmental Fate and Effects Division (7507C)

**TO:** Rosanna Louie
Special Review and Reregistration Division (SRRD) (7505C)

Attached please find the Environmental Fate and Effects Division's (EFED) environmental risk assessment for reregistration of sodium chlorate as an herbicide (defoliant/desiccant) on agricultural commodities and in non-agricultural areas. Sodium chlorate (chlorate) is a non-selective, contact herbicide that can kill all green parts of plants. It penetrates the cuticle causing cell death, probably by altering the metabolic processes. Chlorate has been used in the United States as a defoliant/desiccant at least since the early 1940s. It is used primarily in the southern United States on cotton, but is also used on a number of other agricultural commodities at application rates that range from approximately 4 to 12.5 lbs a.i./Acre. Chlorate is also used for a number of non-agricultural applications at much higher rates (up to 620 lbs a.i./Acre). The end-use products containing sodium chlorate as the active ingredient include soluble concentrates, granular products, and pellets. Sodium chlorate is also an inert ingredient in some pesticide formulations, where it is used because its antimicrobial effects retard biodegradation of the pesticide, resulting in prolonged pesticidal activity.

This risk assessment covers the technical chlorate active ingredient (a.i.), 13 end-use products for non-agricultural uses, and 20 end-use products for agricultural uses. Key findings of this risk assessment are as follows:

- **Fish:** There appears to be no acute risk to fish at levels of concern to the Agency. However, some data suggest that brown trout could be substantially more sensitive than other fish species tested to chlorate's toxicity. It is uncertain if these data are reliable; therefore, additional testing in brown trout would reduce uncertainty in this assessment. No chronic toxicity studies are available to allow for chronic risk to fish to be quantified.

- **Aquatic Invertebrates:** Potential risk to aquatic invertebrates cannot be precluded because a chlorate reduction product, chlorite, is approximately 6000-fold more toxic than chlorate to aquatic invertebrates. There are insufficient data available to characterize potential exposure to and risk from chlorite as a result of chlorate use. Therefore, this potential risk could not be quantified. No chronic toxicity data are available in aquatic invertebrates; therefore, chronic risk to fish or invertebrates could not be assessed.

- **Aquatic Plants:** Data in *Selenastrum capricornutum* (a freshwater green alga) were submitted. Although these data suggest that there is not risk to aquatic plants at levels of concern to the Agency, data on all required aquatic plant species have not been submitted. Therefore, additional data are needed to allow for a full characterization of potential risk to aquatic plants.

- **Birds, acute exposures:** No mortality occurred in the submitted avian subacute toxicity studies at the highest concentration tested (5620 mg/kg-diet). Therefore, risk from chlorate's agricultural uses is presumed lower than the Agency's concern level. However, acute risk to birds cannot be precluded for chlorate's *non-agricultural* uses because environmental concentrations from these uses were estimated to be significantly higher than 5620 mg/kg-diet on some food items.

- **Mammals, acute exposures.** Risk cannot be precluded from chlorate's agricultural or non-agricultural uses. Even though chlorate is of low toxicity to mammals (10% mortality occurred at 5000 mg/kg-bw), some of chlorate's non-agricultural uses could result in ingestion of chlorate at levels that are significantly higher than 5000 mg/kg-bw for some food items. Also, levels of concern could be exceeded for chlorate's agricultural uses if the LD50 is in close proximity to 5000 mg/kg-bw.

- **Birds and mammals, chronic exposures.** No reproduction toxicity data have been submitted to allow for calculation of risk quotients. Chronic risk to birds and mammals are presumably higher than the Agency's level of concern because chronic exposure is possible and repeated-dose toxicity studies in mammals suggest that chlorate's effects are cumulative (toxicity increases as exposure duration increases). These studies suggest that repeated exposures may adversely affect reproduction, survival, or growth at concentrations that are lower than the EECs presented in this assessment.

- **Terrestrial plants:** Adequate data are not available to allow for derivation of risk quotients. However, risk to plants is presumably higher than the Agency's concern level based on chlorate's non-selective mode of action and high labeled application rates.

### Data Gaps and Key Uncertainties

The following major data gaps were noted in this assessment:

***Field dissipation study (164-1)***. Terrestrial field dissipation data are not available and this study was never waived. There are some reports that sodium chlorate can be persistent in the field (6 months to 5 years, depending on rate applied, soil type, fertility, organic matter, moisture, and weather conditions). However, the cited information do not provide any data to support this claim. ("Inorganic Herbicides", Chapter 21 in Weed Science: Principles and Practices , edited by G. Klingman and F. Ashton, Published by Wiley, 1982). Also, several labels report that sodium chlorate is effective for the control of weeds for up to a year, which indicates that chlorate may persist for up to a year. Therefore, the range of persistence of sodium chlorate in the field remains a major uncertainty in the environmental fate behavior of this chemical. Use of sodium chlorate in the field requires that it be applied in conjunction of a fire retardant to minimize fire incidents. It is unclear how the fire retardant could influence the persistence in the field. Therefore, the EFED recommends that field persistence data from actual use sites be submitted to the Agency upon agreement of a protocol to conduct the studies.

***Reproduction toxicity study in bobwhite quail and mallard ducks (71-4).*** Toxicity data were not submitted that allow for calculation of risk quotients. Mammalian toxicity data suggest that chlorate is more toxic after repeated exposures.

***2-Generation reproduction toxicity study in laboratory rats (83-4).*** Toxicity data were not submitted to allow for calculation of risk quotients. Subchronic studies suggest that repeated exposures may adversely affect reproduction, survival, or growth at concentrations that are lower than chlorate's agricultural and non-agricultural estimated environmental concentrations (EECs) calculated in this assessment.

***Chronic toxicity studies in fish and aquatic invertebrates (72-4).*** No chronic studies have been submitted to the Agency. Chlorate is practically non-toxic to fish and aquatic invertebrates after acute exposures.

***Acute toxicity studies in non-guideline fish and aquatic plant species.*** Open literature studies suggest that chlorate may be particularly toxic to brown trout and to brown algae. However, sufficient detail is not available in the study reports identified in the open literature to allow for an adequate assessment of study quality. Therefore, submission of reliable studies in these species could be of considerable value to this assessment.

***Tier II terrestrial plant seedling emergence and vegetative vigor studies (123-1).*** Chlorate is a non-selective herbicide. Submitted Tier I studies suggest that chlorate is toxic to non-target plants at high application rates.

***Tier II aquatic plant toxicity studies (123-2)***. No studies in the following plant species have been submitted, which are required for herbicides: *Lemna gibba* (duckweed), *Skeletonema costatum* (a marine diatom), *Anabaena flos-aquae* (a blue-green bacterium), and a freshwater diatom.

**Additional key uncertainties include the following:**

<u>Fate and Exposure</u>

- Many of the labels are not clear regarding the maximum allowable annual applications (number of applications or total load). The Agency assumed a maximum of 2 annual applications (30-days apart) for cotton and 1 annual application for all other uses. Risk may be under-estimated if these assumptions do not accurately reflect chlorate's applications.

- Many of the non-agricultural uses will likely result in small contiguously treated areas, which would reduce the likelihood that an animal would consume 100% of its diet from chlorate treated areas. This uncertainty likely resulted in an over-estimation of risk.

- Chlorate is a strong oxidizer and may be reduced to other chemically related species under some environmental conditions. The extent and rate to which this occurs will depend on the redox chemical species (including organic matter) in the water or soil. Extensive spatial and temporal variability is expected for the reactions of chlorate in the environment. However, the currently available simulation models do not allow for a quantitative evaluation of the potential exposure levels of each the reduced products of chlorate (i.e., speciation and predominance) and how fast these chemical species may form. Therefore, there is a high degree of uncertainty in the exposure and risk assessment.

This is important because a reduction product of chlorate (chlorite) is expected to be more toxic to most aquatic and terrestrial species, particularly aquatic invertebrates.

- Sodium chlorate could be particularly attractive to salt-thirsty mammals. Therefore, chlorate body burdens could be substantially higher in those mammals resulting in increased risk.

### Toxicity

- Open literature toxicity data were located that suggest that some fish and algal species may be significantly more sensitive to chlorate toxicity than the surrogate species used in this assessment. Therefore, submission of confirmatory studies in non-guideline fish and algal species would reduce uncertainty in this assessment (see Section 3 for additional discussion).

- An LD50 of 1200 mg/kg-day was reported in the open literature for mammals. However, this study report has not been obtained and evaluated by the Agency. If these data are reliable, then risk may have been underestimated.

### Scope of Assessment

- Some formulated products that contain sodium chlorate also contain other active ingredients such as sodium metaborate, and all formulated products contain flame retardants. In some formulated products, sodium chlorate is present at concentrations that are lower than these other active ingredients. Potential effects that these other chemicals may have on chlorate's fate or toxicity is not considered in this assessment. Also, risk from direct effects from these other active ingredients is not within the scope of this risk assessment.

- The effects of prolonged, year-after-year use of sodium chlorate in the same field is not known, particularly in semiarid sites that require irrigation (e.g., Arizona, California), where there is a potential for salt build-up over time.

### Labels

EFED recommends that labels be revised for consistency. Many labels do not allow direct application to water (surface water; intertidal areas), use through irrigation systems, contaminating water by cleaning of equipment or disposal of rinsates, discharge into sewage systems without notifying the pertinent sewage treatment plant authority (PTOW), and carry NPDES license restriction. However, not all of the current labels contain all of the language necessary to protect water resources. This is particularly notorious for the Non-food/non-feed products. Many of the listed uses in this pattern appear to contradict the limitations specified in most of the Food/Feed labels (e.g., drainage systems; sewage systems). Moreover, some of the Non-food/Non-feed labels carry restrictions/warnings that are not included in those for Food/Feed uses, such as ground water restrictions, warnings that the chemical is toxic to aquatic invertebrates, fish, and wildlife, or restricting applications on sandy soils.

# Environmental Fate and Ecological Risk Assessment for the Reregistration of Sodium Chlorate as an Active Ingredient in Terrestrial Food/Feed and Non-food/Non-feed Uses

**Reregistration Case Number 4049**
**PC Code 073301**
Chemical Abstracts Registry No. 7775-09-9

Brian Anderson, Biologist
Silvia C. Termes, Chemist
Ecological Risk Branch 3

James A. Hetrick, Senior Scientist
Ecological Risk Branch 1

Henry Nelson, Chemist
Exposure Assessment Division
Office of Science and Coordination Policy (OSCP/OPPTS/USEPA)

Environmental Fate and Effects Division

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## 1. Environmental Risk Conclusions

Tables 1-1 and 1-2 below summarize the major conclusions from chlorate’s agricultural and non-agricultural uses, respectively. Additional details are in Section 4 (Risk Characterization). Table 1-3 below identifies data gaps and characterizes potential value that additional testing may provide. See Appendix A for the status of all data requirements for chlorate.

**Table 1-1. Summary of Environmental Risk Conclusions for Aquatic and Terrestrial Organisms (Agricultural Uses)**

| Surrogate Species | Duration of Exposure | Summarized Characterization of Potential Risks |
|---|---|---|
| Potential risk to fish[a] | Acute | The submitted data suggest that risk is presumably lower than the Agency's level of concern for acute effects. |
| | Chronic | No chronic toxicity data are available; therefore, chronic risk to fish could not be assessed. |
| Potential Risk to Aquatic Invertebrates[a] | Acute | The Agency's levels of concern for acute effects were not exceeded. However, risk cannot be precluded because chlorite, a reduction product of chlorate, is ≈6000-fold more toxic to daphnids than chlorate, and there are insufficient data available to characterize the potential of chlorite to form under environmental conditions. |
| | Chronic | No chronic toxicity data are available; therefore, chronic risk invertebrates could not be assessed. |
| Potential risk to mammals | Acute | Risk cannot be precluded even though chlorate is of low toxicity to mammals (10% mortality occurred at the highest dose tested of 5000 mg/kg-bw). If the LD50 is in close proximity to 5000 mg/kg-bw there may be potential risk to some mammals at levels of concern to the Agency. |
| | Chronic | No reproduction toxicity data have been submitted to allow for calculation of risk quotients. Chronic risk to terrestrial organisms is presumably higher than the Agency's level of concern because chronic exposure appears possible, and repeated-dose toxicity studies in mammals suggest that chlorate's effects are cumulative (toxicity increases as exposure duration increases). These studies suggest that repeated exposures may adversely affect reproduction, survival, or growth at concentrations that are lower than the EECs presented in this assessment. |
| Potential risk to birds | Acute | Risk is presumably lower than the Agency's level of concern based on chlorate's low acute toxicity to birds. |
| | Chronic | No reproduction toxicity data in birds are available. Studies in mammals suggest that chlorate's effects are cumulative, and repeated exposure appears possible. Therefore, there may be chronic risk to birds at levels of concern to the Agency. |
| Terrestrial Plants | Acute | Adequate data are not available to allow derivation of risk quotients. However, risk to plants is presumably higher than the Agency's concern level based on chlorate's non-selective mode of action and high application rates. |

| Table 1-1. Summary of Environmental Risk Conclusions for Aquatic and Terrestrial Organisms (Agricultural Uses) | | |
|---|---|---|
| **Surrogate Species** | **Duration of Exposure** | **Summarized Characterization of Potential Risks** |
| Potential risk to aquatic plants | Acute and chronic | Risk to endangered or non-endangered algae cannot be precluded. Submitted core algal toxicity data indicate that chlorate is practically non-toxic to green algae; however, green algae is generally a poor surrogate for vascular plants. Data located in the open literature suggest that brown algae are considerably more sensitive than green algae to chlorate. A 14-day EC50 of 0.012 mM (≈1 mg/L) and a NOAEC of <0.005 mM (≈0.42 mg/L) was reported for brown algae (van Wijk et al., 1997, described in Appendix M). Sufficient detail was not available in the published study report to allow for a comprehensive assessment of data adequacy. However, the EECs for chlorate's agricultural uses were as high as 0.91 mg/L, which exceeds the reported NOAEC for brown algae of ≈0.42 mg/L. For this reason, there may be risk to endangered algal species that exceed the Agency's level of concern for aquatic plants. Also, aquatic plant toxicity data in several required species have not been submitted; therefore, potential risk to aquatic plants may have been underestimated. |

[a] Risks are similar for freshwater and saltwater species.

| Table 1-2. Summary of Environmental Risk Conclusions for Aquatic and Terrestrial Organisms (Non-Agricultural Uses) | | |
|---|---|---|
| **Surrogate Species** | **Duration of Exposure** | **Summarized Risk Characterization And Important Uncertainties** |
| Potential Risk to Fish | Acute and chronic | Risk conclusions are equivalent to those presented in Table 1-1. |
| Potential Risk to Aquatic invertebrates | Acute and chronic | Risk conclusions are equivalent to those presented in Table 1-1. |
| Potential Risk to Birds | Acute | Risk cannot be precluded. No mortality occurred in the submitted subacute toxicity studies at the highest concentration tested (5620 mg/kg-diet); however, EECs on several food items for some of the non-agricultural uses are significantly higher than 5620 mg/kg-food item. |
| | Chronic | Risk conclusions are equivalent to those presented in Table 1-1. |

| Table 1-2. Summary of Environmental Risk Conclusions for Aquatic and Terrestrial Organisms (Non-Agricultural Uses) | | |
|---|---|---|
| **Surrogate Species** | **Duration of Exposure** | **Summarized Risk Characterization And Important Uncertainties** |
| Potential Risk to Mammals | Acute | Risk cannot be precluded even though chlorate is of low toxicity to mammals (10% mortality occurred at 5000 mg/kg-bw). Some of the non-agricultural uses could result in ingestion of chlorate at levels that are significantly higher than 5000 mg/kg-bw for some food items. |
| | Chronic | Risk conclusions are equivalent to those presented in Table 1-1. |
| Potential risk to terrestrial plants | Acute | Risk conclusions are equivalent to those presented in Table 1-1. |
| Potential risk to aquatic plants | Acute and chronic | Risk to endangered or non-endangered algae cannot be precluded. Data located in the open literature suggest that brown algae are considerably more sensitive than green algae to chlorate. However, the EECs for the non-agricultural uses ranged from 3.1 to 39 mg/L, which all exceed the reported EC50 for brown algae of ≈ 1 mg/L. For this reason, there may be risk to endangered and non-endangered algal species that exceed the Agency's level of concern for aquatic plants. Also, EFED noted several data gaps in the aquatic plant toxicity data base that may have resulted in an underestimation of risk. |

**Table 1-3. Data Gaps Identified in this Assessment and Value of Additional Testing to This Assessment**

| Data Gap | Value of Additional Testing to Satisfy the Data Gap | Comments |
|---|---|---|
| Field dissipation study<br>(164-1) | High | No field dissipation data have been submitted to the Agency, and this data requirement has not been waived. A core field dissipation study would allow the Agency to determine the likelihood of chronic exposures and to determine the potential of more toxic reduction products such as chlorite to form in the environment. |
| 2-Generation reproduction toxicity study in mammals<br>(83-4) | High[a] | Toxicity data were not submitted to allow for calculation of risk quotients. Subchronic studies suggest that repeated exposures may adversely affect reproduction, survival, or growth at concentrations that are lower than the EECs presented in this assessment. |
| Reproduction toxicity study in birds<br>(71-4) | High[a] | An avian reproduction toxicity study has not been submitted. Mammalian toxicity data suggest that chlorate is more toxic after repeated exposures. |
| Tier II terrestrial plant toxicity studies<br>(123-1) | High | Chlorate is a non-selective herbicide. Submitted Tier I studies suggest that chlorate is toxic to non-target plants at high application rates. |
| Tier II aquatic plant toxicity studies in *Lemna gibba* (duckweed), *Skeletonema costatum* (a marine diatom), *Anabaena flos-aquae* (a blue-green bacterium), and a freshwater diatom.<br>(123-2) | High | Chlorate is a non-selective herbicide that has been shown to be toxic to some aquatic plants. Only data in green algae have been submitted. Studies in the four other aquatic plant species listed are required for herbicides and would substantially reduce uncertainty in this assessment. |
| Acute toxicity studies in guideline fish and aquatic invertebrate species<br>(72-1, 72-2, and 72-3) | Low | No core studies have been submitted. The submitted supplemental studies suggest that chlorate is practically non-toxic to aquatic organisms (EC50/LC50 values >1000 mg/L). Submission of core studies would not likely alter the conclusions of this assessment. |
| Acute toxicity studies in non-guideline fish and algal species | Potentially high | Open literature studies suggest that chlorate may be particularly toxic to brown trout and to brown algae. However, sufficient detail is not available in these studies to allow for a comprehensive assessment of study adequacy. Therefore, submission of reliable studies in these species could be of considerable value to this assessment. |
| Chronic toxicity studies in fish and aquatic invertebrates<br>(72-4) | Moderate[a] | No chronic studies have been submitted to the Agency. Chlorate is practically non-toxic to fish and aquatic invertebrates after acute exposures. |

a If data from a field dissipation study indicate low potential for chronic exposure, then the value of this study could be reduced.

# 2. Problem Formulation

## *2.1. Initial Considerations*

Methods used to assess risk from exposure to a pesticide are dependent on its environmental fate, physicochemical properties, use information (rates, method, and frequency of application), and target crop/site). Some of the important factors considered in this risk assessment are provided in Table 2-1 below.

**Table 2-1. Selected Factors Considered in the Ecological Risk Assessment of Sodium Chlorate**

| Consideration | Sodium Chlorate-Specific Data | Effect on Risk Assessment |
|---|---|---|
| Toxicity Database | Adequate non-target plant toxicity data are not currently available. | Risk to non-target plants cannot be quantified. Because chlorate is an herbicide with a non-selective mode of action, the Agency presumes that risk to non-target plants exists at levels of concern to the Agency for all labeled uses. |
| | Adequate chronic or reproduction toxicity data for use in ecological risk assessment are not available in any aquatic or terrestrial organism. | Chronic exposure values will not be estimated, and the Agency cannot preclude chronic risk to any organism. |
| | Discrete LD50s or LC50s could not be estimated because chlorate did not induce mortality in birds and induced 10% mortality in mammals at the highest chlorate levels tested. | Acute risk quotients will not be calculated because the proximity of the LD50/LC50 to the highest chlorate levels tested cannot be estimated. Potential risk will be qualitatively assessed by comparing the highest levels tested in the toxicity studies to the estimated environmental concentrations (EECs). |
| | Open literature data suggest that chlorate may be particularly toxic to brown algae and brown trout. | These open literature studies are used to qualitatively characterize potential risk to these surrogate species. |
| Environmental Fate Database | There are no guideline environmental fate studies that have been submitted to the Agency. However, the following studies have been waived: Abiotic Hydrolysis (161-1); [Direct] Photodegradation in Water (161-2). The rationale for waiving these data requirements is in Section 3. | The behavior of chlorate in the environment is dependent on the redox conditions of the medium (nature and concentration of reductants; oxic or anoxic conditions). A high spatial and temporal variability is expected throughout the sites where chlorate is used as a defoliant/desiccant. Therefore, extremely conservative assumptions were made for the exposure estimates. |

| Consideration | Sodium Chlorate-Specific Data | Effect on Risk Assessment |
|---|---|---|
| Degradation | It is assumed that chlorate may be persistent in the field under some environmental conditions, but the source of the data is obscure. For example, some labels indicate that chlorate may control plant growth for up to a year.<br>A potential reduction product of chlor**a**te is chlor**i**te. Chlorite is more toxic to some organisms, particularly aquatic invertebrates. | In the absence of data indicating otherwise, the Agency assumes that short-term and long-term exposure to chlorate and its reduced products may occur.<br>However, the distribution and concentration of chlorate and its reduced products in soil and water as a function of time could not be obtained because of lack of kinetics data. It is unlikely that all chlorate converts to all chlorite because other chemical species (e.g., chlorine oxyanions in lower oxidation states) can also form and react further via redox reaction and/or disproportionation).<br>Thermodynamic equilibrium data and predominance diagrams showed that, at chemical equilibrium, the end product is chloride ($Cl^-$). Even though chlorite, other oxyanions, and chloride may be present together, the concentration of chlorite and other species at any given time post-application cannot be estimated because of lack of kinetics data. |
| Application Method | Sodium chlorate may be applied via aerial or ground spray (agricultural) or dispersed as a granule (non-agricultural) or pellet. | Consumption of granules will be considered in this assessment using the LD50/ft$^2$ method in addition to the standard methods used to assess risk from spray applications. EFED does not currently assess chronic risk from exposure to granular pesticides (U.S. EPA, 2004). |
| Number of Annual Applications | The number of annual applications is not specified on many of the labels. | The Agency is assuming that chlorate is to be applied once per year for all uses where the label does not specify the number of annual applications or maximum annual load (except cotton, where the Agency is assuming two applications). |
| Use | Sodium chlorate is labeled for use on a number of agricultural crops and non-agricultural areas of unspecified size. Some non-agricultural uses are “as needed” and some uses are spot treatments. | EFED’s exposure models are not currently designed to predict aquatic concentrations from some of these uses. Therefore, estimated aquatic concentrations may be highly conservative for some uses. |
|  | The maximum labeled application rates of the non-food uses are extremely high (up to 650 lbs a.i./Acre). | Based on the very high application rates, additional exposure analyses may be needed. For example, consumption of contaminated soil could result in high body burdens for some animals. |

## 2.2. Stressor Identification, Source, and Distribution

### *2.2.1. Assessment of Chemicals of Concern*

Sodium chlorate (also referred to as chlorate in this assessment), specifically the chlorate anion, is the chemical stressor to which non-target plant and animal populations may be exposed and is, therefore, the primary focus of this risk assessment.[1] Chlorate is a strong oxidizer and may be reduced to a variety of chemical species depending on the environmental conditions. This assessment also considers potential exposure to and risk from these chemical species. However, the currently available data and the complexity of processes involved in the formation of these chemical species do not allow for a quantitative evaluation of the potential exposure levels to them. Therefore, potential risks from these products are only qualitatively described. The Environmental Fate and Effects Division (EFED) is particularly concerned with potential exposure to chlorite, which has been shown to be considerably more toxic than chlorate to some species, particularly aquatic invertebrates.

Several end-use products of chlorate also contain other active ingredients (e.g., sodium metaborate) in addition to flame retardants. Potential effects that these other chemicals may have on chlorate's fate or toxicity is not considered in this assessment.

### *2.2.2. Physical and Chemical Properties of Sodium Chlorate*

Chlorate, an inorganic salt, is not a naturally occurring chemical. It is made by electrolysis of brine (sodium chloride) under controlled temperature and pH conditions (Appendix B-1) to optimize the efficiency of the process and yield.

Physical and chemical properties of a chemical can be used *a priori* to identify potential routes of exposure. For example, the vapor pressure and Henry's Law Constant provide an indication of the potential to volatilize from soil and water (partitioning into air), and the *n*-octanol/water partition coefficient provides an indication of the potential to bioaccumulate in fish or other aquatic organisms. The physical and chemical properties of chlorate are summarized in Table 2-2.

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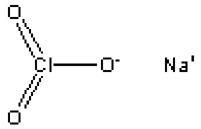
[1] The use of chlorate to generate chlorine dioxide *in-situ* is not considered in this assessment as the two uses have completely different exposure scenarios (Refer to "Environmental Fate section)

**Table 2-2. Physical and Chemical Properties of Chlorate**

| **Physical and/or Chemical Property** | **Data** |
|---|---|
| Selected Synonyms | Soda chlorate; chloric acid, sodium salt |
| Structure |  |
| Chemical Abstract Registry Number | 7775-09-9 |
| Chemical Class | Inorganic Salt<br>Chlorate is one of the oxyanions of chlorine. The oxidation state of chlorine in chlorate is 5, represented as Cl(V) or $Cl^{5+}$<br>Chlorate is a monovalent anion |
| Empirical Formula | $NaClO_3$ |
| Molecular Weight, Daltons | 106.5 |
| Physical State | Crystalline Solid (hygroscopic)[2] |
| Melting Point | 248° C |
| Boiling Point | Not applicable. Decomposes above 300°C, with release of oxygen (violently) |
| Solubility in Water | $1.0 \times 10^{6}$ $mgL^{-1}$ at 25° C<br>(highly soluble) |
| Dissociation Constant | Fully ionized |
| Vapor Pressure, 25° C | Negligible<br>$7.3 \times 10^{-16}$ mm of Hg<br>$9.7 \times 10^{-14}$ Pa |
| Henry's Law Constant | Negligible<br>$1.0 \times 10^{-22}$ atm-$m^3 mole^{-1}$ (Estimated) |
| Log *n*-octanol/water Partition Coefficient (Log Kow) | -7.08 (Estimated) |

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[2] Crystal System: Cubic. The chlorate anion is pyramidal, with Cl at the apex (near $C_{3v}$ symmetry) and the X-ray diffraction pattern serve to identify chlorate, as X-ray diffraction patterns serve as "fingerprint" identification method.

| Table 2-2. Physical and Chemical Properties of Chlorate | |
|---|---|
| **Physical and/or Chemical Property** | **Data** |
| Other | Chlorate is considered a hazardous material. Although stable by itself, it can be highly flammable when in contact with organic material, including agricultural materials such as peat, powdered sulfur and other organic matter. Therefore, end-use products containing chlorate as the active ingredient must also contain a fire retardant |

Based on the low vapor pressure, chlorate is not expected to volatilize from soil. The low log *n*-octanol/water partition coefficient indicates that chlorate has low potential to bioaccumulate. Chlorate is highly soluble and is completely ionized in water, thus producing $Na^+$ and the chlorate ($ClO_3^-$) anion. Anions do not bind readily to soil or sediment particulates[3] and, therefore, are expected to be very mobile. Assuming that chlorate does not undergo any redox reactions, it is expected to be very mobile and to partition predominantly into the water. However, extensive redox reactions are expected to occur in the environment that will reduce the concentration of chlorate in the water column.

The redox chemistry[4] of chlorate affects its behavior in soils and natural water. Therefore, identification of the conditions (pH; redox potential, "$E_h$" or pE) under which chlorate and other oxyanions of chlorine may predominate is an important consideration in the environmental fate and risk assessment of chlorate. The oxidation-reduction reactions of chlorate with organic matter and other inorganic chemical species are very complex and depend on the redox conditions of the media, nature and concentration of reductants, chlorate concentration, temperature, pH, and degree of moisture (soils). Nitrate concentrations in soil and water (as well as other physical and chemical properties of soil and water) play an important role in the redox chemistry of chlorate in the environment.

Open, peer-reviewed chemical literature and descriptive chemistry of the chlorine system were used as the basis for understanding the redox behavior of chlorate (at least on a qualitative basis; Refer to Appendix B-1) and for generating a screening-level environmental fate assessment. Targeted, guideline studies designed to understand the environmental fate of chlorate are not available. Laboratory guideline studies were waived as it was considered that the studies would not provide any additional information above what is already known in the open chemical literature (See Appendix H). However, major spatial and temporal variability in the environmental conditions that may affect the redox chemistry of chlorate is anticipated. Thus,

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[3] Unless they chemisorb to soil or sediment particulates. Chemisorption of chlorate is unlikely.

[4] The term "redox chemistry" is used as an overall term for oxidation and reduction reactions. Other terms that are frequently used for oxidizers are "oxidants", "oxidizing agents". Reductants are frequently referred to as "reducing agents". All redox reactions require an oxidant **and** a reductant. Reductants are electron donors, while oxidants are electron acceptors.

attempts were made to identify geographical locations and seasons where and when chlorate might be more persistent. For this purpose, the USDA's Census of Agriculture (2002) was used to gather information on the number of acres harvested (by state) for specific agricultural commodities on which chlorate is used (See Section 2.2.4, Use Characterization). The number of harvested acres was taken as an indicator of areas of the country where chlorate might be used. Since the degree of soil humidity is important for application of chlorate, the percent of irrigated acres was also estimated for cotton (Appendix D), the crop of major use of chlorate.

### *2.2.3. Mode of Action*

Chlorate is a non-selective, contact herbicide that can kill all green parts of plants. Chlorate is well known to be a strong oxidizing agent. Chlorate is absorbed rapidly by plants through both root and leaf systems. When applied as a foliar spray, chlorate penetrates the cuticle causing cell death, probably by altering the metabolic processes. Soil applications result in translocation through the xylem of living tissue of plant and foliage. As a consequence of its reaction as an oxidant, it generates reduced chloro species (i.e., chlorine in lower oxidation states than chlorate), such as chlorite and/or hypochlorite. These chemical species appear to inactivate the nitrogen reductase enzyme or disrupt other physiological processes. However, the exact mechanisms are not fully understood. In addition, injured plants can cause an increase in production of ethylene, auxins, and abscissic acid, which cause leaf abscission.

### *2.2.4. Use Characterization and End-Use Product*s

Chlorate has a long use history. It has been used in the United States as a defoliant/desiccant at least since the early 1940s, mostly on cotton. In spite of this, behavior of chlorate in the field is not well documented nor are its long-term effects on soils.

The end-use products containing chlorate as the active ingredient include soluble concentrates, granular products, and pellets. Chlorate end-use products must contain a fire retardant because it can ignite readily when in contact with organic matter. No data were located that document the effects of flame retardants on chlorate's toxicity or environmental fate.

There are two terrestrial use patterns for chlorate: Food/Feed Use (agricultural commodities) and Food/Non-Feed (non-agricultural sites). Each use pattern is described below. Chlorate is also an inert ingredient in some pesticide formulations, where it is used because its antimicrobial effects retard biodegradation of the pesticide, resulting in prolonged pesticidal activity. Risk from these uses was not considered in this assessment because exposure of non-target organisms to chlorate from these uses is considered negligible.[5] However, its soil sterilizing properties could have adverse effects on soil quality and productivity over time.

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[5] Confidential business information (CBI) restrictions preclude the Agency from identifying the pesticide formulations in which chlorate is used as an inert ingredient in this assessment.

Agricultural Food/Feed Uses

Currently, chlorate is used primarily as a harvest aid (defoliant[6], desiccant[7], or both). All of the end-use products formulated for agricultural uses are soluble concentrates. The major Food/Feed Use is on cotton (>90% of agricultural uses), but it is also used on other field crops (See Table 2-3). Application rates associated with each agricultural commodity are also in Table 2-3. The data were compiled by the Agency's review of existing labels. A summary of all labeled uses for each registered end-use product is in Appendix E.

**Table 2-3. Summary of Agricultural Commodities and Associated Application Rates for Labeled Sodium Chlorate Formulations**

| **Use** | **Range of Max Labeled Application Rates[a] (lbs a.i./Acre)** | **Comments** |
|---|---|---|
| Pepper<br>(Chili Type) | 8.775 - 12.5 | Maximum number of applications or maximum annual load not specified |
| Potato, White/Irish | 6 - 12.5 | Maximum number of applications or maximum annual load not specified |
| Beans, dried-type<br>Guar; Southern peas; Safflower<br>Sorghum; Soybeans; Sunflower; Flax<br>Corn; Rice (air only) | 6 - 7.5 | Maximum number of applications or maximum annual load not specified |
| Cotton | 4.5 - 7.5 | Two applications of the maximum application rate (30-day interval) assumed by the Agency. Labels that specifically allow multiple applications have lower maximum application rates than 7.5 lbs a.i./Acre. However, multiple applications of 7.5 lbs a.i./Acre are not precluded in the labels and are therefore used as the maximum application rate in this assessment. |
| Cucurbit Vegetables | 6.1875 | Maximum number of applications or maximum annual load not specified |

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[6] Defoliant: Defoliation is the process by which leaves are abscised from the plant. While other process such as drought, low temperature, or disease can induce abscised leaves, the term "defoliant" is used for chemicals that promote the process.

[7] Desiccant: Desiccation by chemicals is the rapid killing or drying of the leaf blades and petioles, with the leaves remaining in a withered state in the plant.

| Use | Range of Max Labeled Application Rates[a] (lbs a.i./Acre) | Comments |
|---|---|---|
| Agricultural fallow / idleland; gourds; wheat[b] | 6 | Maximum number of applications or maximum annual load not specified |

a The loading in terms of sodium ranges from 1.01 to 2.7 lbs per acre.
b Wheat has been covered under a FIFRA Section 18 Emergency Exemption tolerance for 25 years. The current exemption is scheduled to expire on December 31, 2004. The following states have requested a Section 18 wheat tolerance in the past: Arkansas, Georgia, Kansas, Louisiana, Mississippi, Missouri, North Dakota, Nevada, New Mexico, Oklahoma, and Texas.

Many of the labels do not specify the maximum number of applications or annual load; however, some labels for cotton indicate that multiple applications may be necessary. The Agency has assumed that chlorate may be applied twice annually to cotton at all application rates with a 30-day application interval and is applied once annually for all other uses.[8] This assumption may have resulted in an under-estimation of risk if chlorate may be applied more than twice annually (or at shorter application intervals) to cotton or more than once annually to other crops. Typical application rates, number of applications, and application intervals were not located.

Figure 2-1 below illustrates the estimated national annual chlorate usage rate for 1998. Appendix C illustrates all areas in the United States that grow commodities on which chlorate is used where such data are available. Percentage of each agricultural crop on which chlorate is used compared with the total amount of crop grown in the United States is also included in Appendix F.

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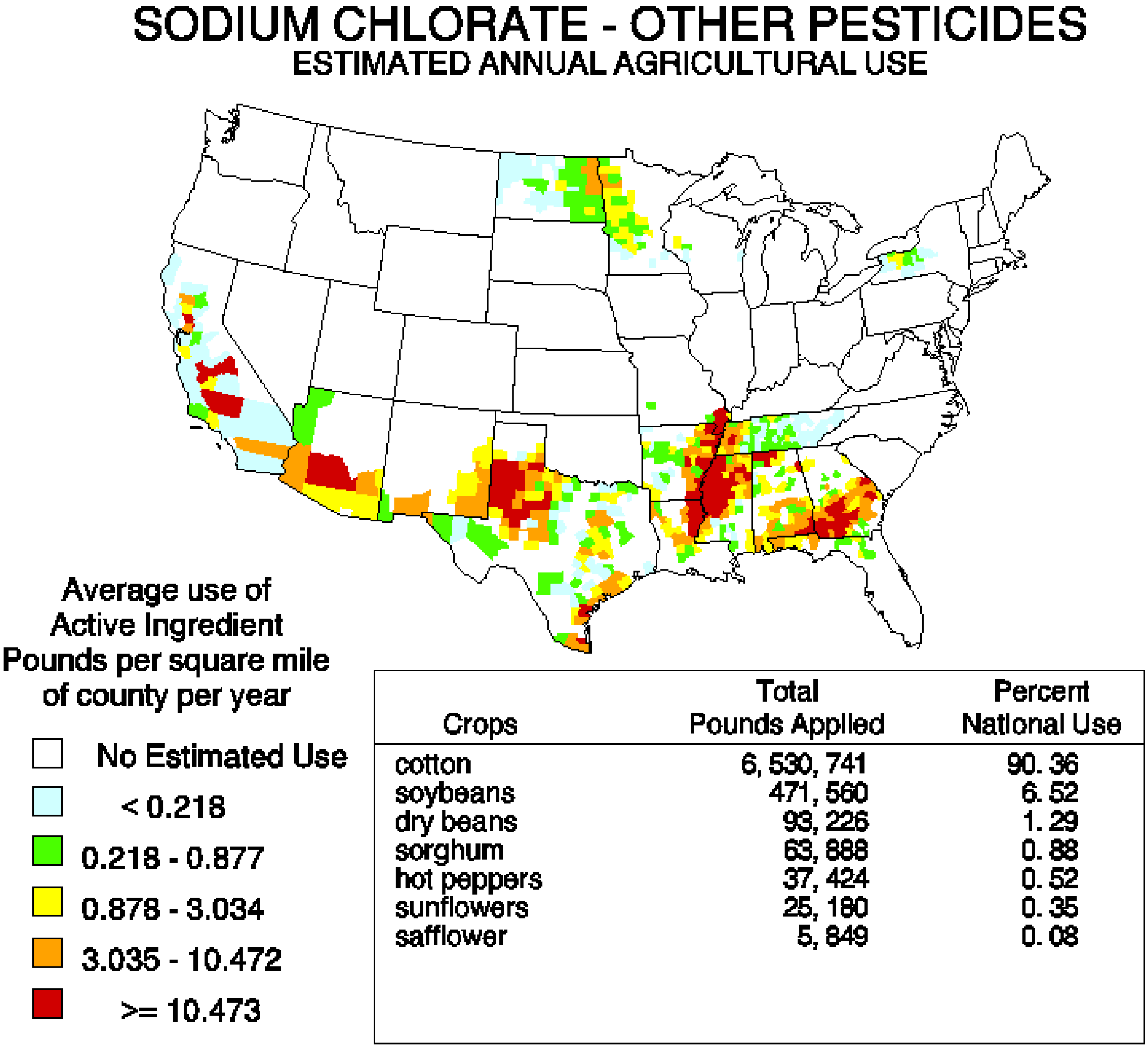
[8] Data from the Office of Pesticide Programs Label Use Information System (LUIS) report, Table A2 “Food/feed Use Patterns Summary for Chlorate (CASE 4049)”. June 14, 2004.



| Crops | Total Pounds Applied | Percent National Use |
|---|---|---|
| cotton | 6,530,741 | 90.36 |
| soybeans | 471,560 | 6.52 |
| dry beans | 93,226 | 1.29 |
| sorghum | 63,888 | 0.88 |
| hot peppers | 37,424 | 0.52 |
| sunflowers | 25,180 | 0.35 |
| safflower | 5,849 | 0.08 |

**Figure 2-1**

**1997 Use Data for Sodium Chlorate**

**Data obtained from the U.S. Geological Survey (USGS) and are available at the following url:**
http://ca.water.usgs.gov/cgi-bin/pnsp/pesticide_use_maps_1997.pl?map=W8004

## Non-Agricultural Uses

Chlorate is used to control perennial weeds (morning glory, Canada thistle, and Johnson grass) in non-agricultural areas and for vegetation control on roadsides, rights of ways, and other public and industrial areas. The maximum labeled application rates for all end-use products are in Table 2-4 below. The Agency assumed a single application per year for the non-agricultural uses. However, many of the labels do not specify the maximum number of annual applications or maximum annual chlorate load. In the absence of such data, EFED assumed a single application. This assumption may have resulted in an under-estimation of risk if multiple applications of chlorate are allowed.

Chlorate is also registered as a biocide for drinking water treatment. There are major and important differences between its use as a biocide and its use as a defoliant/desiccant. As a disinfectant, chlorate is used to generate chlorine dioxide gas *in-situ*, in closed containers and in the absence of light (i.e., formation of stable chlorine dioxide is the goal)[9]. As a defoliant/desiccant, chlorate is applied to an open field. Thus, it is exposed to an open environment (soil, water, air, sunlight). That is, the scenarios are significantly different and, therefore, the dissipation behavior is expected to be different. The present assessment only considers use of chlorate in terrestrial fields. Other uses are assessed by the Office of Pesticide Program's Antimicrobial Division and the Office of Water.

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[9] Chlorine dioxide, $ClO_2$ (Cl oxidation state IV), is a gas. It is a highly energetic molecule and a free radical even in dilute aqueous solutions. At high concentrations it reacts violently with reductants. It is only stable in dilute solutions and in the absence of light (i.e., it photolyzes).

## Table 2-4. Maximum Application Rates for Sodium Chlorate's Non-Agricultural Uses

| Product | Max App. Rate (lbs a.i./Acre)[a] | Use Description | Formulation |
|---|---|---|---|
| Ferti-Lome Special Vegetation Killer | 650<br>(under asphalt)<br>325<br>(other uses) | Brick walks, patios, parking areas, along fences, curbs, gutters, around building, graveled pathways, driveways, under asphalt paving | Liquid (SC) |
| Perkerson's Tri-Ate Weed Killer | 520 | Parking lots, under asphalt paving, fence lines, building perimeters, ditch banks, picnic areas, vacant lots, wood decks, bleachers, cemeteries, fuel tanks, runways, helo pads, etc. | Granular<br>(may be dissolved) |
| Barespot Monobor Chlorate | 520 | Bleachers, fence lines, fire hydrants, guard rails, parking lots, under driveways, sidewalks, asphalt | Granular<br>(may be dissolved) |
| Barespot weed and grass | 390 | Bleachers, bridge abutments, buildings, guard rails, helo pads, under asphalt, concrete, gravel, driveways, sidewalks, wood decks. | Granular |
| Bareground BD | 240 | Industrial sites, rights of way, lumberyards, petroleum tank farms, around farm buildings, along fence lines, and similar areas | Liquid (SC) |
| Barespot Ureabor | 240 | Bleachers, fence lines, fire hydrants, helo pads, parking lots, runways, vacant lots. | Granular |
| Grass, weed, and vegetation killer | 220 | Driveways, walks, patios, tennis courts, curbs, garages, etc. | Liquid (SC) |
| Tri-Kil nonselective weed and grass killer | 160 | Fence rows, rights-of-ways and similar areas | Liquid (SC) |
| AllPro Baracide 5PS Pelleted Herbicide | 160 | Around buildings, storage areas, fences, recreational areas, guard rails, highway medians, industrial sites. | Pelleted/Tableted |
| Prometon 5PS; Pramitol 5 PS | 160 | Around buildings, storage areas, fences, pumps, machinery, fuel tanks, recreational areas, roadways, guard rails, airports, rights of ways. | Pelleted/Tableted |
| Riverdale Killsall Liquid | 140 | Driveways, parking lots, walks, around fences, curbs, similar areas. Not for use on lawns. | Liquid (SC) |
| Perkerson's Tri-Chlor Weed Killer | 52 | Industrial sites such as driveways, paths, brick walks, cobble gutters, tennis courts | Liquid (SC) |

a Application rates were generally given in lbs a.i./100 $ft^2$ and were converted to lbs a.i./Acre (100 $ft^2$ = 0.0023 acres).

The labels for the non-agricultural terrestrial uses preclude direct application to water. Therefore, risk to aquatic organisms from direct application to water was not assessed.

### *2.2.5. Persistence, Bioaccumulation, and Toxicity (PBT) Screen for Sodium Chlorate*

Chlorate is toxic to plants and may be persistent under some environmental conditions; however, its low bioconcentration potential precludes it from meeting the screening level characteristics of a PBT chemical.[10] See Section 3 (Analysis) for a discussion of chlorate's relevant environmental fate properties that relate to its persistence and bioaccumulation potential and for a discussion on the available toxicity data.

## 2.3. Exposure Assessment Approach

### *2.3.1. Aquatic Organism Exposure Approach*

The GENeric Expected Environmental Concentration (GENEEC-2) model was used to calculate EECs for all uses included in this assessment. The GENEEC-2 program is a simple model that uses a chemical's soil/water partition coefficient and degradation half-life values to estimate runoff from a ten hectare field into a one hectare by two meter deep pond. It should be noted that none of EFED's current surface water simulation models that calculate EECs are designed for inorganic chemicals such as chlorate for which formation of reaction products is controlled by pH and redox potential nor are they capable of indicating the distribution and concentration of the reduced products. In addition, GENEEC-2 estimates will likely be very conservative for the non-agricultural uses because the model assumes that a contiguous drainage basin flows into a pond that is10-times smaller than the treated area. The application scenarios for the non-agricultural uses may not be consistent with the scenario assumed by GENEEC-2.

The rate and extent of formation of reduction products of chlorate will be dependent on the chemical nature and concentration of environmental reductants present in the environment in which chlorate is released. However, data on chlorate-specific reductant reaction rates (i.e., kinetics) are scarce and mostly under conditions not relevant to the environment (e.g., very acid or very alkaline media; reductants not likely to be found in the environment). Therefore, EFED calculated peak EECs under the assumption that chlorate remains stable. This assumption likely resulted in high-end chlorate concentrations in aquatic systems. Chronic exposure values (21- or 60-day) are not presented in this assessment because no chronic toxicity data are available for comparison.

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[10] Although a bioconcentration study has not been submitted to the Agency, the extremely low Log Kow of chlorate indicates that it will not bioconcentrate or bioaccumulate.

Attempts were made to refine the aquatic EECs using higher tier models such as PRZM and EXAMS[11]. However, none were found to be adequate simulation models for chlorate as they cannot adequately handle redox systems. Given that there is a major uncertainty in the kinetics and reaction products under field conditions, the use of higher tier simulation models or other approaches  may give a perception of higher confidence in the aquatic EECs than is justified by the available data.

Other approaches using available thermodynamics data were also attempted (Section 3.1). However, all were considered to be inappropriate as they were not able to determine the speciation (i.e., which chemical species will form and their distribution) and predominance (relative amount of each of the potential chemical species) that may occur under environmental conditions.  Thermodynamics data only indicate which chemical species **can** form, but do not indicate that they **will** form and at what rate.  Nevertheless, EFED used thermodynamic data to estimate which of the chlorine species could be found within the pH-pE range of natural waters (see Section 3.1).

EFED did not use its interim rice model to calculate EECs from chlorate use on rice because the model calculates EECs in a flooded rice paddy.  As a desiccant, chlorate will likely be applied after the rice fields have been drained.  Therefore, GENEEC-2 was used to calculate EECs from all uses considered in this assessment.

### *2.3.2.   Terrestrial Organism Exposure Approach*

Chlorate may be applied as a spray or as granules.  EFED's methods for assessing  exposure to terrestrial organisms are different for each of these application methods and are discussed below.

Spray Applications

The focus of terrestrial wildlife exposure estimates is for birds and mammals with an exposure route emphasis on uptake through the diet.  For exposure to terrestrial organisms, the Agency estimates the residue concentrations of pesticides on food items and assumes that organisms are exposed to one active ingredient in a given exposure scenario.  For chlorate spray applications, estimation of pesticide concentrations in wildlife food items focuses on quantifying possible dietary ingestion of residues on vegetative matter and insects.  The residue estimates are based on nomograms that relates food item residues to pesticide application rate (Fletcher et al., 1994). The nomograms are incorporated into a first-order residue decline model, "ELL-FATE", which allows determination of residue dissipation over time by incorporating degradation half-life.  Two nomograms are used in this ecological risk assessment: One is based on the maximum residue concentrations and one based on mean residue concentrations reported by Fletcher et al. (1994).

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[11] Although EXAMS has some capability to introduce redox data, kinetics data is also needed. Given the lack of chlorate- specific reductant kinetics data, at this time EXAMS is not adequate to handle inorganic chemicals that can exist in more than one oxidation state.

Residues may be compared directly with dietary toxicity data or converted to an oral dose, as is the case for small mammals. For mammals, the residue concentration is converted to daily oral dose based on fractions of body weight consumed daily as estimated through mammalian allometric relationships. In all screening-level assessments, the organisms are assumed to consume 100% of their diet as one food type. These exposure estimates are only applicable to the applied pesticide, chlorate. It is uncertain to what extent exposure to reduced species of chlorate, such as chlorite, may occur.

Granular applications

For granular applications, estimation of chlorate loading per unit area (mg/ft$^2$) are calculated. This approach, which is intended to represent exposure via multiple routes (e.g., incidental ingestion of contaminated soil, dermal contact with treated seed surfaces and soil during activities in the treated areas, preening activities, and ingestion of drinking water contaminated with pesticide) and not just direct ingestion, considers observed effects in toxicity studies and relates them to the pesticide applied to surface area. The maximum labeled application rate for the active ingredient is the basis for the exposure term.

### *2.3.3. Terrestrial Plant Exposure Approach*

Adequate toxicity data are not available to perform a risk assessment (see Section 3, Analysis); therefore, risk to non-target terrestrial plants was not quantified. Based on chlorate's non-selective mode of action, EFED presumes high risk to all non-target plants pending receipt of adequate toxicity data.

## 2.4. Conceptual Model

In order for a chemical to pose an ecological risk, it must reach ecological receptors in biologically significant concentrations. An exposure pathway is the means by which a contaminant moves in the environment from a source to an ecological receptor. For an ecological exposure pathway to be complete, it must have a source, a release mechanism, an environmental transport medium, a point of exposure for ecological receptors, and a feasible route of exposure. The assessment of ecological exposure pathways, therefore, includes an examination of the source and potential migration pathways for constituents, and the determination of potential exposure routes (e.g., ingestion, inhalation, dermal absorption).

Ecological receptors that may potentially be exposed to chlorate and its degradates include wildlife and plants in terrestrial and semiaquatic areas (e.g., mammals, birds, reptiles, invertebrates). In addition to terrestrial ecological receptors, aquatic receptors (e.g., freshwater and estuarine/marine fish and invertebrates, amphibians, reptiles) may also be exposed to potential migration of pesticides from the site of application to various watersheds and other aquatic environments via runoff and spray drift.

The source and mechanism of release of chlorate is application via foliar spray (ground or aerial application) on agricultural crops or chlorate application of foliar spray or distribution of granules to non-agricultural areas. Based on the expected high mobility of chlorate, surface water runoff from the areas of application is assumed to be the primary route of exposure in aquatic systems. Additional release mechanisms include spray drift, and wind erosion of soil containing residues of chlorate, which may potentially transport site-related contaminants to the surrounding area. Potential emission of volatile compounds is not considered as a viable release mechanism for chlorate because it has a negligible vapor pressure and a very high solubility in water. Therefore volatilization is not expected to be a transport route for chlorate[12]. The conceptual model below generically depicts the potential source of chlorate, release mechanisms, receiving media, and biological receptors for chlorate's use.

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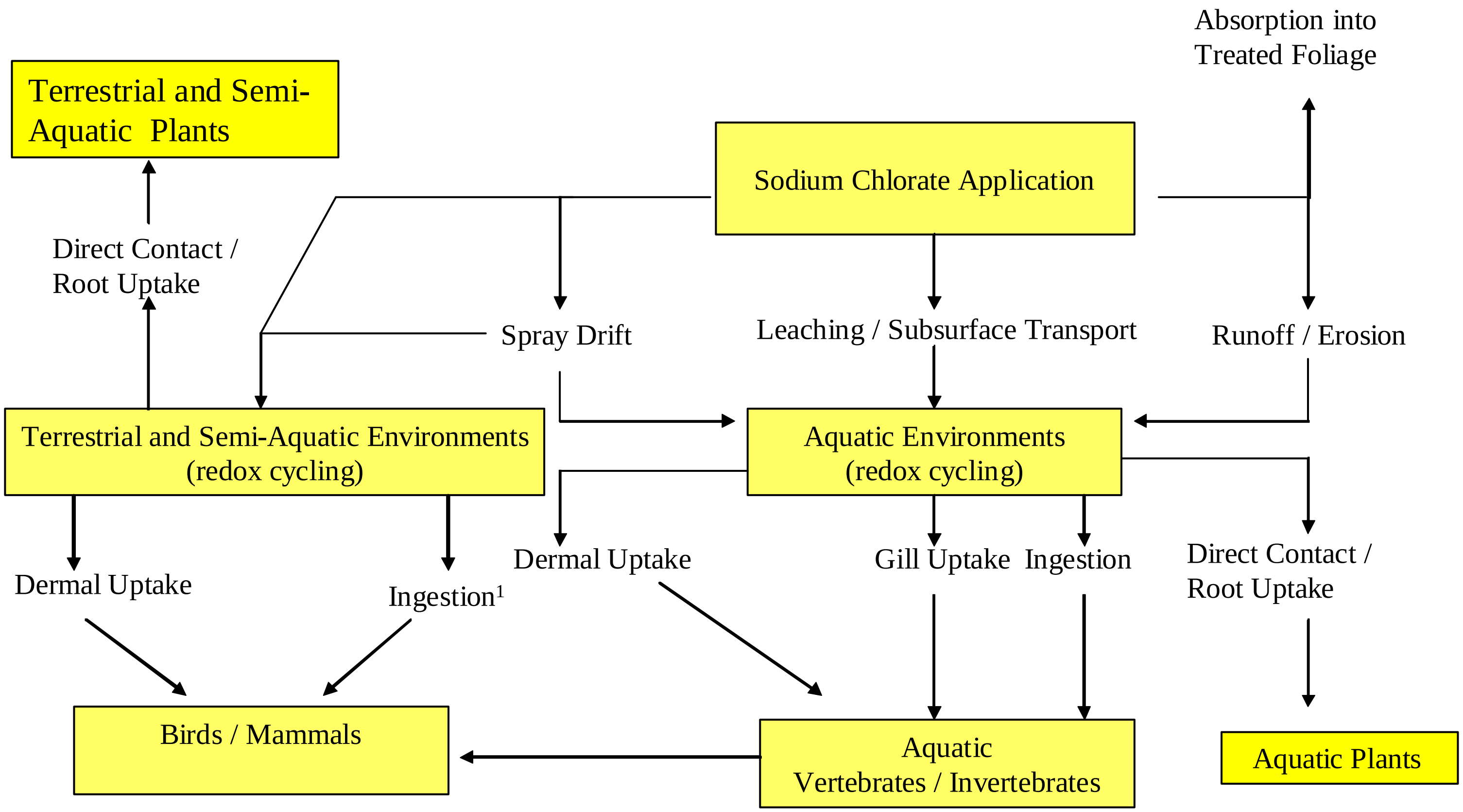
[12] Chlorine dioxide (gas) is among the chemical species that can result from reduction of chlorate. However, photolysis is a major and rapid dissipation pathway for chlorine dioxide.



1 Direct ingestion of granules or ingestion of contaminated food items.
Spray drift is considered negligible for granular applications

## 2.5. Effects Assessment Approach

Assessment endpoints are defined as "explicit expressions of the actual environmental value that is to be protected (U.S. EPA, 2004)." Defining an assessment endpoint involves two steps: 1) identifying the valued attributes of the environment that are considered to be at risk, and 2) operationally defining the assessment endpoint in terms of an ecological entity (i.e., a community of fish and aquatic invertebrates) and its attributes (i.e., survival and reproduction). Therefore, selection of the assessment endpoints is based on valued entities (i.e., ecological receptors), the ecosystems potentially at risk, the migration pathways of pesticides, and the routes by which ecological receptors are exposed to pesticide-related contamination. The selection of clearly defined assessment endpoints is important because they provide direction and boundaries in the risk assessment for addressing risk management issues of concern.

The typical assessment endpoints for screening-level ecological risk assessments include reduced survival and impairment of reproductive and growth of freshwater and saltwater organisms and terrestrial species. Potential effects on a set of surrogate species are used to extrapolate risk to all species. Surrogate aquatic organisms include freshwater and saltwater fish and invertebrates. Benthic organisms were not specifically assessed for chlorate because it is not expected to partition to the sediment. In the absence of toxicity data on amphibians, it is assumed that aquatic-phase amphibians are approximately as sensitive as fish to potential effects of a pesticide. Surrogate terrestrial animal species include birds and mammals. This screening-level assessment assumes that reptiles and terrestrial-phase amphibians are approximately as sensitive to pesticide-induced effects as birds. For both aquatic and terrestrial animal species, direct acute and direct chronic effects are considered. Indirect effects to listed/endangered species resulting from direct effects on food-items and habitat are also considered.

Each assessment endpoint requires one or more "measures of ecological effect," which are defined as changes in the attributes of an assessment endpoint itself or changes in a surrogate entity or attribute in response to exposure to a pesticide. Ecological measurement endpoints for the screening level risk assessment are based on a suite of toxicity studies performed on a limited number of organisms in the broad groupings indicated in Table 2-5 below. Within each of those very broad taxonomic groups in animals, an acute and chronic endpoint is selected from the available test data, as the data sets allow. Chronic effects in plants is not currently assessed by EFED.

A summary of the assessment and measurement endpoints selected to characterize potential ecological risks associated with exposure to chlorate is provided in Table 2-5 below. A more comprehensive discussion of all toxicity data available for this risk assessment and the resulting measurement endpoints selected for each taxonomic group are included in Appendix M of this document.

| Table 2-5. Summary of Assessment and Measurement Endpoints | | | |
|---|---|---|---|
| **Surrogate Species** | **Assessment Endpoint** | **Measurement Endpoint**[a] | **Substance Tested** |
| Birds | Abundance (i.e., survival, reproduction, and growth) of bird populations | **Acute Exposures:** LD50 in mallard ducks and bobwhite quail<br>**Short-term (Subacute) Exposures:** LC50 in mallard ducks and bobwhite quail<br>**Chronic Exposures:** No available data | TGAI[b]<br>TGAI[b] |
| Mammals | Abundance (i.e., survival, reproduction, and growth) of mammal populations | **Acute Exposures:** Laboratory rat acute oral $LD_{50}$ (mg/kg-bw)<br>**Chronic Exposures:** Developmental toxicity study; subchronic toxicity studies*****<br>***** A 2-generation reproduction toxicity study in rodents is typically used by EFED to estimate potential risk to mammals from chronic exposures; however, such data on sodium chlorate were not available. | TGAI[b] |
| Freshwater Aquatic Organisms | Survival and reproduction of freshwater fish and invertebrate communities | **Acute Exposures:** Daphnia Magna, rainbow trout, and bluegill sunfish.<br>**Chronic Exposures:** No chronic studies were submitted. | TGAI[b]<br>NA |
| Estuarine/ marine organisms | Survival and reproduction of estuarine/marine fish and invertebrate communities | **Acute Exposures:** Acute studies in fish (sheepshead minnows) and invertebrates (mysid shrimp and oysters).<br>**Chronic Exposures:** No chronic studies were submitted. | NA |
| Plants (terrestrial and semi-aquatic environments) | Perpetuation of populations of non-target terrestrial and semi-aquatic species (crops and non-crop plant species) | Adequate toxicity data are not available for screening level assessment. | TGAI |
| Plants (aquatic environments) | Maintenance and growth of standing crop or biomass of aquatic plant populations | EC50 and NOAEC from 96-hour study in green algae. | TGAI |

[a] $LD_{50}$ = Lethal dose to 50% of the test population.
NOAEC = No observed adverse effect concentration.
LOAEC = Lowest observed adverse effect concentration
$LC_{50}$ = Lethal concentration to 50% of the test population.
$EC_{50}$ = Effect concentration to 50%/25% of the test population.

[b] TGAI = Technical grade active ingredient

## 2.6. Risk Characterization Approach

Risk characterization is the integration of exposure and effects characterization to determine the ecological risk from the use of the pesticide and the likelihood of effects on aquatic life, wildlife, and plants based on varying pesticide-use scenarios. The risk characterization provides an estimation and a description of the risk; articulates risk assessment assumptions, limitations, and uncertainties; synthesizes an overall conclusion; and provides the risk managers with information to make regulatory decisions regarding a pesticide.

Results of the exposure and toxicity effects data are used to evaluate the likelihood of adverse ecological effects on non-target species. For the screening level assessment of chlorate risks, the risk quotient (RQ) method is used to compare exposure and measured toxicity values. Estimated environmental concentrations (EECs) are divided by acute and chronic toxicity values to derive risk quotients. The RQs are compared to the Agency's levels of concern (LOCs). These LOCs are the Agency's interpretive policy and are used to analyze potential risk to non-target organisms and the need to consider refinement or regulatory action. These criteria are used to indicate when a pesticide is used as directed on the label has the potential to cause adverse effects on non-target organisms. Appendix G of this document summarizes the LOCs used in this risk assessment. Risk characterization is composed of risk estimation and risk description. Risk quotients are calculated in the risk estimation section for each endpoint, and characterization and interpretation of risk is described in the risk description section for each endpoint assessed.

## 2.7. Key Uncertainties and Information Gaps in This Assessment

The following uncertainties and information gaps were identified as part of the problem formulation (additional uncertainties identified in this assessment are reported in the individual sections of this report):

Fate and Exposure

- Many of the labels are not clear regarding the maximum allowable annual applications (number of applications or total load). The Agency assumed a maximum of 2 annual applications (30 days apart) for cotton and 1 annual application for all other uses for this assessment. Risk may be under-estimated if these assumptions do not accurately reflect chlorate's applications.

- Chlorate is a strong oxidizer and may be reduced to other chemically related species under some environmental conditions. The extent and rate to which this occurs will depend on the redox chemical species (including organic matter) in the water or soil. Extensive spatial and temporal variability is expected for the reactions of chlorate in the environment. However, the currently available simulation models do not allow for a quantitative evaluation of the potential exposure levels of each the reduced products of chlorate (i.e., speciation and predominance). Therefore, there is a high degree of uncertainty in the exposure and risk assessment.

- Terrestrial field dissipation data have not been submitted (164-1). There are some reports that chlorate can be persistent in the field (6 months to 5 years, depending on rate applied, soil type, fertility, organic matter, moisture, and weather conditions)[13]. However, the cited information is not readily available to assess the validity of the claims. Also, several labels report that chlorate is effective for the control of weeds for up to a year, which indicates that chlorate may persist for up to a year. Therefore, the range of persistence of chlorate in the field remains as a major uncertainty in the environmental fate behavior of this chemical.

Toxicity

- The toxicity database is limited. No chronic or reproductive toxicity data (aquatic or terrestrial organisms) considered adequate for screening level ecological risk assessment were available. These limitations in the toxicity database introduce considerable uncertainty in this risk assessment.

- Adequate non-target terrestrial plant data are not available for this assessment. Therefore, risks to non-target plants were not quantified. In the absence of such data, and based on the non-specific mode of action of chlorate, EFED presumes considerable risk to non-target plants.

- Open literature toxicity data were located that suggest that some fish and algal species may be more sensitive to chlorate toxicity than the surrogate species used in this assessment. Therefore, submission of confirmatory studies in non-guideline fish and algal species would reduce uncertainty in this assessment (see Section 3 for additional discussion). Also, a lower LD50 value in rats than used in this assessment has been reported. The Agency was unsuccessful in locating this study report for evaluation, but the data could suggest that risk to mammals may have been under-estimated.

Scope of Assessment

- Surrogate organisms were used to predict potential risks for species with no data (i.e., reptiles and amphibians). It was assumed that use of surrogate toxicity data are sufficiently

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[13] See for example the documents on chlorate found at the following URLs:

http://extoxnet.orst.edu/pips/sodiumch.htm
(For the issue of persistence in the field (6 months to 5 years), primary references cited in this review were consulted, but the basis of these claims are not documented. Therefore, the issue of persistence in the field remains uncertain).
http://wlapwww.gov.bc.ca/wat/wq/BCguidelines/chlorate.html#properties
http://www.ams.usda.gov/nop/NationalList/TAPReviews/SodiumChlorate.pdf

conservative and would capture the distribution of toxicity to the broad range of species within taxonomic groups. As previously discussed, some data located in the open literature suggest that there may be more sensitive fish and algal species than the surrogate species used in this assessment.

- Inhalation and dermal pathways for birds and mammals were not evaluated. Exposures from these pathways are assumed to be negligible given the low volatility and limited expected dermal absorption (based on physicochemical properties) of chlorate.

- Risks to top-level carnivores were not evaluated. Ingestion of grass, plants, fruits, insects, and seeds by terrestrial wildlife was considered; however, consumption of small mammals and birds by carnivores was not evaluated. In addition, food chain exposures for aquatic receptors (i.e., fish consumption of aquatic invertebrates and/or aquatic plants) were also not considered. However, chlorate's low Kow suggests that the substance is not likely to bioaccumulate.

- Sodium Chlorate is formulated with other active ingredients and with flame retardants. Potential effects that these other chemicals may have on chlorate's fate or toxicity is not considered in this assessment. However, the fire retardant may affect the persistence of chlorate in the field.[14]

- The effects of prolonged, year-after-year use of chlorate in the same field is not known, particularly in semiarid sites that require irrigation (e.g., Arizona, California), where there is a potential for salt build-up over time.

- Although some "greenhouse" studies performed in the early 1940s claim that there are no soil sterility issues, it is uncertain how many years of use at the same sites have affected the soil physical and chemical properties and microbial population.

## 3. Analysis

### *3.1. Environmental Fate*

Environmental fate data from target, guideline laboratory studies are not available. EFED has previously waived the following data requirements: (161-1), Abiotic Hydrolysis; (161-2) [Direct]

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[14] Review articles on the use of sodium chlorate as a defoliant/desiccant mention that chlorate can be persistent in the field (6 months to as long as 5 years). However, the primary references do not provide any supporting data for these claims.(See Footnote 13).

Chlorate can be highly flammable when in contact with organic material, including agricultural materials such as peat, powdered sulfur and other organic matter. Therefore, end-use products containing chlorate as the active ingredient must also contain a fire retardant, which in turn may prolong the activity of chlorate after application.

Photodegradation in Water; (161-3), Photodegradation on Soil; (162-1/162-2), Aerobic/Anaerobic Soil Metabolism; (162-3/162-4), Anaerobic/Aerobic Aquatic Metabolism ; (163-1) Mobility in Soil. Also, neither the vapor pressure nor the *n*-octanol water partition coefficient trigger the need for volatility from soil (163-2) and bioaccumulation in fish (165-4) studies. These study requirements were waived because they were not likely to produce results beyond what is already known about chlorate's environmental fate. Discussion on the justification for waiving these data requirements is in Appendix H. However, the field dissipation study requirement has never been waived and remains a data gap. Based on the lack of guideline environmental fate studies, this environmental fate assessment provides a qualitative overview of chlorate's expected environmental fate.

### 3.1.1. Environmental Fate Assessment of Sodium Chlorate

Chlorate is fully ionized in water, and is expected to dissociate immediately when added to moist soil. The very low vapor pressure and very high solubility of chlorate in water suggest that volatilization of chlorate from soil and water is an unlikely transport route. In addition, the very low *n*-octanol/water partition coefficient indicates that it is not a lipophilic chemical and therefore, has low potential to bioaccumulate in fish or other aquatic organisms.

As an anion, chlorate is not likely to adsorb to soil/sediment particulates. Therefore, on this basis alone, chlorate has a high leaching and run-off potential, particularly when heavy rainfall occurs immediately after application, where it can be washed out of the site of applications. These general routes of dissipation assume that chlorate remains as "chlorate". That is, that redox reactions of chlorate are not taken into account.

The pesticide active species in chlorate is the chlorate anion ($ClO_3^-$)[15]. Chlorate is a strong oxidizer (electron acceptor) and its mode of action as a defoliant/desiccant is linked to its oxidizing properties. As an oxidizer (electron acceptor), the reactions of chlorate in the environment are dominated by natural electron donor chemical species (reductants). Knowledge of the redox chemistry of chlorate is key in understanding its behavior in the environment, at least qualitatively. Appendix B-1 contains an expanded discussion of the redox chemistry of chlorate and related chemical species. However, an attempt has been made to qualitatively identify conditions at which chlorate may be less persistent and the products that may potentially form.

The following considerations were taken into account to qualitatively characterize the behavior of chlorate in the environment and are discussed below:

A. Redox conditions in the environment
B. Identification of electron donors (reductants) and electron acceptors (oxidizers) in the environment (inorganic and organic).

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[15] The EFED considered loading of $Na^+$ to soils and concluded that it did not have an impact in soils under most use conditions (See Appendix I).

## C. Potential reduction products of chlorate in the environment

### *A. Reducing and Oxidizing Conditions in the Environment.*

Chlorate is more stable under alkaline than acidic conditions[16]. Thus, based on pH dependence alone, chlorate would be predicted to be less persistent in acidic than alkaline natural waters. However, when a chemical element, such as chlorine, can exist in two or more oxidation states, it must also be considered whether the aqueous environment is well aerated (oxidizing environment) or polluted with organic wastes or other chemical species that may serve as electron donors (reducing environment). That is, the predominance of specific reduction products of chlorate is dependent on pH **and** redox potential ($E_h$) of the media. The redox potential can also be expressed in a p$E$ scale, which is the notation used in this assessment[17]. Likewise, the redox environment of the soil is also expected to control the redox behavior of chlorate in soils.

### *Redox Conditions in Natural Waters*

The following redox conditions have been identified for abiotic transformation in water and are classified based on their redox potential (in mV).

**Table 3-1. Redox Potentials in Water***

| Redox Conditions | Redox Potentials, mV |
|---|---|
| Strongly Oxidizing | +400 to + 800 |
| Moderately Oxidizing | + 200 to + 400 |
| Moderately Reducing | - 50 to +200 |
| Reducing | -200 to -50 |
| Strongly Reducing | - 400 to -200 |

* Wolfe, N., *et al*. 1990. Abiotic transformations in water, sediments and soil. In Pesticides in the Soil Environment, Soil Science Society of America, pp. 103-110.

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[16] Chlorate is obtained via electrolytic reactions of brine (NaCl).The efficiency of chlorate formation by this process is controlled by temperature and pH., with stability (as measured by yield) increasing with increasing pH. However, the presence of chemical species that can act as reductants (such as some ionic transition metals) decrease the efficiency of the process. This is a good example of how the presence of reductants can control the stability of chlorate.

[17] The p$E$ (p$E$= -log $E$) scale is analogous to that of pH.

The redox conditions of the water body can control the persistence of chlorate. In reducing environments (i.e., low *E*; p*E*), chlorate would be less persistent than in oxidizing environments (high *E*; p*E*). Therefore, a seasonal and geographical variability in the nature and concentration of redox species and pH is expected across the use area and time of application. Table 3-2 shows how redox conditions of natural waters may vary in natural water throughout the year. The pH of natural waters in the United States also vary by region. Generally, acidic waters are found east and alkaline waters west of the Mississippi River.

**Table 3-2. pH, pE, and Seasonal Variability**

| pH | p*E* | Seasonal Variability of pE |
|---|---|---|
| < 7 | Low | Summer; Early Fall<br>(High concentration of organic species) |
| < 7 | High | Winter; Early spring |
| > 7 | Low | Summer; Early Fall<br>(High concentration of organic species) |
| > 7 | High | Winter; Early spring |

Chlorate is used as a harvest aid. For most agricultural crops in the US, harvest time takes place in late Summer to early Fall. Therefore, based on the table above, the conditions at time of application are such that they would favor reduction of chlorate (reduce persistence) in receiving water bodies. At that time of the year, the levels of dioxygen in natural waters are low and organic matter (mostly from plant debris) are high. These two conditions favor anoxic (reducing) environments. For example, for cotton grown in the Mississippi Basin or the Eastern states, heavy rainfall and high temperatures occur at that time of the year. Assuming that all chlorate reaches surface water by runoff, the anoxic conditions would in principle reduce the persistence of chlorate in the receiving water body. EFED does not have sufficient information for all crops or for non-food/non-feed uses to correlate the timing of use and seasonal conditions affecting persistence of chlorate in natural water.

### *Redox Conditions in Soils*

If a pH of 9 is taken as the upper bound for a soil solution, the lower extreme value of p*E* in soil is -9. However, a p*E* range of - 6 (“strongly reduced”) to +12 (“strongly oxidized”) is more representative. Like for natural waters, the redox environment/behavior of the soil depends on the nature, concentration, and pH-p*E* dependence of redox species. The following redox environments can be distinguished in soils (Table 3-3).

**Table 3-3. pE and Redox Conditions in Soils**

| Medium | pE |
|---|---|
| Soil, oxic | $+7 < pE$ |
| Soil, suboxic | $+2 < pE < +7$ |
| Soil, anoxic | $pE < +2$ |

In general, chlorate is expected to be less persistent in anoxic than in oxic soils.

### B. *Electron Acceptors (Oxidizers) and Electron Donors (Reductants) in Natural Water and Soils*

#### *Organic Species*

In natural waters and in soil, organic matter is present at percentage amounts and is likely to be the dominant source of reducing potential. Even though the actual organic matter fractions may not be fully characterized, many functional groups present in organic matter can act as electron donors (reductants) or electron acceptors (oxidizers). Appendix B-1 identifies organic functional groups that are capable of undergoing redox reactions[18]. Other factors controlling the redox chemistry of a natural environment include the population of aerobic and anaerobic microorganisms.

#### *Inorganic Species*

Another factor controlling the redox environment in soils and natural water is the nature and concentration of inorganic redox species. Major chemical species associated with reducing environments are transition metals in low oxidation states (e.g., Fe(II), Mn(II)), N-species in low oxidation states ($NO_2^-$; $NH_4^+$); S(-II) (e.g $HS^-$, $S^{2-}$; polysulfido species), and others. Major chemical species associated with oxidizing environments are dissolved dioxygen ($O_2$), transition metals in high oxidation states such as Fe(III); Mn(III, IV), sulfate, and nitrate. In addition to "straight" redox reactions, many of the redox species in natural waters may also act as photosensitizers, which can accelerate the photodegradation of organic compounds. In addition, many of the transition metals may be present as mineral phases that could be involved in interfacial redox reactions (i.e., a reductant or oxidizer reacting at the mineral surface)[19].

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[18] The functional groups included in Appendix B-1 represent only potential redox moieties. They may or may not be present in all soil/natural water organic matter.

[19] For example, surface reactions of some chemical species dithiolates with semiconducting minerals (e.g., galena). For interfacial reactions such as these, the particle size distribution of the mineral phase is an important controlling factor. These reactions are very important in the separation of minerals by froth flotation.

### *C. Potential Chlorate Reaction Products in Environmental Media*

The following chlorine chemical species (bold characters) could form in the environment, when focusing only on those formed by reduction of chlorate and when considering thermodynamics data alone (Table3-4). The source of the electrons ($e^-$) can be any oxidizable moiety, be it organic matter or inorganic species. It should be noted that in the environment it is unlikely that a single reductant is present in the soil or natural water. Therefore, competitive kinetics in natural water/soil is important in determining which are the predominant reaction products. Even if a reaction product is thermodynamically favored (i.e., that it <u>can</u> form), it does not imply that it <u>will</u> form.

The chlorine chemical species also are assessed regarding the likelihood of their formation and their persistence (since each of the products are potent oxidizers themselves). In natural waters and soils, organic matter and inorganic species in soils and water are available to be oxidized by any of the reaction products, with the final likely redox product being chloride ion ($Cl^-$).

**Table 3-4. Reactions Involving Chlorate anion. (The Oxidation State in Chlorate is V)**

| Redox Half-Cell | Name of the Products | Under environmental conditions, is the product likely to . . . | |
|---|---|---|---|
| | | **Occur?** | **Persist?** |
| 1. $ClO_3^- + \rightarrow 3H_2O + 6e^- \rightarrow \mathbf{Cl^-} + 6\ OH^-$ | Chloride; Cl (-I) | Yes | Yes |
| 2 $ClO_3^- + 12\ H^+ + 10e^- \rightarrow \mathbf{Cl_2\ (g)} + 6H_2O$ | Chlorine; Cl (0) | Possibly | No,<br>It can undergo further reactions (redox; disproportionation) |
| 3. $ClO_3^- + 2H_2O + 4e^- \rightarrow \mathbf{ClO^-} + 4\ OH^-$ | Hypochlorite; Cl(I) | Possibly | No,<br>It can undergo further reactions (redox; disproportionation) |
| 4. $ClO_3^- + 3H^+ + 3e^- \rightarrow \mathbf{HClO_2} + H_2O$ | Chlorous acid[1]; Cl(II) | Possibly | No,<br>It can undergo further reactions (redox; disproportionation) |
| 5. $ClO_3^- + H_2O + 2e^{-1} \rightarrow \mathbf{ClO_2^-} + 2OH$ | Chlorite; Cl (II) | Possibly | Possibly, but like chlorate, it can undergo further reactions (redox; disproportionation) |
| 6. $ClO_3^- + 2\ H^+ + e^- \rightarrow \mathbf{ClO_2\ (g)} + H_2O$<br>7. $ClO_3^- + H_2O + e^{-1} \rightarrow \mathbf{ClO_2\ (g)} + 2OH$ | Chlorine dioxide; Cl(IV) | Possibly | No<br>Chlorine Dioxide photoreacts under sunlight |
| 8. $ClO_4^- + 2\ H^+ + 2e^{-1} \rightarrow \mathbf{ClO_3^-} + H_2O$<br>9. $ClO_4^- + H_2O + 2e^{-1} \rightarrow \mathbf{ClO_3^-} + 2OH^-$ | Perchlorate; Cl (VII) | Not Possible[2] | - |

1 Forms only in solution (i.e., cannot be isolated)
2 Disproportionation reactions[20] of chlorate indicate that chlorite and perchlorate (the highest oxidation state of chlorine) would be the reaction products. Even though formation of perchlorate from chlorate is a reaction favored by thermodynamics, it is so slow (even at 100° C) that perchlorate cannot be readily formed. Disproportionation of hypochlorite to yield chlorite is not thermodynamically favored. Therefore, formation of perchlorate from chlorate (or other oxyanions of chlorine) in the environment are not likely to occur.
3 All of the oxyanions of chlorine are strong oxidizers and, therefore, they also react with reductants.

These equations represent only half-cell reactions (Refer to Appendix B-1 for their Standard Electrode Potentials, *E*°, and other pertinent information). Although these chemical species can

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[20] Disproportionation reactions occur in when chemical species of an element can exist in multiple oxidation states (e.g. the chlorine system). The disproportionation products are a chemical species in a lower and another in a higher oxidation state than the reactant.

occur, the concentration of chlorate as well as the nature and concentration of the environmental reductants and the pH of the media are also important. As indicated earlier, very high variability in the nature and concentration of environmental reductants in soil and water is expected throughout the vast use area of chlorate. Again, it is because of this variability that the assessment can only be made at a qualitative level. Even at the laboratory level, chemical reactions of chlorine species are extremely complex to study, particularly their reaction kinetics. Laboratory studies are mainly focused on reactions with single reductants[21].

In summary, the chlorate reduction products in the environment are oxyanions of chlorine (chlorite, hypochlorite), chlorous acid, and chlorine dioxide. These products are in themselves strong oxidizers that can react in the environment and generate products in lower oxidation states. For this reason, a hundred percent conversion of chlorate to chlorite alone or to other species in lower oxidation states is unlikely. While pH/pE chlorine-species predominance diagrams can be generated for aqueous solutions at thermodynamic equilibrium, the distribution of chlorine species in actual natural waters at any given time may deviate substantially from those in the diagrams because natural waters are not themselves at equilibrium and very rarely approach equilibrium. (See Appendix B-1)

Based on thermodynamic equilibrium alone, the end reduced product of chlorate, chlorite, chlorous acid, hypochlorite, and chlorine dioxide is chloride, but how fast all of these chemical species convert to chloride cannot be estimated.

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[21] In the environment, it is unlikely that a single reductant is present in the soil or natural water. Therefore, competitive kinetics in natural water/soil would important in determining which are the predominant reaction products. Even if a reaction product is thermodynamically favored (i.e., that it can form), it does not imply that it will form.

## 3.2. Exposure

### *3.2.1. Aquatic Organisms*

Aquatic Exposure Assessment

At the present time, there is no methodology to estimate exposure concentrations in water for non-metal inorganic chemical species that can be found in different oxidation states[22] (e.g., for inorganic chemical species that can exhibit an extensive pH-pE dependent redox chemistry, such as the chlorine system). As an approximation on the impact of chlorate on surface water quality, the Tier I GENEEC-2 simulation model was used to estimate exposure concentrations in aquatic systems. Extreme assumptions in the environmental persistence of chlorate were made that resulted in high-end exposure concentrations in standard ecological pond scenario (See Table 3-6). The predicted chlorate concentrations are believed to be high because the chemical speciation of chlorate was not considered in the assessment. As discussed in Appendix B-2, under thermodynamic equilibrium conditions, chloride is likely the predominant species in natural environments. This analysis, however, indicates that chlorate can be reduced to chloride, but not how fast the reduction will occur. Appendix J-2 presents pE/pH predominance and 3D activity fraction diagrams for aqueous chlorine-system species at thermodynamic equilibrium[23] and it is an extension of the mole fraction computations of chlorine species mole fractions used in the Drinking Water Assessment (D303556; 01/05/05).

Tier I- GENEEC-2 Concentrations in Aquatic Environments

Aquatic estimated environmental concentrations (EECs) were calculated using the GENEEC-2 model, which assumes removal of a bulk of the pesticide at one time from a 10 hectare field into a 1 acre standard ecological pond.[24] Additional details on this model may be obtained from the following url:

www.epa.gov/oppefed1/models/water/index.htm .

*Agricultural Uses*

Aquatic EECs from agricultural uses ranged from 0.36 to 0.91 mg/L (360 to 910 ug/L) and are presented in Table 3-5 below. GENEEC-2 model inputs are presented in Table 3-6. It should be noted that there are no input parameters that take into account the redox behavior of chlorate.

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[22] The EFED, however, has utilize chemical speciation models to identify predominant copper species in aquatic media, but models exist to handle speciation of metals as a function of pE-pH (MINTEQ).

[23] For a definition of activity and activity coefficients see Appendix B-1

[24] 20,000 $m^3$ (20,000,000 L) water volume, 2-meter deep pond with no outlets

Therefore, it was assumed that unchanged chlorate runs off into surface water, where it remains as chlorate.

**Table 3-5. Aquatic EECs of Sodium Chlorate Calculated by GENEEC-2 Agricultural Uses**

| Maximum Application Rate (No. Of Applications / Interval) | Crops | Predicted Peak EEC (ug/L)[a] |
|---|---|---|
| 7.5 lbs a.i./Acre (2/30) | Cotton | 910*<br>*Assuming virtually no degradation between applications |
| 12.5 lbs a.i./Acre Single application | Chili peppers; potatoes | 760 |
| 7.5 lbs a.i./Acre Single application | Dried beans; corn; cotton, flax, guar; southern peas; safflower; sorghum; soybeans; sunflower | 450 |
| 6 lbs a.i./Acre Single application | Agricultural fallow land; dried beans; corn; cucurbits[b], flax, gourds; guar; southern peas; white/Irish potatoes; rice; safflower; sorghum; soybeans; sunflower, wheat | 360 |

[a] Chronic EECs are not presented because no chronic toxicity values are available

[b] The application rate for cucurbits is 6.1875 lbs a.i./Acre

**Table 3-6. Selected Input Parameters Used in the GENEEC-2 Estimates**

| Information Needed by GENEEC | Input Parameter | Comment |
|---|---|---|
| Method of application<br>Maximum application rate (lbs ai/A) | Aerial | All labels allow for aerial applications for agricultural uses. |
| Kd | 0 | Chlorate is an anion. Thus, it is expected to be very mobile in soils (high leaching and runoff potential)<br>In addition, it has a very low potential to volatilize from soils and water (very low vapor pressure and extremely high solubility in water) |

**Table 3-6. Selected Input Parameters Used in the GENEEC-2 Estimates**

| Information Needed by GENEEC | Input Parameter | Comment |
|---|---|---|
| Aerobic Soil Metabolism | 0 | Persistence in soil is highly dependent on type of soil, pH, other chemical species present in soil, soil moisture temperature, precipitation (i.e. high spatial and temporal variability). The only persistence information comes from a USDA report, which is not reported in terms of half-lives. Because persistence was expressed in terms of "toxic persistence" and that this ranged from 6 to 12 months *ad minimum* the half-life was assumed to be zero. In addition, chlorate is a soil sterilant. |
| Aerobic Aquatic Metabolism | 0 | See comment under "Hydrolysis" |
| [Direct] Photolysis in Water | 0 | The chlorate anion does not absorb energy in the wavelength range of sunlight. Therefore, it lacks the necessary condition for a chemical to undergo direct photolysis. See comment under "Hydrolysis". |
| Hydrolysis (abiotic) | 0 | The chlorate anion is not expected to react with water.[a] |
| Solubility in water ($mgL^{-1}$; ppm) | $1 \times 10^6$ at 25° C | Chlorate is a fully ionized salt in water |

[a] Theoretically, it may be possible to estimate the redox potential(s) conditions at which formation chlorite may be most favored. The "chlorine-chlorine anions-oxyanions" redox chemistry is well known. GENEEC, FIRST and SCI-GROW do not have the capability to handle redox data and to predict the distribution and predominance of reduction products of chlorate. Even EXAMS cannot provide such information.

The behavior of chlorate (an oxidant) is controlled by the nature and concentration of reducing (i.e., electron donors) chemical species in water and other environmental media. A major chemical species that control the redox behavior of chlorate in aqueous media is the concentration of nitrate. An important reduced species of chlorate is chlorite ($ClO_2^-$). In addition, some of the constituents of natural waters have the potential to act as photosensitizers

## Non-Agricultural Uses

A range of chlorate EECs from its non-agricultural uses is in Table 3-7. Model inputs are equivalent to those in Table 3-6 except that ground, instead of aerial, application was modeled. EECs predicted by GENEEC-2 ranged from 3.1 to 39 mg/L. These EECs are likely very conservative because the model assumes that a contiguous drainage basin flows into a pond that is10-times smaller than the treated area. The application scenarios for the non-agricultural uses may not be consistent with the scenario assumed by GENEEC-2. Also, the environmental fate data are not adequate to allow for further refinement of aquatic EECs using higher tier models such as PRZM/EXAMS as discussed in the problem formulation.

| Table 3-7. Range of Aquatic EECs for Sodium Chlorate Calculated by GENEEC-2 (Non-Agricultural Uses) | | |
|---|---|---|
| **Application Rate** | **Use** | **Predicted Peak EEC (ug/L)[a]** |
| 52 to 650 lbs a.i./Acre (single applications)[b] | All non-Agricultural uses | 3,100 to 39,000 |

[a] Chronic EECs are not reported because no chronic toxicity values are available for comparison

[b] The application rate of 650 lbs a.i. acre is only labeled for pre-paving uses, which will not likely result in exposure to aquatic organisms. The highest application rate that would likely result in exposure to aquatic organisms is 520 lbs a.i./acre. Uses for this rate include fence lines, building perimeters, ditch banks, picnic areas, vacant lots, and cemeteries. The peak EEC for this application rate is 31,000 ug/L.

### *3.2.2. Exposure to Terrestrial Organisms - Agricultural Uses*

ELL-FATE predicted upper 90th percentile and mean chlorate EECs on selected terrestrial animal food items are presented in Table 3-8 below. In accordance with EFED policy, the default foliar dissipation half-life of 35 days was used to calculate chlorate's decline in residue concentrations between applications because no adequate foliar dissipation half-life data were submitted. This only affects the EEC for cotton because other uses were not modeled using multiple applications.

| Table 3-8. EECs (mg ai/kg-food item) for Terrestrial Animal Risk Assessment Calculated by ELL-FATE v. 1.4 Agricultural Uses | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Max. Labeled Application Rate (No. Of Applications / Interval) | Crops | Predicted 90th Percentile Residue Levels | | | | Predicted Mean Residue Levels | | | |
| | | short grass | tall grass | broadleaf forage, small insects | fruit, pods, seeds, small insects | short grass | tall grass | broadleaf forage, small insects | fruit, pods, seeds, small insects |
| 12.5 lbs a.i./Acre Single application | Chili peppers; white/Irish potatoes | 3000 | 1400 | 1700 | 190 | 1100 | 450 | 560 | 88 |
| 7.5 lbs a.i./Acre (2/30) | Cotton | 2800 | 1300 | 1600 | 170 | 990 | 420 | 520 | 81 |
| 7.5 lbs a.i./Acre Single application | Corn; flax, guar; southern peas; rice; safflower; sorghum; soybeans; sunflower | 1800 | 830 | 1000 | 110 | 640 | 270 | 340 | 53 |
| 6 lbs a.i./Acre Single application | Agricultural fallow land; dried beans; corn; cucurbits[a], flax, gourds; guar; southern peas; white/Irish potatoes; rice; safflower; sorghum; soybeans; sunflower | 1400 | 660 | 810 | 90 | 510 | 220 | 270 | 42 |

a The application rate for cucurbits is 6.1875 lbs a.i./Acre

### *3.2.3. Terrestrial Organisms - Non-Agricultural Uses*

End-use products for the non-agricultural uses include granule (broadcast applications) and soluble concentrates (spray applications). EFED uses different methods to assesses exposure to terrestrial animals for each of these end-use products.

Spray Applications

EECs for the spray applications were determined using the same methods described for the agricultural uses. EECs on selected food items resulting from application rates labeled for non-agricultural uses are listed in Table 3-9 below. Only the highest and lowest EECs from these uses are presented. EECs from all non-agricultural uses are in Appendix K.

**Table 3-9. EECs (mg ai/kg-food item) for Terrestrial Animal Risk Assessment Calculated by ELL-FATE v. 1.4**
**(Non-Agricultural Uses)**

| **Use** | **Application rate (lbs/Acre)** | **Predicted 90th Percentile Residue Levels** | | | | **Predicted Mean Residue Levels** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **Short grass** | **Tall grass** | **Broadleaf forage, small insects** | **Fruit, pods, seeds, small insects** | **Short grass** | **Tall grass** | **Broadleaf forage, small insects** | **Fruit, pods, seeds, small insects** |
| Industrial sites such as driveways, paths, brick walks, cobble gutters, tennis courts | 52 | 12500 | 5700 | 7000 | 780 | 4400 | 1900 | 2300 | 360 |
| Parking lots, fence lines, building perimeters, ditch banks, picnic areas, vacant lots, wood decks, bleachers, cemeteries, fuel tanks, runways, helo pads, etc. | 520[a] | 125,000 | 57,000 | 70,000 | 7800 | 44,000 | 19,000 | 23,000 | 3600 |

[a] The application rate for pre-paving is 650 lbs a.i./Acre; however, this use pattern would not likely result in exposure to terrestrial organisms.

Granular Applications

For granular applications, estimation of pesticide loading per unit area (mg/ft$^2$) was calculated (Table 3-10 below). This approach is intended to represent exposure via multiple routes (e.g., incidental ingestion of contaminated soil, dermal contact with treated seed surfaces and soil during activities in the treated areas, preening activities, and ingestion of drinking water contaminated with pesticide) and not just direct ingestion. It should be noted, however, that most of chlorate's exposure will be via the oral route because it is not volatile and it is not expected to appreciably absorb through the skin. Although a bird's or mammal's habitat is not limited to a square foot, there is presumably a direct correlation between the concentration of a pesticide in the environment (mg/ft$^2$) and the chance that an animal will be exposed to a concentration that could adversely affect its survival. Further description of the mg/ft$^2$ index is in U.S. EPA, 2004 and U.S. EPA, 1992. Chlorate granules are applied via broadcast treatment; therefore, EFED assumes that 100% of the granules are unincorporated for the exposure assessment. EFED does not currently assess chronic risk from long-term exposure to granules.

**Table 3-10. Range of Terrestrial EECs (Granular Applications) for Sodium Chlorate Non-Agricultural Uses**

| Use | Application Rate (lbs a.i./Acre) | EEC (mg/ft$^2$)$^{a,b}$ |
|---|---|---|
| Parking lots, under asphalt paving, fence lines, building perimeters, ditch banks, picnic areas, vacant lots, wood decks, bleachers, cemeteries, fuel tanks, runways, helo pads, etc. | 520 | 5400 |
| Around buildings, storage areas, fences, pumps, machinery, fuel tanks, recreational areas, roadways, guard rails, airports, rights of ways. | 160 | 1700 |

a EEC = Application rate (lbs/Acre) x 453,000 mg/lb ÷ 43,600 sq ft/Acre
b Only calculations for the high and low extreme application rates are presented

### *3.2.4. Terrestrial Organisms, Non-Target Plants*

Adequate toxicity data are not available to allow for a characterization of potential risk to non-target plants. Therefore, exposure to non-target plants was not estimated.

### 3.2.5. Uncertainties in the Exposure Assessment

A number of uncertainties were identified in this exposure assessment:

### Aquatic and Terrestrial EECs

- Stability of chlorate in terrestrial and aquatic environments is uncertain, but it is expected to exhibit wide spatial and seasonal variability. Some labels indicate that chlorate may be effective as an herbicide after a single application for up to a year, which suggests that there is potential for chronic exposure.

- As discussed in the problem formulation (Section 2), there is considerable uncertainty in the rate of formation/decline of redox products of chlorate (i.e., the kinetics of formation/decline). Although thermodynamics indicates which products *can* form (i.e., speciation), it does not imply that they *will* form and at what rate. Redox kinetics of the "chlorine system" is very complex, studies are very difficult, and most of the data available are not suitable for estimating speciation and predominance in terrestrial and aquatic environments. GENEEC-2 and PRZM-EXAMS are not ideal simulation models for chemicals in which one of the elements that can exist in more than one oxidation state. Therefore, conservative assumptions were made that likely resulted in an over-estimation of exposure to chlorate. Even simulation models used in drinking water chlorination are not adequate for open field environments.

- Chlorate as a defoliant on cotton is used in the late summer to early fall, where the redox conditions in water and soil favor dissipation of chlorate by reduction. That is, high temperature and humidity, as well as higher reducing conditions of the media are such that chlorate can be reduced to other related chemical species. However, no adequate information was made available to the Agency about the time of the year when chlorate is used for other crops (that is, the typical harvest time across the crop sites). Therefore, it is uncertain if the seasonal redox conditions favor dissipation of chlorate for these crops.

### Terrestrial EECs

- Many of the non-agricultural uses will likely result in small contiguously treated areas, which would reduce the likelihood that an animal would consume 100% of its diet from chlorate treated areas.

- Inhalation and dermal exposure pathways for birds and mammals were not evaluated. Exposures from these pathways are assumed to be negligible given the low volatility and limited expected dermal absorption of chlorate.

- Because the herbicide is absorbed by plants relatively rapidly and kills most exposed plants within several days to several weeks after exposure, some food items may not be attractive to herbivores for an extended period of time after treatment.

Aquatic EECs

- GENEEC-2 assumes no foliar interception, which likely resulted in an over-estimation of exposure. Foliar interception is likely to occur because chlorate absorbs into plants. Any chlorate that absorbs into the plant will not likely enter surface water.

- GENEEC-2 assumes a contiguous drainage basin that flows into a pond that is10-times smaller than the treated area. The application scenarios for the non-agricultural uses may not be consistent with the scenario assumed by GENEEC-2.

## 3.3. Ecological Effects Characterization

### *3.3.1. Aquatic Toxicity*

Fish

Supplemental[25] acute 96-hour flow-through toxicity studies in bluegill and sheepshead minnows have been submitted (MRIDs 418872-02 and 418872-07) and are summarized in Table 3-11. LC50s from these studies were >1000 mg/L, consistent with a "practically non-toxic" designation. No effects were observed in sheepshead minnows or bluegill at up to 1000 mg/L (nominal concentrations).

A supplemental 96-hour acute flow-through study in rainbow trout was also submitted (MRID 418872-03). The NOAEC in this study was 600 mg/L (1/10 rainbow trout died at 1000 mg/L). However, the fish appear to have been exposed to lower concentrations towards the end of the study as indicated by a reduction in conductivity between study days 3 and 4. Conductivity is directly related to aqueous chlorate concentration. Because the chlorate concentration associated with mortality observed in this study is uncertain, submission of a confirmatory study would reduce uncertainty in this assessment.

Appendix L summarizes publically available toxicity data on chlorate as reported in EPA's ECOTOX database.[26] Published acute toxicity data in fish are generally consistent with a "practically non-toxic" classification. All reported LC50 values are >1000 mg/L with a single exception. Woodiwiss et al. (1974) (summarized in Appendix L) reported a 48-hour LC50 of 7.3 mg/L in brown trout for chlorate, which indicates that brown trout could be considerably more sensitive to chlorate than other fish species. No other studies in brown trout were located, and sufficient information was not available in the publication to allow for an evaluation of data quality. Also, it appears that chlorate was tested in the presence of another unspecified flame

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[25] Most of the aquatic toxicity studies were previously considered invalid, but were upgraded based on the results of a confirmatory acute static toxicity study in daphnids.

[26] http://www.epa.gov/ecotox

retardant. Therefore, it is uncertain if the toxicity observed in this study was caused by chlorate, the other unidentified chemical, or a combination of the two. Nonetheless, these data *could* suggest that there may be considerable variability in species sensitivity to chlorate toxicity. Alternatively, these data could suggest that some formulated products are more toxic to fish because all chlorate formulations contain fire retardants.

No chronic toxicity studies have been submitted to the Agency or were identified in the ECOTOX database. Chronic toxicity in freshwater and saltwater fish remains a data gap.

Aquatic Invertebrates

Two supplemental 48-hour studies in daphnids (MRIDs 418872-04 and 438748-01) have been submitted to the Agency. The EC50s were >1000 mg/L and 920 mg/L, respectively (consistent with a "practically non-toxic" designation). In MRID 418872-04, no effects were observed at any concentration up to 1000 mg/L (nominal). In MRID 438748-01, the NOAEC was 410 mg/L (55% mortality was observed at 1020 mg/L). This study was considered supplemental because the pH was 8.2 to 8.4, which is higher than recommended by EPA guidelines (7.2 - 7.6). The higher pH in this study may have resulted in an underestimation of toxicity because lower pH conditions are expected to promote reduction of chlorate. It is uncertain if higher concentrations of more toxic reduction products such as chlorite may form at pH environments of 7.2 - 7.6 compared with the pH environments used in MRID 438748-01. The EC50 of chlorite in a core study submitted to the Agency (MRID 940680-09) was 0.15 mg/L. Therefore, the higher pH in this study may have resulted in an underestimation of chlorate's toxicity under some environmental conditions.

The submitted study in mysid shrimp (MRID 418872-06) produced results that were consistent with the results from the submitted daphnid studies. The 96-hour LC50 in mysid shrimp was >1000 mg/L; 2/20 mysids died at 1000 mg/L, and 1/20 died at 590 mg/L. No other mortalities or signs of toxicity were noted at any concentration tested. This study is classified as **supplemental** because the test substance concentrations were not analytically confirmed. Additional details are included in Appendix M.

Also, EC50s for Eastern oysters exposed to chlorate via flow through conditions were >1000 mg/L (MRID 418872-05). No treatment related mortalities occurred. Shell growth at 250, 500, and 1000 mg/L was 10%, 15%, and 30% lower than controls, respectively. Shell growth at all other concentrations was equivalent to or greater than controls. Additional details are included in Appendix M of this assessment. This study is classified as **supplemental**.

Publically available studies identified using the Agency's ECOTOX database are summarized in Appendix L. No studies were located that report toxicity values that are more sensitive than the submitted studies in daphnids. Therefore, these data were not used in this assessment. No chronic studies in aquatic invertebrates have been submitted to the Agency or were identified in the ECOTOX database.

Aquatic Plants

A **core** 96-hour static study in green algae (MRID 418872-01) was submitted. The EC50 in this study was 133 mg/L, which is consistent with a “practically non-toxic” designation. The NOAEC was 62.5 mg/L. It should be noted that green algae are generally poor (insensitive) surrogates for aquatic vascular plants. No studies in the following plant species have been submitted, which are required for herbicides: *Lemna gibba* (duckweed), *Skeletonema costatum* (a marine diatom), *Anabaena flos-aquae* (a blue-green bacterium), and a freshwater diatom.

Publically available studies identified using the Agency’s ECOTOX database are summarized in Appendix L. Data located in the open literature suggest that brown algae may be considerably more sensitive than green algae to chlorate. A 14-day EC50 of 0.012 mM (≈1 mg/L) and NOAEC of <0.005 mM (≈0.42 mg/L) was reported for brown algae (van Wijk et al., 1997, described in Appendix M). Sufficient detail was not available in the published study report to allow for a comprehensive assessment of data adequacy.[27] Nonetheless, these data suggest that brown algae may be considerably more sensitive than green algae to chlorate toxicity. Other aquatic plant toxicity values identified in the open literature were not more sensitive than the EC50 from the submitted study in green algae.

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[27] Key missing details included whether the study conduct followed standard guidelines, whether chlorate concentrations were analytically confirmed, the test concentrations, dose-response information from each concentration, water quality parameters from individual cultures.

| Table 3-11. Aquatic Toxicity Profile for Sodium Chlorate | | | | |
|---|---|---|---|---|
| **Endpoint** | **Environment/ Species** | **Toxicity Value Used in Risk Assessment** | **Reference** | **Comment** |
| Acute Toxicity to Fish | Freshwater/ Rainbow trout | LC50>1000 mg/L | MRID 418872-03 | **Supplemental.** The NOAEC was 600 mg/L in this 96-hour flow-through study (1/10 fish died at 1000 mg/L). Based on conductivity data (conductivity increases as chlorate concentrations increase), the fish appear to have been exposed to lower concentrations between days 3 and 4 of the study, which may have resulted in an underestimation of toxicity. Chlorate concentrations were not analytically confirmed. |
| | Bluegill | LC50>1000 mg/L | MRID 418872-02 | **Supplemental.** Chlorate concentrations were not analytically confirmed. No effects were observed at any concentration. |
| | Saltwater/ Sheepshead minnow | LC50 >1000 mg/L | MRID 418872-07 | **Supplemental**. The NOAEC was 1000 mg/L. Test concentrations were not analytically confirmed. |
| Chronic Toxicity to Fish | Freshwater | No Data | Not applicable | No data are available. Chlorate may be persistent under some environmental conditions. Therefore, submission of chronic toxicity data would reduce uncertainty in this assessment. |
| | Saltwater | No Data | Not applicable | |
| Acute Toxicity to Invertebrates | Freshwater *Daphnia magna* | 48-hr EC50: 920 mg/L | MRIDs 438748-01; 418872-04 | **Supplemental.** In MRID 438748-01, *Daphnia magna* were tested in a 48-hour static study. The NOAEC and LOAEC was 410 mg/L and 1000 mg/L, respectively (55% mortality occurred at 1000 mg/L). The study is supplemental because the pH in the study was 8.2 to 8.4, which is higher than EPA guidelines (7.2 - 7.6). The pH conditions used may have resulted in an underestimation of chlorate's toxicity because some reduction products of chlorate are considerably more toxic to invertebrates.<br>In MRID 418872-04, no effects occurred at up to 1000 mg/L. |
| | Saltwater Mysid shrimp | 96 hr LC50: >1000 mg/L | MRID 418872-06 | **Supplemental.** The test concentrations were not analytically confirmed. The LC50 in this study was >1000 mg/L; 10% (2/20) mortality occurred at 1000 mg/L. |

**Table 3-11. Aquatic Toxicity Profile for Sodium Chlorate**

| Endpoint | Environment/ Species | Toxicity Value Used in Risk Assessment | Reference | Comment |
|---|---|---|---|---|
| | Saltwater<br>Eastern oyster | EC50 >1000 mg/L | MRID 418872-05 | **Supplemental**. Test concentrations were not analytically confirmed in this 96-hr flow-through study. A 10%, 15%, and 30% reduction in shell growth was observed at 250, 500, and 1000 mg/L, respectively. |
| Chronic Toxicity to Invertebrates | Freshwater | No Data | Not applicable | No studies were submitted. |
| | Saltwater | No Data | Not applicable | No studies were submitted. |
| Toxicity to Aquatic Plants | Freshwater<br>*Selenastrum capricornutum* | EC50: 133 mg/L<br>NOAEC: 62.5 mg/L | MRID 418872-01 | **Core.** The NOAEC and LOAEC was 62.5 and 125 mg/L, respectively. No other aquatic plant toxicity studies have been submitted. Data in four other aquatic plant species are required for herbicides (see Table 1-3). |

Toxicity of Sodium Chlorite to Aquatic Organisms

Chlorite has been shown to more toxic than chlorate to fish and aquatic invertebrates. Scientifically valid chlorite toxicity data that have been submitted to and evaluated by the Agency (D16650) are summarized below.

Acute toxicity to fish (96-hr LC50s): Rainbow trout (MRID 94068007): **360 mg/L**
Bluegill (MRID 94068006): **420 mg/L**

Acute toxicity to aquatic invertebrates (48-hr EC50): Daphnids (MRID 94068009): **0.15 mg/L**

### *3.3.2. Terrestrial Organism Toxicity*

Birds

The data indicate that chlorate is practically non-toxic to birds after acute oral gavage or subacute dietary exposures (Table 3-12). No mortalities or signs of toxicity were observed in the submitted acute or subacute toxicity studies in mallard ducks or bobwhite quail at levels that exceeded the limit dose for the type of study submitted.

No reproduction toxicity studies in birds have been submitted.

## Mammals

Chlorate is practically non-toxic to mammals after single oral gavage administration. An LD50 of >5000 mg/kg-bw was reported in an acceptable acute oral toxicity study in rats. In this study, 1/10 animals died at 5000 mg/kg-bw. Necropsy findings of the only rat that died during the study showed green discoloration of the intestines, a light green fluid on the stomach, pink liquid in the abdominal cavity and dark red lung discoloration. No gross lesions were observed in the 9/10 rats that survived to study termination.

A 2-generation reproduction toxicity study in mammals is not available for use in risk assessment; however, multiple subchronic and chronic studies are available (Appendix M). EFED does not use these types of studies to calculate risk quotients. In the absence of a 2-generation toxicity study, short-term and subchronic studies were used to qualitatively characterize risk to mammals (data summarized in Table 3-12 below and further described in Appendix M). These studies demonstrate that repeated oral exposures to chlorate have induced effects in laboratory animals that could affect fecundity, growth, or reproductive success at daily doses of $\geq \approx$100 mg/kg-bw. Common effects observed in these studies include reductions in growth rate, pituitary and thyroid effects, and blood toxicity. NOAELs from repeated-dose oral toxicity studies ranged from approximately 30 mg/kg-day to 100 mg/kg-day. Study duration ranged from 21 days to 90 days. Submitted developmental toxicity studies suggest that chlorate is not a developmental toxicant.

**Table 3-12. Terrestrial Toxicity Profile for Sodium Chlorate**

| Assessment Endpoint | Species | Toxicity Value Used in Risk Assessment | Reference | Comment |
|---|---|---|---|---|
| Acute toxicity to birds, LD50 | Mallard duck | >2510 mg/kg-bw | MRID 421494-01 | **Supplemental study.** No mortality and no clinical signs of toxicity were observed in this study. Treated birds generally consumed less food than controls; however, a clear dose-response relationship was not observed. The study was supplemental because chlorate's purity was not reported. |
| Subacute toxicity to birds, LC50 | Mallard and bobwhite | >5620 mg/kg-feed (both species) | MRID 418199-07 and 418199-08 | **Acceptable studies.** No effects were observed in these studies. |
| Reproductive toxicity to birds | **No available data** | | | |
| Acute toxicity to mammals | Rat | LD50: >5000 mg/kg-bw | MRID 41819901 | **Acceptable study**. At 5000 mg/kg-bw, 1/10 animals died. |

**Table 3-12. Terrestrial Toxicity Profile for Sodium Chlorate**

| Assessment Endpoint | Species | Toxicity Value Used in Risk Assessment | Reference | Comment |
|---|---|---|---|---|
| Reproductive Toxicity in Mammals | Sufficient data not available | None used | Not applicable | A 2-generation toxicity study is not available. Developmental toxicity studies (MRID 40460401; NTP, 2002) suggest that chlorate is not a developmental toxicant (summarized in Appendix M). |
| Chronic toxicity to mammals | Rat | None used | MRID 40444801;<br>MRID 40460402;<br>McCauley *et al*, 1995;<br>Kurokawa *et al*, 1985;<br>Heywood *et al*, 1972<br>NTP, 1999 | Commonly reported toxic effects include blood toxicity, thyroid effects (hypertrophy and thyroid hormone level changes), pituitary toxicity, and body weight reduction (See Appendix M). NOAELs ranged from approximately 30 mg/kg-day to 100 mg/kg-day. |

Terrestrial Plants

Tier I studies were submitted to the Agency that showed an application of 348 lbs a.i./Acre was toxic to monocots and dicots. These studies are summarized below and are further described in Appendix M. Effects of a single application of chlorate at 348 lbs a.i./Acre was evaluated in 10 plant species. In the vegetive vigor study, almost all plants were dead by 11 days (all species). Phytotoxic effects included chlorosis, necrosis and stunting. Cucumber exhibited the greatest reduction for a dicot, with 95.4% mean fresh weight inhibition and sorghum exhibited the greatest reduction for a monocot, with 83.1% mean fresh weight inhibition. The $EC_{25}$ and NOAEC were <348 lbs a.i./A for all test species.

In the seed germination and seedling emergence studies, an increase in the number of plants that failed to germinate compared with controls for all test species was observed compared to the controls by Day 5. The 348 lbs a.i./A treatment group percent inhibitions exceeded 25% for the mean fresh weights of all test species. Phytotoxic effects included chlorosis, necrosis, stunting, and distortion. Cucumber exhibited the greatest reduction for a dicot, with 98% mean fresh weight inhibition, and corn exhibited the greatest reduction for a monocot, with 90% mean fresh weight inhibition. The $EC_{25}$ and NOAEC for this study were <348 lb a.i./A for all test species.

Although these Tier I studies were adequately conducted, the data do not allow for derivation of EC25, EC05, or NOAEC values, precluding their use in quantitative risk assessment.

Toxicity of Chlorite to Terrestrial Organisms

Chlorite has been shown to more toxic to mammals and birds than chlorate. Chlorite toxicity data that have been submitted to and evaluated and considered valid by the Agency are summarized below.

*Acute toxicity to birds (LD50):* Bobwhite quail (MRID 254177): **467 mg/kg-bw**
*Subacute toxicity to birds (LC50):* Bobwhite quail (MRID 94068008): **>5000 mg/kg-diet**
*Subacute toxicity to birds (LC50):* Mallard duck (MRID 94068005): **>5000 mg/kg-diet**
*Acute toxicity to mammals (LD50):* **105-136 mg/kg-bw**[26]
*Chronic toxicity to mammals (NOAEC from a 2-generation toxicity study in rats)*: **70 mg/kg-diet**[28]

### 3.3.3. Incident Data Review

A review of the EIIS database for ecological incidents involving chlorate was completed on October 25, 2004. There were no chlorate incidents in the database.

## 4. Risk Characterization

### 4.1. Aquatic Organisms

Summary of Conclusions

- Risk (acute exposure) to fish is presumably lower than the Agency's level of concern for all labeled chlorate uses.
- No acute risk to aquatic invertebrates was identified at levels of concern to the Agency from exposure to chlorate; however, formation of chlorite could result in risk to aquatic invertebrates at levels of concern to the Agency. These potential risks cannot be quantified.
- No toxicity data are available to allow for characterization of potential risk to aquatic organisms from chronic exposures.

### 4.1.1. Fish, Freshwater and Saltwater

Risk Estimation

Formal risk quotients were not calculated for fish because the proximity of the LC50 to the highest concentration tested (1000 mg/L) could not be estimated. However, 1000 mg/L was considered a toxic concentration to fish because it induced 10% mortality in rainbow trout

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[28] Data were taken from EFED's science chapter for reregistration eligibility decision for sodium chlorite (D16650, 1993) and from U.S. EPA's Drinking Water Health Advisory for chlorine dioxide, chlorite and chlorate (1996).

(418872-03).[29] Table 4-1 below presents ratios of chlorate's EECs to the toxic concentration of 1000 mg/L. Because these values are not LC50s, which are the toxicity values usually used to derive risk quotients, they can be used to estimate high-end risk to exposed fish.

**Table 4-1. Proximity of Chlorate's EECs to the Toxic Concentration of 1000 mg/L in Fish (Agricultural and Non-Agricultural Uses)**

| Use | Highest EEC | Toxic Concentration[a] | Ratio of EEC to the Toxic Concentration |
|---|---|---|---|
| All agricultural uses | ≤0.91 mg/L | 1000 mg/L | <0.01 |
| All non-Agricultural | ≤39 mg/L | 1000 mg/L | ≤0.039 |

[a] LC50s are from supplemental studies in bluegill, rainbow trout, and sheepshead minnows. No evidence of toxicity was observed at up to 1000 mg/L in bluegill or sheepshead minnows; 10% mortality was observed in rainbow trout (418872-03) at 1000 mg/L. Therefore, 1000 mg/L was considered to represent a potentially toxic concentration to some fish species. The proximity of the LC50 to 1000 mg/L is uncertain. However, the conductivity data suggest that fish exposed at the nominal concentration of 1000 mg/L may have been exposed to lower concentrations (see Section 3 for details).

Risk Description - Interpretation of Direct Effects

All EECs were more than 20-fold lower than the toxic concentration observed in fish of 1000 mg/L (all risk quotients would be <0.05). Therefore, the currently labeled chlorate uses presumably do not pose risk at levels of concern to the Agency from agricultural or non-agricultural uses. Uncertainties in this assessment are discussed in Section 4.1.4.

### *4.1.2. Aquatic Invertebrates*

Risk Estimation

Risk quotients based on an EC50 from a supplemental 48-hour acute toxicity study in daphnids and EECs calculated by GENEEC-2 are presented in Table 4-2 below. Formal risk quotients were not calculated for saltwater invertebrates because the proximity of the LC50 from a supplemental 96-hr study (MRID 438748-01) to the highest concentration tested (1000 mg/L) could not be estimated. However, 1000 mg/L was considered a toxic concentration to the surrogate saltwater invertebrate mysid shrimp because it induced 10% mortality at that concentration. Table 4-3 below presents ratios of chlorate's EECs to the toxic concentration of 1000 mg/L.

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| Table 4-2. Acute Freshwater Aquatic Invertebrate Risk Quotients<br>Agricultural and Non-Agricultural Uses of Sodium Chlorate | | | | | |
|---|---|---|---|---|---|
| **Use** | **Application Rate** | **Maximum EEC** | **EC50[a]** | **RQ** | **LOC Exceedance** |
| Agricultural uses | All labeled rates | ≤0.91 mg/L | 920 mg/L | <0.01 | No LOC exceeded |
| | | | | <0.01 | No LOC exceeded |
| Non-agricultural uses | All labeled rates | ≤39 mg/L | 920 mg/L | ≤0.041 | No LOC exceeded |
| | | | | <0.039 | No LOC exceeded |

[a] The freshwater invertebrate EC50 used in this analysis was based on a supplemental acute 48-hour study in daphnids (438748-01); 55% mortality occurred at 1000 mg/L.

| Table 4-3. Proximity of Chlorate's EECs to the Toxic Concentration of 1000 mg/L in Saltwater Invertebrates<br>Agricultural and Non-Agricultural Uses of Sodium Chlorate | | | | |
|---|---|---|---|---|
| **Use** | **Application Rate** | **Maximum EEC** | **Toxic Concentration[a]** | **Ratio of EEC to the Toxic Concentration** |
| Agricultural uses | All labeled rates | ≤0.91 mg/L | Saltwater: >1000 mg/L[a] | <0.01 |
| | | | | <0.01 |
| Non-agricultural uses | All labeled rates | ≤39 mg/L | Saltwater: >1000 mg/L[a] | ≤0.041 |
| | | | | <0.039 |

[a] The saltwater invertebrate LC50 was >1000 mg/L; 10% (2/20) mortality at 1000 mg/L (MRID 418872-06).

Risk Description - Interpretation of Direct Effects

For chlorate's agricultural and non-agricultural uses, the acute risk quotients for freshwater aquatic invertebrates indicate that there is no risk that exceed the Agency's level of concern. The data also suggest that there is no risk to saltwater invertebrates at the Agency's level of concern from any of chlorate's labeled uses. Uncertainties in this assessment are discussed in Section 4.1.4.

### *4.1.3. Aquatic Plants*

Risk Estimation

Risk quotients based on a vascular plant EC50 of 133 mg/L and a NOAEC of 62.5 mg/L and EECs calculated by GENEEC-2 are in Table 4-4 and Table 4-5 below.

**Table 4-4. Non-Endangered Species Algal Risk Quotients**
**Agricultural and Non-Agricultural Uses**

| Use | Application Rate | Maximum Peak EEC | EC50 or LC50 | RQ | LOC Exceedance |
|---|---|---|---|---|---|
| Agricultural uses | All labeled rates | ≤0.9 mg/L | 133 mg/L | <0.01 | No LOC exceeded |
| Non-Agricultural | All labeled rates | ≤39 mg/L | 133 mg/L | ≤0.29 | No LOC exceeded |

**Table 4-5. Endangered Species Algal Risk Quotients**
**Agricultural and Non-Agricultural Uses**

| Use | Application Rate | Maximum Peak EEC$^a$ | NOAEC | RQ | LOC Exceedance |
|---|---|---|---|---|---|
| Agricultural uses | All labeled rates | ≤0.9 mg/L | 62.5 mg/L | ≤0.014 | No LOC exceeded |
| Non-Agricultural | All labeled rates | ≤39 mg/L | 62.5 mg/L | ≤0.62 | No LOC exceeded |

Risk Description - Interpretation of Direct Effects

No LOCs were exceeded from chlorate's agricultural or non-agricultural uses. Also, the NOAEC from the green algae study was 62.5 mg/L, which is lower than the peak chlorate EEC of 39 mg/L. Therefore, risk to endangered species is also presumably lower than the Agency's level of concern. However, risk to algae cannot be precluded. No studies in the following plant species have been submitted, which are required for herbicides: *Lemna gibba* (duckweed), *Skeletonema costatum* (a marine diatom), *Anabaena flos-aquae* (a blue-green bacterium), and a freshwater diatom.

Also, data located in the open literature suggest that brown algae are considerably more sensitive than green algae to chlorate. A 14-day EC50 of 0.012 mM (≈1 mg/L) was reported for brown algae (van Wijk et al., 1997, described in Appendix M). Sufficient detail was not available in the published study report to allow for a comprehensive assessment of data adequacy.[30] However, the EECs for the non-agricultural uses ranged from 3.1 to 39 mg/L, which all exceed the reported EC50 for brown algae of ≈1 mg/L. For this reason, there may be risk to some algal species that exceed the Agency's level of concern for aquatic plants. As previously discussed, however, additional data are needed to address the considerable uncertainty in the aquatic EECs and uncertainty in the toxicity data before risk can be definitively assessed.

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[30] Key missing details included whether the study conduct followed standard guidelines, whether chlorate concentrations were analytically confirmed, the test concentrations, dose-response information from each concentration, and water quality parameters from individual cultures.

### *4.1.4. Uncertainties in the Aquatic Organism Risk Assessment*

There are a number of areas of uncertainty in the aquatic organism risk assessment that merit discussion. These include the following:

*Uncertainties that may have caused an under-estimation of risk*

- **The risk assessment only considers the most sensitive species *tested*.** Aquatic acute and chronic risks are based on acceptable toxicity data for the most sensitive fish, invertebrate, and plant species tested. Responses to a toxicant can be expected to be variable across species. Sensitivity differences between species can be considerable (several orders of magnitude) for some chemicals (Mayer and Ellersieck 1986). It is uncertain if the tested laboratory species is representative of most species' sensitivities to chlorate toxicity.

  Open literature toxicity data were located that suggest that some fish and algal species may be more sensitive to chlorate toxicity than the surrogate species used in this assessment. Therefore, submission of confirmatory studies in non-guideline fish and algal species would reduce uncertainty in this assessment (see Section 3 for additional discussion).

- **The risk assessment only considered a subset of possible use scenarios.** Although chlorate has a label for a limited number of crops and non-agricultural uses, they encompass a large geographic area. Also, the non-agricultural uses may presumably be used without geographic limits. Some uses that may pose higher risks include those occurring in sensitive locations (close proximity to aquatic environments and high runoff potentials).

- **The risk quotients assume that exposure only occurs to chlorate.** In some environments, chlorate may be reduced to chlorite, which has been shown to be more toxic to aquatic organisms than chlorate. This is of particular concern for invertebrates because the chlorite EC50 for daphnids is 0.15 mg/L, which is approximately 6000-fold lower than the EC50 for chlorate of 920 mg/L. Therefore, formation of even small amounts of chlorite could result risk to endangered and non-endangered aquatic invertebrates at levels of concern to the agency.

- **The effect of pH on chlorate toxicity is uncertain.** The available toxicity studies used pH environments that are slightly alkaline. The toxicity of chlorate is expected to be dependent on pH as well as redox condition. Therefore, submission of data that characterizes the effect of pH and redox condition of the media on chlorate toxicity to invertebrates would be of considerable value to this assessment, provided that the chemical species in the test media are adequately characterized (qualitatively and quantitatively). Submission of such chlorate in toxicity studies for aquatic invertebrates would reduce uncertainty in this assessment because pH conditions as low as 5.5 are not uncommon, particularly in the Northeastern United States.

- Many of the labels do not specify the maximum number of applications or annual load; however, some labels for cotton indicate that multiple applications may be necessary. The Agency has assumed that chlorate may be applied twice annually to cotton at all application rates with a 30-day application interval and is applied once annually for all other uses. This assumption may have resulted in an under-estimation of risk if chlorate may be applied more than twice annually (or at shorter application intervals) to cotton or more than once annually to other crops.

*Uncertainties that may have resulted in an over-estimation of risk*

- As previously discussed, there is considerable uncertainty in the rate of formation/decline of redox products of chlorate (i.e., the kinetics of formation/decline). Redox kinetics of the chlorine system is complex, studies are very difficult, and most of the data available are not suitable for estimating speciation and predominance in terrestrial and aquatic environments. GENEEC-2 and PRZM-EXAMS are not ideal simulation models for chemicals in which one of the elements that can exist in more than one oxidation state. Therefore, conservative assumptions were made that likely resulted in an over-estimation of exposure to chlorate.

- GENEEC-2 assumes a contiguous drainage basin that flows into a pond that is10-times smaller than the treated area. The application scenarios for the non-agricultural uses may not be consistent with the scenario assumed by GENEEC-2.

- GENEEC-2 assumes no foliar interception, which likely resulted in an over-estimation of exposure. Foliar interception is likely to occur because chlorate absorbs into plants. Any chlorate that absorbs into the plant will not likely enter surface water.

*Uncertainties that may have resulted in an under-estimation or an over-estimation of risk*

- **Surrogate species were used to predict potential risks for species with no data (i.e., reptiles and amphibians).** It was assumed that use of surrogate species toxicity data are sufficiently conservative to apply the broad range of species within taxonomic groups. If other species are more or less sensitive to chlorate and its degradates than the surrogates, risks may be under- or over-estimated, respectively.

### *4.2. Risks to Birds, Acute and Chronic Exposures*

Summary of Conclusions

- **Agricultural Uses:** Based on chlorate's low acute and subacute toxicity to birds (LD50 >2510 mg/kg-bw; LC50 >5620 mg/kg-feed), risk to endangered and non-endangered birds is presumably lower than the Agency's level of concern for all agricultural uses.

- **Non-agricultural Uses:** Even though chorate is of low acute toxicity to birds, EECs for chlorate's non-agricultural uses were as high as 125,000 ppm. Therefore, acute risk to birds cannot be precluded. However, such risks cannot be quantified.

- Absence of reproduction toxicity data precludes a quantitative assessment of chronic risk to birds. However, mammalian data suggest that chlorate's effects are cumulative (more toxic after repeated exposures). Therefore, the Agency presumes that potential risk to birds exists.

#### 4.2.1. Risk Estimation - Integration of Exposure and Effects Data

Acute risk quotients were not calculated because no mortality or signs of toxicity were observed in the submitted subacute or acute toxicity studies at concentrations that are above the limit for these types of studies.

Chronic risk quotients were not calculated because a reproduction toxicity study has not been submitted to the Agency.

#### 4.2.2. Risk Description - Interpretation of Direct Effects

No acute risk to birds was identified at levels of concern to the Agency from chlorate's agricultural uses based on its low acute toxicity to birds. However, EFED cannot preclude acute risk from the non-agricultural uses. Chlorate is applied at rates of 52 to 520 lbs/Acre for these uses.[31] The corresponding EECs are 12,500 and 125,000 ppm, respectively, which are approximately 2.5 to 25-fold higher than the highest concentration tested in the subacute bird toxicity studies. Therefore, acute risk to birds from these high application rates cannot be precluded.

EFED cannot preclude chronic risk because no reproduction toxicity data are available. A field dissipation study has not been submitted; therefore, the potential for chronic exposure has not been fully assessed. However, chlorate is expected to be persistent under some environmental conditions; therefore, the Agency assumes that repeated exposure is possible. The available

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[31] The application rate for pre-paving is 650 lbs a.i./Acre; however, this use pattern would not likely result in exposure to birds.

studies in mammals suggest that chlorate is significantly more toxic after repeated exposures compared with single exposures (i.e., toxicity increases as study duration increases). A similar relationship between exposure duration and toxicity is presumed in birds as well. Therefore, lack of reproduction toxicity data is an important data gap.

### *4.3. Risk to Mammals, Acute Exposures*

Summary of Conclusions

- Risk from acute exposure cannot be precluded for chlorate's agricultural or non-agricultural uses.
- A 2-generation reproduction toxicity study is not available to allow for derivation of chronic risk quotients, and other studies were considered inappropriate for risk quotient calculations. However, based on subchronic toxicity studies, there appears to be risk to mammals at levels of concern to the Agency from both agricultural and non-agricultural uses.

#### 4.3.1. Risk Estimation, Integration of Exposure and Effects Data

Acute risk quotients were not calculated for mammals. The LD50 from a core acute oral toxicity study in rats was >5000 mg/kg-bw (MRID 418199-01). In this study, 10% (1/10) of the rats administered 5000 mg/kg died. Mortality was not observed at any other dose. Therefore, the data were not sufficient to allow for characterization of the dose-response relationship, and the proximity of the LD50 to 5000 mg/kg-bw is uncertain. For this reason, formal risk quotients were not calculated. However, Tables 4-6 and 4-7 below, respectively, present a comparison of the body weight adjusted LD50s to the agricultural and non-agricultural EECs. These ratios can be used to estimate high-end risk to exposed mammals.

**Table 4-6. Proximity of the lowest observed acute toxic dose in mammals to the upper 90th percentile EEC (mg/kg-bw) for small (15-gram), medium (35-gram), and large (1000-gram) mammals (Range of Maximum Application Rate for all Agricultural Uses).**

| **Food Item** | **Size of Mammal (grams)** | **Adjusted lowest observed toxic dose from MRID 41819901 (mg/kg-bw)[a]** | **Range of EECs (mg/kg-bw)[b]** | **Ratio of lowest observed toxic dose to the upper 90th percentile EEC (unitless)** |
|---|---|---|---|---|
| Short grass | 15 | 10,989 | 1400 - 2900 | 0.13 - 0.26 |
| | 35 | 8891 | 950 - 2000 | 0.11 - 0.22 |
| | 1000 | 3846 | 200 - 450 | 0.052 - 0.12 |
| Tall grass | 15 | 10,989 | 630 - 1300 | 0.057 - 0.12 |
| | 35 | 8891 | 440 - 910 | 0.049 - 0.10 |
| | 1000 | 3846 | 99 - 210 | 0.026 - 0.055 |
| Broadleaf plants/small insects | 15 | 10,989 | 770 - 1600 | 0.070 - 0.15 |
| | 35 | 8891 | 540 - 1100 | 0.061 - 0.12 |
| | 1000 | 3846 | 120 - 250 | 0.031 - 0.065 |
| Fruits, pods, large insects | 15 | 10989 | 86 - 180 | <0.01 - 0.016 |
| | 35 | 8891 | 59 - 120 | <0.01 - 0.013 |
| | 1000 | 3846 | 14 - 28 | <0.01 - <0.01 |

[a] The acute oral toxic dose was adjusted for body weight based on the formula recommended by Mineau *et al.* 1996:Adj. $LD_{50} = LD_{50}\ (TW/AW)^{0.25}$ : TW=weight of test organism (reference body weight of adult rat is ≈350 grams); AW = weight of assessed organism.

[b] EECs were calculated by assuming that small, medium, and large mammals consume 95%, 66%, and 15% of their body weight daily. Only the highest and lowest EECs from chlorate's agricultural uses are used in this assessment. These values are based on EECs presented in Table 3-8.

**Table 4-7. Proximity of the lowest observed acute toxic dose in mammals to the predicted EEC (mg/kg-bw) for small (15-gram), medium (35-gram), and large (1000-gram) mammals (Based on the Range of Maximum Application Rates for all Non-Agricultural Uses).**

| Food Item | Size of Mammal (weight, grams) | Adjusted lowest observed toxic dose (mg/kg-bw)[a] | Range of EECs (mg/kg-bw)[b] | Ratio of lowest observed toxic dose to the upper 90th percentile EEC (unitless) |
|---|---|---|---|---|
| Short grass | 15 | 10989 | 11,900 - 119,000 | 1.1 - 11 |
| | 35 | 8891 | 8200 - 82,000 | 0.93 - 9.3 |
| | 1000 | 3846 | 1900 - 19,000 | 0.49 - 4.9 |
| Tall grass | 15 | 10989 | 5400 - 54,000 | 0.49 - 4.9 |
| | 35 | 8891 | 3800 - 38,000 | 0.43 - 4.3 |
| | 1000 | 3846 | 860 - 8600 | 0.22 - 2.2 |
| Broadleaf plants/small insects | 15 | 10989 | 6700 - 67,000 | 0.61 - 6.1 |
| | 35 | 8891 | 4600 - 46,000 | 0.52 - 5.2 |
| | 1000 | 3846 | 1100 - 11,000 | 0.27 - 2.7 |
| Fruits, pods, large insects | 15 | 10989 | 740 - 7400 | 0.07 - 0.7 |
| | 35 | 8891 | 520 - 5200 | 0.06 - 0.6 |
| | 1000 | 3846 | 120 - 1200 | 0.03 - 0.3 |

[a] The acute oral toxic dose was adjusted for body weight based on the formula recommended by Mineau *et al.* 1996 for adjusting $LD_{50}$s:Adj. $LD_{50} = LD_{50}\ (TW/AW)^{0.25}$ : TW=weight of test organism (reference body weight of adult rat is 350 grams); AW = weight of assessed organism.

[b] EECs were calculated by assuming that small, medium, and large mammals consume 95%, 66%, and 15%, respectively, of their body weight daily, and were calculated using the highest and lowest labeled application rates (52 lbs a.i./Acre and 520 lbs a.i./Acre) that are most likely to result in exposure.

### 4.3.2. Risk Description - Interpretation of Direct Effects

*Agricultural Uses*

For chlorate's agricultural uses, the ratio of the lowest body weight adjusted observed toxic dose in mammals (5000 mg/kg-bw) to the upper 90th percentile EEC was as high as 0.26 for small mammals, 0.22 for medium sized mammals, and 0.12 for large mammals (short grass food items). For other food items, the ratios were ≤0.15. If the LD50 is in close proximity to 5000 mg/kg-day, there may be potential risk at levels of concern to the Agency to non-endangered small and medium sized mammals that forage on short grass and potential risk to large (1000 grams) endangered mammals that feed on short grass and small and medium-sized endangered mammals that forage on several other food items. However, proximity of the LD50 to 5000 mg/kg-day cannot be determined based on the submitted data. Additional uncertainties in this assessment are discussed in Section 4.7.

*Non-Agricultural Uses, Spray Applications*

The ratios presented in Table 4-7 above suggest that there could be considerable risk to mammals of all sizes that forage in the area where chlorate is used for the non-agricultural applications. However, potential risk was likely over-estimated for the following reasons:

- An LD50 has not been established. The highest dose tested in the available toxicity studies (5000 mg/kg-bw) induced 10% mortality. The proximity of the LD50 to 5000 mg/kg-bw is uncertain.
- Many of the non-agricultural uses will likely result in small contiguously treated areas. Therefore, the likelihood that an animal will consume 100% of its diet from chlorate treated areas is low for some of these uses.

Nonetheless, the EECs were predicted to be up to 11 times higher than the toxic dose of 5000 mg/kg-bw for the non-agricultural uses. Therefore, there appears to be risk to mammals at levels of concern to the Agency.

Also, based on the very high application rates associated with the non-agricultural uses of chlorate, ingestion of contaminated soil could represent a significant exposure pathway. Therefore, incidental ingestion via contaminated soil was estimated. Based on a maximum application rate of 650 lbs a.i./Acre and a soil density of 1.3 grams/cm$^3$ (Campbell 1985),[32] chlorate concentrations in the first 3 centimeters of soil could be as high as 1500 mg/kg-soil (ppm).[33] This application rate is only labeled for pre-paving, which is not likely to result in exposure. Also, this calculation assumes no foliar interception (direct application to soil). For these reasons, this calculation represents a high-end estimate. Using daily food intake, as estimated by Nagy (1987) (**EQ 1**), a 20-gram mammal is estimated to consume approximately 3.7 grams of food (wet weight) daily:

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[32] Campbell G S. 1985. *Soil Physics with BASIC. Developments in Soil Science 14.* Elsevier publishers. New York NY, USA. This soil density is considered a representative, mid-range value.

[33] 650 lbs a.i./Acre × 0.37 kg/lb = 240.5 kg a.i./Acre × 1E6 mg/kg = 2.4E8 mg a.i./Acre
1.2E8 cm$^3$/Acre x 1.3 g soil/cm$^3$ = 1.6 E8 g soil/Acre (1.6E5 kg soil/Acre)
2.4E8 mg a.i./Acre ÷ 1.6E5 kg soil/Acre = **1500 mg a.i./kg-soil**

$$F = \frac{0.621 * BW^{0.564}}{(1 - W)}$$

where F is the food intake in grams of fresh weight per day, BW is the body mass (wet weight) of the organism in grams, and W is the mass fraction of water in the food (assumed to be 0.1). Therefore, the estimated dose of chlorate from dietary consumption of 100% soil would be 5.6 mg/day (3.7 g soil $day^{-1} \times 0.001$ kg $g^{-1} \times 1500$ mg a.i. $kg^{-1}$). This intake level corresponds to a body weight adjusted internal dose of 280 mg/kg-day for a 20-gram mammal (5.6 mg/day ÷ 0.02 kg = 280 mg/kg-day). Direct comparison of this maximum possible soil intake value to the body weight adjusted acute oral LD50 of >10,989 mg/kg-bw[34] would not result in risk to mammals at levels of concern to the Agency.

In addition, Beyer et al. (1994) reported that high-end mammals with respect to soil consumption (e.g., armadillos) consume $\leq 17\%$ soil in their diet, and small mammals (mice and voles) consume less than 2.5% soil in their diet. Therefore, this analysis likely resulted in an over-estimation of exposure and risk. However, risk from repeated ingestion of contaminated soil cannot be precluded, because adequate toxicity data are not available for comparison to these exposure values.

Non-Agricultural Uses, Granular Applications

*Risk Estimation*

Formal risk quotients were not calculated for reasons previously discussed. However, Table 4-8 below presents a comparison of the body weight adjusted lowest observed toxic dose in rats of 5000 mg/kg-day from MRID 41819901 to the granular application EECs (mg/$ft^2$). These ratios are used to qualitatively describe potential risk.

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[34] Extrapolations from one mammal species to another needs to consider differences in the scaling of toxicity for differences in body weight. Therefore, the acute oral $LD_{50}$ was adjusted for body weight based on the formula recommended by Mineau *et al.* 1996:Adj. $LD_{50} = LD_{50} (TW/AW)^{0.25}$ : TW=weight of test organism (reference body weight of adult rat is $\approx 350$ grams); AW = weight of assessed organism.

**Table 4-8. Range of Ratios of Chlorate's Body Weight Adjusted LD50 to Granular EECs (mg/ft$^2$) for Sodium Chlorate's Non-Agricultural Uses (Granular Formulations)**

| Use | Body Weight (g) | Rat LD50$_{Adj}$ mg/kg-bw[a] | EEC (mg/ft$^2$)[b] | Ratio of LD50adj to EEC[c] |
|---|---|---|---|---|
| Parking lots, under asphalt paving, fence lines, building perimeters, ditch banks, picnic areas, vacant lots, wood decks, bleachers, cemeteries, fuel tanks, runways, helo pads, etc.<br>520 lbs a.i./Acre | 15 | 10,989 | 5400 | 33 |
| | 35 | 8891 | 5400 | 17 |
| | 1000 | 3846 | 5400 | 1.4 |
| Around buildings, storage areas, fences, pumps, machinery, fuel tanks, recreational areas, roadways, guard rails, airports, rights of ways.<br>160 lbs a.i./Acre | 15 | 10,989 | 1700 | 10 |
| | 35 | 8891 | 1700 | 5.4 |
| | 1000 | 3846 | 1700 | 0.43 |

a Adj. $LD_{50} = LD_{50}\,(TW/AW)^{0.25}$ : TW=weight of test organism (reference body weight of adult rat is ≈350 grams); AW = weight of assessed organism.
b EEC = Application rate (lbs/Acre) x 453,000 mg/lb ÷ 43,600 sq ft/Acre
c Ratio = EEC ÷ (LD50$_{adj}$ × bw in kg)

### *Risk Description*

Granular applications of chlorate appear to pose risk to small, medium, and large mammals at levels of concern to the Agency. It was estimated that granular applications would result in chlorate concentrations that are between 0.42- and 33-times the mass of chlorate in every ft$^2$ of chlorate-treated areas that has been shown to be toxic to mammals. Although the habitat and feeding area of mammals are substantially greater than a ft$^2$, the mg/ft$^2$ index is used to evaluate whether there is sufficient mass of chlorate within a treated area to potentially cause adverse effects to exposed mammals. U.S. EPA 1992 and U.S. EPA 2004 can be referenced for additional discussion on the LD50/ft$^2$ index.

The LD50/ft$^2$ method is used to encompass exposure via all routes (oral, dermal, inhalation). However, as an ionic salt, chlorate will not likely appreciably absorb through the skin, and its low Henry's law constant and volatility suggest that inhalation will likely be negligible. Therefore, exposure will likely be limited largely to the oral route (drinking water, contaminated food items, direct consumption of granules, preening activity). Although chlorate is a strong oxidant, it is not a strong irritant; therefore, mammals are not expected to intentionally avoid chlorate. In fact, chlorate could be particularly attractive to salt-thirsty mammals resulting in higher chlorate body burdens in these mammals.

Other uncertainties in this assessment are presented in Section 4.7.

### *4.4. Potential Risk to Mammals, Chronic Exposures*

Sufficient toxicity data are not available to allow for risk quotient calculations. However, the available subchronic data suggest that mammals may be at considerable risk from repeated exposures to chlorate. Chlorate is presumably stable under some environmental conditions; therefore, repeated exposures to chlorate is possible. Subchronic toxicity studies ranging in duration from 21 to 90 days suggest that chlorate may induce effects that could affect the growth, survival, or reproduction in exposed mammals at doses of approximately 100 mg/kg-bw per day, which is a dose that is 50 times lower than the acute oral LD50 of >5000 mg/kg-bw. Effects observed in the repeated-dose toxicity studies included decreased body weight (up to approximately 30% decrease compared with control (unexposed) animals), blood toxicity, and pituitary and thyroid effects (including changes in hormone levels).

### *4.5. Endocrine Disruption Potential*

Effects observed in repeated-dose toxicity studies in mammals indicate that chlorate could affect the endocrine system. For example, thyroid hormone levels were affected in rats maintained on drinking water supplemented with chlorate for 90 days.

EPA is required under the Federal Food, Drug, and Cosmetic Act (FFDCA), as amended by the Food Quality Protection Act (FQPA), to develop a screening program to determine whether certain substances (including all pesticide active and other ingredients) *"may have an effect in humans that is similar to an effect produced by a naturally occurring estrogen, or other such endocrine effects as the Administrator may designate."* Following the recommendations of its Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC), EPA determined that there was scientific bases for including, as part of the program, the androgen and thyroid hormone systems, in addition to the estrogen hormone system. EPA also adopted EDSTAC’s recommendation that the Program include evaluations of potential effects in wildlife. For pesticide chemicals, EPA will use The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and, to the extent that effects in wildlife may help determine whether a substance may have an effect in humans, FFDCA authority to require the wildlife evaluations. As the science develops and resources allow, screening of additional hormone systems may be added to the Endocrine Disruptor Screening Program (EDSP). When the appropriate screening and/or testing protocols being considered under the Agency’s EDSP have been developed, chlorate may be subjected to additional screening and/or testing to better characterize effects related to endocrine disruption.

### *4.6. Potential Risk to Terrestrial Plants*

Based on chlorate’s non-selective mode of action and lack of adequate toxicity data, EFED presumes risk to non-target plants at levels above the Agency’s level of concern for all uses. However, such risks cannot be quantified based on the currently available data.

### *4.7. Uncertainties in the Terrestrial Organism Risk Assessment*

There are a number of areas of uncertainty in the terrestrial risk assessment that merit discussion, which were previously discussed in Sections 2 and 3. These are summarized below.

Exposure

- Many of the labels are not clear regarding the maximum allowable annual applications (number of applications or total load). The Agency assumed a maximum of 2 annual applications (30-days apart) for cotton and 1 annual application for all other uses. Risk may be under-estimated if these assumptions do not accurately reflect chlorate's applications.

- Stability of chlorate in terrestrial and aquatic environments is uncertain, but it is expected to exhibit wide spatial and seasonal variability.

- There is considerable uncertainty in the rate of formation/decline of redox products of chlorate (i.e., the kinetics of formation/decline).

- Many of the non-agricultural uses will likely result in small contiguously treated areas, which would reduce the likelihood that an animal would consume 100% of its diet from chlorate treated areas.

- Chlorate is a dessicant that kills parts of plants that are generally edible to herbivorous organisms. Because the herbicide is absorbed by plants relatively rapidly and kills most exposed plants within several days to several weeks after exposure, some contaminated food items may not be attractive to herbivores for an extended period of time after treatment.

- The risk assessment assumes that 100% of the exposure organism's diet is relegated to single food types foraged only from treated fields. These assumptions are likely to be conservative for many species and will tend to overestimate potential risks. The assumption of 100% diet from a treated area may be realistic for acute exposures, but long-term exposures modeled as single food types composed entirely of material from a treated field is uncertain.

Toxicity

- The toxicity database is limited. No chronic or reproductive toxicity data (aquatic or terrestrial organisms) considered adequate for screening level ecological risk assessment were available.

- Adequate non-target terrestrial plant data are not available for this assessment. In the absence of such data, and based on the non-specific mode of action of chlorate, EFED presumes considerable risk to non-target plants.

- None of the submitted acute toxicity studies in rats, mysid shrimp, or fish produced toxicity at or above the LD50 or LC50 (<50% of tested organisms were affected by exposure) resulting in an over-estimation of risk. The available data from these studies do not allow for an approximation of the highest dose or concentration tested to the LD50 or LC50. Therefore, the magnitude of the over-estimation of risk on the risk assessment from using these toxicity values is uncertain.

- An LD50 of 1200 mg/kg-day in rats has been reported in secondary sources.[35] However, this study report has not been obtained and evaluated by the Agency. If these data are reliable, then risks characterized in this assessment may have been under-estimated.

Scope of Assessment

- Surrogate organisms were used to predict potential risks for species with no data (i.e., reptiles and amphibians).

- The risk assessment only considers the most sensitive species tested. Terrestrial acute and chronic risks are based on toxicity data for the most sensitive bird, mammal, and plant species tested. Responses to a toxicant can be expected to be variable across species. The position of the tested species relative to the distribution of all species' sensitivities to chlorate is unknown.

- Sodium Chlorate is formulated with other active ingredients and with flame retardants. Potential effects that these other chemicals may have on chlorate's fate or toxicity is not considered in this assessment. The effects of prolonged, year-after-year use of chlorate in the same field is not known, particularly in semiarid sites that require irrigation (e.g., Arizona, California), where there is a potential for salt build-up over time.

### *4.8. Potential Risk to Threatened and/or Endangered Species*

#### 4.8.1. Aquatic Organisms

There are no geographical limitations on the non-agricultural chlorate uses; therefore, the Agency assumes that there is considerable potential for exposure to endangered aquatic species. No chronic toxicity data are available in freshwater or saltwater fish or invertebrates; therefore, chronic risk to these surrogate organisms cannot be precluded. Although levels of concern were not exceeded, potential risk to listed fish, aquatic invertebrates, or aquatic plants cannot be precluded for the following reasons:

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[35] Hayes, Wayland J., Jr. Pesticides Studied in Man. Baltimore/London: Williams and Wilkins, 1982..

- *Fish.* The data located in the open literature suggest that brown trout could be considerably more sensitive than other fish species that have been tested. Woodiwiss et al. (1974) (summarized in Appendix M) reported a 48-hour LC50 of 7.3 mg/L in brown trout for chlorate. No other studies in brown trout were located, and sufficient information was not available in the publication to allow for an evaluation of data quality. However, this LC50 would trigger endangered species concerns for all chlorate agricultural and non-agricultural uses. Also, it appears that chlorate was tested in the presence of another unspecified flame retardant in this study. Therefore, it is uncertain if the toxicity observed in this study was caused by chlorate, the other unidentified chemical, or a combination of the two. Nonetheless, these data *could* suggest that there may be considerable variability in species sensitivity to chlorate toxicity. Alternatively, these data could suggest that formulated products are more toxic to fish because all chlorate formulations contain fire retardants.

- *Aquatic Invertebrates.* Chlorite could form from the reduction of chlorate in the environment. Chlorite is 6000-fold more toxic than chlorate to daphnids.[36] However, the currently available data do not allow for a realistic estimation of the amount of chlorite that may form in the environment. Therefore, submission of data that characterize the potential for chlorate to be reduced to chlorite in natural waters would be of considerable value to this assessment.

- *Aquatic Plants.* The data located in the open literature suggest that brown algae are considerably more sensitive than green algae to chlorate. A 14-day EC50 of 0.012 mM (≈1 mg/L) was reported for brown algae (van Wijk et al., 1997). The EECs for the non-agricultural uses ranged from 3.1 to 39 mg/L, which exceed the EC50 for brown algae of ≈1 mg/L. Therefore, there may be risk to some algal species that exceeds the Agency's level of concern for aquatic plants. As previously discussed, however, additional data are needed to address the considerable uncertainty in the aquatic EECs before risk can be definitively characterized. Also, no studies in the following plant species have been submitted, which are required for herbicides: *Lemna gibba* (duckweed), *Skeletonema costatum* (a marine diatom), *Anabaena flos-aquae* (a blue-green bacterium), and a freshwater diatom..

Uncertainties in this assessment are equivalent to those presented in Section 4.1.4. Listed species that reside in areas where chlorate may be used were not located because its uses have no geographical restrictions. For example, rights-of-ways and airport fields are located in virtually every county in the United States. Therefore, the Agency presumes that there is considerable potential for exposure to chlorate by listed species.

### 4.8.2. Terrestrial Organisms

*Potential Risk to Endangered Birds*

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[36] The 48-hour acute EC50 in daphnids is 0.15 mg/L (MRID 940680-09).

No effects were observed in subacute dietary studies in mallard ducks or bobwhite quail at up to 5620 mg/kg-diet. However, acute risk to endangered birds cannot be precluded for chlorate's non-agricultural uses because the EECs were significantly higher (up to 125,000 mg/kg-food item) than the highest concentration tested in subacute dietary toxicity studies.

No reproduction toxicity data are available to allow for an estimation of risk from chronic exposures to chlorate. However, mammalian toxicity data indicate that chlorate is more toxic after repeated exposures. The Agency presumes that chlorate is also more toxic to birds after repeated exposures. Therefore, chronic risk to birds cannot be precluded.

*Potential Acute Risk to Endangered Mammals*

For chlorate's agricultural uses, the ratio of the lowest observed toxic dose to mammals (5000 mg/kg-bw) to the upper 90th percentile EEC was as high as 0.26 for small mammals, 0.22 for medium sized mammals, and 0.12 for large mammals (short grass food items). For other food items, the ratios were $\leq 0.15$. If the LD50 is in close proximity to 5000 mg/kg-day, there may be risk at levels of concern to the Agency to endangered small, medium, and large mammals that forage on short grass and risk to small and medium sized endangered mammals that forage on several other food items.

There appears to be considerable potential acute risk to endangered mammals of all sizes that forage in the area where chlorate is used for the non-agricultural applications. The EECs were up to 11 times higher than the toxic dose of 5000 mg/kg-bw for the non-agricultural uses. Therefore, there appears to be risk to mammals at levels of concern to the Agency.

A number of uncertainties were noted in this assessment, which have previously been described in detail and are summarized in Section 4.7.

*Potential Chronic Risk to Endangered Birds and Mammals*

No chronic toxicity data have been submitted to the Agency or are available in the open literature for any surrogate species used in this assessment; therefore, risk cannot be precluded for any species assessed. The available studies in mammals suggest that chlorate is significantly more toxic after repeated exposures compared with single exposures (i.e., toxicity increases as study duration increases). A similar relationship between exposure duration and toxicity is presumed in birds as well. Based on the expected persistence of chlorate under some environmental conditions and the demonstrated cumulative toxicity observed in mammals, risk to endangered birds and mammals is presumed to exceed the Agency's level of concern.

The Agency presumes that there is potential for exposure to a large number and large variety of endangered species because these uses would presumably encompass every county in the United States. Therefore, states or counties with endangered species that reside in areas that may be treated with chlorate were not identified as part of this screening level assessment.

### *Potential Risk to Endangered Terrestrial Plants*

Sufficient toxicity data have not been submitted to the Agency to allow for a characterization of potential risk to terrestrial plants. Based on chlorate's non-selective toxicity to plants, the Agency presumes that there is risk to endangered plants at levels of concern to the Agency from the use of chlorate on agricultural and non-agricultural areas.

### *Critical Habitat*

In the evaluation of pesticide effects on designated critical habitat, consideration is given to the physical and biological features (constituent elements) of a critical habitat identified by the U.S Fish and Wildlife and National Marine Fisheries Services as essential to the conservation of a listed species and which may require special management considerations or protection. The evaluation of impacts for a screening level pesticide risk assessment focuses on the biological features that are constituent elements and is accomplished using the screening-level taxonomic analysis (risk quotients, RQs) and listed species levels of concern (LOCs) that are used to evaluate direct and indirect effects to listed organisms.

The screening-level risk assessment has identified potential concerns for indirect effects on listed species for those organisms dependant upon species at risk from chlorate exposure. Considerable uncertainty in the potential for direct effects to listed species from chlorate's use identified in this assessment precludes a meaningful analysis of the potential of indirect effects to listed species. In light of the potential for indirect effects, the next step for EPA and the Service(s) is to identify which listed species and critical habitat are potentially implicated. Analytically, the identification of such species and critical habitat can occur in either of two ways. First, the agencies could determine whether the action area overlaps critical habitat or the occupied range of any listed species. If so, EPA would examine whether the pesticide's potential impacts on non-endangered species would affect the listed species indirectly or directly affect a constituent element of the critical habitat. Alternatively, the agencies could determine which listed species depend on biological resources, or have constituent elements that fall into, the taxa that may be directly or indirectly impacted by the pesticide. Then EPA would determine whether use of the pesticide overlaps the critical habitat or the occupied range of those listed species. At present, the information reviewed by EPA does not permit use of either analytical approach to make a definitive identification of species that are potentially impacted indirectly or critical habitats that is potentially impacted directly by the use of the pesticide. EPA and the Service(s) are working together to conduct the necessary analysis.

This screening-level risk assessment for critical habitat provides a listing of potential biological features that, if they are constituent elements of one or more critical habitats, would be of potential concern. These correspond to the taxa identified above as being of potential concern for indirect effects. This list should serve as an initial step in problem formulation for further assessment of critical habitat impacts outlined above, should additional work be necessary.

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# Appendices

# Environmental Fate and Ecological Risk Assessment
for the Reregistration of Sodium Chlorate as an Active Ingredient in
Terrestrial Food/Feed and Non-food/Non-feed Uses

# Appendix A. Status of Data Requirements for Sodium Chlorate

**Table A-1.** **Status of Data Requirements for Sodium Chlorate (Food/Feed and Non-food/Non-feed Uses. (Waivers: EFGWB DPBarcode D186156, 03/15/93; Transmittal Memo to SRRD 05/05/93)**

| Data Requirement | Status | Comment |
|---|---|---|
| **Environmental Fate Data** | | |
| 161-1 Abiotic Hydrolysis | Waived | The chemistry of chlorate in water is dominated by redox reactions that require the presence of reductants (inorganic and/or organic). Because the 161-1 Hydrolysis study is conducted in abiotic media and in types of buffer solutions that are not likely to act as reductants, this study was waived as it was concluded that the study was not going provide any useful or very limited information, unless known environmental reductants were included in the aqueous media. Moreover, the redox chemistry of chlorate in water is extensively documented in the chemical literature. |
| 161-2 Direct Photolysis in Water | Waived | The 161-2 study is conducted in the absence of chemical photosensitizers. That is, this study is designed to address the role of <u>direct</u> photolysis in aqueous media. A necessary, but not sufficient, condition for direct photolysis in environmentally significant aqueous media is that the chemical must absorb energy (photon) in the sunlight wavelength range. Chlorate does not absorb energy in this range. Therefore, the 161-2 study was waived because it does not the necessary condition for direct photolysis.[37]. |
| 161-3 Photolysis on Soil | Waived | The 161-2 study is conducted in the absence of chemical photosensitizers. That is, this study is designed to address the role of <u>direct</u> photolysis in aqueous media. A necessary, but not sufficient, condition for direct photolysis in environmentally significant aqueous media is that the chemical must absorb energy (photon) in the sunlight wavelength range. Chlorate does not absorb energy in this range. Therefore, the 161-2 study was waived because it does not the necessary condition for direct photolysis.. |

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[37] Photoreactions induced by transfer of energy from photosensitizers in natural water and soils may contribute to the transformation of chlorate in the environment (that is, indirect photolysis contribution). Many chemical reductants present in natural environments may also behave as photoreductants.

| Data Requirement | Status | Comment |
|---|---|---|
| 162-1 Aerobic Soil Metabolism[38] | Waived | This study, if conducted according to existing guidelines, would not likely produce useful information due to sodium chlorate antimicrobial properties that can destroy the microbial populations in soil. If the microbial population is destroyed, the study cannot adequately address the role of microorganisms in the degradation of chlorate. It is more likely that the nature and concentration of redox species control the chemistry of chlorate in soils |
| 162-2 Anaerobic Soil Metabolism | Waived | This study, if conducted according to existing guidelines, would not likely produce useful information due to sodium chlorate antimicrobial properties that can destroy the microbial populations in soil. If the microbial population is destroyed, the study cannot adequately address the role of microorganisms in the degradation of chlorate. It is more likely that the nature and concentration of redox species control the chemistry of chlorate in soils |
| 162-3 Anaerobic Aquatic Metabolism | Waived | This study, if conducted according to existing guidelines, would not likely produce useful information due to sodium chlorate antimicrobial properties that can destroy the microbial populations in water-sediment systems. If the microbial population is destroyed, the study cannot adequately address the role of microorganisms in the degradation of chlorate. It is more likely that the nature and concentration of redox species control the chemistry of chlorate in water-sediment systems. |
| 162-4 Aerobic Aquatic Metabolism | Waived | This study, if conducted according to existing guidelines, would not likely produce useful information due to sodium chlorate antimicrobial properties that can destroy the microbial populations in water-sediment systems. If the microbial population is destroyed, the study cannot adequately address the role of microorganisms in the degradation of chlorate. It is more likely that the nature and concentration of redox species control the chemistry of chlorate in water-sediment systems. |
| 163-1 Mobility in Soil | Waived | Sodium chlorate is fully ionized in water. The chlorate anion is not likely to adsorb onto soils or sediments. Therefore, high mobility was anticipated. Guideline studies would not provide additional information. |
| 163-2/-3 Volatility from Soil | Waived | The very low vapor pressure of sodium chlorate ($9.7 \times 10^{-14}$ Pa at 25° C) does not trigger the volatility from soil data requirement |

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[38] Although laboratory studies conducted on soils could, in principle, provide useful information on the persistence of chlorate on soil, there is a major drawback and concern in the case of chlorate because sodium chlorate can react violently with organic material and cause fire. Therefore, performing these studies is not recommended.

The persistence of chlorate in the field remains an issue and an uncertainty. While there are claims that it could persist as long as 5 years, there are no actual data to support this claim. Use of sodium chlorate as a desiccant/defoliant requires that it is used in conjunction with a fire retardant. Thus, how the fire retardant influences the persistence of chlorate in the field is unknown. Therefore, a field study is recommended according to agree upon protocols. Terrestrial field dissipation studies must be conducted with a typical end-use product formulation.

| Data Requirement | Status | Comment |
|---|---|---|
| **164-1 Terrestrial Field Dissipation** | **Not Waived** | **This data requirement has never been waived. There is major uncertainty on how long sodium chlorate (formulated) may remain active in the field. Of particular concern is persistence in use sites in semiarid areas. Additional information and/or actual field studies is needed. The open literature information submitted by the registrant in not sufficient to decrease the uncertainty on field persistence of sodium chlorate products**. (Refer to Footnote 2) |
| 165-4 Bioaccumulation in Fish | There is no waiver request for this data requirement. Although this data requirement may be waived, the registrant must formally request the waiver | Sodium chlorate is a highly hydrophilic chemical. Its extremely low Log *n*-octanol/water partition coefficient of -7 does not trigger this data requirement. |

### Table A-2. Status of Ecotoxicity Data Requirements

| Data Requirement | Does EPA Have Data To Complete a Risk Assessment? (Yes, No) | Bibliographic Citation | Are additional data needed? | Comment |
|---|---|---|---|---|
| 71-1(a,b) Acute Avian Oral, Quail/Duck | Yes | 421494-01 | No | |
| 71-2(a) Acute Avian Diet, Quail | Yes | 418199-08 | No | |
| 71-2(b) Acute Avian Diet, Duck | Yes | 418199-07 | No | |
| 71-3 Wild Mammal Toxicity | No | N/A | No | |
| **71-4(a) Avian Reproduction Quail** | **No** | **N/A** | **Yes** | |
| **71-4(b) Avian Reproduction Duck** | **No** | **N/A** | **Yes** | |
| 71-5(a) Simulated or Actual Terrestrial Field Study | No | N/A | No | |
| 72-1(a,b) Acute Fish Toxicity Rainbow trout and Bluegill | Yes | 418872-02<br>418872-03 | No | |
| 72-2(a,b) Acute Freshwater Invertebrate Toxicity | Yes | 438748-01;<br>418872-04 | No | |

## Table A-2. Status of Ecotoxicity Data Requirements

| Data Requirement | Does EPA Have Data To Complete a Risk Assessment? (Yes, No) | Bibliographic Citation | Are additional data needed? | Comment |
|---|---|---|---|---|
| 72-3(a) Acute Estuarine/Marine Toxicity to Fish | Yes | 418872-07 | No | |
| 72-3(b) Acute Estu/Marine Invertebrate | Yes | 418872-05<br>418872-06 | No | |
| **72-4(a) Early Life-Stage Fish** | **No** | **N/A** | **Yes** | |
| **72-4(b) Life-Cycle Aquatic Invertebrate** | **No** | **N/A** | **Yes** | |
| 72-5 Life-Cycle Fish | No | N/A | No | |
| 72-6 Aquatic Org. Accumulation | No | N/A | No | |
| 72-7(a) Simulated Aquatic Field Study | No | N/A | No | |
| 72-7(b) Actual Aquatic Field Study | No | N/A | No | |
| 122-1(a) Seed Germ./Seedling Emerg. Tier I | Yes | 463008-02 | No | |
| 122-1(b) Vegetative Vigor, Tier I | Yes | 463008-01 | No | |
| 122-2 Aquatic Plant Growth, Tier I | No | N/A | No | |
| **123-1(a) Seed Germ./Seedling Emerg., Tier II** | **No** | **N/A** | **Yes** | |
| **123-1(b) Vegetative Vigor , Tier II** | **No** | **N/A** | **Yes** | |
| **123-2 Aquatic Plant Growth , Tier II** | **Yes** | **418872-01** | **Yes** | **Only data on green algae were submitted. Studies in four other aquatic plant species are required for herbicides.** |
| 124-1 Terrestrial Field Study | No | N/A | No | |
| 124-2 Aquatic Field Study | No | N/A | No | |
| **141-1 Honey Bee Acute Contact** | **Yes** | **N/A** | **Yes** | **Study was submitted; however, a new copy of the study needs to be submitted to the Agency for evaluation because a readable copy no longer exists.** |

| Table A-2. Status of Ecotoxicity Data Requirements | | | | |
|---|---|---|---|---|
| **Data Requirement** | **Does EPA Have Data To Complete a Risk Assessment? (Yes, No)** | **Bibliographic Citation** | **Are additional data needed?** | **Comment** |
| 141-2 Honey Bee Residue on Foliage | No | N/A | No | |
| 141-5 Field Test for Pollinators | No | N/A | No | |
| OECD, Section 2 #207<br>Earthworm Acute Toxicity Test | No | N/A | No | |

## Appendix B-1.  The Chemistry of Chlorate

## A. Oxidation States of Chlorine

Chlorine (oxidation state 0) can form chemical species that include chlorine in different oxidation states. In aqueous media, the predominant species, their concentration, and reaction kinetics depend on pH, temperature, and the presence and nature of chemical species that can undergo redox reactions. That is, chlorine speciation (i.e., reduced and oxidized forms) in aqueous media is driven by thermodynamics (equilibria) as well as by kinetics. Table B-1 shows the oxidation states of chlorine and the names given to these species[39].

**Table B-1. Chlorine and Chlorine Species in Aqueous Media[40].**

| Oxidation State | Name of the Acid Form | Chemical Representatiof the Acid Form | Chemical Name of the Anion/Salts | Chemical Representation of the Anion |
|---|---|---|---|---|
| 0 | Not Applicable | Elemental chlorine, $Cl_2$ (gas) | Not Applicable | Not Applicable |
| -I (-1) | Hydrochloric acid | HCl | Chloride/ Chlorides | $Cl^-$ |
| I (+1) | Hypochlorous acid[a] | HOCl | Hypochlorite[b]/ Hypochlorites | "$ClO^-$" |
| III (+3) | Chlorous acid[a] | HOClO | Chlorite[b]/Chlorites | $ClO_2^-$ |
| V (+5) | Chloric Acid[a] | $HOClO_2$ | Chlorate[b]/Chlorates | $ClO_3^-$ |
| VII (+7) | Perchloric Acid | $HOClO_3$ | Perchlorate[b]/ Perchlorates | $ClO_4^-$ |

[a] Stable only in aqueous solutions; [b] Oxyanion.
The oxidation state of chlorine in chlorine dioxide ($ClO_2$) is IV

## Synthesis of Sodium Chlorate

Sodium chlorate is not a naturally occurring material. It is prepared by electrolysis of sodium chloride (NaCl brine) and it is an energy-intensive process. It requires 6 Faradays to produce one

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[39] The convention of using Roman numerals to express the oxidation state of an element that can exist in more than one oxidation states has the advantage of identifying the oxidation state of oxidants and reductants regardless of their chemical nature. For example, aqua ions, complexes, amorphous or crystalline mineral phase.

[40] The most important oxides of chlorine are "Chlorine Monoxide, $Cl_2O$" and "Chlorine Dioxide, $ClO_2$". Both are gases at room temperature. "$Cl_2O$" is the anhydride of hypochlorous acid. Chlorine dioxide is explosive as a liquid or concentrated gas and, for this reason it is generated *in-situ* when it is used as antimicrobial or wood-pulp bleaching agents. It is usually prepared by reducing sodium chlorate. The oxidation state of chlorine in chlorine dioxide, $ClO_2$, is IV (+4).

mole of chlorate and the reaction is endothermic (in practice, it takes 5 kW·hr to generate 1 kg of chlorate). The reaction proceeds via intermediates in a higher oxidation state than chloride, such as chlorine (oxidation state -I) and hypochlorite/hypochlorous acid (oxidation state I). The efficiency of chlorate formation by an electrolytic process is controlled by temperature and pH. The efficiency of chlorate formation may also decrease by non-electrolytic processes, such as by the presence of some ionic transition metal species that can act as reductants that can reduce chlorate to chloro species in lower oxidation states. Transition metals are metals that can exist in two or more oxidation states, such as Fe and Mn. Chloric acid, the corresponding acid form of chlorate, exists only in solution and it is a strong acid.

The electrochemical reactions involved in the preparation of sodium chlorate are:
Anode: Oxidation of Chloride to chlorine ($Cl^- \rightarrow ½\ Cl_2 + e^-$); Cathode: $H_2O + e^- \rightarrow ½H_2 + OH^-$
Mixing: $Cl_2 + 2\ OH^- \rightarrow Cl^- + O\ Cl^- + H_2O$ (disproportionation, i.e., reaction producing chemical species at a lower and a higher oxidation state)
Further disproportionation: $3O\ Cl^- \rightarrow ClO_3^- + Cl^-$
Further anodic oxidation: $O\ Cl^- + 2\ H_2O \rightarrow ClO_3^- + 2\ H_2$

Source: Kirk-Othmer Encyclopedia of Chemical Technology
Cotton, F.A. and Wilkinson, G. “Advanced Inorganic Chemistry”, 5th Edition, Wiley Interscience, 1988.
Greenwood and Earnshaw, “Chemistry of the Elements”, Pergamon

## B. Oxidation-Reduction (Redox) Chemistry of Chlorate

Chlorate is a strong oxidizing agent (oxidant; oxidizer). As such, chlorate can oxidize chemical species considered to be in their “reduced” state. That is, any oxidation requires a reductant. As a result, the oxidizer gets reduced and the reductant gets oxidized. Therefore, an oxidizer is an electron acceptor and the reductant is the electron donor.

The standard electrode potential ($E^o$, defined in terms of standard state conditions of reactants and products; Standard state conditions are 25° C, 298° K , 1 atm, and activity = 1.0 for all reactants and products) represents a redox reaction whose left-hand electrode is a hydrogen electrode. By convention, the hydrogen electrode half reaction is represented as $H^+$ (aqueous [41]at activity a= 1) + $e^-$ at equilibrium with ½ $H_2$ (g, 1 atm) and taken as 0.0 Volt[42]. The redox couples presented here follow the IUPAC convention[43] ($E^o$ is also represented as $E^o_h$ ). Thus, the electrode potential of a

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[41] “$H^+$” represents the hydrated proton, “$H_3O^+$”.

[42] The standard hydrogen electrode (SHE) is also represented by the symbol “NHE” (normal hydrogen electrode)

[43] Chlorate, an oxidizing agent, accepts electrons and generates Cl species at oxidation states lower than V(i.e, it gets reduced). In all redox reactions there is an electron donor (reducing agent; reductant) and an electron acceptor (oxidizing agent; oxidizer; oxidant). Thus, the electron donor species gets oxidized while the electron acceptor gets reduced. That is, redox processes involves electron transfer.

cell (*E*) is taken as the potential of the right-hand terminal with respect to that of the left-hand terminal. If the cell is written down in the opposite direction, the sign of *E* must be reversed.

The standard electrode potentials for reactions involving chlorate are presented in Table B-2 Equations 1 through 7 represent potentials at which chlorate is reduced (i.e., accepts electrons) and which are the reduced products at different electrode potentials. Equations 8 and 9 represent the reduction of perchlorate to chlorate. Note that the nature and redox potential for the reduced products of chlorate are pH and well as temperature dependent.

**Table B-2. Standard Electrode Potentials for Redox Reactions of Chlorate (Half-cell Potentials)**

| Redox Couple[a] | $E°/E°_b$, volts (V) | d $E°$ ($E°_b$)/dT, mVK $^{-1}$ (K= °Kelvin) |
|---|---|---|
| $ClO_3^- + \rightarrow 3H_2O + 6e^- \rightarrow Cl^- + 6\ OH^-$ (1) | $E°_b$, = 0.622 | $dE°_b)/dT$ = - 1.333 |
| $2\ ClO_3^- + 12\ H^+ + 10e^- \rightarrow Cl_2\ (g) + 6H_2O$ (2) | $E°$ = 1.468 | $dE°/dT$ = - 0.347 |
| $ClO_3^- + 2H_2O + 4e^- \rightarrow ClO^- + 4\ OH^-$ (3) | $E°_b$,= 0.488 | $dE°_b/dT$ = -1.467 |
| $ClO_3^- + 3H^+ + 3e^- \rightarrow HClO_2 + H_2O$ (4) | $E°$ = 1.181 | $dE°/dT$ = - 0.180 |
| $ClO_3^- + H_2O + 2e^{-1} \rightarrow ClO_2^- + 2OH^-$ (5) | $E°_b$, = 0.295 | $dE°_b/dT$= -1.467 |
| $ClO_3^- + 2\ H^+ + e^- \rightarrow ClO_2\ (g) + H_2O$ (6) | $E°$ = 1.175 | $dE°/dT$ = 1.026 |
| $ClO_3^- + H_2O + e^{-1} \rightarrow ClO_2\ (g) + 2OH^-$ (7) | $E°_b$, = - 0.481 | $dE°_b/dT$ = - 0.646 |
| $ClO_4^- + 2\ H^+ + 2e^{-1} \rightarrow ClO_3^- + H_2O$ (8) | $E°$ = 1.201 | $dE°/dT$ = -0.416 |
| $ClO_4^- + H_2O + 2e^{-1} \rightarrow ClO_3^- + 2OH^-$ (9) | $E°_b$, = 0.374 | $dE°_b/dT$ = -1.252 |

[a] Defined as any pair of the same element in different oxidation states. Source: **Standard Potentials in Aqueous Solutions**. Edited by Bard, A.J., Parsons, R., and Jordan, J. IUPAC, Commission on Electrochemistry and Electroanalytical Chemistry, Published by Marcel Dekker, Inc., New York, 1985. Most of these redox couples were experimentally determined

## Redox Reactions- General

The tendency for a redox reaction to proceed is determined by the electromotive potential (*emf*).That is, the *emf* is the driving force of the reaction. Because redox reactions involve chemical species that get reduced and chemical species that get oxidized, any redox reaction can be written as the sum of two half-reactions. Under real conditions, the activity of reactants and products deviate from the unit activity[44] of standard conditions. Therefore, $E^o$ needs to be corrected. This is done using the Nernst relationship[45]. For any redox reaction at 25° C (298° K)

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[44] The activity of ions in water is the effective concentration and it is thermodynamically more precise than the molar concentration. The activity of any ion $a_i$, is related to the concentration $c_i$ by the activity coefficient $\gamma_i$, ($a_i = \gamma_i\ c_i$). Discussion of methods for calculating $\gamma_i$ are beyond the scope of this Appendix.

[45] The Nernst equation correlates the *emf* with the Gibbs Free Energy, $\triangle G$. The $\triangle G$.is the negative value of the maximum electric work, $W$ ($\triangle G = - W = q \triangle E$ ), where $q$ is related to the amount of charge transferred at the completion of the reaction and $q$ is related to the number of electrons, n, involved in the reaction. Thus, $q = nF$, where $F$ is the Faraday Constant,

between *a* moles of reactant *A* and *b* moles of *B* to produce *c* moles of *C* and *d* moles of *D* (i.e, $aA + bB = cC + dD$),

$$E = E° - (0.059/n) \ln [C]^c [D]^d / [A]^a [B]^b = E° - (0.059/n) \ln \mathrm{K},$$

where K is the Equilibrium Constant

If $[\mathrm{D}] = [\mathrm{H}^+]$ and $[\mathrm{B}] = [\mathrm{H}_2]$ and since $[\mathrm{H}^+] = [\mathrm{H}_2] = 1$, the equation reduces to

$$E = E° - (0.059/n) \ln [C]^c/[A]^a$$

where [C]= [R]= concentration of the reduced form and [A]= the concentration of the oxidized form, both corrected for activity (γ),

$$E = E° - (0.059/n) \ln [\mathrm{R}]^{\gamma}{}_{\mathrm{R}}/[\mathrm{O}]^{\gamma}{}_{\mathrm{O}}$$

Since all oxidation reactions result in reduction of the oxidizer[46], the overall redox has also to consider the half-cell of the reductant. The sum of the two half-cells (i.e., the standard reduction and oxidation half-cells) give the *net* potential ($E_{net}$). It is $E_{net}$ what determines the thermodynamic feasibility of specific redox reactions,

$\triangle G = -n\mathrm{F}(E_{net}) = -n\mathrm{F}(E_{red} + E_{ox})$, where *n* is the number of electrons exchanged in the net reaction

Reactions with a negative $\triangle G$ ($\triangle G < 0$; or $E_{net} > 0$) can occur spontaneously.

## Predominance of Chemical Species in the Environment

The effects of pH on the form in which an element in a given oxidation state exists in natural waters can be summarized with chemical species predominance diagrams. Knowledge of the environmental pH is not sufficient for predicting the form (i.e., oxidation state; chemical species; phase) in which an element, the chlorine system in this case, will exist in natural waters. When a chemical element can exist in two or more oxidation states, it must also be taken into consideration whether the aqueous environment is well aerated (oxidizing) or polluted with organic wastes (reducing). Therefore, it becomes necessary to add the redox variable to expand the predominance diagram to include the reduction potential of the environment as well as the pH.

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which is the charge of each mole of electrons ($F$= 96,485 Coulombs/mole). Therefore, $\triangle G = -nF \triangle E$ and $\triangle G° = -nF \triangle E°$ for standard conditions and "0.059" applies only to the standard temperature of 298° K.

[46] Likewise, all reduction reactions result in oxidation of the reductant.

This type of predominance diagram is known as a Pourbaix-diagram or *E-pH* diagram[47], which can also be expressed in a p*E* scale. The p*E* (p*E*= -log *E*) scale is analogous to that of pH. It represents the concentration of the standard reducing agent and is obtained from the reduction potential by dividing by 0.059. Low *E* (p*E*) values represent a reducing environment, while high *E* (p*E*) values represent an oxidizing environment.

*Thermodynamics versus Kinetics*

The Standard Redox Potentials, as well as the predominance diagrams are based on equilibria relationships (i.e., thermodynamics). In the environment, particularly in heterogeneous media such as soils, suspended particulates in natural water, redox species are not generally in equilibrium and the concentrations of ionic species deviate from unit activity. In addition, redox potentials do not tell how fast the redox reactions take place (i.e., the kinetics of the redox reactions). Thus, a redox reaction that may be thermodynamically favored might be kinetically very slow[48]. In summary, the redox reactions based on thermodynamic equilibria indicates that the reaction *can* occur, but it does not mean that they *will* occur and how fast.

## Natural Redox Environments

A major factor controlling the redox environment is the nature and concentration of redox species. Major chemical species associated with reducing environments are transition metals in low oxidation states (e.g., Fe(II), Mn(II)), N-species in low oxidation states ($NO_2^-$; $NH_4^+$); S(-II) (e.g $HS^-$, $S^{2-}$; polysulfido species), and organic matter[49]. Major chemical species associated with oxidizing environments are dissolved dioxygen ($O_{2;}$ moleular oxygen), transition metals in high oxidation states such as Fe(III); Mn(III, IV), sulfate, and nitrate. In addition to “straight” redox reactions, many of the redox species in natural waters may also act as photosensitizers. Other factors controlling the redox chemistry of a natural environment are the population of aerobic and anaerobic microorganisms. In addition, many of the transition metals may be present as mineral phases that could be involved in surface-catalyzed reactions[50]. The half-cell reactions for important environmental reductants are presented below for selected species

Nitrogen System

**Table B-3. Half-cell reactions for important environmental reductants**

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[47] Pourbaix, M. Atlas d’équilibres èlectrochimiques à 25°C. Gauthier-Villars, Paris, 1963. Pourbaix diagrams are routinely used in corrosion and minerals processing work.

[48] For example, the conversion of Diamond-carbon to Graphite carbon is favored thermodynamically, but has a very slow kinetics.

[49] See “Reactions with Organic Matter”

[50] For example, surface reactions with minerals that are semiconductors (galena). For interfacial reactions such as these, the particle size distribution of the mineral phase is an important controlling factor

| **Redox Couple,** | **E°/E°$_b$, volts (V)** |
|---|---|
| $NO_3^- + 2H^+ + 2e^{-1} \rightarrow NO_2^- + H_2O$ | E° = 0.835<br>= 0.965 (pH 4-7) |
| $NO_3^{-+} + H_2O + 2e^{-1} \rightarrow NO_2^- + 2OH^-$ | E°$_b$ = 0.01 |
| $NO_3^{-+} + H_2O + 2e^{-1} \rightarrow NO_2^- + 2OH^-$ | E°$_b$ = 0.01 |
| $NO_3^- + 10H^+ + 6e^{-1} \rightarrow NH_4^+ + 3 H_2O$ | E° = 0.87 |
| $NO_2^- + 8H^+ + 8e^{-1} \rightarrow NH_4^+ + 2 H_2O$ | E° = 0.897 |
| $NO_2^- + 7H^+ + 8e^{-1} \rightarrow NH_3(aq) + 2 H_2O$ | E° = 0.806 |
| $NO_2^- + 6H^+ + 8e^{-1} \rightarrow NH_3 (g)$ | E° = 0.789 |

## The Iron System

In aqueous solutions, Fe(II) and Fe(III) are the common oxidation states, yet the chemistry of Fe(II)/Fe(III) is extremely complex. In addition to pH-pE dependent reactions, Fe(II)/Fe(III) can generate a wide range of chemical species than can occur as discreet aqua ions, colloidal species, and distinct mineral phases of varied composition, all of which can undergo specific redox reactions. In acid solutions (pH < 2 and in the absence of complexing anions, the predominant species is the hexaaqua Fe(II) complex , $[Fe(H_2O)_6]^{2+}$, which hydrolyzes to first form $FeOH^+$ . With increasing pH, oxidation of Fe(II) to Fe(III) species takes place via a series of hydroxo complexes, precipitated hydroxides, and mineral oxides/hydroxyoxides (e.g., hematite/magnetite; goethite). While oxidation involving dioxygen (molecular oxygen) occurs, other oxidants can also oxidize Fe(II). Given the complexity of natural systems in terms of types and concentration of natural oxidants (e.g., nitrate/nitrite), competitive redox reactions are expected to occur in the environment.

In acid solution (pH 0),

$$\text{Fe(III)} + e \rightarrow \text{Fe (II)}, \qquad E° = +0.771 \text{ V}$$

In alkaline solution,

$$\text{Fe (III) (as } FeO_4^{2-}) + e \rightarrow \text{Fe (III) (as } FeO_2^{-}) \qquad E° = +0.55 \text{ V}$$

## The Sulfur System

Like with chlorine, sulfur can exist in more than one oxidation states. The oxidation state of sulfur in the sulfide system is -II. The inorganic sulfide species that might be present in anoxic natural waters are: $H_2S$ (hydrogen sulfide, gas; hydrogen sulfide aqueous), $HS^-$, and $S^{2-}$. The predominance of each of these species depends on pH and is governed by the dissociation constants, $K_1$ and $K_2$, of hydrogen sulfide in water[51]. In addition, polysulfides $S_n^{2-}$ may be present in some aqueous environment. Sulfide species are often found as complexes with some metal ions. Higher oxidation states of sulfur (e.g., II, IV, VI) are more predominant in oxic systems, of which sulfate ($SO_4^{2-}$, S(VI)) is an example. Like for chlorine, the higher oxidation states of sulfur are oxyanions, but the sulfur oxyanions are more numerous and complex than those of chlorine.

Organic Material

The reactions below are examples of how different functional groups undergo redox reactions. Many of these functional groups are present in natural organic matter, for example, hydroxyl groups in humic acids, but other simpler organic species such as oxalate may also be present in natural water.

**Table B-4. Redox Reactions with Organic Functional Groups**

| Type of Oxidation Reactions | Type of Reduction Reactions |
|---|---|
| Alkanes to alcohols (R-H → R-OH) | Reductive dehalogenation (R-X → R-H) |
| Alcohols to aldehydes (R-OH → RCHO) | Vicinal dehalogenation (X-R-R-X→ R=R) |
| Aldehydes to acids (RCHO → RCOOH) | Nitro reduction ($R\text{-}NO_2 \rightarrow R\text{-}NH_2$) |
| Dehydrogenation (-CH-CH- → -C=C-) | Azo reduction ($Ar\text{-}N{=}N\text{-}Ar \rightarrow 2Ar\text{-}NH_2$) |
| Oxidative coupling (2R-OH→ R-O-R) | Disulfide to thiol ( R-S-S-R→ 2R-SH) |
| Hydroquinones to quinones (HO-Phenyl-OH→ O=Phenyl=O) | Deoxygenation of sulfoxo and sulfoxides<br>($R\text{-}SO_2\text{-}R \rightarrow R\text{-}SO\text{-}R \rightarrow R\text{-}S\text{-}R$) |
| Thiooxidation (R-S-R→ R-SO-R; $R\text{-}SO_2\text{-}R$) | Nitrosamine Reduction ($R_2N\text{-}N{=}O \rightarrow R_2N\text{-}H + HNO$) |
| Fomation of disulfide linkages (2R-SH → R-S-S-R) | Quinones to hydroquinones (O=Phenyl=O→HO-Phenyl-OH) |
| - | Dealkylation (R-Y-R’ → R-YH + R’H) |

## Redox Conditions in Soils and Water Controlling the Behavior of Chlorate in the Environment

### *Soils*

If a pH=9 is taken as the upper bound of a soil solution, the lower extreme value of p*E* is -9 (assuming that $H_2$, gas, is at the state of 1 atm and 298° K). The theoretical range of p*E* in soil is- $9 < pE < +16.6$. However, a p*E* range of $-6 < pE < 12$ is more realistic. A pE of -6 corresponds to the “strongly reduced” boundary and + 12 to the “strongly oxidized” boundary. Like for

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[51] At 18° C in water, $K_1 = 9.1 \times 10^{-8}$, $H_2S\ (aq) \rightarrow H^+ + HS^-$
$K_2 = 1.2 \times 10^{-12}$, $HS^- \rightarrow H^+ + S^{2-}$

natural waters, the redox environment/behavior of the soil depends on the nature, concentration and $E_h$- pH dependence of redox species.

Table B-5. pE and Redox Conditions of Soils

| **Medium** | **pE** |
|---|---|
| Soil, suboxic | $+2 < pE < +7$ |
| Soil, oxic | $+7 < pE$ |
| Soil, anoxic | $pE < +2$ |

*Water*

Chlorate is more stable under alkaline than acidic conditions. Thus, based on pH dependence alone, it would be less persistent in acidic than alkaline natural waters. In general, it could be said that it would be less persistent in areas of the country where the pH of natural water is < 7. Acidic natural waters are predominantly found east of the Mississippi River, with acidity increasing with latitude[52]. Likewise, chlorate would be more persistent in the more alkaline water bodies West of the Mississippi River.

However, as previously indicated, pH is not the only controlling factor in the persistence of chlorate because pH-dependent redox reactions must be taken into consideration. Thus, the redox conditions of the water body also controls the persistence of chlorate. In reducing environments (i.e., low $E$; p$E$), chlorate would be less persistent than in oxidizing environments (high $E$; p$E$).

In general, the variability in persistence of chlorate in natural waters has a spatial and temporal component. Spatial variability would be related to the geographical location of the use site (pH and nature of redox species) and temporal (seasonal variations and concentration of redox species). Therefore, where, when, and how the chemical is used are contributing factors to the persistent of chlorate in water.

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[52] Factors contributing to the acidity of natural waters in the Middle Atlantic/ Northeast of the USA are acid mine drainaged and/or deposition of acid rain.

**Table B-6. Spatial and temporal variability related to the geographical location use site**

| pH | pE | pH of Natural Water Systems | Seasonal Variability of pE |
|---|---|---|---|
| < 7 | Low | East of the Mississippi River, particularly in the Mid-Atlantic and Northeastern regions | Summer; Early Fall (High concentration of organic species) |
| < 7 | High | East of the Mississippi River, particularly in the Mid-Atlantic and Northeastern regions | Winter; Early spring |
| > 7 | Low | West of the Mississippi River | Summer; Early Fall (High concentration of organic species) |
| > 7 | High | West of the Mississippi River | Winter; Early spring |

A spatial and temporal variability of chlorate is also expected in soils. Factors like pH, organic matter content and type, moisture content, microbial population.

# Appendix B-2. Discussion on Chlorate Redox Chemistry as it Relates to Exposure to Aquatic Organisms in the Environment

**MEMORANDUM:** January 27, 2005

**SUBJECT:** pE/pH Predominance and 3D activity ratio diagrams for aqueous chlorine species at thermodynamic equilibrium

**TO:** Daniel Rieder, Chief
Environmental Risk Branch 3
Environmental Fate and Effects Division/Office of Pesticide Programs/USEPA

Silvia Termes, Ph.D., Chemist
Environmental Risk Branch 3
Environmental Fate and Effects Division/Office of Pesticide Programs/USEPA

**FROM:** Henry Nelson, Ph.D., Chemist
Exposure Assessment Division
Office of Science and Coordination Policy (OSCP/OPPTS/USEPA)

This memo provides pE/pH predominance and 3D activity fraction diagrams for aqueous chlorine species at thermodynamic equilibrium. Chlorine species distributions in actual natural waters at any given time may deviate substantially from such equilibrium computations since natural waters are not at equilibrium and very rarely even approach equilibrium.

Aqueous chlorine reactions considered along with associated equilibrium expressions and equations used to generate activity ratios and redox pair boundary lines in the formation of predominance diagrams are listed in Attachment A. A thermodynamic spreadsheet used to compute $\Delta G^0_{rxn}$ and log $K_{equil} = \Delta G^0_{rxn}/(-2.3RT)$ (where $K_{eq}$ = thermodynamic activity based equilibrium constant) for the various reactions listed in Attachment A is provided in Attachment B. The format of the thermodynamic spreadsheet provided in Attachment B was developed by Dr. Jim Hetrick. Free energies of formation are in kJ/mol. This memo is an extension of Dr. Hetrick's computations of chlorine species mole fractions.

Mixed equilibrium constants are referred to as "mixed" because their expressions contain chemical species concentrations but $H^+$ and $e^-$ activities. Mixed equilibrium constants are often used in equilibrium computations (Jensen 2004) because while the use of concepts such as mass balance generally requires the use of chemical species concentrations rather than activities, pH and redox electrodes respond to $H^+$ and $e^-$ activities rather than concentrations where

$$pH = -\log(H^+) \qquad pE = -\log(e^-)$$

Thermodynamic activity based equilibrium constants are equal to the product of the quotient of activity coefficients for the chemical species times mixed equilibrium constants. For example consider the following reaction:

$$Cl^- + H_2O \leftrightarrow ClO^- + 2H^+ + 2e^- \qquad \text{(eq. 1)}$$

The thermodynamic activity based equilibrium constant for the reaction is related to the mixed equilibrium constant for the reaction by:

$$K_{eq} = \frac{(ClO^{-})(H^{+})^{2}(e^{-})^{2}}{(Cl^{-})} = \frac{\gamma_{ClO^{-}}[ClO^{-}](H^{+})^{2}(e^{-})^{2}}{\gamma_{Cl^{-}}[Cl^{-}]} = \frac{\gamma_{ClO^{-}}}{\gamma_{Cl^{-}}}K_{mixed} \qquad \text{(eq. 2)}$$

where

$$K_{mixed} = \frac{[ClO^{-}](H^{+})^{2}(e^{-})^{2}}{[Cl^{-}]} \qquad \text{(eq. 3)}$$

and

$\gamma$ = activity coefficients
( ) = designates activities
[ ] = designates concentrations

The construction of predominance diagrams relies on considerations of mass balance and assumptions of equivalence of molar concentrations along redox couple boundaries which in turn requires the use of chemical species concentrations instead of activities. At the same time it is convenient to maintain the $H^{+}$ and $e^{-}$ levels as activities as previously discussed. The most accurate way of generating predominance diagrams is to convert thermodynamic activity based equilibrium constants (which are computed from standard free energies of formation) to mixed thermodynamic activity based and concentration based equilibrium constants by dividing the activity based equilibrium constants by quotients of the activity coefficients of the chemical species. For example, from eq. 2 above, it can be seen that the $K_{mix}$ for the eq. 1 reaction is given by:

$$K_{mix} = \frac{K_{eq}}{\left(\gamma_{ClO^{-}}/\gamma_{Cl^{-}}\right)} = \frac{\gamma_{Cl^{-}}}{\gamma_{ClO^{-}}}K_{eq} \qquad \text{(eq. 4)}$$

The mixed equilibrium constants are then set equal to mixed quotients that use concentrations for the chemical species but activities for $H^{+}$ and $e^{-}$. However, predominance diagrams are semi-qualitative (they predict general predominance areas rather than the actual activities or concentrations of various species). Therefore, equations for generating predominance diagrams are often approximations based on the assumption that the expressions for the mixed equilibrium constants are approximately equal to the thermodynamic equilibrium constants. That assumption is used in the generation of the predominance diagrams in this document. The accuracy of that assumption depends upon how close the quotient of activity coefficients is to one. The chlorine species considered here are either neutral or univalent. Most freshwaters have ionic strengths between 0.001 M and 0.01 M (Jensen 2004). In freshwaters with ionic strengths between 0.001 and 0.01 M, the activity coefficients of neutral species will be close to one. Based on the use of the Debye-Huckel equation for ionic strengths up to 0.005 M and the extended Debye-Huckel equation for ionic strengths between 0.005 M and 0.01 M, the activity coefficients of univalent ions range from approximately 0.9 in waters with ionic strength = 0.01 M to close to one in waters with ionic strengths = 0.001 M (Langmuir 2002). Therefore, the assumption that the expressions for the mixed equilibrium constants are approximately equal to the thermodynamic equilibrium constants are generally adequate for generating semi-qualitative pE/pH predominance diagrams for freshwaters.

In addition to generating predominance diagrams, activity fractions are generated for various chlorine species as a function of pE and pH. This is done by rearranging the equations in Attachment A to give the activity of each chlorine species considered in terms of the activity of a common chlorine species ($Cl^-$ is used here but any of the species could have served as the common species). The ratio of the activity of each chlorine species (in terms of the $Cl^-$ activity) to the total activity of chlorine species (in terms of the $Cl^-$ activity) is then computed. By performing computations for pHs $\geq 4$, $Cl_{2(aq)}$ does not have to be included in the activity ratio computations because the construction of predominance diagrams indicates that $Cl_{2(aq)}$ will be predominant (if at all - see discussion of Case 1 versus Case 2 below) at pEs above the stability of water and at pHs < 2 well below the lower pH limit of natural waters (pH 5) and well below the lower pH limit of our calculations (pH 4). Not including $Cl_{2(aq)}$ in the activity fraction computations allows for complete cancellation of the $Cl^-$ activity from the numerator and denominator of each ratio. The activity fractions are in terms of the thermodynamic activity based equilibrium constants (computed in the Attachment B thermodynamic spreadsheet), pH, and pE.

Mole fractions could not be computed because they would be in terms of the mixed equilibrium constants which were not computed (only thermodynamic activity based equilibrium constants were computed). However, for low ionic strength waters, the activity fractions provide an approximate estimate of mole fractions.

Two cases are considered. Case 1 considers only the lower oxidation state chlorine species ($Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO). Case 2 considers higher oxidation state chlorine species ($ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$) as well as the lower oxidation state chlorine species ($Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO). Case 1 is included in this memo only because it is the case considered by several aquatic chemistry texts. **However, Case 1 is misleading** because it results in predominance and activity fraction diagrams that shows predominance areas and areas of high activity fractions for $ClO^-$, and HClO that are not reflected in the much more accurate Case 2 predominance and activity fraction diagrams that consider higher oxidation state chlorine species as well as lower oxidation state chlorine species.

The more accurate Case 2 shows predominance areas and high activity fractions for only $ClO_4^-$ and $Cl^-$. **Although Case 1 and Case 2 differ substantially for $ClO^-$, HClO, and $ClO_4^-$, they both show $Cl^-$ as the only predominant species at thermodynamic equilibrium within the pE and pH ranges of natural waters.**

**Case 1:** Case 1 considers only the lower oxidation state chlorine species ($Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO). A pE/pH predominance diagram considering only those lower oxidation state chlorine species is provided in several aquatic chemistry texts (e.g., Stumm and Morgan 1995; Pankow 1991; Snoeyink 1980; Jensen 2004). That diagram is recreated independently here (Chart 1a) using a more systematic approach involving the separate determination of predominance areas for each chlorine species (Attachment C, Charts 1b through 1e) and then combining the separate diagrams into one predominance diagram (Chart 1a). The general use of such a systematic approach for generating pE/pH predominance diagrams was recommended by Benjamin (2002).

Because of the 2 to 1 chlorine stoichiometry of $Cl_{2(aq)}$ compared to other aqueous chlorine species considered in Case 1, the development of a predominance area for $Cl_{2(aq)}$ in an overall pE/pH predominance diagram for aqueous chlorine species requires consideration of chlorine mass balance and an assumption concerning total chlorine (Stumm and Morgan 1995; Pankow 1991; Snoeyink 1980; Jensen 2004).

Chart 1a was generated using the same assumption (total chlorine concentration = 0.04 M) as used in those references. A total chlorine concentration of 0.04 M is somewhat higher than typical chlorine background concentrations in freshwater. However, the use of a higher assumed total chlorine results in a slightly larger $Cl_{2(aq)}$ predominance area in Chart 1a that is easier to illustrate than when using a smaller assumed total chlorine. It is somewhat academic in that the the $Cl_{2(aq)}$ predominance area in Chart 1a is still small and still occurs at high pEs/ low pH well outside the pE & pH ranges of natural waters.

In addition to a small predominance area for $Cl_{2(aq)}$ at high pEs and very low pHs, Chart 1a for Case 1 predicts predominance areas for HClO at high pEs (outside those of natural waters) and acidic pHs, for $ClO^-$ at high pEs (also outside those of natural waters) and alkaline pHs, and **for $Cl^-$ at lower pEs including those within the range of pE and pH of natural waters (region ABCD in Chart 1a).** The Case 1 predominance diagram Chart 1a is misleading because it shows predominance areas for $ClO^-$, and HClO that are not reflected in the Case 2 predominance diagram that considers higher oxidation state chlorine species as well as lower oxidation state chlorine species.

Case 1 activity fraction diagrams were generated for $Cl^-$, $ClO^-$, and HClO for pHs between 4 and 10 and for pEs between -10 and 30. The Case 1 $Cl^-$ activity fraction was generated from equation 5 below. The Case 1 $ClO^-$ and HClO activity fractions were generated from equations 2f and 3f, respectively in Attachment A.

$$f_{Cl^-(Case1)} = \frac{(Cl^-)}{(Cl^-)+(ClO^-)+(HClO)} = \frac{(Cl^-)}{(Cl^-)+\frac{K_{eq2}(Cl^-)}{(H^+)^2(e^-)^2}+\frac{K_{eq3}(Cl^-)}{(H^+)(e^-)^2}} = \frac{1}{1+\frac{K_{eq2}}{(H^+)^2(e^-)^2}+\frac{K_{eq3}}{(H^+)(e^-)}} =$$

$$\frac{1}{1+\frac{10^{\log K_{eq2}}}{(10^{-pH})^2(10^{-pE})^2}+\frac{10^{\log K_{eq3}}}{(10^{-pH})(10^{-pE})^2}} = \frac{1}{1+\frac{10^{-58.1}}{(10^{-pH})^2(10^{-pE})^2}+\frac{10^{-50.6}}{(10^{-pH})(10^{-pE})^2}}$$

(eq. 5)

As expected, the Case 1 activity fraction diagrams for $Cl^-$, $ClO^-$, and HClO (Charts 2a, 2b, and 2c, respectively) are consistent with the Case 1 predominance diagram 1a with high activity fractions approaching 1 in areas of pE and pH where the Case 1 predominance diagram 1a indicates they are the predominant species. However, like Case 1 predominance diagram Chart 1a, Case 1 activity fraction diagrams Charts 2b and 2c are misleading because they show areas of high activity fractions for $ClO^-$, and HClO that are not reflected in the Case 2 activity fraction diagrams that consider higher oxidation state chlorine species as well as lower oxidation state chlorine species.

**Case 2:** Case 2 is much more accurate than Case 1 because it considers higher oxidation state chlorine species ($ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$) as well as the lower oxidation state chlorine species ($Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO). A pE/pH predominance diagram considering the higher oxidation state chlorine species as well as the lower oxidation state chlorine species is provided in Chart 3a. A systematic approach was used involving the separate determination of predominance areas for each chlorine species (Attachment D, Charts 3b through 3i) and then combining the separate diagrams into one predominance diagram (Chart 3a). As previously indicated, the general use of such a systematic approach for generating pE/pH predominance diagrams was recommended by Benjamin (2002).

Chart 3a for Case 2 predicts predominance areas for only $ClO_4^-$ at high pEs (above those of natural waters), and **for $Cl^-$ at lower pEs including those within the range of pE and pH of natural waters (region ABCD in Chart 3a).**

Case 2 activity fraction diagrams were generated for $Cl^-$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$ for pHs between 4 and 10 and for pEs between -10 and 30. The Case 2 $Cl^-$ activity fraction was generated from equation 6 below. The Case 2 $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$ activity ratios were generated from equations 2g, 3g, 4f, 5f, 6f, and 7f, respectively, in Attachment A.

$$f_{Cl^-(Case\,2)} = \frac{(Cl^-)}{(Cl^-)+(ClO^-)+(HClO)+(ClO_2^-)+(ClO_{2(aq)})+(ClO_3^-)+(ClO_4^-)} =$$

$$\frac{(Cl^-)}{(Cl^-)+\frac{K_{eq2}(Cl^-)}{(H^+)^2(e^-)^2}+\frac{K_{eq3}(Cl^-)}{(H^+)(e^-)^2}+\frac{K_{eq4}(Cl^-)}{(H^+)^4(e^-)^4}+\frac{K_{eq5}(Cl^-)}{(H^+)^4(e^-)^5}+\frac{K_{eq6}(Cl^-)}{(H^+)^6(e^-)^6}+\frac{K_{eq7}(Cl^-)}{(H^+)^8(e^-)^8}} =$$

$$\frac{1}{1+\frac{K_{eq2}}{(H^+)^2(e^-)^2}+\frac{K_{eq3}}{(H^+)(e^-)^2}+\frac{K_{eq4}}{(H^+)^4(e^-)^4}+\frac{K_{eq5}}{(H^+)^4(e^-)^5}+\frac{K_{eq6}}{(H^+)^6(e^-)^6}+\frac{K_{eq7}}{(H^+)^8(e^-)^8}} =$$

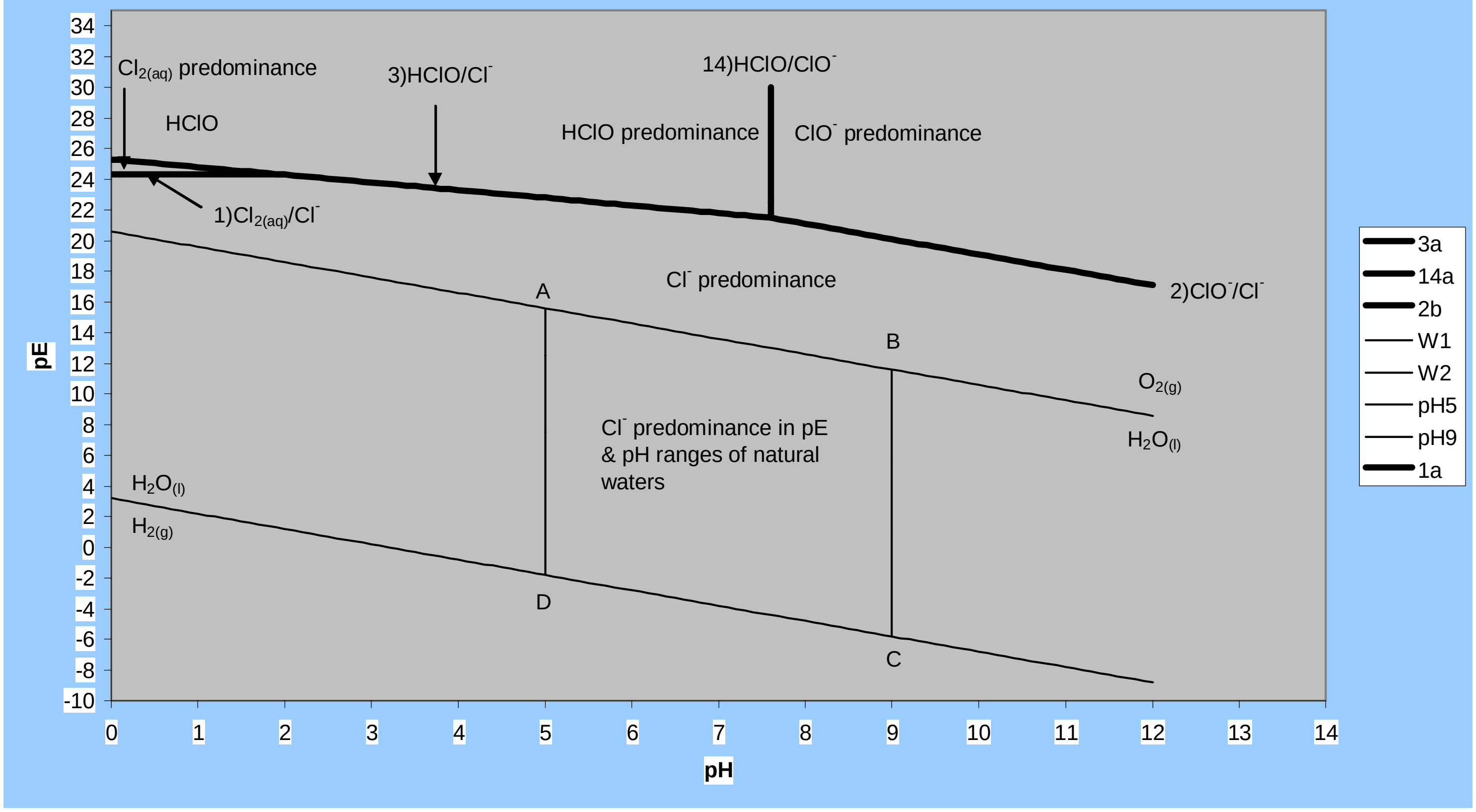
$$\frac{1}{1+\frac{10^{\log K_{eq2}}}{(10^{-pH})^2(10^{-pE})^2}+\frac{10^{\log K_{eq3}}}{(10^{-pH})(10^{-pE})^2}+\frac{10^{\log K_{eq4}}}{(10^{-pH})^4(10^{-pE})^4}+\frac{10^{\log K_{eq5}}}{(10^{-pH})^4(10^{-pE})^5}+\frac{10^{\log K_{eq6}}}{(10^{-pH})^6(10^{-pE})^6}+\frac{10^{\log K_{eq7}}}{(10^{-pH})^8(10^{-pE})^8}} =$$

$$\frac{1}{1+\frac{10^{-58.1}}{(10^{-pH})^2(10^{-pE})^2}+\frac{10^{-50.6}}{(10^{-pH})(10^{-pE})^2}+\frac{10^{-109.1}}{(10^{-pH})^4(10^{-pE})^4}+\frac{10^{-126.8}}{(10^{-pH})^4(10^{-pE})^5}+\frac{10^{-147.1}}{(10^{-pH})^6(10^{-pE})^6}+\frac{10^{-187.8}}{(10^{-pH})^8(10^{-pE})^8}}$$

(eq. 6)

As expected, the Case 2 activity fraction diagrams for predominant species $Cl^-$ and $ClO_4^-$ (Charts 4a and 4b) are consistent with the Case 2 predominance diagram 3a with high activity fractions approaching 1 in areas of pE and pH where the Case 2 predominance diagram 3a indicates they are the predominant species. The Case 2 activity fraction diagrams for the other species ($ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, and $ClO_3^-$) (Charts 4c through 4g in Attachment E) are also consistent with the Case 2 predominance diagram 3a in that none are shown as predominant in Case 2 predominance diagram 3a and none have activity ratios > $10^{-6}$.

**Chart 1a: Case 1 aqueous chlorine species predominance diagram: (Considering only $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO); Chart 1a from combination of Charts 1b - 1e in Attachment C ; $Cl^-$ predominant in region ABCD representing pE & pH ranges of natural waters.**



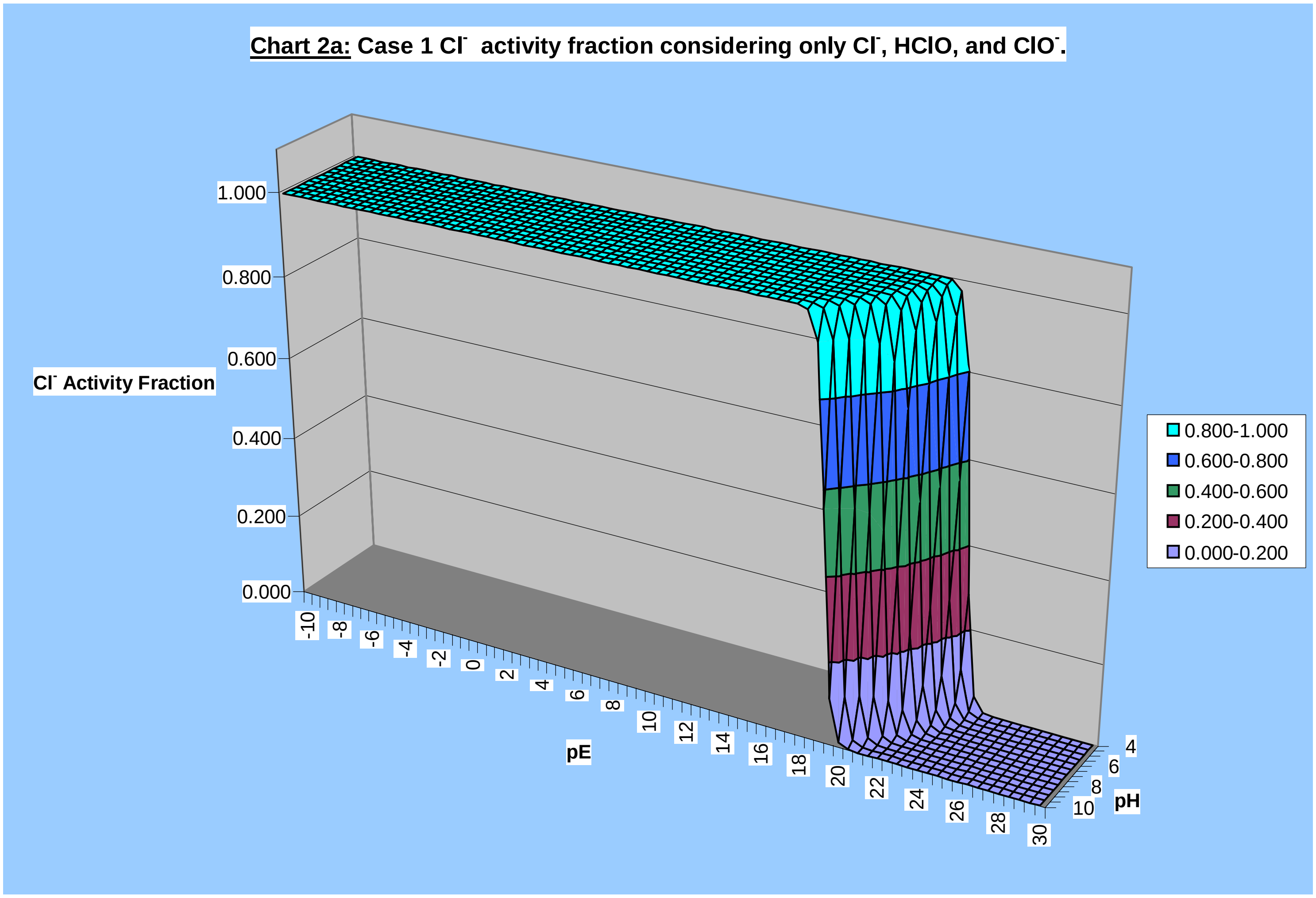


**Chart 2a:** Case 1 $Cl^-$ activity fraction considering only $Cl^-$, HClO, and $ClO^-$.

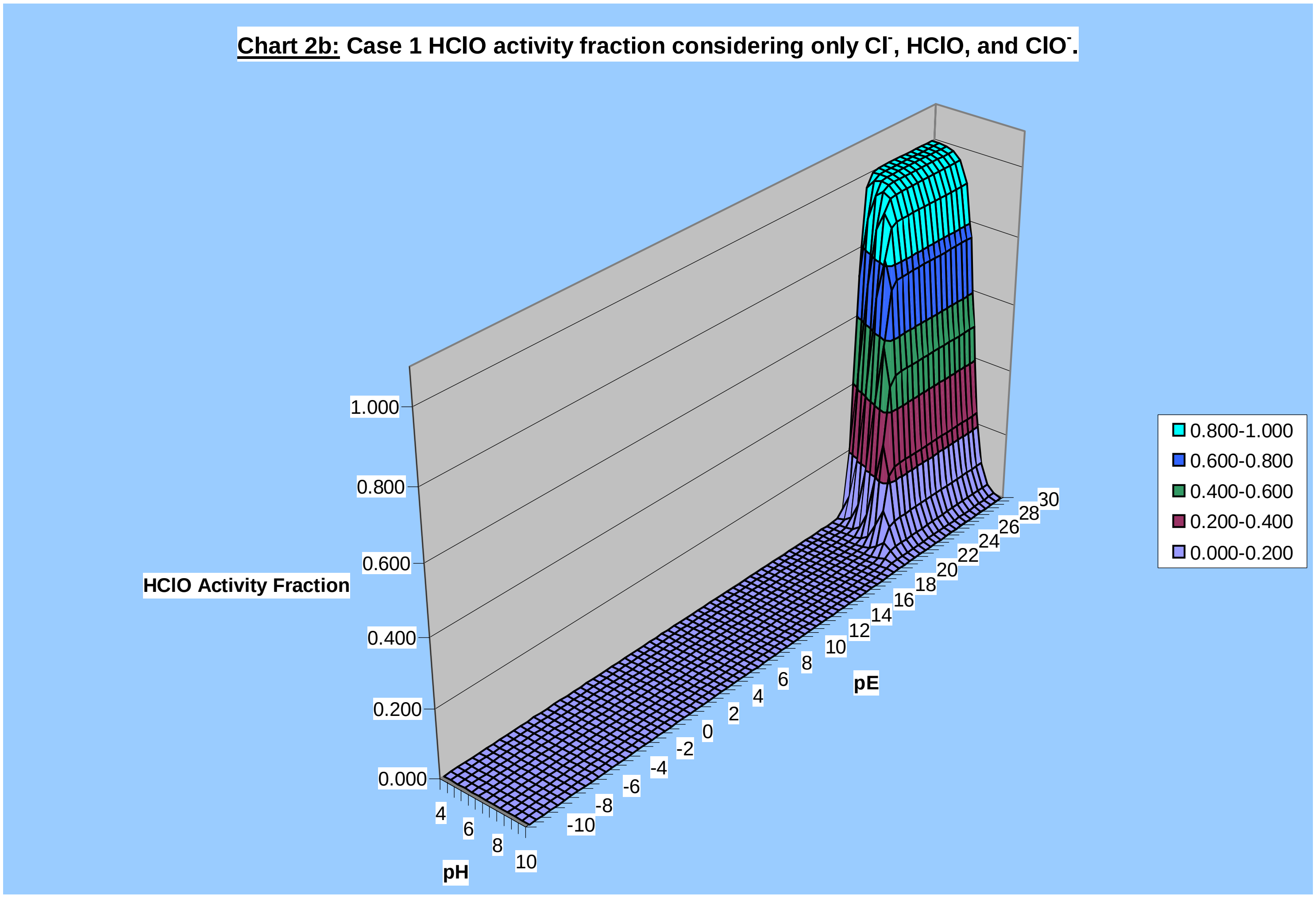


**Chart 2b:** **Case 1 HClO activity fraction considering only $Cl^-$, HClO, and $ClO^-$.**

**Chart 2c: Case 1 ClO$^-$ activity fraction considering only Cl$^-$, HClO, and ClO$^-$.**

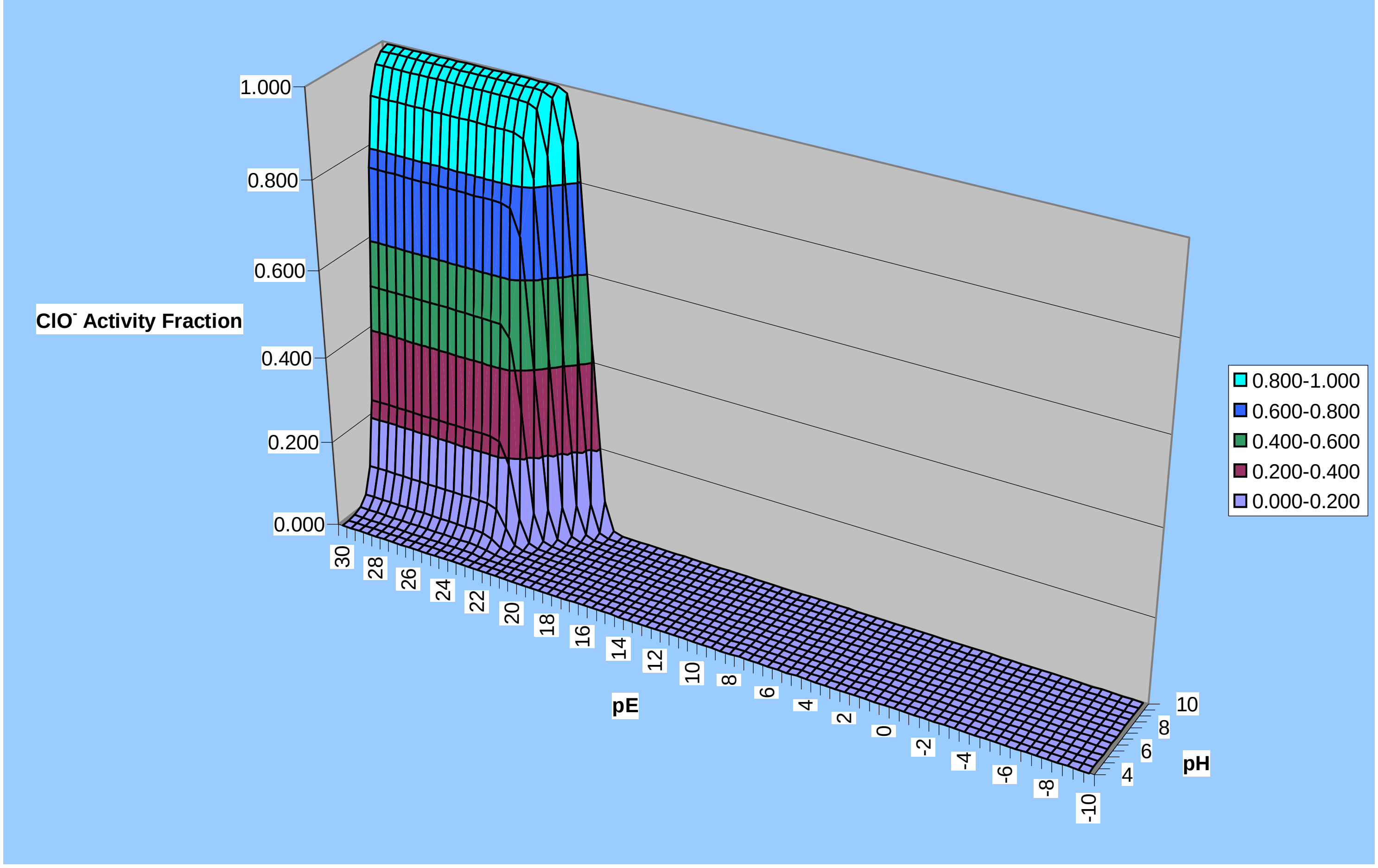
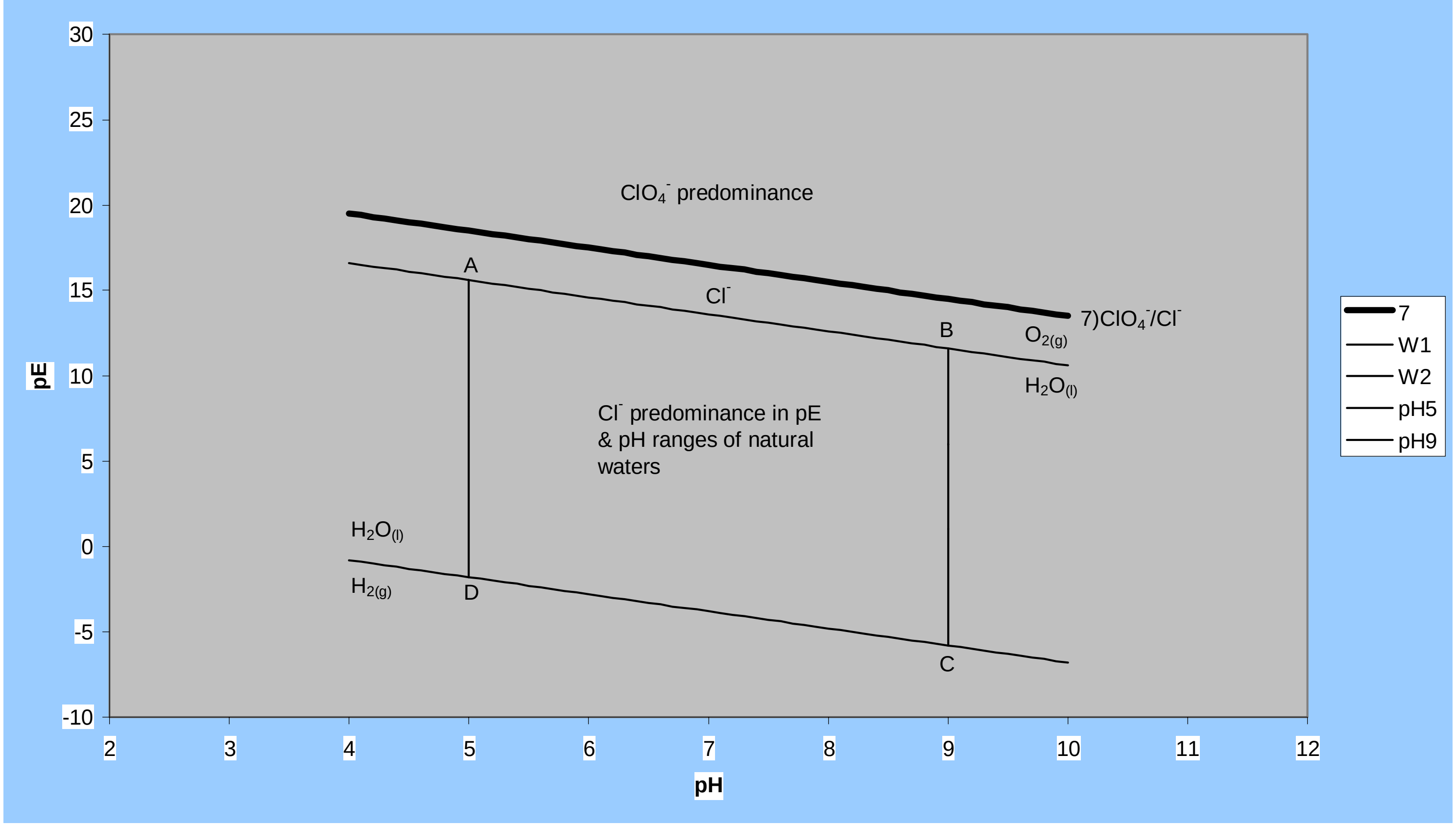


**Chart 3a: Case 2 aq. chlorine species predominance diagram: (Considering Cl-, $Cl_{2(aq)}$, ClO-, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$); Based on Charts 3b - 3i in Attachment D; Cl- predominant in region ABCD representing pE & pH ranges of natural waters.**



## ATTACHMENT A to Appendix B-2:

### Primary chlorine species in aqueous solution:

The primary chlorine species in aqueous solution are $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$ in which Cl exhibits oxidation states of -I, 0, I, III, IV, V, and VII, respectively. $HClO_3$ and $HClO_4$ are completely dissociated strong acids and $HClO_2$ has a $pK_a = 2$. Therefore they are not further considered here for computations at pHs $\geq 4$.

Provided below are:

(a) 28 reactions between each aqueous chlorine species.
(b) Equations for the thermodynamic activity based equilibrium constant for each reaction
(c) Equations for the mixed equilibrium constant for each reaction
(d) The logarithm of the approximate equation for the equilibrium constant for each reaction
(e) Equations for boundary lines used in generating pE/pH predominance diagrams for aqueous chlorine species. These equations are derived by substituting the value of the logarithm of the equilibrium constant into the previous equation and assuming that along the boundary the concentration of the species on one side of the boundary = the concentration of the species on the other side of the boundary.
(f) Equations for Case 1 and Case 2 activity fractions for each reaction

The thermodynamic activity based equilibrium constant computations were performed using the Attachment B Excel spreadsheet. The format of the spreadsheet used for thermodynamic computations was developed by Dr. Jim Hetrick.

### Reactions 1 - 7 (reactions involving $Cl^-$):

**Rxn 1:** $2Cl^- \leftrightarrow Cl_{2(aq)} + 2e^-$ (eq. 1a)

$$K_{eq1} = \frac{\left(Cl_{2(aq)}\right)\left(e^-\right)^2}{\left(Cl^-\right)^2} \quad \text{(eq. 1b)}$$

$$K_{mix1} = \frac{\left[Cl_{2(aq)}\right]\left(e^-\right)^2}{\left[Cl^-\right]^2} \quad \text{(eq. 1c)}$$

For generating predominance diagrams, assume that $K_{eq1} \sim K_{mix1}$ such that

$$\log K_{eq1} \approx \log K_{mix1} = \log \frac{\left[Cl_{2(aq)}\right]}{\left[Cl^-\right]} + 2\log\left(e^-\right) = \log \frac{\left[Cl_{2(aq)}\right]}{\left[Cl^-\right]} - 2pE \qquad \text{(eq. 1d)}$$

Along the $Cl_{2(aq)}/Cl^-$ boundary line, it is reasonable to assume that $[Cl_{tot}] \sim [Cl^-] + 2[Cl_{2(aq)}]$. Therefore, along the boundary for a total chlorine concentration $[Cl_{tot}] = 0.04$ mol/L, $[Cl^-] \sim 0.02$ mol/L and $[Cl_{2(aq)}] \sim 0.01$ mol/L. From the attached thermodynamic spreadsheet, $\log K_{eq1} = -47.2$. Substituting those values into eq. 1d and rearranging gives the following equation for the $Cl_{2(aq)}$ $/Cl^-$ boundary line:

$$2pE = 47.2 + \log \frac{[0.01]}{[0.02]^2} = 47.2 + \log(25) = 47.2 + 1.4 = 48.6 \Rightarrow \quad pE = 24.3$$

(eq. 1e)

**<u>Rxn 2:</u>** $Cl^- + H_2O \leftrightarrow ClO^- + 2H^+ + 2e^-$ (eq. 2a)

$$K_{eq2} = \frac{\left(ClO^-\right)\left(H^+\right)^2\left(e^-\right)^2}{\left(Cl^-\right)} \qquad \text{(eq. 2b)}$$

$$K_{mix2} = \frac{\left[ClO^-\right]\left(H^+\right)^2\left(e^-\right)^2}{\left[Cl^-\right]} \qquad \text{(eq. 2c)}$$

For generating predominance diagrams, assume that $K_{eq2} \sim K_{mix2}$ such that

$$\log K_{eq2} \approx \log K_{mix2} = \log \frac{\left[ClO^-\right]}{\left[Cl^-\right]} + 2\log\left(H^+\right) + 2\log\left(e^-\right) = \log \frac{\left[ClO^-\right]}{\left[Cl^-\right]} - 2pH - 2pE$$

(eq. 2d)

Along the $ClO^-/Cl^-$ boundary line, $[ClO^-] = [Cl^-]$ so $\log\{[ClO^-]/[Cl^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq2} = -58.1$. Substituting those values into eq. 2d and rearranging gives the following equation for the $ClO^-/Cl^-$ boundary line:

$$2pE = 58.1 - 2pH \Rightarrow \quad pE = 29.1 - pH \qquad \text{(eq. 2e)}$$

$$f_{ClO^-(Case1)} = \frac{(ClO^-)}{(Cl^-)+(ClO^-)+(HClO)} = \frac{\frac{K_{eq2}(Cl^-)}{(H^+)^2(e^-)^2}}{(Cl^-)+\frac{K_{eq2}(Cl^-)}{(H^+)^2(e^-)^2}+\frac{K_{eq3}(Cl^-)}{(H^+)(e^-)^2}} = \frac{\frac{K_{eq2}}{(H^+)^2(e^-)^2}}{1+\frac{K_{eq2}}{(H^+)^2(e^-)^2}+\frac{K_{eq3}}{(H^+)(e^-)}} =$$

$$\frac{\frac{10^{\log K_{eq2}}}{(10^{-pH})^2(10^{-pE})^2}}{1+\frac{10^{\log K_{eq2}}}{(10^{-pH})^2(10^{-pE})^2}+\frac{10^{\log K_{eq3}}}{(10^{-pH})(10^{-pE})^2}} = \frac{\frac{10^{-58.1}}{(10^{-pH})^2(10^{-pE})^2}}{1+\frac{10^{-58.1}}{(10^{-pH})^2(10^{-pE})^2}+\frac{10^{-50.6}}{(10^{-pH})(10^{-pE})^2}}$$

(eq. 2f)

$$f_{ClO^-(Case2)} = \frac{(ClO^-)}{(Cl^-)+(ClO^-)+(HClO)+(ClO_2^-)+(ClO_{2(aq)})+(ClO_3^-)+(ClO_4^-)} =$$

$$\frac{\frac{K_{eq2}(Cl^-)}{(H^+)^2(e^-)^2}}{(Cl^-)+\frac{K_{eq2}(Cl^-)}{(H^+)^2(e^-)^2}+\frac{K_{eq3}(Cl^-)}{(H^+)(e^-)^2}+\frac{K_{eq4}(Cl^-)}{(H^+)^4(e^-)^4}+\frac{K_{eq5}(Cl^-)}{(H^+)^4(e^-)^5}+\frac{K_{eq6}(Cl^-)}{(H^+)^6(e^-)^6}+\frac{K_{eq7}(Cl^-)}{(H^+)^8(e^-)^8}} =$$

$$\frac{\frac{K_{eq2}}{(H^+)^2(e^-)^2}}{1+\frac{K_{eq2}}{(H^+)^2(e^-)^2}+\frac{K_{eq3}}{(H^+)(e^-)^2}+\frac{K_{eq4}}{(H^+)^4(e^-)^4}+\frac{K_{eq5}}{(H^+)^4(e^-)^5}+\frac{K_{eq6}}{(H^+)^6(e^-)^6}+\frac{K_{eq7}}{(H^+)^8(e^-)^8}} =$$

$$\frac{\frac{10^{\log K_{eq2}}}{(10^{-pH})^2(10^{-pE})^2}}{1+\frac{10^{\log K_{eq2}}}{(10^{-pH})^2(10^{-pE})^2}+\frac{10^{\log K_{eq3}}}{(10^{-pH})(10^{-pE})^2}+\frac{10^{\log K_{eq4}}}{(10^{-pH})^4(10^{-pE})^4}+\frac{10^{\log K_{eq5}}}{(10^{-pH})^4(10^{-pE})^5}+\frac{10^{\log K_{eq6}}}{(10^{-pH})^6(10^{-pE})^6}+\frac{10^{\log K_{eq7}}}{(10^{-pH})^8(10^{-pE})^8}} =$$

$$\frac{\frac{10^{-58.1}}{(10^{-pH})^2(10^{-pE})^2}}{1+\frac{10^{-58.1}}{(10^{-pH})^2(10^{-pE})^2}+\frac{10^{-50.6}}{(10^{-pH})(10^{-pE})^2}+\frac{10^{-109.1}}{(10^{-pH})^4(10^{-pE})^4}+\frac{10^{-126.8}}{(10^{-pH})^4(10^{-pE})^5}+\frac{10^{-147.1}}{(10^{-pH})^6(10^{-pE})^6}+\frac{10^{-187.8}}{(10^{-pH})^8(10^{-pE})^8}}$$

(eq 2g)

**Rxn 3:** $Cl^- + H_2O \leftrightarrow HClO + H^+ + 2e^-$ (eq. 3a)

$$K_{eq3} = \frac{(HClO)(H^+)(e^-)^2}{(Cl^-)}$$ (eq. 3b)

$$K_{mix3} = \frac{[HClO](H^+)(e^-)^2}{[Cl^-]}$$ (eq. 3c)

For generating predominance diagrams, assume that $K_{eq3} \sim K_{mix3}$ such that

$$\log K_{eq3} \approx \log K_{mix3} = \log\frac{[HClO]}{[Cl^-]} + \log\left(H^+\right) + 2\log\left(e^-\right) = \log\frac{[HClO]}{[Cl^-]} - pH - 2pE$$

(eq. 3d)

Along the HClO/Cl$^-$ boundary line, [HClO] = [Cl$^-$] so log{[HClO]/[Cl$^-$]} = log 1 = 0. From the attached thermodynamic spreadsheet, $\log K_{eq3} = -50.6$. Substituting those values into eq. 3d and rearranging gives the following equation for the HClO/Cl$^-$ boundary line:

$$2pE = 50.6 - pH \Rightarrow pE = 25.3 - 0.5pH \qquad \text{(eq. 3e)}$$

$$f_{HClO(Case1)} = \frac{(HClO)}{\left(Cl^-\right) + \left(ClO^-\right) + (HClO)} = \frac{\dfrac{K_{eq3}\left(Cl^-\right)}{\left(H^+\right)\left(e^-\right)^2}}{\left(Cl^-\right) + \dfrac{K_{eq2}\left(Cl^-\right)}{\left(H^+\right)^2\left(e^-\right)^2} + \dfrac{K_{eq3}\left(Cl^-\right)}{\left(H^+\right)\left(e^-\right)^2}} = \frac{\dfrac{K_{eq3}}{\left(H^+\right)\left(e^-\right)^2}}{1 + \dfrac{K_{eq2}}{\left(H^+\right)^2\left(e^-\right)^2} + \dfrac{K_{eq3}}{\left(H^+\right)\left(e^-\right)}} =$$

$$\frac{\dfrac{10^{\log K_{eq3}}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}}{1 + \dfrac{10^{\log K_{eq2}}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2} + \dfrac{10^{\log K_{eq3}}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}} = \frac{\dfrac{10^{-50.6}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}}{1 + \dfrac{10^{-58.1}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2} + \dfrac{10^{-50.6}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}}$$

(eq. 3f)

$$f_{HClO(Case2)} = \frac{(HClO)}{\left(Cl^-\right) + \left(ClO^-\right) + (HClO) + \left(ClO_2^-\right) + \left(ClO_{2(aq)}\right) + \left(ClO_3^-\right) + \left(ClO_4^-\right)} =$$

$$\frac{\dfrac{K_{eq3}\left(Cl^-\right)}{\left(H^+\right)\left(e^-\right)^2}}{\left(Cl^-\right) + \dfrac{K_{eq2}\left(Cl^-\right)}{\left(H^+\right)^2\left(e^-\right)^2} + \dfrac{K_{eq3}\left(Cl^-\right)}{\left(H^+\right)\left(e^-\right)^2} + \dfrac{K_{eq4}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^4} + \dfrac{K_{eq5}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^5} + \dfrac{K_{eq6}\left(Cl^-\right)}{\left(H^+\right)^6\left(e^-\right)^6} + \dfrac{K_{eq7}\left(Cl^-\right)}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{K_{eq3}}{\left(H^+\right)\left(e^-\right)^2}}{1 + \dfrac{K_{eq2}}{\left(H^+\right)^2\left(e^-\right)^2} + \dfrac{K_{eq3}}{\left(H^+\right)\left(e^-\right)^2} + \dfrac{K_{eq4}}{\left(H^+\right)^4\left(e^-\right)^4} + \dfrac{K_{eq5}}{\left(H^+\right)^4\left(e^-\right)^5} + \dfrac{K_{eq6}}{\left(H^+\right)^6\left(e^-\right)^6} + \dfrac{K_{eq7}}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{10^{\log K_{eq3}}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}}{1 + \dfrac{10^{\log K_{eq2}}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2} + \dfrac{10^{\log K_{eq3}}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2} + \dfrac{10^{\log K_{eq4}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4} + \dfrac{10^{\log K_{eq5}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5} + \dfrac{10^{\log K_{eq6}}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6} + \dfrac{10^{\log K_{eq7}}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}} =$$

$$\frac{\dfrac{10^{-50.6}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}}{1 + \dfrac{10^{-58.1}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2} + \dfrac{10^{-50.6}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2} + \dfrac{10^{-109.1}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4} + \dfrac{10^{-126.8}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5} + \dfrac{10^{-147.1}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6} + \dfrac{10^{-187.8}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}}$$

(eq. 3g)

**Rxn 4:** $Cl^- + 2H_2O \leftrightarrow ClO_2{}^- + 4H^+ + 4e^-$ (eq. 4a)

$$K_{eq4} = \frac{\left(ClO_2^-\right)\left(H^+\right)^4\left(e^-\right)^4}{\left(Cl^-\right)} \qquad \text{(eq. 4b)}$$

$$K_{mix4} = \frac{\left[ClO_2^-\right]\left(H^+\right)^4\left(e^-\right)^4}{\left[Cl^-\right]} \qquad \text{(eq. 4c)}$$

For generating predominance diagrams, assume that $K_{eq4} \sim K_{mix4}$ such that

$$\log K_{eq4} \approx \log K_{mix4} = \log\frac{\left[ClO_2^-\right]}{\left[Cl^-\right]} + 4\log\left(H^+\right) + 4\log\left(e^-\right) = \log\frac{\left[ClO_2^-\right]}{\left[Cl^-\right]} - 4pH - 4pE$$

(eq. 4d)

Along the $ClO_2^-/Cl^-$ boundary line, $[ClO_2^-] = [Cl^-]$ so $\log\{[ClO_2^-]/[Cl^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq4} = -109.1$. Substituting those values into eq. 4d and rearranging gives the following equation for the $ClO_2^-/Cl^-$ boundary line:

$$4pE = 109.1 - 4pH \;\Rightarrow\; pE = 27.3 - pH \qquad \text{(eq. 4e)}$$

$$f_{ClO_2^-(Case\,2)} = \frac{\left(ClO_2^-\right)}{\left(Cl^-\right)+\left(ClO^-\right)+\left(HClO\right)+\left(ClO_2^-\right)+\left(ClO_{2(aq)}\right)+\left(ClO_3^-\right)+\left(ClO_4^-\right)} =$$

$$\frac{\dfrac{K_{eq4}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^4}}{\left(Cl^-\right)+\dfrac{K_{eq2}\left(Cl^-\right)}{\left(H^+\right)^2\left(e^-\right)^2}+\dfrac{K_{eq3}\left(Cl^-\right)}{\left(H^+\right)\left(e^-\right)^2}+\dfrac{K_{eq4}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^4}+\dfrac{K_{eq5}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^5}+\dfrac{K_{eq6}\left(Cl^-\right)}{\left(H^+\right)^6\left(e^-\right)^6}+\dfrac{K_{eq7}\left(Cl^-\right)}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{K_{eq4}}{\left(H^+\right)^4\left(e^-\right)^4}}{1+\dfrac{K_{eq2}}{\left(H^+\right)^2\left(e^-\right)^2}+\dfrac{K_{eq3}}{\left(H^+\right)\left(e^-\right)^2}+\dfrac{K_{eq4}}{\left(H^+\right)^4\left(e^-\right)^4}+\dfrac{K_{eq5}}{\left(H^+\right)^4\left(e^-\right)^5}+\dfrac{K_{eq6}}{\left(H^+\right)^6\left(e^-\right)^6}+\dfrac{K_{eq7}}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{10^{\log K_{eq4}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4}}{1+\dfrac{10^{\log K_{eq2}}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2}+\dfrac{10^{\log K_{eq3}}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}+\dfrac{10^{\log K_{eq4}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4}+\dfrac{10^{\log K_{eq5}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5}+\dfrac{10^{\log K_{eq6}}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6}+\dfrac{10^{\log K_{eq7}}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}} =$$

$$\frac{\dfrac{10^{-109.1}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4}}{1+\dfrac{10^{-58.1}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2}+\dfrac{10^{-50.6}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}+\dfrac{10^{-109.1}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4}+\dfrac{10^{-126.8}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5}+\dfrac{10^{-147.1}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6}+\dfrac{10^{-187.8}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}}$$

(eq. 4f)

**Rxn 5:** $Cl^- + 2H_2O \leftrightarrow ClO_{2(aq)} + 4H^+ + 5e^-$ (eq. 5a)

$$K_{eq5} = \frac{\left(ClO_{2(aq)}\right)\left(H^+\right)^4\left(e^-\right)^5}{\left(Cl^-\right)} \qquad \text{(eq. 5b)}$$

$$K_{mix5} = \frac{\left[ClO_{2(aq)}\right]\left(H^+\right)^4\left(e^-\right)^5}{\left[Cl^-\right]} \qquad \text{(eq. 5c)}$$

For generating predominance diagrams, assume that $K_{eq5} \sim K_{mix5}$ such that

$$\log K_{eq5} \approx \log K_{mix5} = \log\frac{\left[ClO_{2(aq)}\right]}{\left[Cl^-\right]} + 4\log\left(H^+\right) + 5\log\left(e^-\right) = \log\frac{\left[ClO_{2(aq)}\right]}{\left[Cl^-\right]} - 4pH - 5pE$$

(eq. 5d)

Along the $ClO_{2(aq)}/Cl^-$ boundary line, $[ClO_{2(aq)}] = [Cl^-]$ so $\log\{[ClO_{2(aq)}]/[Cl^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq5} = -126.8$. Substituting those values into eq. 5d and rearranging gives the following equation for the $ClO_{2(aq)}/Cl^-$ boundary line:

$$5pE = 126.8 - 4pH \Rightarrow pE = 25.4 - 0.8pH \qquad \text{(eq. 5e)}$$

$$f_{ClO_{2(aq)}(Case\,2)} = \frac{\left(ClO_{2(aq)}\right)}{\left(Cl^-\right) + \left(ClO^-\right) + \left(HClO\right) + \left(ClO_2^-\right) + \left(ClO_{2(aq)}\right) + \left(ClO_3^-\right) + \left(ClO_4^-\right)} =$$

$$\frac{\dfrac{K_{eq5}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^5}}{\left(Cl^-\right) + \dfrac{K_{eq2}\left(Cl^-\right)}{\left(H^+\right)^2\left(e^-\right)^2} + \dfrac{K_{eq3}\left(Cl^-\right)}{\left(H^+\right)\left(e^-\right)^2} + \dfrac{K_{eq4}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^4} + \dfrac{K_{eq5}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^5} + \dfrac{K_{eq6}\left(Cl^-\right)}{\left(H^+\right)^6\left(e^-\right)^6} + \dfrac{K_{eq7}\left(Cl^-\right)}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{K_{eq5}}{\left(H^+\right)^4\left(e^-\right)^5}}{1 + \dfrac{K_{eq2}}{\left(H^+\right)^2\left(e^-\right)^2} + \dfrac{K_{eq3}}{\left(H^+\right)\left(e^-\right)^2} + \dfrac{K_{eq4}}{\left(H^+\right)^4\left(e^-\right)^4} + \dfrac{K_{eq5}}{\left(H^+\right)^4\left(e^-\right)^5} + \dfrac{K_{eq6}}{\left(H^+\right)^6\left(e^-\right)^6} + \dfrac{K_{eq7}}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{10^{\log K_{eq5}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5}}{1 + \dfrac{10^{\log K_{eq2}}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2} + \dfrac{10^{\log K_{eq3}}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2} + \dfrac{10^{\log K_{eq4}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4} + \dfrac{10^{\log K_{eq5}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5} + \dfrac{10^{\log K_{eq6}}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6} + \dfrac{10^{\log K_{eq7}}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}} =$$

$$\frac{\dfrac{10^{-126.8}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5}}{1 + \dfrac{10^{-58.1}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2} + \dfrac{10^{-50.6}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2} + \dfrac{10^{-109.1}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4} + \dfrac{10^{-126.8}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5} + \dfrac{10^{-147.1}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6} + \dfrac{10^{-187.8}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}}$$

(eq. 5f)

**Rxn 6:** $Cl^- + 3H_2O \leftrightarrow ClO_3^- + 6H^+ + 6e^-$ (eq. 6a)

$$K_{eq6} = \frac{\left(ClO_3^-\right)\left(H^+\right)^6\left(e^-\right)^6}{\left(Cl^-\right)}$$ (eq. 6b)

$$K_{mix6} = \frac{\left[ClO_3^-\right]\left(H^+\right)^6\left(e^-\right)^6}{\left[Cl^-\right]}$$ (eq. 6c)

For generating predominance diagrams, assume that $K_{eq6} \sim K_{mix6}$ such that

$$\log K_{eq6} \approx \log K_{mix6} = \log\frac{\left[ClO_3^-\right]}{\left[Cl^-\right]} + 6\log\left(H^+\right) + 6\log\left(e^-\right) = \log\frac{\left[ClO_3^-\right]}{\left[Cl^-\right]} - 6pH - 6pE$$

(eq. 6d)

Along the $ClO_3^-/Cl^-$ boundary line, $[ClO_3^-] = [Cl^-]$ so $\log\{[ClO_3^-]/[Cl^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq6} = -147.1$. Substituting those values into eq. 6d and rearranging gives the following equation for the $ClO_3^-/Cl^-$ boundary line:

$$6pE = 147.1 - 6pH \;\Rightarrow\; pE = 24.5 - pH$$

(eq. 6e)

$$f_{ClO_3^-(Case\,2)} = \frac{\left(ClO_3^-\right)}{\left(Cl^-\right)+\left(ClO^-\right)+\left(HClO\right)+\left(ClO_2^-\right)+\left(ClO_{2(aq)}\right)+\left(ClO_3^-\right)+\left(ClO_4^-\right)} =$$

$$\frac{\dfrac{K_{eq6}\left(Cl^-\right)}{\left(H^+\right)^6\left(e^-\right)^6}}{\left(Cl^-\right)+\dfrac{K_{eq2}\left(Cl^-\right)}{\left(H^+\right)^2\left(e^-\right)^2}+\dfrac{K_{eq3}\left(Cl^-\right)}{\left(H^+\right)\left(e^-\right)^2}+\dfrac{K_{eq4}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^4}+\dfrac{K_{eq5}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^5}+\dfrac{K_{eq6}\left(Cl^-\right)}{\left(H^+\right)^6\left(e^-\right)^6}+\dfrac{K_{eq7}\left(Cl^-\right)}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{K_{eq6}}{\left(H^+\right)^6\left(e^-\right)^6}}{1+\dfrac{K_{eq2}}{\left(H^+\right)^2\left(e^-\right)^2}+\dfrac{K_{eq3}}{\left(H^+\right)\left(e^-\right)^2}+\dfrac{K_{eq4}}{\left(H^+\right)^4\left(e^-\right)^4}+\dfrac{K_{eq5}}{\left(H^+\right)^4\left(e^-\right)^5}+\dfrac{K_{eq6}}{\left(H^+\right)^6\left(e^-\right)^6}+\dfrac{K_{eq7}}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{10^{\log K_{eq6}}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6}}{1+\dfrac{10^{\log K_{eq2}}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2}+\dfrac{10^{\log K_{eq3}}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}+\dfrac{10^{\log K_{eq4}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4}+\dfrac{10^{\log K_{eq5}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5}+\dfrac{10^{\log K_{eq6}}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6}+\dfrac{10^{\log K_{eq7}}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}} =$$

$$\frac{\dfrac{10^{-147.8}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6}}{1+\dfrac{10^{-58.1}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2}+\dfrac{10^{-50.6}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2}+\dfrac{10^{-109.1}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4}+\dfrac{10^{-126.8}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5}+\dfrac{10^{-147.1}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6}+\dfrac{10^{-187.8}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}}$$

(eq. 6f)

**Rxn 7:** $Cl^- + 4H_2O \leftrightarrow ClO_4^- + 8H^+ + 8e^-$ (eq. 7a)

$$K_{eq7} = \frac{\left(ClO_4^-\right)\left(H^+\right)^8\left(e^-\right)^8}{\left(Cl^-\right)} \qquad \text{(eq. 7b)}$$

$$K_{mix7} = \frac{\left[ClO_4^-\right]\left(H^+\right)^8\left(e^-\right)^8}{\left[Cl^-\right]} \qquad \text{(eq. 7c)}$$

For generating predominance diagrams, assume that $K_{eq7} \sim K_{mix7}$ such that

$$\log K_{eq7} \approx \log K_{mix7} = \log\frac{\left[ClO_4^-\right]}{\left[Cl^-\right]} + 8\log\left(H^+\right) + 8\log\left(e^-\right) = \log\frac{\left[ClO_4^-\right]}{\left[Cl^-\right]} - 8pH - 8pE$$

(eq. 7d)

Along the $ClO_4^-/Cl^-$ boundary line, $[ClO_4^-] = [Cl^-]$ so $\log\{[ClO_4^-]/[Cl^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq7} = -187.8$. Substituting those values into eq. 7d and rearranging gives the following equation for the $ClO_4^-/Cl^-$ boundary line:

$$8pE = 187.8 - 8pH \Rightarrow pE = 23.5 - pH \qquad \text{(eq. 7e)}$$

$$f_{ClO_4^-(Case2)} = \frac{\left(ClO_4^-\right)}{\left(Cl^-\right) + \left(ClO^-\right) + \left(HClO\right) + \left(ClO_2^-\right) + \left(ClO_{2(aq)}\right) + \left(ClO_3^-\right) + \left(ClO_4^-\right)} =$$

$$\frac{\dfrac{K_{eq7}\left(Cl^-\right)}{\left(H^+\right)^8\left(e^-\right)^8}}{\left(Cl^-\right) + \dfrac{K_{eq2}\left(Cl^-\right)}{\left(H^+\right)^2\left(e^-\right)^2} + \dfrac{K_{eq3}\left(Cl^-\right)}{\left(H^+\right)\left(e^-\right)^2} + \dfrac{K_{eq4}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^4} + \dfrac{K_{eq5}\left(Cl^-\right)}{\left(H^+\right)^4\left(e^-\right)^5} + \dfrac{K_{eq6}\left(Cl^-\right)}{\left(H^+\right)^6\left(e^-\right)^6} + \dfrac{K_{eq7}\left(Cl^-\right)}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{K_{eq7}}{\left(H^+\right)^8\left(e^-\right)^8}}{1 + \dfrac{K_{eq2}}{\left(H^+\right)^2\left(e^-\right)^2} + \dfrac{K_{eq3}}{\left(H^+\right)\left(e^-\right)^2} + \dfrac{K_{eq4}}{\left(H^+\right)^4\left(e^-\right)^4} + \dfrac{K_{eq5}}{\left(H^+\right)^4\left(e^-\right)^5} + \dfrac{K_{eq6}}{\left(H^+\right)^6\left(e^-\right)^6} + \dfrac{K_{eq7}}{\left(H^+\right)^8\left(e^-\right)^8}} =$$

$$\frac{\dfrac{10^{\log K_{eq7}}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}}{1 + \dfrac{10^{\log K_{eq2}}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2} + \dfrac{10^{\log K_{eq3}}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2} + \dfrac{10^{\log K_{eq4}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4} + \dfrac{10^{\log K_{eq5}}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5} + \dfrac{10^{\log K_{eq6}}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6} + \dfrac{10^{\log K_{eq7}}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}} =$$

$$\frac{\dfrac{10^{-187.8}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}}{1 + \dfrac{10^{-58.1}}{\left(10^{-pH}\right)^2\left(10^{-pE}\right)^2} + \dfrac{10^{-50.6}}{\left(10^{-pH}\right)\left(10^{-pE}\right)^2} + \dfrac{10^{-109.1}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^4} + \dfrac{10^{-126.8}}{\left(10^{-pH}\right)^4\left(10^{-pE}\right)^5} + \dfrac{10^{-147.1}}{\left(10^{-pH}\right)^6\left(10^{-pE}\right)^6} + \dfrac{10^{-187.8}}{\left(10^{-pH}\right)^8\left(10^{-pE}\right)^8}}$$

(eq. 7f)

**Reactions 8 - 13 (remaining reactions involving Cl$_{2(aq)}$:**

**Rxn 8:** $Cl_{2(aq)} + 2H_2O \leftrightarrow 2ClO^- + 4H^+ + 2e^-$ (eq. 8a)

$$K_{eq8} = \frac{(ClO^-)^2(H^+)^4(e^-)^2}{\left(Cl_{2(aq)}\right)}$$ (eq. 8b)

$$K_{mix8} = \frac{[ClO^-]^2(H^+)^4(e^-)^2}{\left[Cl_{2(aq)}\right]}$$ (eq. 8c)

For generating predominance diagrams, assume that K$_{eq8}$ ~ K$_{mix8}$ such that

$$\log K_{eq8} \approx \log K_{mix8} = \log\frac{[ClO^-]^2}{\left[Cl_{2(aq)}\right]} + 4\log(H^+) + 2\log(e^-) = \log\frac{[ClO^-]^2}{\left[Cl_{2(aq)}\right]} - 4pH - 2pE$$

(eq. 8d)

Along the ClO$^-$/Cl$_{2(aq)}$ boundary line, it is reasonable to assume that [Cl$_{tot}$] ~ [ClO$^-$] + 2[Cl$_{2(aq)}$]. Therefore, along the boundary for a total chlorine concentration [Cl$_{tot}$] = 0.04 mol/L, [ClO$^-$] ~ 0.02 mol/L and [Cl$_{2(aq)}$] ~ 0.01 mol/L. From the attached thermodynamic spreadsheet, logK$_{eq8}$ = -69.0. Substituting those values into eq. 8d and rearranging gives the following equation for the ClO$^-$/Cl$_{2(aq)}$ boundary line:

$$2pE = 69.0 + \log\frac{[0.02]^2}{[0.01]} - 4pH = 69.0 - 1.4 - 4pH = 67.6 - 4pH \Rightarrow$$ (eq. 8e)

$$2pE = 67.6 - 4pH \Rightarrow pE = 33.8 - 2pH$$

**Rxn 9:** $Cl_{2(aq)} + 2H_2O \leftrightarrow 2HClO + 2H^+ + 2e^-$ (eq. 9a)

$$K_{eq9} = \frac{(HClO)^2(H^+)^2(e^-)^2}{\left(Cl_{2(aq)}\right)}$$ (eq. 9b)

$$K_{mix9} = \frac{[HClO]^2 (H^+)^2 (e^-)^2}{\left[Cl_{2(aq)}\right]} \qquad \text{(eq. 9c)}$$

For generating predominance diagrams, assume that $K_{eq9}$ ~ $K_{mix9}$ such that

$$\log K_{eq9} \approx \log K_{mix9} = \log \frac{[HClO]^2}{\left[Cl_{2(aq)}\right]} + 2\log(H^+) + 2\log(e^-) = \log \frac{[HClO]^2}{\left[Cl_{2(aq)}\right]} - 2pH - 2pE$$

(eq. 9d)

Along the HClO/$Cl_{2(aq)}$ boundary line, it is reasonable to assume that $[Cl_{tot}]$ ~ [HClO] + 2$[Cl_{2(aq)}]$. Therefore, along the boundary for a total chlorine concentration $[Cl_{tot}]$ = 0.04 mol/L, [HClO] ~ 0.02 mol/L and $[Cl_{2(aq)}]$ ~ 0.01 mol/L. From the attached thermodynamic spreadsheet, $\log K_{eq9}$ = -53.9. Substituting those values into eq. 9d and rearranging gives the following equation for the HClO/$Cl_{2(aq)}$ boundary line:

$$2pE = 53.9 + \log \frac{[0.02]^2}{[0.01]} - 2pH = 53.9 - 1.4 - 2pH = 52.5 - 2pH \Rightarrow \qquad \text{(eq. 9e)}$$
$$2pE = 52.5 - 2pH \Rightarrow pE = 26.3 - pH$$

**<u>Rxn 10:</u>** $Cl_{2(aq)} + 4H_2O \leftrightarrow 2ClO_2^- + 8H^+ + 6e^-$ (eq. 10a)

$$K_{eq10} = \frac{(ClO_2^-)^2 (H^+)^8 (e^-)^6}{\left(Cl_{2(aq)}\right)} \qquad \text{(eq. 10b)}$$

$$K_{eq10} = \frac{[ClO_2^-]^2 (H^+)^8 (e^-)^6}{\left[Cl_{2(aq)}\right]} \qquad \text{(eq. 10c)}$$

For generating predominance diagrams, assume that $K_{eq10}$ ~ $K_{mix10}$ such that

$$\log K_{eq10} \approx \log \frac{[ClO_2^-]^2}{\left[Cl_{2(aq)}\right]} + 8\log(H^+) + 6\log(e^-) \approx \log \frac{[ClO_2^-]^2}{\left[Cl_{2(aq)}\right]} - 8pH - 6pE$$

(eq. 10d)

Along the $ClO_2^-$ /$Cl_{2(aq)}$ boundary line, it is reasonable to assume that [$Cl_{tot}$] ~ [$ClO_2^-$ ] + 2[$Cl_{2(aq)}$]. Therefore, along the boundary for a total chlorine concentration [$Cl_{tot}$] = 0.04 mol/L, [$ClO_2^-$ ] ~ 0.02 mol/L and [$Cl_{2(aq)}$] ~ 0.01 mol/L. From the attached thermodynamic spreadsheet, $\log K_{eq10}$ = -171.1. Substituting those values into eq. 10d and rearranging gives the following equation for the $ClO_2^-$ /$Cl_{2(aq)}$ boundary line:

$$6pE = 171.1 + \log\frac{[0.02]^2}{[0.01]} - 8pH = 171.1 - 1.4 - 8pH = 169.7 - 8pH \Rightarrow$$ (eq. 10e)

$$6pE = 169.7 - 8pH \Rightarrow \quad pE = 28.3 - 1.33pH$$

**Rxn 11:** $Cl_{2(aq)} + 4H_2O \leftrightarrow \; 2ClO_{2(aq)} + 8H^+ + 8e^-$ (eq. 11a)

$$K_{eq11} = \frac{\left(ClO_{2(aq)}\right)^2\left(H^+\right)^8\left(e^-\right)^8}{\left(Cl_{2(aq)}\right)}$$ (eq. 11b)

$$K_{mix11} = \frac{\left[ClO_{2(aq)}\right]^2\left(H^+\right)^8\left(e^-\right)^8}{\left[Cl_{2(aq)}\right]}$$ (eq. 11c)

For generating predominance diagrams, assume that $K_{eq11}$ ~ $K_{mix11}$ such that

$$\log K_{eq11} \approx \log K_{mix11} = \log\frac{\left[ClO_{2(aq)}\right]^2}{\left[Cl_{2(aq)}\right]} + 8\log\left(H^+\right) + 8\log\left(e^-\right) = \log\frac{\left[ClO_{2(aq)}\right]^2}{\left[Cl_{2(aq)}\right]} - 8pH - 8pE$$

(eq. 11d)

Along the $ClO_{2(aq)}$ /$Cl_{2(aq)}$ boundary line, it is reasonable to assume that [$Cl_{tot}$] ~ [$ClO_{2(aq)}$ ] + 2[$Cl_{2(aq)}$]. Therefore, along the boundary for a total chlorine concentration [$Cl_{tot}$] = 0.04 mol/L, [$ClO_{2(aq)}$ ] ~ 0.02 mol/L and [$Cl_{2(aq)}$] ~ 0.01 mol/L. From the attached thermodynamic spreadsheet, $\log K_{eq11}$ = -206.3. Substituting those values into eq. 11d and rearranging gives the following equation for the $ClO_{2(aq)}$ /$Cl_{2(aq)}$ boundary line:

$$8pE = 206.3 + \log\frac{[0.02]^2}{[0.01]} - 8pH = 206.3 - 1.4 - 8pH = 204.9 - 8pH \Rightarrow$$ (eq. 11e)

$$8pE = 204.9 - 8pH \Rightarrow \quad pE = 25.6 - pH$$

**Rxn 12:** $Cl_{2(aq)} + 6H_2O \leftrightarrow 2ClO_3^- + 12H^+ + 10e^-$ (eq. 12a)

$$K_{eq12} = \frac{\left(ClO_3^-\right)^2\left(H^+\right)^{12}\left(e^-\right)^{10}}{\left(Cl_{2(aq)}\right)}$$ (eq. 12b)

$$K_{mix12} = \frac{\left[ClO_3^-\right]^2\left(H^+\right)^{12}\left(e^-\right)^{10}}{\left[Cl_{2(aq)}\right]}$$ (eq. 12c)

For generating predominance diagrams, assume that $K_{eq12} \sim K_{mix12}$ such that

$$\log K_{eq12} \approx \log K_{mix12} = \log\frac{\left[ClO_3^-\right]^2}{\left[Cl_{2(aq)}\right]} + 12\log\left(H^+\right) + 10\log\left(e^-\right) = \log\frac{\left[ClO_3^-\right]^2}{\left[Cl_{2(aq)}\right]} - 12pH - 10pE$$

(eq. 12d)

Along the $ClO_3^-$ /$Cl_{2(aq)}$ boundary line, it is reasonable to assume that $[Cl_{tot}] \sim [ClO_3^-] + 2[Cl_{2(aq)}]$. Therefore, along the boundary for a total chlorine concentration $[Cl_{tot}]$ = 0.04 mol/L, $[ClO_3^-] \sim$ 0.02 mol/L and $[Cl_{2(aq)}] \sim$ 0.01 mol/L. From the attached thermodynamic spreadsheet, $\log K_{eq12}$ = -247.0. Substituting those values into eq. 12d and rearranging gives the following equation for the $ClO_3^-$ /$Cl_{2(aq)}$ boundary line:

$$10pE = 247.0 + \log\frac{[0.02]^2}{[0.01]} - 12pH = 247.0 - 1.4 - 12pH = 245.6 - 12pH \Rightarrow$$

$$10pE = 245.6 - 12pH \Rightarrow \quad pE = 24.6 - 1.2pH$$

(eq. 12e)

**Rxn 13:** $Cl_{2(aq)} + 8H_2O \leftrightarrow 2ClO_4^- + 16H^+ + 14e^-$ (eq. 13a)

$$K_{eq13} = \frac{\left(ClO_4^-\right)^2\left(H^+\right)^{16}\left(e^-\right)^{14}}{\left(Cl_{2(aq)}\right)} \qquad \text{(eq. 13b)}$$

$$K_{mix13} = \frac{\left[ClO_4^-\right]^2\left(H^+\right)^{16}\left(e^-\right)^{14}}{\left[Cl_{2(aq)}\right]} \qquad \text{(eq. 13c)}$$

For generating predominance diagrams, assume that $K_{eq13} \sim K_{mix13}$ such that

$$\log K_{eq13} \approx \log K_{mix13} = \log\frac{\left[ClO_4^-\right]^2}{\left[Cl_{2(aq)}\right]} + 16\log\left(H^+\right) + 14\log\left(e^-\right) = \log\frac{\left[ClO_4^-\right]^2}{\left[Cl_{2(aq)}\right]} - 16pH - 14pE$$

(eq. 13d)

Along the $ClO_4^-$ /$Cl_{2(aq)}$ boundary line, it is reasonable to assume that [$Cl_{tot}$] ~ [$ClO_4^-$ ] + 2[$Cl_{2(aq)}$]. Therefore, along the boundary for a total chlorine concentration [$Cl_{tot}$] = 0.04 mol/L, [$ClO_4^-$ ] ~ 0.02 mol/L and [$Cl_{2(aq)}$] ~ 0.01 mol/L. From the attached thermodynamic spreadsheet, $\log K_{eq13}$ = -328.3. Substituting those values into eq. 13d and rearranging gives the following equation for the $ClO_4^-$ /$Cl_{2(aq)}$ boundary line:

$$14pE = 328.3 + \log\frac{[0.02]^2}{[0.01]} - 16pH = 328.3 - 1.4 - 16pH = 326.9 - 16pH \Rightarrow$$

$$14pE = 326.9 - 16pH \Rightarrow \quad pE = 23.4 - 1.14pH$$

(eq. 13e)

**<u>Reactions 14 -18 (remaining reactions involving $ClO^-$):</u>**

**<u>Rxn 14:</u>** $ClO^- + H^+ \rightarrow HClO$ (eq. 14a)

$$K_{eq14} = \frac{(HClO)}{\left(ClO^-\right)\left(H^+\right)} \qquad \text{(eq. 14b)}$$

$$K_{mix14} = \frac{[HClO]}{\left[ClO^-\right]\left(H^+\right)} \qquad \text{(eq. 14c)}$$

For generating predominance diagrams, assume that $K_{eq14} \sim K_{mix14}$ such that

$$\log K_{eq14} \approx \log K_{mix14} = \log \frac{[HClO]}{[ClO^-]} - \log(H^+) = \log \frac{[HClO]}{[ClO^-]} + pH \qquad \text{(eq. 14d)}$$

Along the HClO/ClO$^-$ boundary line, [HClO] = [ClO$^-$] so log{[HClO]/[ClO$^-$]} = log 1 = 0. From the attached thermodynamic spreadsheet, $\log K_{eq14} = 7.6$. Substituting the values into eq. 14d and rearranging gives the following equation for the HClO/ClO$^-$ boundary line:

$$pH = 7.6 \qquad \text{(eq. 14e)}$$

**<u>Rxn 15:</u>** $ClO^- + H_2O \leftrightarrow ClO_2^- + 2H^+ + 2e^-$ (eq. 15a)

$$K_{eq15} = \frac{(ClO_2^-)(H^+)^2(e^-)^2}{(ClO^-)} \qquad \text{(eq. 15b)}$$

$$K_{mix15} = \frac{[ClO_2^-](H^+)^2(e^-)^2}{[ClO^-]} \qquad \text{(eq. 15c)}$$

For generating predominance diagrams, assume that $K_{eq15} \sim K_{mix15}$ such that

$$\log K_{eq15} \approx \log K_{mix15} = \log \frac{[ClO_2^-]}{[ClO^-]} + 2\log(H^+) + 2\log(e^-) = \log \frac{[ClO_2^-]}{[ClO^-]} - 2pH - 2pE$$

(eq. 15d)

Along the ClO$_2^-$/ClO$^-$ boundary line, [ClO$_2^-$] = [ClO$^-$] so log{[ClO$_2^-$]/[ClO$^-$]} = log 1 = 0. From the attached thermodynamic spreadsheet, $\log K_{eq15} = -51.0$. Substituting the values into eq. 15d and rearranging gives the following equation for the ClO$_2^-$/ClO$^-$ boundary line:

$$2pE = 51.0 - 2pH \Rightarrow pE = 25.5 - pH \qquad \text{(eq. 15e)}$$

**<u>Rxn 16:</u>** $ClO^- + H_2O \leftrightarrow ClO_{2(aq)} + 2H^+ + 3e^-$ (eq. 16a)

$$K_{eq16} = \frac{\left(ClO_{2(aq)}\right)\left(H^+\right)^2\left(e^-\right)^3}{\left(ClO^-\right)}$$ (eq. 16b)

$$K_{mix16} = \frac{\left[ClO_{2(aq)}\right]\left(H^+\right)^2\left(e^-\right)^3}{\left[ClO^-\right]}$$ (eq. 16c)

For generating predominance diagrams, assume that $K_{eq16} \sim K_{mix16}$ such that

$$\log K_{eq16} \approx \log K_{mix16} = \log\frac{\left[ClO_{2(aq)}\right]}{\left[ClO^-\right]} + 2\log\left(H^+\right) + 3\log\left(e^-\right) = \log\frac{\left[ClO_{2(aq)}\right]}{\left[ClO^-\right]} - 2pH - 3pE$$

(eq. 16d)

Along the $ClO_{2(aq)}/ClO^-$ boundary line, $[ClO_{2(aq)}] = ClO^-$ so $\log\{[ClO_{2(aq)}]/[ClO^-]\} = \log 1 = 0$. From the thermodynamic spreadsheet, $\log K_{eq16} = -68.6$. Substituting the values into eq. 16d and rearranging gives the following equation for the $ClO_{2(aq)}/ClO^-$ boundary line:

$$3pE = 68.6 - 2pH \Rightarrow pE = 22.9 - 0.67pH$$ (eq. 16e)

**Rxn 17:** $ClO^- + 2H_2O \leftrightarrow ClO_3^- + 4H^+ + 4e^-$ (eq. 17a)

$$K_{eq17} = \frac{\left(ClO_3^-\right)\left(H^+\right)^4\left(e^-\right)^4}{\left(ClO^-\right)}$$ (eq. 17b)

$$K_{mix17} = \frac{\left[ClO_3^-\right]\left(H^+\right)^4\left(e^-\right)^4}{\left[ClO^-\right]}$$ (eq. 17c)

For generating predominance diagrams, assume that $K_{eq17} \sim K_{mix17}$ such that

$$\log K_{eq17} \approx \log K_{mix17} = \log\frac{\left[ClO_3^-\right]}{\left[ClO^-\right]} + 4\log\left(H^+\right) + 4\log\left(e^-\right) = \log\frac{\left[ClO_3^-\right]}{\left[ClO^-\right]} - 4pH - 4pE$$

(eq. 17d)

Along the $ClO_3^-/ClO^-$ boundary line, $[ClO_3^-] = [ClO^-]$ so $\log\{[ClO_3^-]/[ClO^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq17} = -89.0$. Substituting those values into eq. 17d and rearranging gives the following equation for the $ClO_3^-/ClO^-$ boundary line:

$$4pE = 89.0 - 4pH \Rightarrow pE = 22.3 - pH \qquad \text{(eq. 17e)}$$

**Rxn 18:** $ClO^- + 3H_2O \leftrightarrow ClO_4^- + 6H^+ + 6e^-$ (eq. 18a)

$$K_{eq18} = \frac{(ClO_4^-)(H^+)^6(e^-)^6}{(ClO^-)} \qquad \text{(eq. 18b)}$$

$$K_{mix18} = \frac{[ClO_4^-](H^+)^6(e^-)^6}{[ClO^-]} \qquad \text{(eq. 18c)}$$

For generating predominance diagrams, assume that $K_{eq18} \sim K_{mix18}$ such that

$$\log K_{eq18} \approx \log K_{mix18} = \log\frac{[ClO_4^-]}{[ClO^-]} + 6\log(H^+) + 6\log(e^-) = \log\frac{[ClO_4^-]}{[ClO^-]} - 6pH - 6pE$$

(eq. 18d)

Along the $ClO_4^-/ClO^-$ boundary line, $[ClO_4^-] = [ClO^-]$ so $\log\{[ClO_4^-]/[ClO^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq18} = -129.7$. Substituting those values into eq. 18d and rearranging gives the following equation for the $ClO_4^-/ClO^-$ boundary line:

$$6pE = 129.7 - 6pH \Rightarrow pE = 21.6 - pH \qquad \text{(eq. 18e)}$$

**Reactions 19 -22 (remaining reactions involving HClO):**

**Rxn 19:** $HClO + H_2O \leftrightarrow ClO_2^- + 3H^+ + 2e^-$ (eq. 19a)

$$K_{eq19} = \frac{(ClO_2^-)(H^+)^3(e^-)^2}{(HClO)} \qquad \text{(eq. 19b)}$$

$$K_{mix19} = \frac{\left[ClO_2^-\right]\left(H^+\right)^3\left(e^-\right)^2}{[HClO]} \qquad \text{(eq. 19c)}$$

For generating predominance diagrams, assume that $K_{eq19} \sim K_{mix19}$ such that

$$\log K_{eq19} \approx \log K_{mix19} = \log\frac{\left[ClO_2^-\right]}{[HClO]} + 3\log\left(H^+\right) + 2\log\left(e^-\right) = \log\frac{\left[ClO_2^-\right]}{[HClO]} - 3pH - 2pE$$

(eq. 19d)

Along the $ClO_2^-$ /HClO boundary line, $[ClO_2^-]$ = [HClO] so log{$[ClO_2^-]$/[HClO]} = log 1 = 0. From the attached thermodynamic spreadsheet, $\log K_{eq19} = -58.6$. Substituting the values into eq. 19d and rearranging gives the following equation for the $ClO_2^-$ /HClO boundary line:

$$2pE = 58.6 - 3pH \Rightarrow pE = 29.3 - 1.5pH \qquad \text{(eq. 19e)}$$

**Rxn 20:** $HClO + H_2O \leftrightarrow ClO_{2(aq)} + 3H^+ + 3e^-$ (eq. 20a)

$$K_{eq20} = \frac{\left(ClO_{2(aq)}\right)\left(H^+\right)^3\left(e^-\right)^3}{(HClO)} \qquad \text{(eq. 20b)}$$

$$K_{mix20} = \frac{\left[ClO_{2(aq)}\right]\left(H^+\right)^3\left(e^-\right)^3}{[HClO]} \qquad \text{(eq. 20c)}$$

For generating predominance diagrams, assume that $K_{eq20} \sim K_{mix20}$ such that

$$\log K_{eq20} \approx \log K_{mix20} = \log\frac{\left[ClO_{2(aq)}\right]}{[HClO]} + 3\log\left(H^+\right) + 3\log\left(e^-\right) = \log\frac{\left[ClO_{2(aq)}\right]}{[HClO]} - 3pH - 3pE$$

(eq. 20d)

Along the $ClO_{2(aq)}$ /HClO boundary line, $[ClO_{2(aq)}]$ = [HClO] so log{$[ClO_{2(aq)}]$/[HClO]} = log 1 = 0. From the attached thermodynamic spreadsheet, $\log K_{eq20} = -76.2$. Substituting the values into eq. 20d and rearranging gives the following equation for the $ClO_{2(aq)}$ /HClO boundary line:

$$3pE = 76.2 - 3pH \Rightarrow pE = 25.4 - pH \qquad \text{(eq. 20e)}$$

**Rxn 21:** $HClO + 2H_2O \leftrightarrow ClO_3^- + 5H^+ + 4e^-$ (eq. 21a)

$$K_{eq21} = \frac{(ClO_3^-)(H^+)^5(e^-)^4}{(HClO)}$$ (eq. 21b)

$$K_{mix21} = \frac{[ClO_3^-](H^+)^5(e^-)^4}{[HClO]}$$ (eq. 21c)

For generating predominance diagrams, assume that $K_{eq21} \sim K_{mix21}$ such that

$$\log K_{eq21} \approx \log K_{mix21} = \log\frac{[ClO_3^-]}{[HClO]} + 5\log(H^+) + 4\log(e^-) = \log\frac{[ClO_3^-]}{[HClO]} - 5pH - 4pE$$

(eq. 21d)

Along the $ClO_3^-$ /HClO boundary line, $[ClO_3^-]$ = [HClO] so log{$[ClO_3^-]$/[HClO]} = log 1 = 0. From the attached thermodynamic spreadsheet, $\log K_{eq21} = -96.6$. Substituting the values into eq. 21d and rearranging gives the following equation for the $ClO_3^-$ /HClO boundary line:

$$4pE = 96.6 - 5pH \Rightarrow pE = 24.2 - 1.25pH$$ (eq. 21e)

**Rxn 22:** $HClO + 3H_2O \leftrightarrow ClO_4^- + 7H^+ + 6e^-$ (eq. 22a)

$$K_{eq22} = \frac{(ClO_4^-)(H^+)^7(e^-)^6}{(HClO)}$$ (eq. 22b)

$$K_{mix22} = \frac{[ClO_4^-](H^+)^7(e^-)^6}{[HClO]}$$ (eq. 22c)

For generating predominance diagrams, assume that $K_{eq22} \sim K_{mix22}$ such that

$$\log K_{eq22} \approx \log K_{mix22} = \log\frac{[ClO_4^-]}{[HClO]} + 7\log(H^+) + 6\log(e^-) = \log\frac{[ClO_4^-]}{[HClO]} - 7pH - 6pE$$

(eq. 22d)

Along the $ClO_4^-$ /HClO boundary line, $[ClO_4^-] = [HClO]$ so $\log\{[ClO_4^-]/[HClO]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq22} = -137.2$. Substituting the values into eq. 22c and rearranging gives the following equation for the $ClO_4^-$ /HClO boundary line:

$$6pE = 137.2 - 7pH \;\Rightarrow\; pE = 22.9 - 1.17pH \qquad \text{(eq. 22e)}$$

**Reactions 23 - 25 (remaining reactions involving $ClO_2^-$ ):**

**Rxn 23:** $ClO_2^- \leftrightarrow ClO_{2(aq)} + e^-$ (eq. 23a)

$$K_{eq23} = \frac{\left(ClO_{2(aq)}\right)\left(e^-\right)}{\left(ClO_2^-\right)} \qquad \text{(eq. 23b)}$$

$$K_{mix23} = \frac{\left[ClO_{2(aq)}\right]\left(e^-\right)}{\left[ClO_2^-\right]} \qquad \text{(eq. 23c)}$$

For generating predominance diagrams, assume that $K_{eq23} \sim K_{mix23}$ such that

$$\log K_{eq23} \approx \log K_{mix23} = \log\frac{\left[ClO_{2(aq)}\right]}{\left[ClO_2^-\right]} + \log\left(e^-\right) = \log\frac{\left[ClO_{2(aq)}\right]}{\left[ClO_2^-\right]} - pE$$

(eq. 23d)

Along the $ClO_{2(aq)}$ /$ClO_2^-$ boundary line, $[ClO_{2(aq)}] = [ClO_2^-]$ so $\log\{[ClO_{2(aq)}]/[ClO_2^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq23} = -17.6$. Substituting the values into eq. 23d and rearranging gives the following equation for the $ClO_{2(aq)}$ /$ClO_2^-$ boundary line:

$$pE = 17.6 \qquad \text{(eq. 23e)}$$

**Rxn 24:** $ClO_2^- + H_2O \leftrightarrow ClO_3^- + 2H^+ + 2e^-$ (eq. 24a)

$$K_{eq24} = \frac{\left(ClO_3^-\right)\left(H^+\right)^2\left(e^-\right)^2}{\left(ClO_2^-\right)} \qquad \text{(eq. 24b)}$$

$$K_{mix24} = \frac{\left[ClO_3^-\right]\left(H^+\right)^2\left(e^-\right)^2}{\left[ClO_2^-\right]}$$ (eq. 24c)

For generating predominance diagrams, assume that $K_{eq24} \sim K_{mix24}$ such that

$$\log K_{eq24} \approx \log K_{mix24} = \log\frac{\left[ClO_3^-\right]}{\left[ClO_2^-\right]} + 2\log\left(H^+\right) + 2\log\left(e^-\right) = \log\frac{\left[ClO_3^-\right]}{\left[ClO_2^-\right]} - 2pH - 2pE$$

(eq. 24d)

Along the $ClO_3^-$ /$ClO_2^-$ boundary line, [$ClO_3^-$] = [$ClO_2^-$] so log{[$ClO_3^-$]/[$ClO_2^-$]} = log 1 = 0. From the attached thermodynamic spreadsheet, log$K_{eq24}$ = -38.0. Substituting the values into eq. 24d and rearranging gives the following equation for the $ClO_3^-$ /$ClO_2^-$ boundary line:

$$2pE = 38.0 - 2pH \Rightarrow pE = 19.0 - pH$$ (eq. 24e)

**Rxn 25:** $ClO_2^- + 2H_2O \leftrightarrow ClO_4^- + 4H^+ + 4e^-$ (eq. 25a)

$$K_{eq25} = \frac{\left(ClO_4^-\right)\left(H^+\right)^4\left(e^-\right)^4}{\left(ClO_2^-\right)}$$ (eq. 25b)

$$K_{mix25} = \frac{\left[ClO_4^-\right]\left(H^+\right)^4\left(e^-\right)^4}{\left[ClO_2^-\right]}$$ (eq. 25c)

For generating predominance diagrams, assume that $K_{eq25} \sim K_{mix25}$ such that

$$\log K_{eq25} \approx \log K_{mix25} = \log\frac{\left[ClO_4^-\right]}{\left[ClO_2^-\right]} + 4\log\left(H^+\right) + 4\log\left(e^-\right) = \log\frac{\left[ClO_4^-\right]}{\left[ClO_2^-\right]} - 4pH - 4pE$$

(eq. 25d)

Along the $ClO_4^-$ /$ClO_2^-$ boundary line, [$ClO_4^-$] = [$ClO_2^-$] so log{[$ClO_4^-$]/[$ClO_2^-$]} = log 1 = 0. From the attached thermodynamic spreadsheet, log$K_{eq25}$ = -78.6. Substituting the values into eq. 25c and rearranging gives the following equation for the $ClO_4^-$ /$ClO_2^-$ boundary line:

$$4pE = 78.6 - 4pH \Rightarrow pE = 19.7 - pH$$ (eq. 25e)

**Reactions 26 - 27 (remaining reactions involving $\mathbf{ClO_{2(aq)}}$):**

**Rxn 26:** $ClO_{2(aq)} + H_2O \leftrightarrow ClO_3^- + 2H^+ + e^-$ (eq. 26a)

$$K_{eq26} = \frac{(ClO_3^-)(H^+)^2(e^-)}{(ClO_{2(aq)})} \quad \text{(eq. 26b)}$$

$$K_{mix26} = \frac{[ClO_3^-](H^+)^2(e^-)}{[ClO_{2(aq)}]} \quad \text{(eq. 26c)}$$

For generating predominance diagrams, assume that $K_{eq26} \sim K_{mix26}$ such that

$$\log K_{eq26} \approx \log K_{mix26} = \log\frac{[ClO_3^-]}{[ClO_{2(aq)}]} + 2\log(H^+) + \log(e^-) = \log\frac{[ClO_3^-]}{[ClO_{2(aq)}]} - 2pH - pE$$

(eq. 26d)

Along the $ClO_3^-$ /$ClO_{2(aq)}$ boundary line, $[ClO_3^-] = [ClO_{2(aq)}]$ so $\log\{[ClO_3^-]/[ClO_{2(aq)}]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq26} = -20.4$. Substituting the values into eq. 26d and rearranging gives the following equation for the $ClO_3^-$ /$ClO_{2(aq)}$ boundary line:

$$pE = 20.4 - 2pH \quad \text{(eq. 26e)}$$

**Rxn 27:** $ClO_{2(aq)} + 2H_2O \leftrightarrow ClO_4^- + 4H^+ + 3e^-$ (eq. 27a)

$$K_{eq27} = \frac{(ClO_4^-)(H^+)^4(e^-)^3}{(ClO_{2(aq)})} \quad \text{(eq. 27b)}$$

$$K_{mix27} = \frac{[ClO_4^-](H^+)^4(e^-)^3}{[ClO_{2(aq)}]} \quad \text{(eq. 27c)}$$

For generating predominance diagrams, assume that $K_{eq27} \sim K_{mix27}$ such that

$$\log K_{eq27} \approx \log K_{mix27} = \log\frac{\left[ClO_4^-\right]}{\left[ClO_{2(aq)}\right]} + 4\log\left(H^+\right) + 3\log\left(e^-\right) = \log\frac{\left[ClO_4^-\right]}{\left[ClO_{2(aq)}\right]} - 4pH - 3pE$$

(eq. 27d)

Along the $ClO_4^-$ /$ClO_{2(aq)}$ boundary line, $[ClO_4^-] = [ClO_{2(aq)}]$ so $\log\{[ClO_4^-]/[ClO_{2(aq)}]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq27} = -61.0$. Substituting the values into eq. 27d and rearranging gives the following equation for the $ClO_4^-$ /$ClO_{2(aq)}$ boundary line:

$$3pE = 61.0 - 4pH \Rightarrow pE = 20.3 - 1.33pH \qquad \text{(eq. 27e)}$$

**<u>Reaction 28 (last remaining reaction involving $ClO_3^-$ ):</u>**

**<u>Rxn 28:</u>** $ClO_3^- + H_2O \leftrightarrow ClO_4^- + 2H^+ + 2e^-$ (eq. 28a)

$$K_{eq28} = \frac{\left(ClO_4^-\right)\left(H^+\right)^2\left(e^-\right)^2}{\left(ClO_3^-\right)} \qquad \text{(eq. 28b)}$$

$$K_{mix28} = \frac{\left[ClO_4^-\right]\left(H^+\right)^2\left(e^-\right)^2}{\left[ClO_3^-\right]} \qquad \text{(eq. 28c)}$$

For generating predominance diagrams, assume that $K_{eq28} \sim K_{mix28}$ such that

$$\log K_{eq28} \approx \log K_{mix28} = \log\frac{\left[ClO_4^-\right]}{\left[ClO_3^-\right]} + 2\log\left(H^+\right) + 2\log\left(e^-\right) = \log\frac{\left[ClO_4^-\right]}{\left[ClO_3^-\right]} - 2pH - 2pE$$

(eq. 28d)

Along the $ClO_4^-$ /$ClO_3^-$ boundary line, $[ClO_4^-] = [ClO_3^-]$ so $\log\{[ClO_4^-]/[ClO_3^-]\} = \log 1 = 0$. From the attached thermodynamic spreadsheet, $\log K_{eq28} = -40.6$. Substituting the values into eq. 28d and rearranging gives the following equation for the $ClO_4^-$ /$ClO_3$ boundary line:

$$2pE = 40.6 - 2pH \rightarrow pE = 20.3 - pH \qquad \text{(eq. 28e)}$$

**<u>See Next Page</u>**

**Water oxidation and reduction reactions (Benjamin 2002):**

**Rxn 1W Oxidation of Water:** $2H_2O \rightarrow O_{2(g)} + 4H^+ + 4e^-$ (eq. 1Wa)

$$K_{eqW1} = \left(O_{2(aq)}\right)\left(H^+\right)^4\left(e^-\right)^4$$ (eq. 1Wb)

$$\log K_{eqW1} = \log\left(O_{2(g)}\right) + 4\log\left(H^+\right) + 4\log\left(e^-\right) = \log\left(O_{2(g)}\right) - 4pH - 4pE$$
(eq. 1Wc)

$$4pE = 83.1 + \log(0.21) - 4pH \Rightarrow pE = 20.6 - pH$$ (eq. 1Wd)

**Rxn 2W Reduction of Water:** $2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-$ (eq. 2Wa)

$$K_{eqW2} = \frac{\left(H_{2(g)}\right)\left(OH^-\right)^2}{\left(e^-\right)^2}$$ (eq. 2Wb)

$$\log K_{eqW2} = \log\left(H_{2(g)}\right) + 2\log(OH^-) - 2\log\left(e^-\right) = \log\left(H_{2(g)}\right) - 2pOH + 2pE =$$
$$\log\left(H_{2(g)}\right) - 2(14 - pH) + 2pE = \log\left(H_{2(g)}\right) + 2pH + 2pE - 28$$
(eq. 2Wc)

$$2pE = -\log\left(5\times 10^{-7}\right) - 2pH \Rightarrow 2pE = 6.30 - 2pH$$
$$\Rightarrow pE = 3.2 - pH$$ (eq. 2Wd)

Attachment C to Appendix B-2: Charts 1b through 1e

**<u>Attachment B:</u> Computations of delta $G^0$ of reactions and equilbrium constants for aqueous chlorine species reactions and for oxidation and reduction of water reactions. (Spreadsheet format developed by Dr. Jim Hetrick).**

| | **Reactants** | **# mols** | **del$G^0_{form}$** | **del$G^0_{reacts}$** | **Products** | **# mols** | **del$G^0_{form}$** | **del$G^0_{prods}$** | **del$G^0_{rxn}$** | **log$K_{eq}$** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Rxn 1** | $Cl^-$ | 2 | -131.3 | -262.6 | $Cl_{2(aq)}$ | 1 | 6.9 | 6.9 | | |
| | | | | 0 | $e^-$ | 2 | 0 | 0 | | |
| | | | | | | | | 0 | | |
| | | | | -262.6 | | | | 6.9 | 269.5 | -47.2 |
| **Rxn 2** | $Cl^-$ | 1 | -131.3 | -131.3 | $ClO^-$ | 1 | -36.8 | -36.8 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 2 | 0 | 0 | | |
| | | | | | $e^-$ | 2 | 0 | 0 | | |
| | | | Sum(rea): | -368.48 | | | Sum(pro): | -36.8 | 331.7 | -58.1 |
| **Rxn 3** | $Cl^-$ | 1 | -131.3 | -131.3 | HClO | 1 | -79.9 | -79.9 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 1 | 0 | 0 | | |
| | | | | | $e^-$ | 2 | 0 | 0 | | |
| | | | Sum(rea): | -368.48 | | | Sum(pro): | -79.9 | 288.6 | -50.6 |
| **Rxn 4** | $Cl^-$ | 1 | -131.3 | -131.3 | $ClO_2^-$ | 1 | 17.1 | 17.1 | | |
| | $H_2O$ | 2 | -237.18 | -474.36 | $H^+$ | 4 | 0 | 0 | | |
| | | | | | $e^-$ | 4 | 0 | 0 | | |
| | | | Sum(rea): | -605.66 | | | Sum(pro): | 17.1 | 622.8 | -109.1 |
| **Rxn 5** | $Cl^-$ | 1 | -131.3 | -131.3 | $ClO_{2(aq)}$ | 1 | 117.6 | 117.6 | | |
| | $H_2O$ | 2 | -237.18 | -474.36 | $H^+$ | 4 | 0 | 0 | | |
| | | | | | $e^-$ | 5 | 0 | 0 | | |
| | | | Sum(rea): | -605.66 | | | Sum(pro): | 117.6 | 723.3 | -126.8 |
| **Rxn 6** | $Cl^-$ | 1 | -131.3 | -131.3 | $ClO_3^-$ | 1 | -3.35 | -3.35 | | |
| | $H_2O$ | 3 | -237.18 | -711.54 | $H^+$ | 6 | 0 | 0 | | |
| | | | | | $e^-$ | 6 | 0 | 0 | | |
| | | | Sum(rea): | -842.84 | | | Sum(pro): | -3.35 | 839.5 | -147.1 |
| **Rxn 7** | $Cl^-$ | 1 | -131.3 | -131.3 | $ClO4^-$ | 1 | -8.62 | -8.62 | | |
| | $H_2O$ | 4 | -237.18 | -948.72 | $H^+$ | 8 | 0 | 0 | | |
| | | | | | $e^-$ | 8 | 0 | 0 | | |
| | | | Sum(rea): | -1080.02 | | | Sum(pro): | -8.62 | 1071.4 | -187.8 |
| **Rxn 8** | $Cl_{2(aq)}$ | 1 | 6.9 | 6.9 | $ClO^-$ | 2 | -36.8 | -73.6 | | |
| | $H_2O$ | 2 | -237.18 | -474.36 | $H^+$ | 4 | 0 | 0 | | |
| | | | | | $e^-$ | 2 | 0 | 0 | | |
| | | | Sum(rea): | -467.46 | | | Sum(pro): | -73.6 | 393.9 | -69.0 |
| **Rxn 9** | $Cl_{2(aq)}$ | 1 | 6.9 | 6.9 | HClO | 2 | -79.9 | -159.8 | | |
| | $H_2O$ | 2 | -237.18 | -474.36 | $H^+$ | 2 | 0 | 0 | | |
| | | | | | $e^-$ | 2 | 0 | 0 | | |
| | | | Sum(rea): | -467.46 | | | Sum(pro): | -159.8 | 307.7 | -53.9 |
| **Rxn 10** | $Cl_{2(aq)}$ | 1 | 6.9 | 6.9 | $ClO_2^-$ | 2 | 17.1 | 34.2 | | |
| | $H_2O$ | 4 | -237.18 | -948.72 | $H^+$ | 8 | 0 | 0 | | |
| | | | | | $e^-$ | 6 | 0 | 0 | | |
| | | | Sum(rea): | -941.82 | | | Sum(pro): | 34.2 | 976.0 | -171.1 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Rxn 11** | $Cl_{2(aq)}$ | 1 | 6.9 | 6.9 | $ClO_{2(aq)}$ | 2 | 117.6 | 235.2 | | |
| | $H_2O$ | 4 | -237.18 | -948.72 | $H^+$ | 8 | 0 | 0 | | |
| | | | | | $e^-$ | 8 | 0 | 0 | | |
| | | | Sum(rea): | -941.82 | | | Sum(pro): | 235.2 | 1177.0 | -206.3 |
| **Rxn 12** | $Cl_{2(aq)}$ | 1 | 6.9 | 6.9 | $ClO_3^-$ | 2 | -3.35 | -6.7 | | |
| | $H_2O$ | 6 | -237.18 | -1423.08 | $H^+$ | 12 | 0 | 0 | | |
| | | | | | $e^-$ | 10 | 0 | 0 | | |
| | | | Sum(rea): | -1416.18 | | | Sum(pro): | -6.7 | 1409.5 | -247.0 |
| **Rxn 13** | $Cl_{2(aq)}$ | 1 | 6.9 | 6.9 | $ClO4^-$ | 2 | -8.62 | -17.24 | | |
| | $H_2O$ | 8 | -237.18 | -1897.44 | $H^+$ | 16 | 0 | 0 | | |
| | | | | | $e^-$ | 14 | 0 | 0 | | |
| | | | Sum(rea): | -1890.54 | | | Sum(pro): | -17.24 | 1873.3 | -328.3 |
| **Rxn 14** | $ClO^-$ | 1 | -36.8 | -36.8 | HClO | 1 | -79.9 | -79.9 | | |
| | $H^+$ | 1 | 0 | 0 | | | | | | |
| | | | | | | | | | | |
| | | | Sum(rea): | -36.8 | | | Sum(pro): | -79.9 | -43.1 | 7.6 |
| **Rxn 15** | $ClO^-$ | 1 | -36.8 | -36.8 | $ClO_2^-$ | 1 | 17.1 | 17.1 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 2 | 0 | 0 | | |
| | | | | | $e^-$ | 2 | 0 | 0 | | |
| | | | Sum(rea): | -273.98 | | | Sum(pro): | 17.1 | 291.1 | -51.0 |
| **Rxn 16** | $ClO^-$ | 1 | -36.8 | -36.8 | $ClO_{2(aq)}$ | 1 | 117.6 | 117.6 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 2 | 0 | 0 | | |
| | | | | | $e^-$ | 3 | 0 | 0 | | |
| | | | Sum(rea): | -273.98 | | | Sum(pro): | 117.6 | 391.6 | -68.6 |
| **Rxn 17** | $ClO^-$ | 1 | -36.8 | -36.8 | $ClO_3^-$ | 1 | -3.35 | -3.35 | | |
| | $H_2O$ | 2 | -237.18 | -474.36 | $H^+$ | 4 | 0 | 0 | | |
| | | | | | $e^-$ | 4 | 0 | 0 | | |
| | | | Sum(rea): | -511.16 | | | Sum(pro): | -3.35 | 507.8 | -89.0 |
| **Rxn 18** | $ClO^-$ | 1 | -36.8 | -36.8 | $ClO4^-$ | 1 | -8.62 | -8.62 | | |
| | $H_2O$ | 3 | -237.18 | -711.54 | $H^+$ | 6 | 0 | 0 | | |
| | | | | | $e^-$ | 6 | 0 | 0 | | |
| | | | | -748.34 | | | | -8.62 | 739.7 | -129.6 |
| **Rxn 19** | HClO | 1 | -79.9 | -79.9 | $ClO_2^-$ | 1 | 17.1 | 17.1 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 3 | 0 | 0 | | |
| | | | | | $e^-$ | 2 | 0 | 0 | | |
| | | | Sum(rea): | -317.08 | | | Sum(pro): | 17.1 | 334.2 | -58.6 |
| **Rxn 20** | HClO | 1 | -79.9 | -79.9 | $ClO_{2(aq)}$ | 1 | 117.6 | 117.6 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 3 | 0 | 0 | | |
| | | | | | $e^-$ | 3 | 0 | 0 | | |
| | | | Sum(rea): | -317.08 | | | Sum(pro): | 117.6 | 434.7 | -76.2 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Rxn 21** | HClO | 1 | -79.9 | -79.9 | $ClO_3^-$ | 1 | -3.35 | -3.35 | | |
| | $H_2O$ | 2 | -237.18 | -474.36 | $H^+$ | 5 | 0 | 0 | | |
| | | | | | $e^-$ | 4 | 0 | 0 | | |
| | | | Sum(rea): | -554.26 | | | Sum(pro): | -3.35 | 550.9 | -96.6 |
| **Rxn 22** | HClO | 1 | -79.9 | -79.9 | $ClO4^-$ | 1 | -8.62 | -8.62 | | |
| | $H_2O$ | 3 | -237.18 | -711.54 | $H^+$ | 7 | 0 | 0 | | |
| | | | | | $e^-$ | 6 | 0 | 0 | | |
| | | | Sum(rea): | -791.44 | | | Sum(pro): | -8.62 | 782.8 | -137.2 |
| **Rxn 23** | $ClO_2^-$ | 1 | 17.1 | 17.1 | $ClO_{2(aq)}$ | 1 | 117.6 | 117.6 | | |
| | | | | 0 | $e^-$ | 1 | 0 | 0 | | |
| | | | | | | | | 0 | | |
| | | | | 17.1 | | | | 117.6 | 100.5 | -17.6 |
| **Rxn 24** | $ClO_2^-$ | 1 | 17.1 | 17.1 | $ClO_3^-$ | 1 | -3.35 | -3.35 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 2 | 0 | 0 | | |
| | | | | | $e^-$ | 2 | 0 | 0 | | |
| | | | Sum(rea): | -220.08 | | | Sum(pro): | -3.35 | 216.7 | -38.0 |
| **Rxn 25** | $ClO_2^-$ | 1 | 17.1 | 17.1 | $ClO4^-$ | 1 | -8.62 | -8.62 | | |
| | $H_2O$ | 2 | -237.18 | -474.36 | $H^+$ | 4 | 0 | 0 | | |
| | | | | | $e^-$ | 4 | 0 | 0 | | |
| | | | Sum(rea): | -457.26 | | | Sum(pro): | -8.62 | 448.6 | -78.6 |
| **Rxn 26** | $ClO_{2(aq)}$ | 1 | 117.6 | 117.6 | $ClO_3^-$ | 1 | -3.35 | -3.35 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 2 | 0 | 0 | | |
| | | | | | $e^-$ | 1 | 0 | 0 | | |
| | | | Sum(rea): | -119.58 | | | Sum(pro): | -3.35 | 116.2 | -20.4 |
| **Rxn 27** | $ClO_{2(aq)}$ | 1 | 117.6 | 117.6 | $ClO4^-$ | 1 | -8.62 | -8.62 | | |
| | $H_2O$ | 2 | -237.18 | -474.36 | $H^+$ | 4 | 0 | 0 | | |
| | | | | | $e^-$ | 3 | 0 | 0 | | |
| | | | Sum(rea): | -356.76 | | | Sum(pro): | -8.62 | 348.1 | -61.0 |
| **Rxn 28** | $ClO_3^-$ | 1 | -3.35 | -3.35 | $ClO4^-$ | 1 | -8.62 | -8.62 | | |
| | $H_2O$ | 1 | -237.18 | -237.18 | $H^+$ | 2 | 0 | 0 | | |
| | | | | | $e^-$ | 2 | 0 | 0 | | |
| | | | Sum(rea): | -240.53 | | | Sum(pro): | -8.62 | 231.9 | -40.6 |
| **Rxn** | $H_2O$ | 2 | -237.18 | -474.36 | $O_{2(g)}$ | 1 | 0 | 0 | | |
| **1W** | | | | | $H^+$ | 4 | 0 | 0 | | |
| | | | | | $e^-$ | 4 | 0 | 0 | | |
| | | | Sum(rea): | -474.36 | | | Sum(pro): | 0 | 474.4 | -83.1 |
| **Rxn** | $H_2O$ | 2 | -237.18 | -474.36 | $H_{2(g)}$ | 1 | 0 | 0 | | |
| **2W** | $e^-$ | 2 | 0 | | $OH^-$ | 2 | -157.3 | -314.6 | | |
| | | | | | | | | 0 | | |
| | | | Sum(rea): | -474.36 | | | Sum(pro): | -314.6 | 159.8 | -28.0 |

# Attachment C to Appendix B-2: Charts 1b through 1e

**Chart 1b: Case 1 $Cl^-$ predominance (below bolded lines) considering only $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO.**

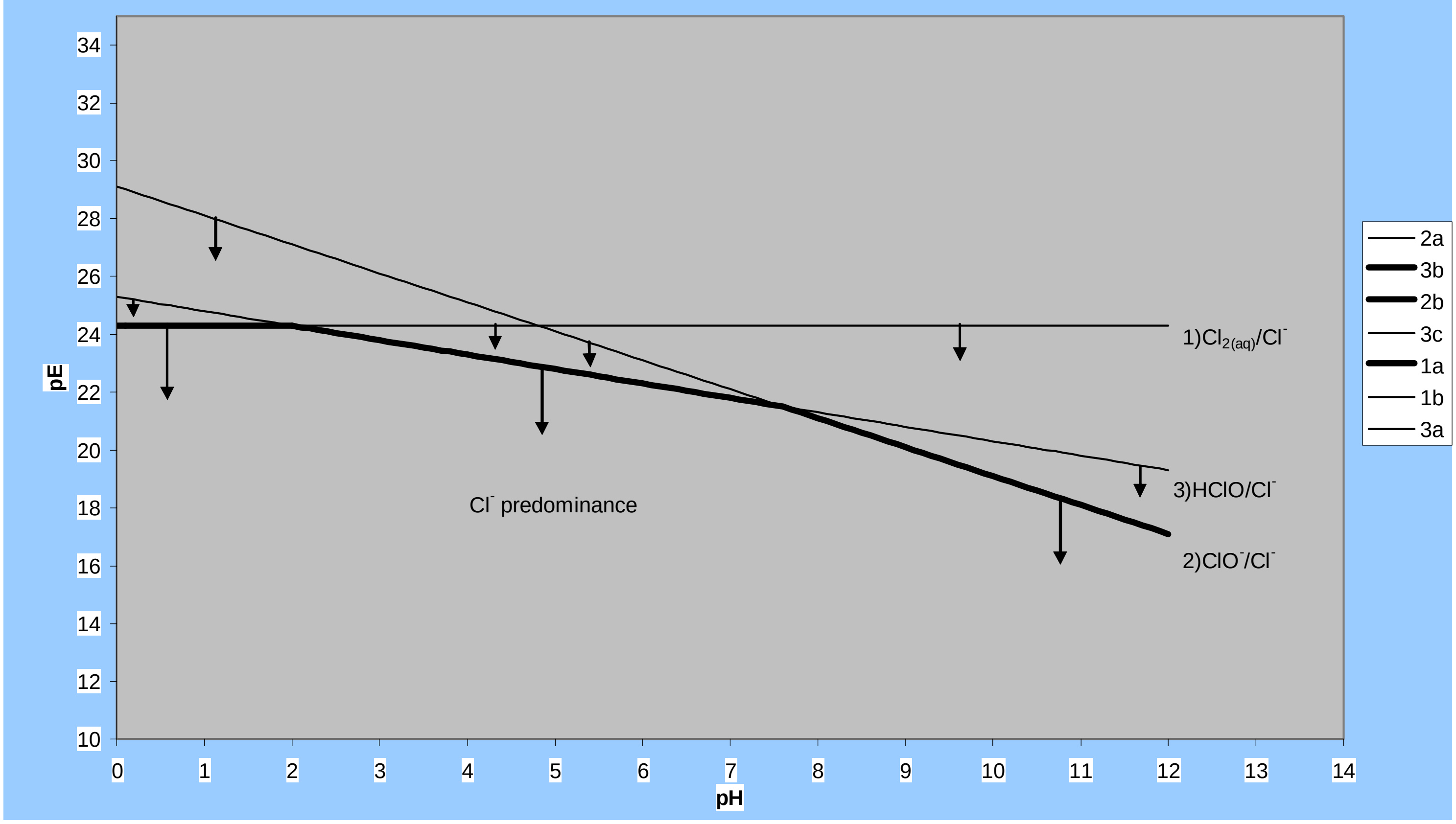


**Chart 1c:** **Case 1 $Cl_{2(aq)}$ predominance considering only $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO.**

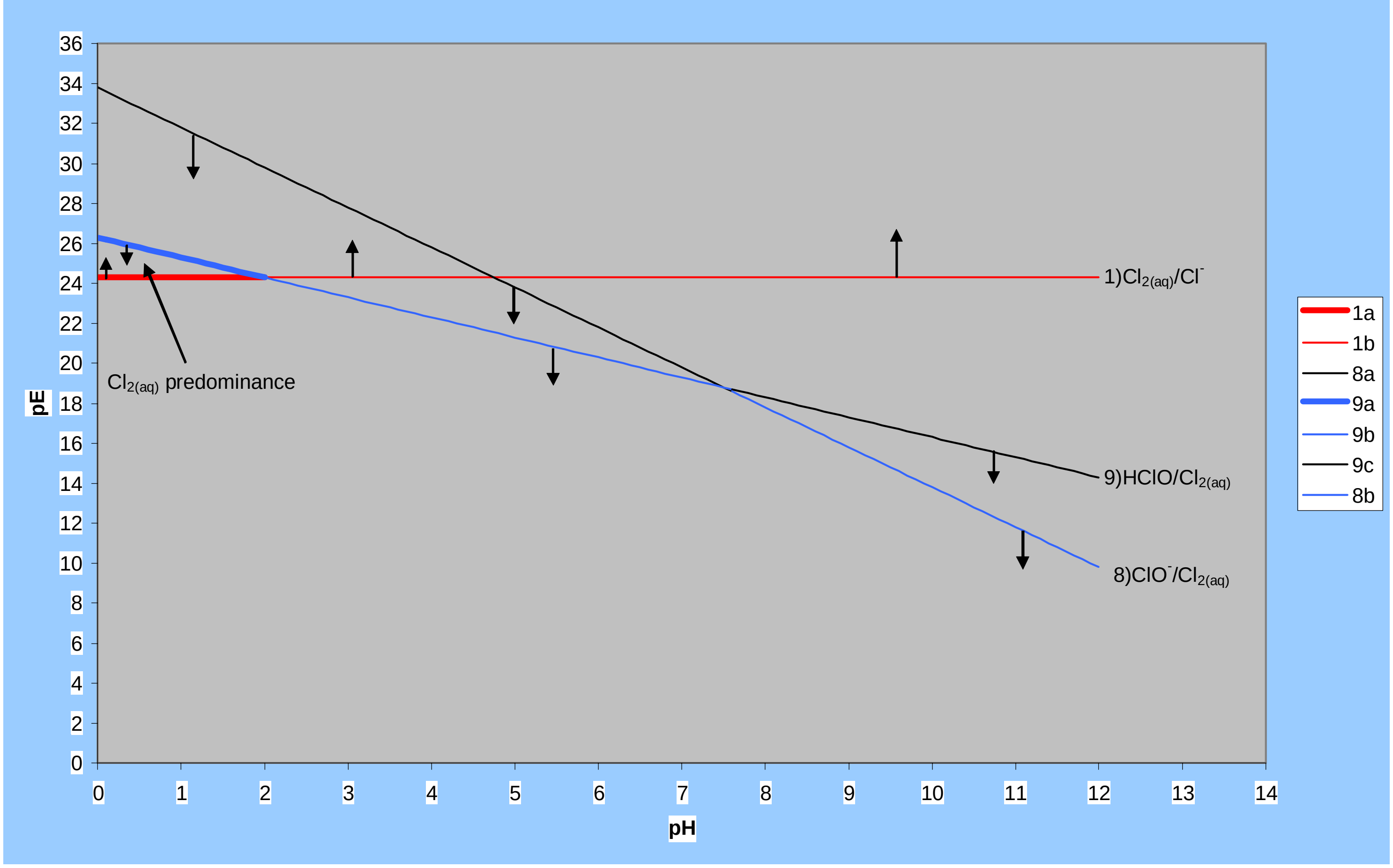


**Chart 1d:** **Case 1 $ClO^-$ predominance (enclosed by bolded lines) considering only $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO.**

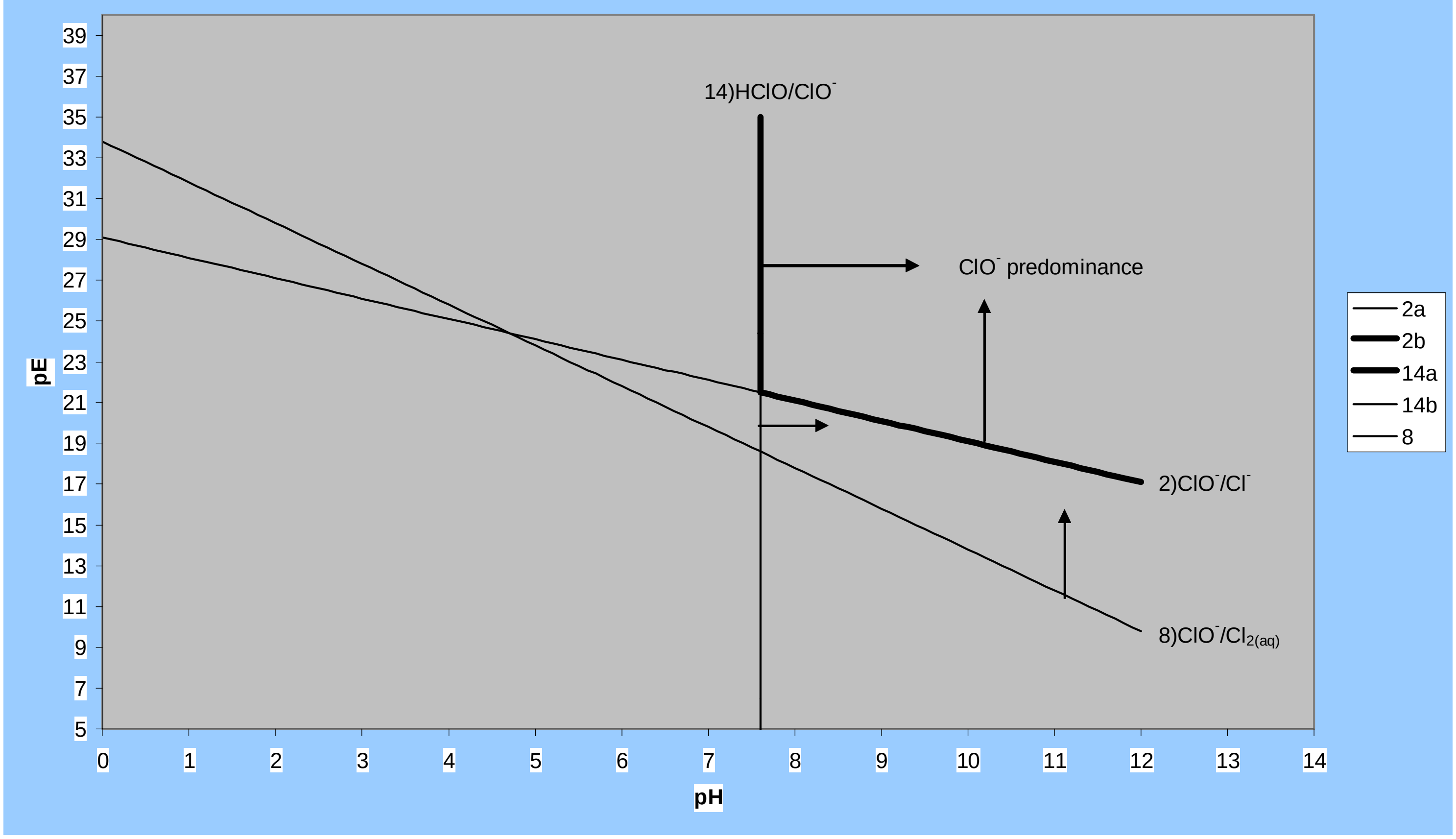
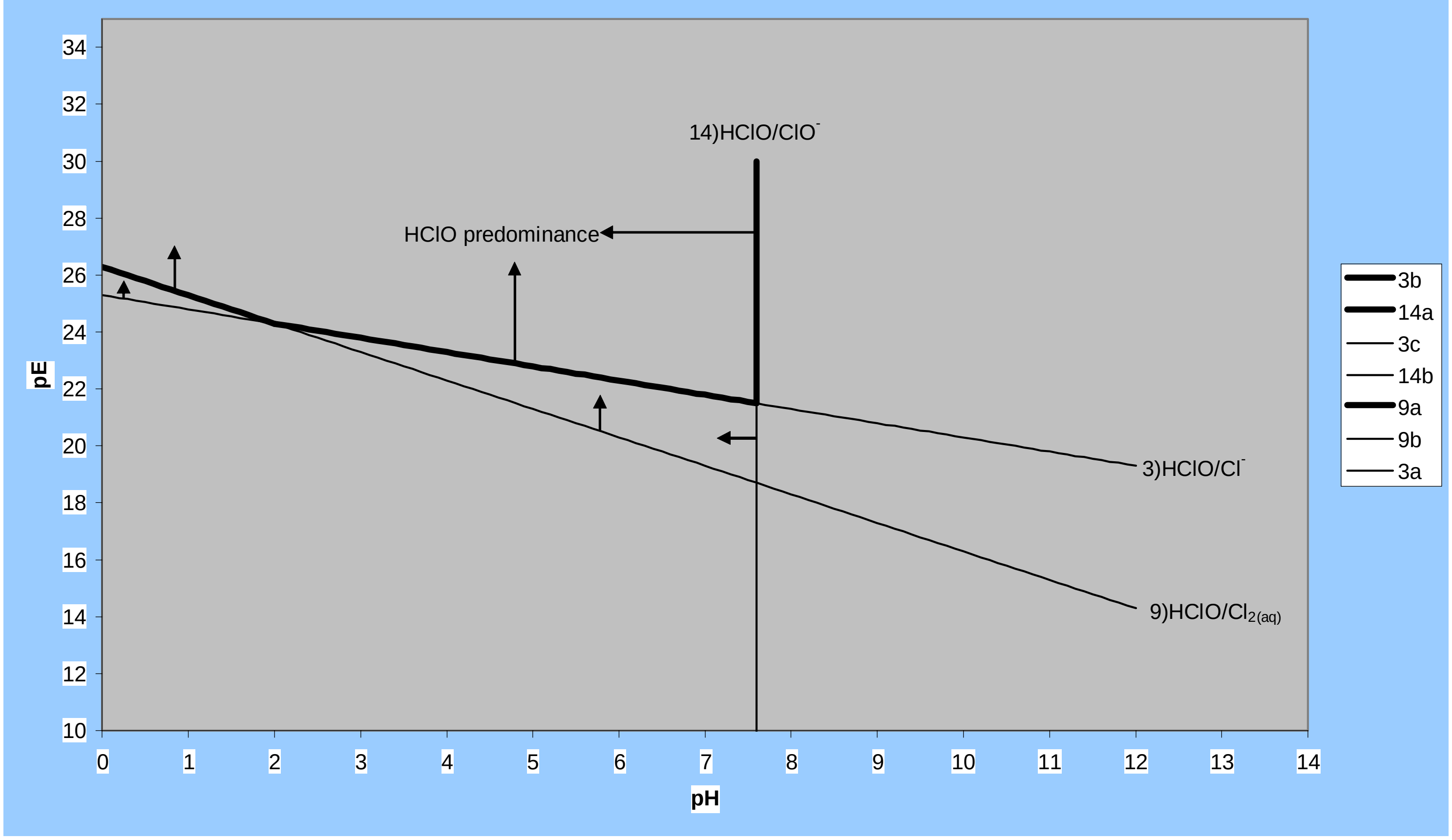
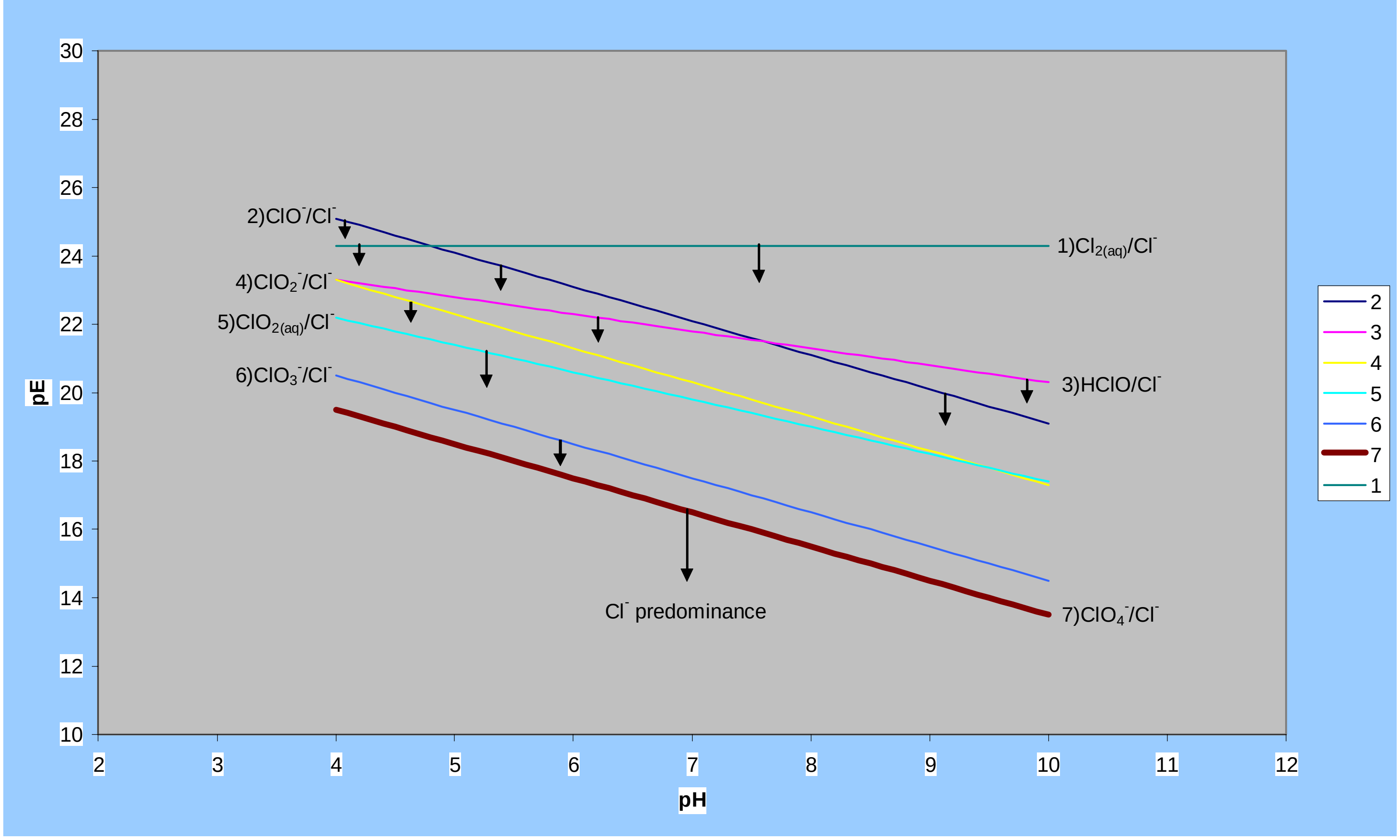


**Chart 1e:** **Case 1 HClO predominance (enclosed by bolded lines) considering only $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, and HClO.**

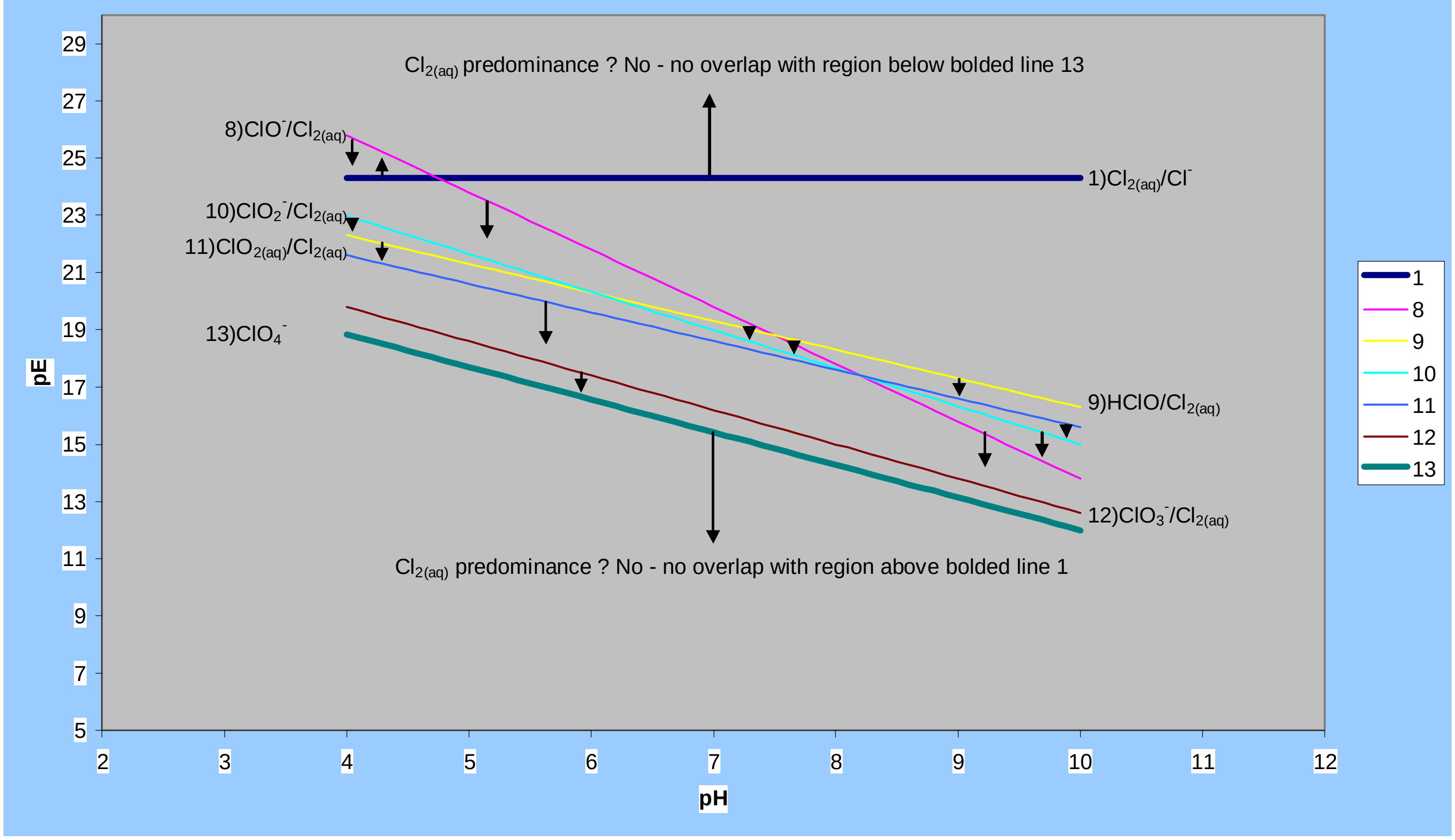


## Attachment D to Appendix B-2. Charts 3b to 3i.

**Chart 3b:** **Case 2 $Cl^-$ predominance (below the bolded line) considering Cl-, $Cl_{2(aq)}$, HClO, $ClO^-$, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**



**<u>Chart 3c:</u> Case 2 $Cl_{2(aq)}$ predominance (none - no overlap between $Cl_{2(aq)}$ regions above and below bolded lines) considering $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**



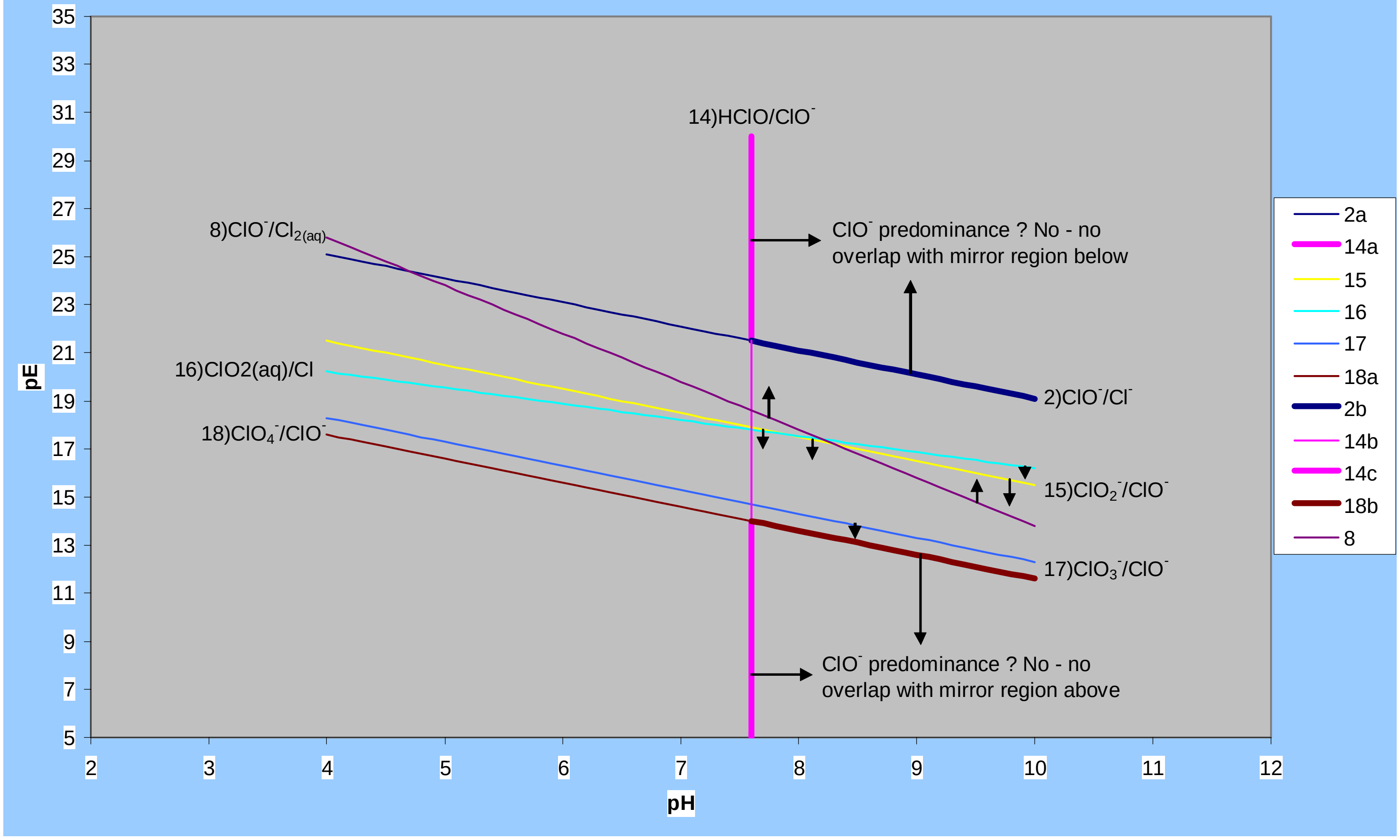
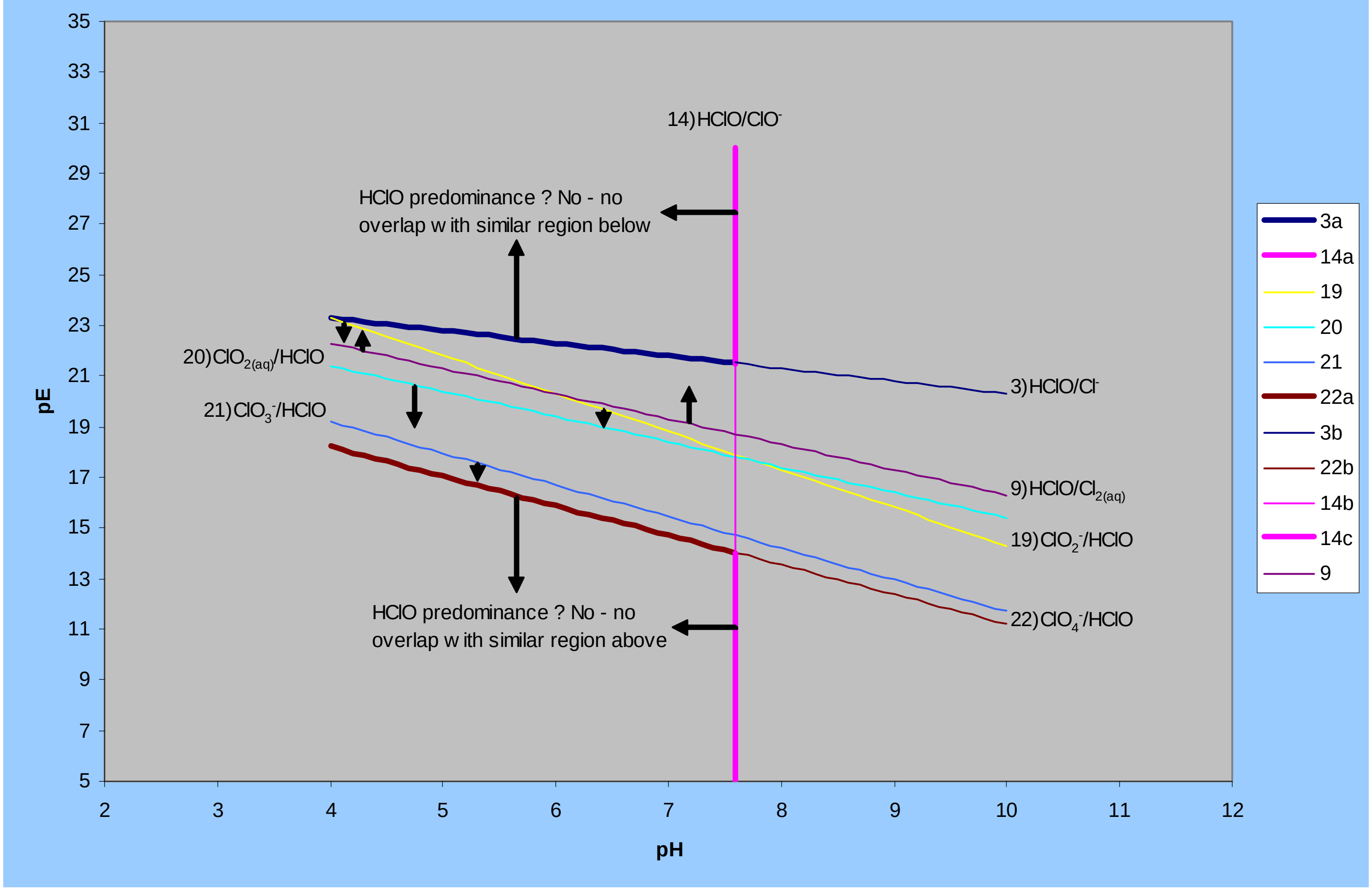


**Chart 3d: Case 2 ClO$^-$ predominance (none - no overlap between ClO$^-$ regions bordered by bolded lines) considering Cl$^-$, $Cl_{2(aq)}$, ClO$^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$**

**Chart 3e: Case 2 HClO predominance (none - no overlap between HClO regions bordered by bolded lines) considering $Cl^-$, $Cl_{2(aq)}$ $ClO^-$, HClO, $ClO_2^-$, $ClO_3^-$, and $ClO_4^-$.**



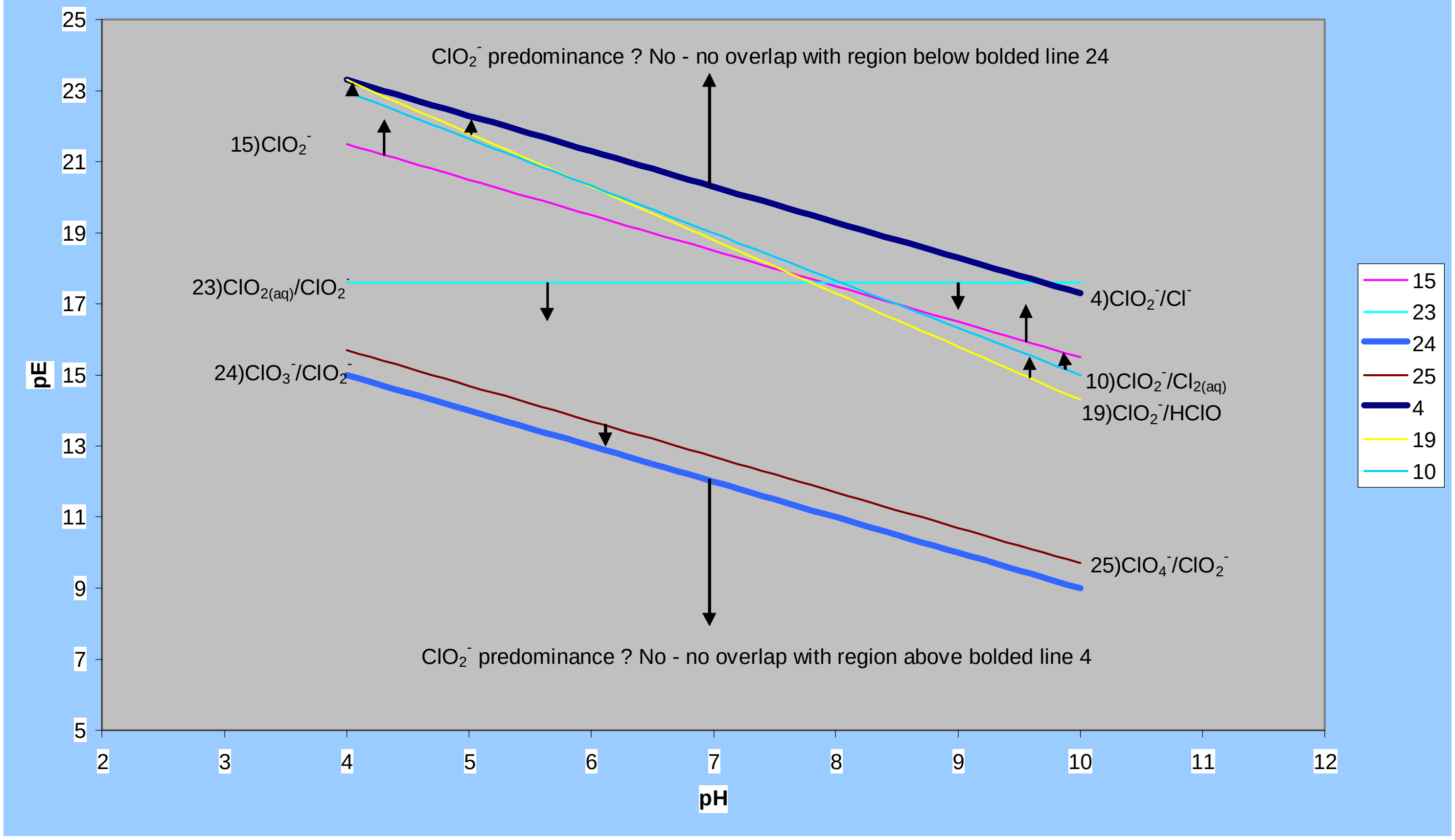


**Chart 3f:** **Case 2 $ClO_2^-$ predominance (none - no overlap between $ClO_2^-$ regions above and below bolded lines) considering $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**

**Chart 3g:** **Case 2 $ClO_{2(aq)}$ predominance (none - no overlap between $ClO_{2(aq)}$ regions above and below bolded lines) considering $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**

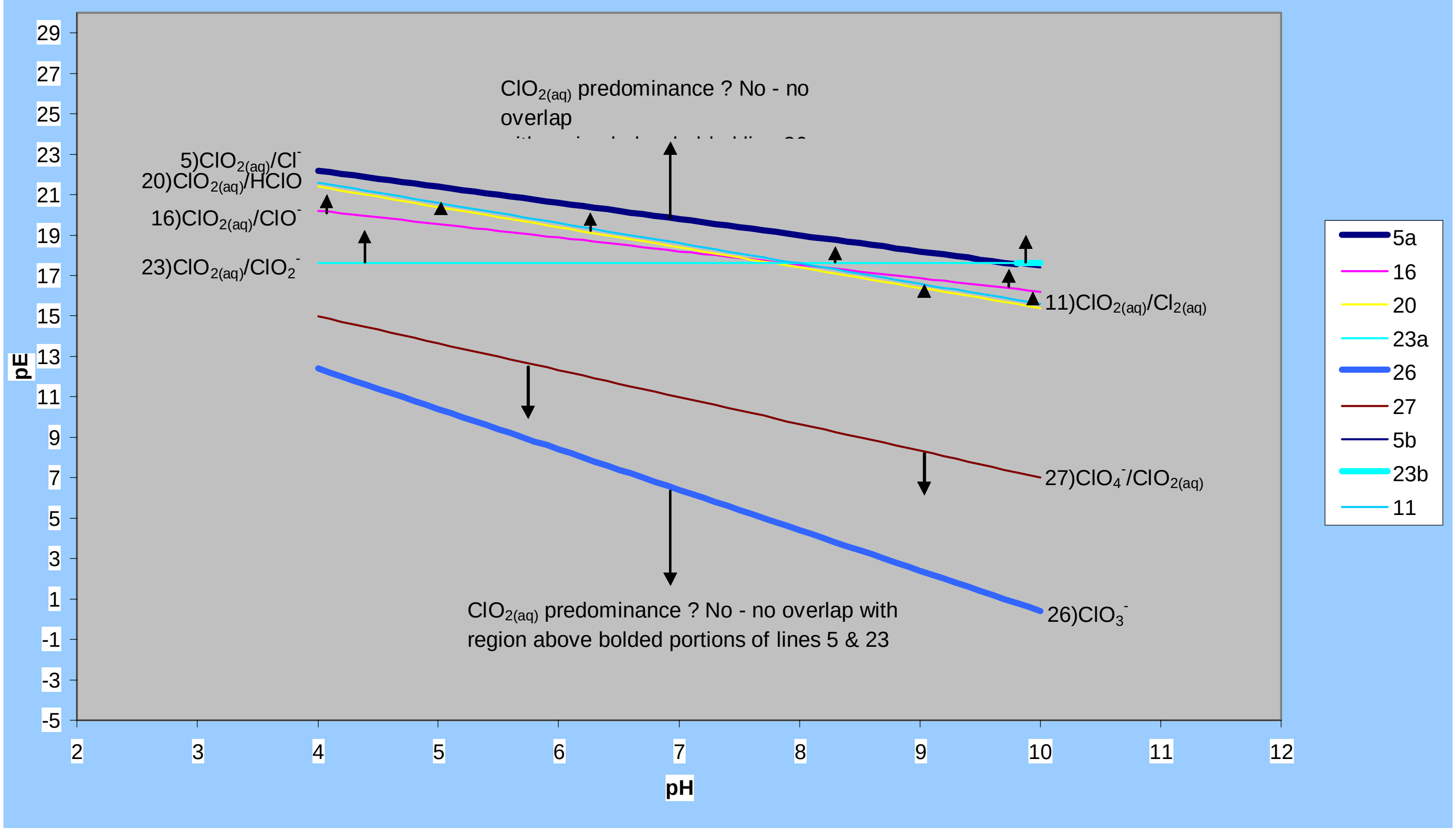


**Chart 3h: Case 2 $ClO_3^-$ predominance (none - no overlap between $ClO_3^-$ regions above and below bolded lines) considering $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**

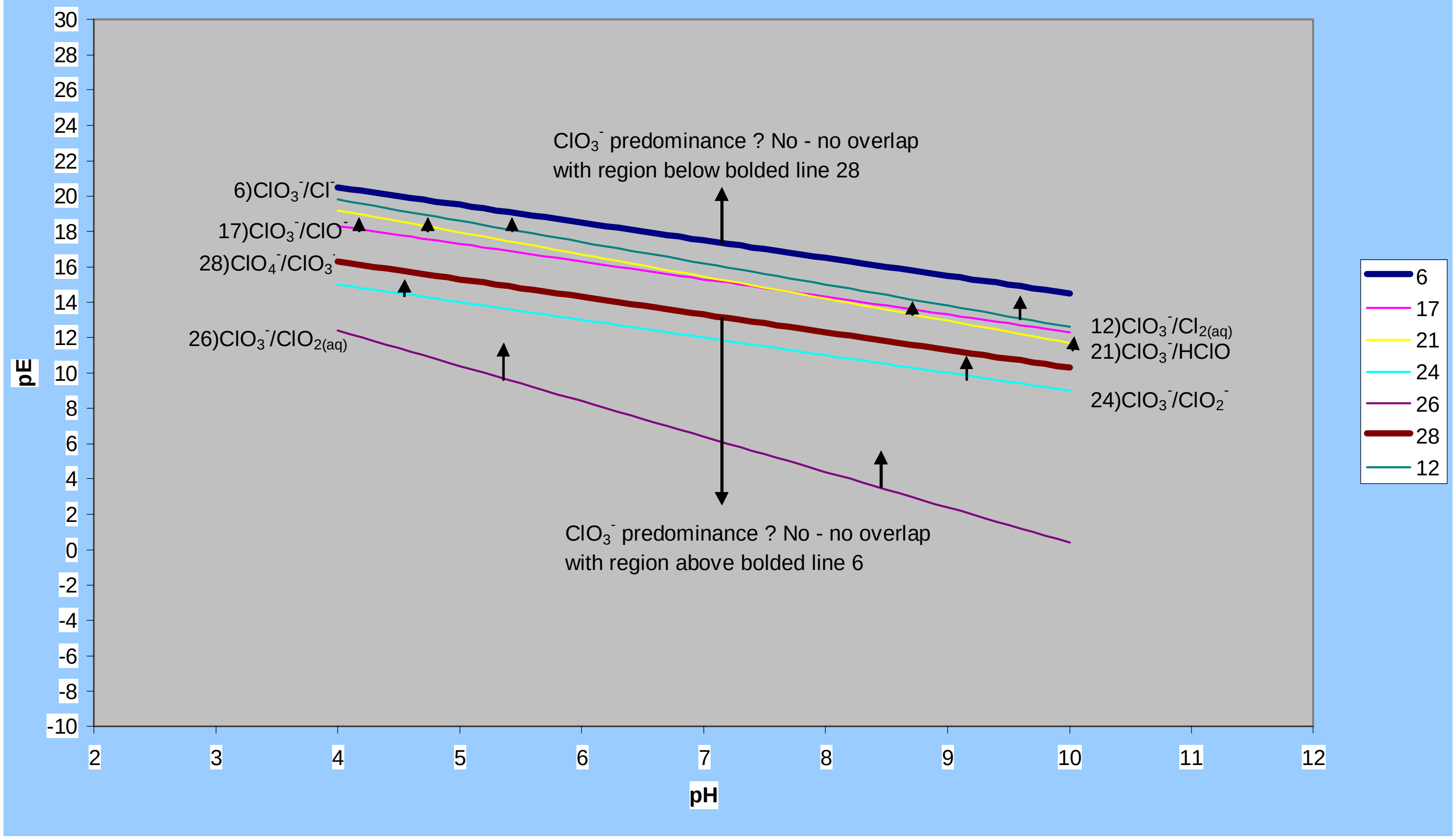
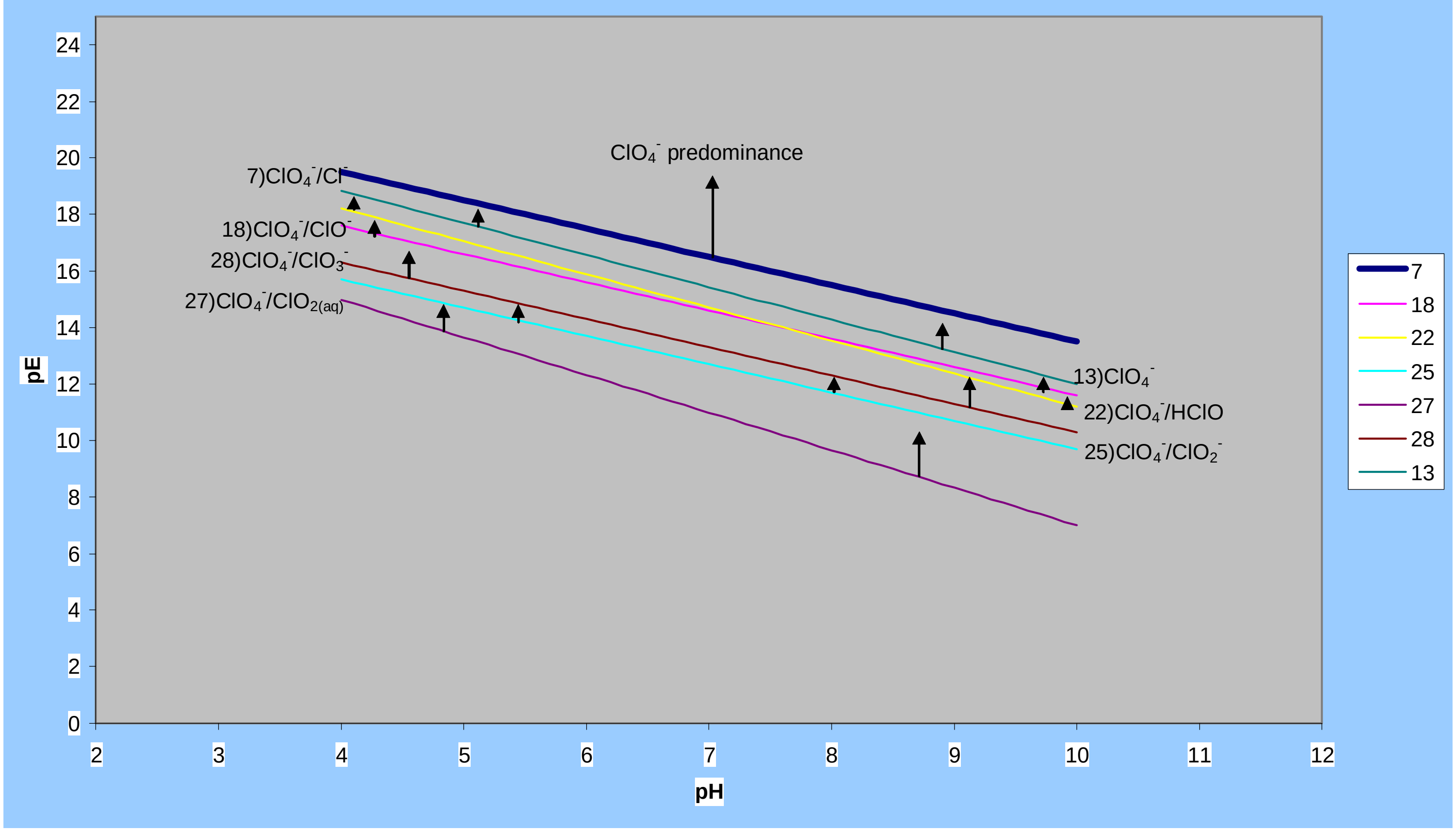


**Chart 3i:** **Case 2 $ClO_4^-$ predominance (above the bolded line) considering $Cl^-$, $Cl_{2(aq)}$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**



## Attachment E to Appendix B-2.  Charts 4c to 4g

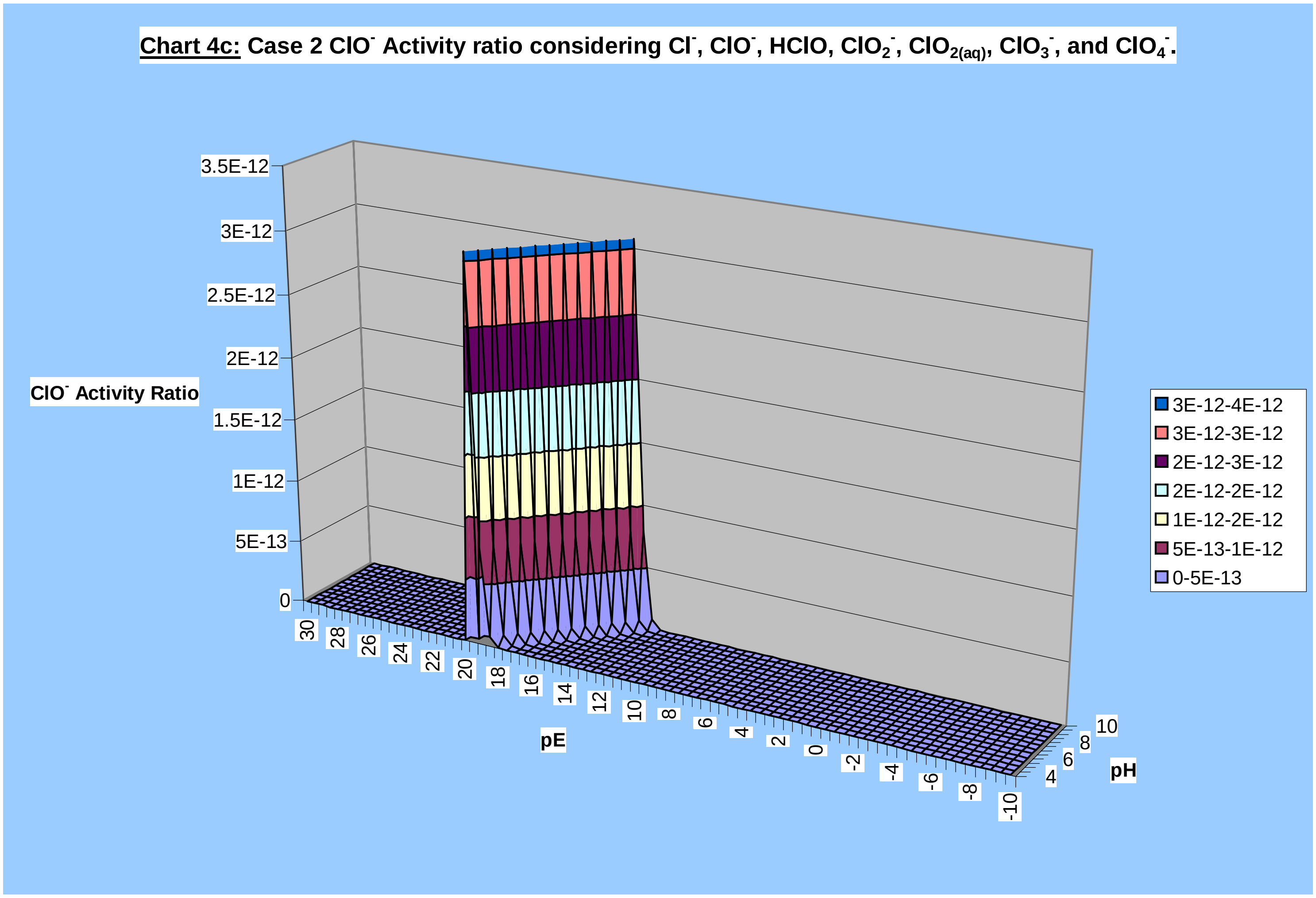
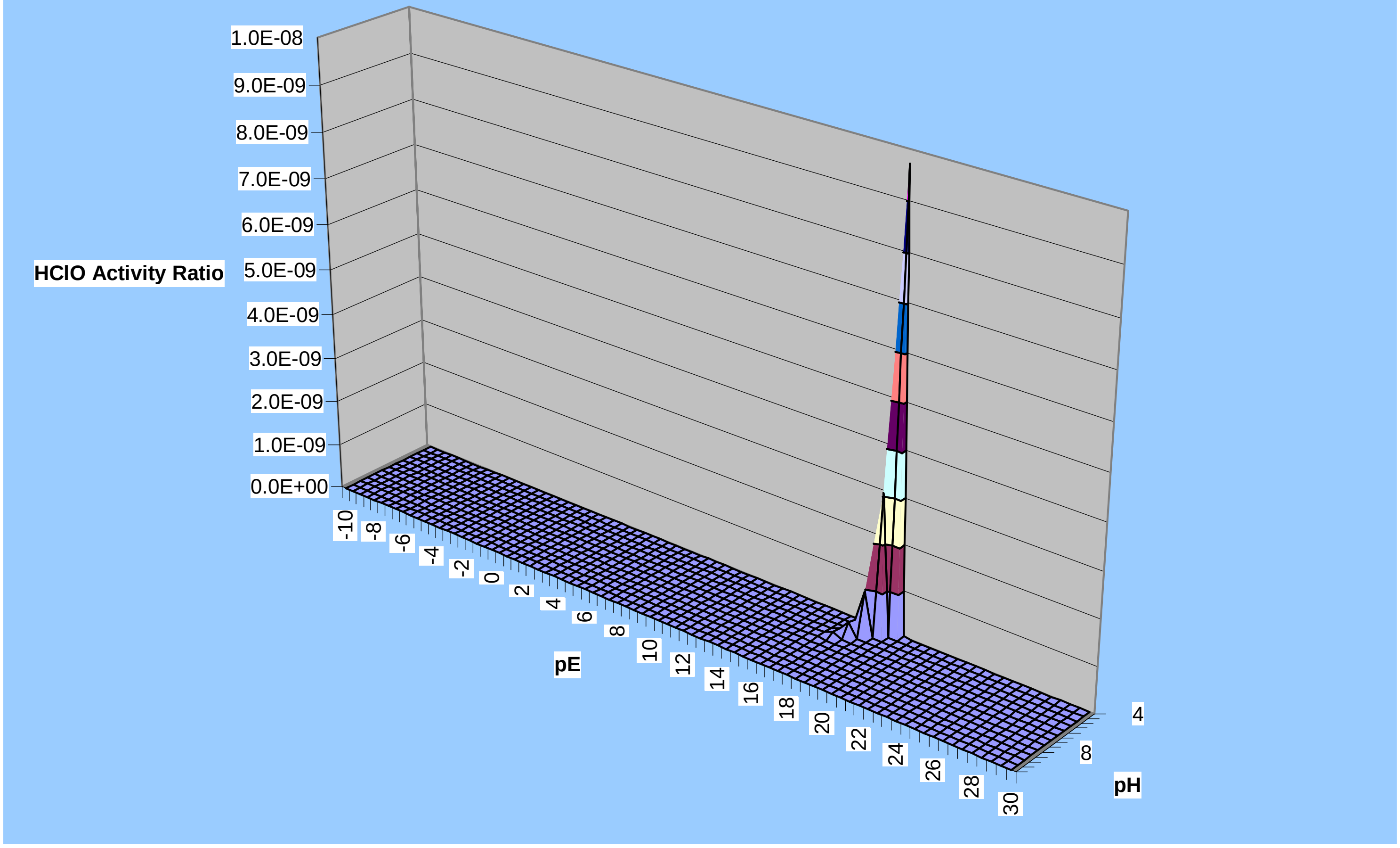


**Chart 4c:** **Case 2 $ClO^-$ Activity ratio considering $Cl^-$, $ClO^-$, $HClO$, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**

**Chart 4d:** **Case 2 HClO Activity ratio considering $Cl^-$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**



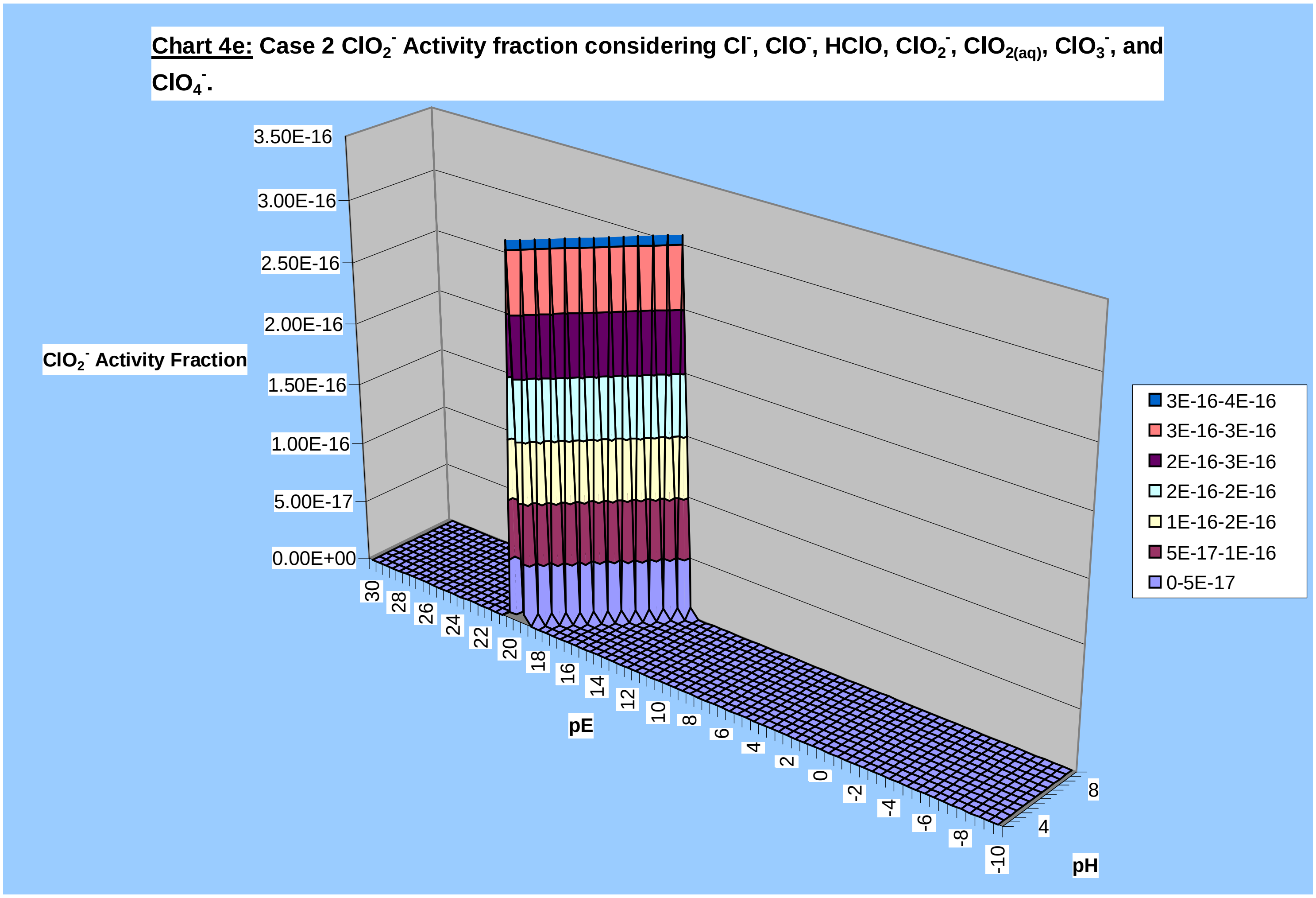


**Chart 4e:** **Case 2 $ClO_2^-$ Activity fraction considering $Cl^-$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**

**Chart 4f: Case 2 $ClO_{2(aq)}$ Activity fraction considering $Cl^-$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**

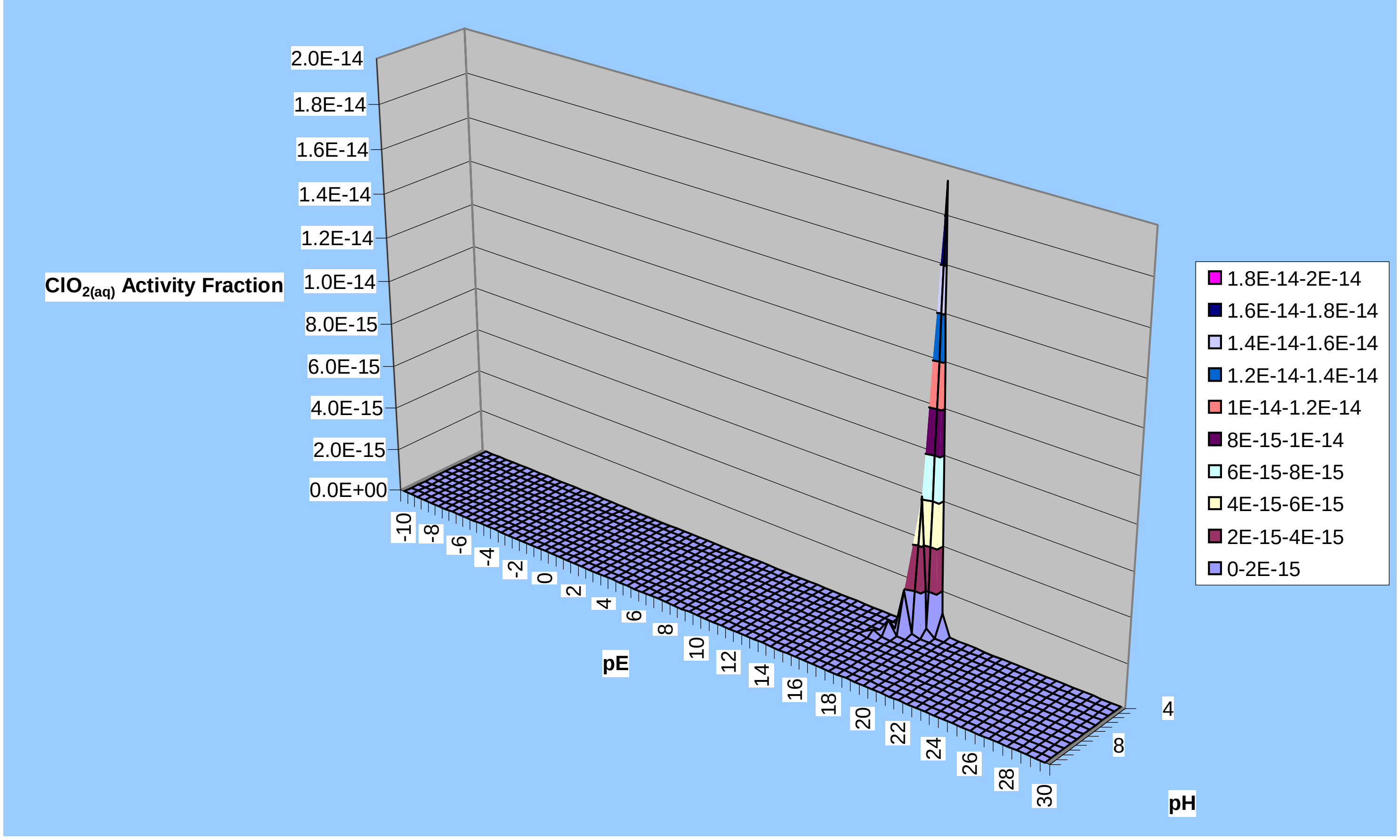
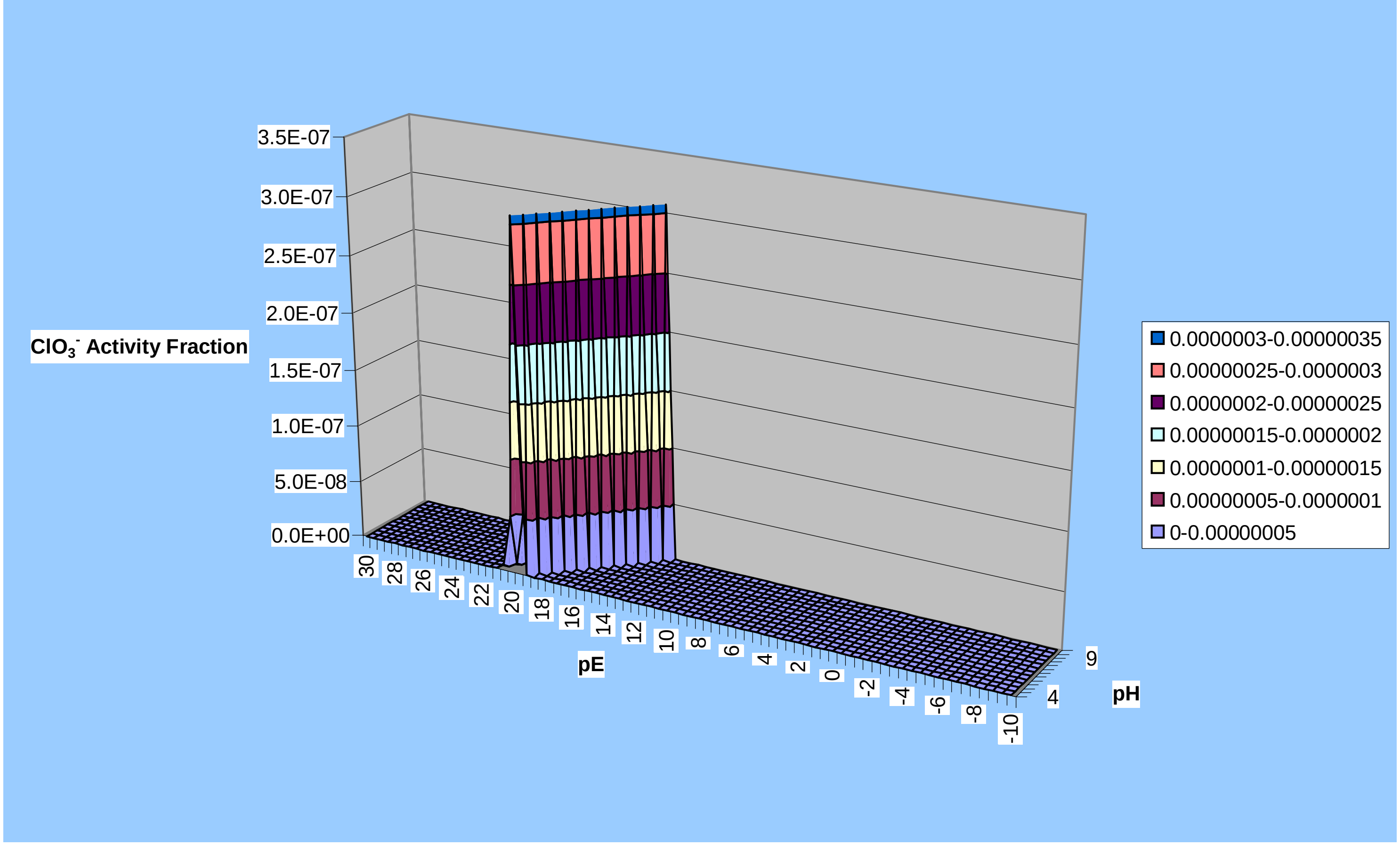
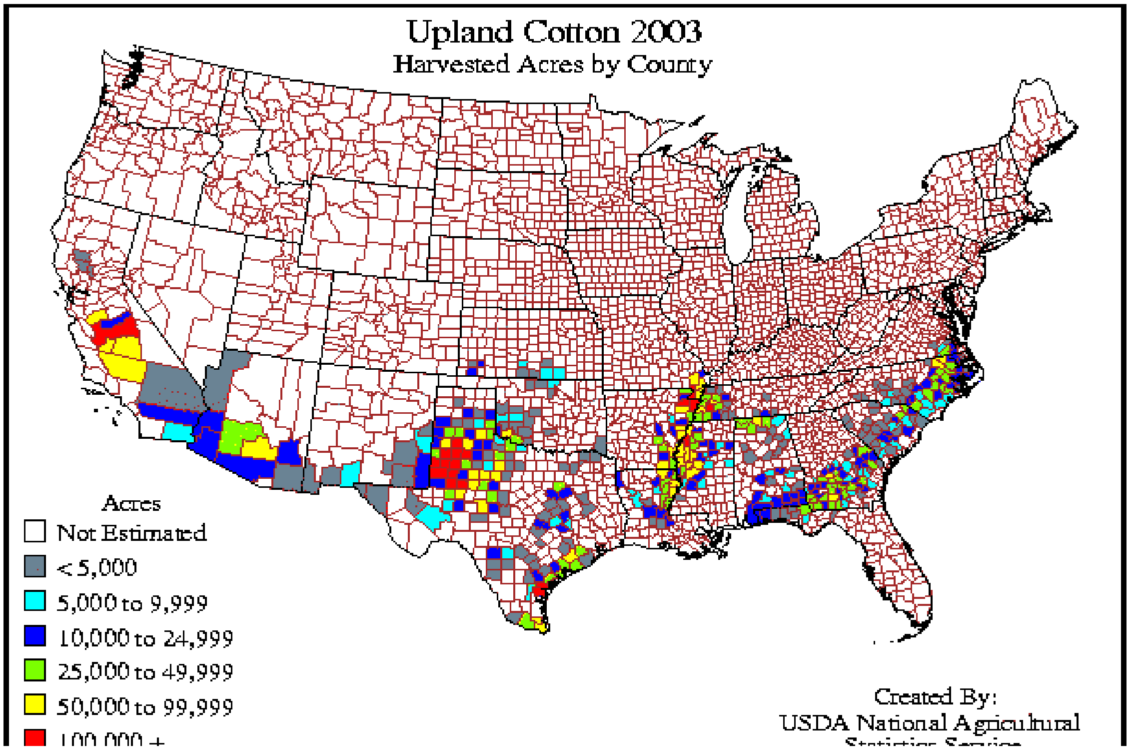
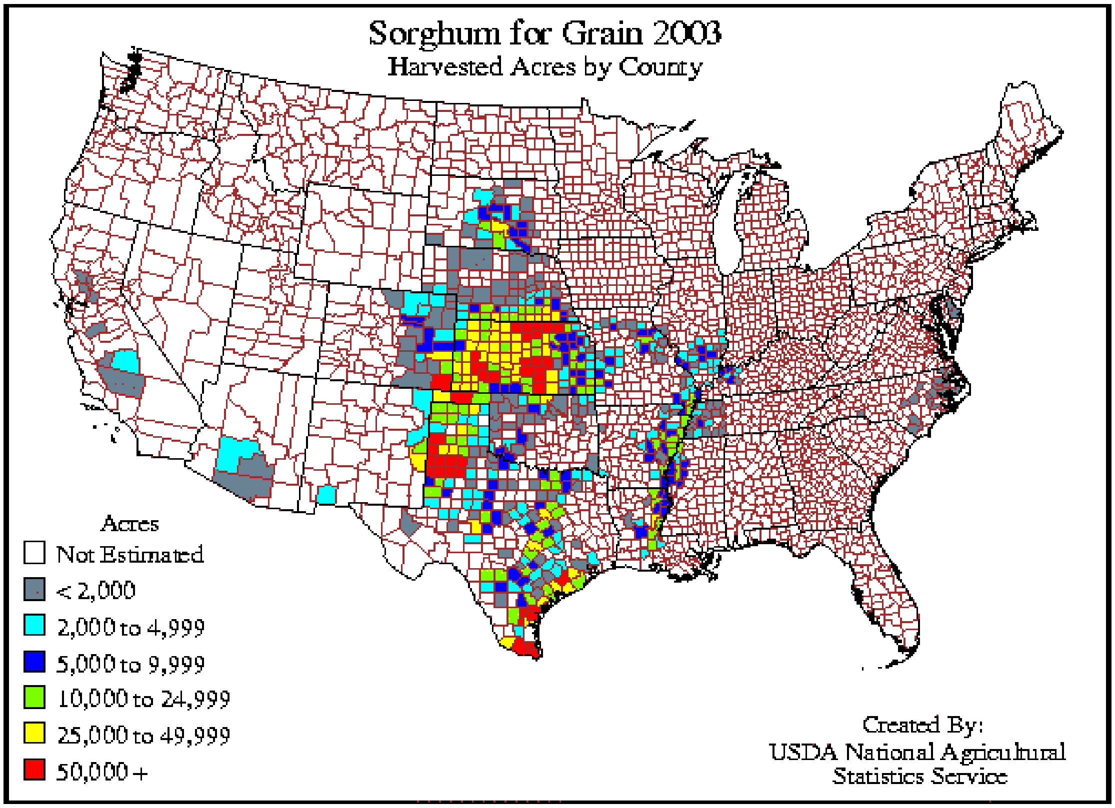


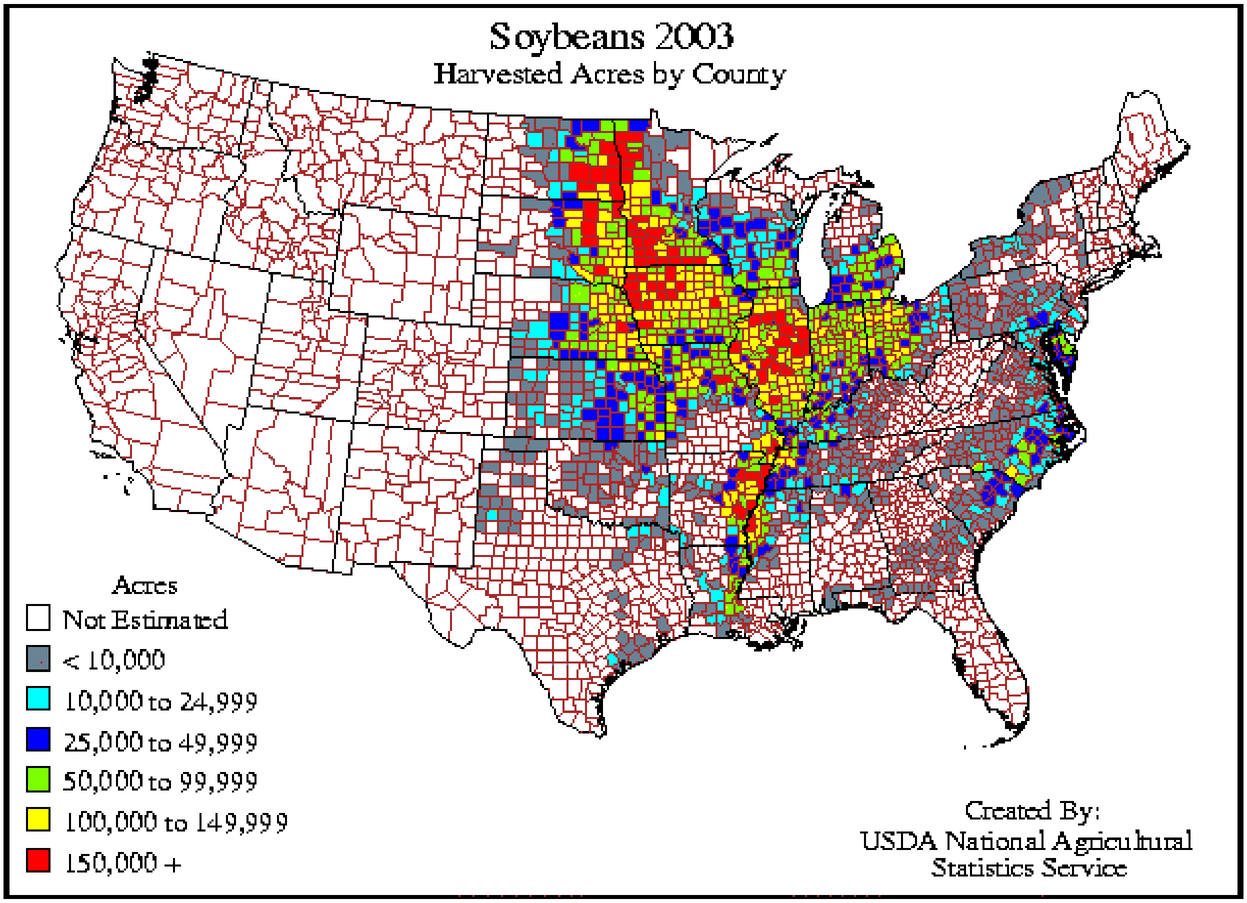
**Chart 4g:** **Case 2 $ClO_3^-$ Activity fraction considering $Cl^-$, $ClO^-$, HClO, $ClO_2^-$, $ClO_{2(aq)}$, $ClO_3^-$, and $ClO_4^-$.**

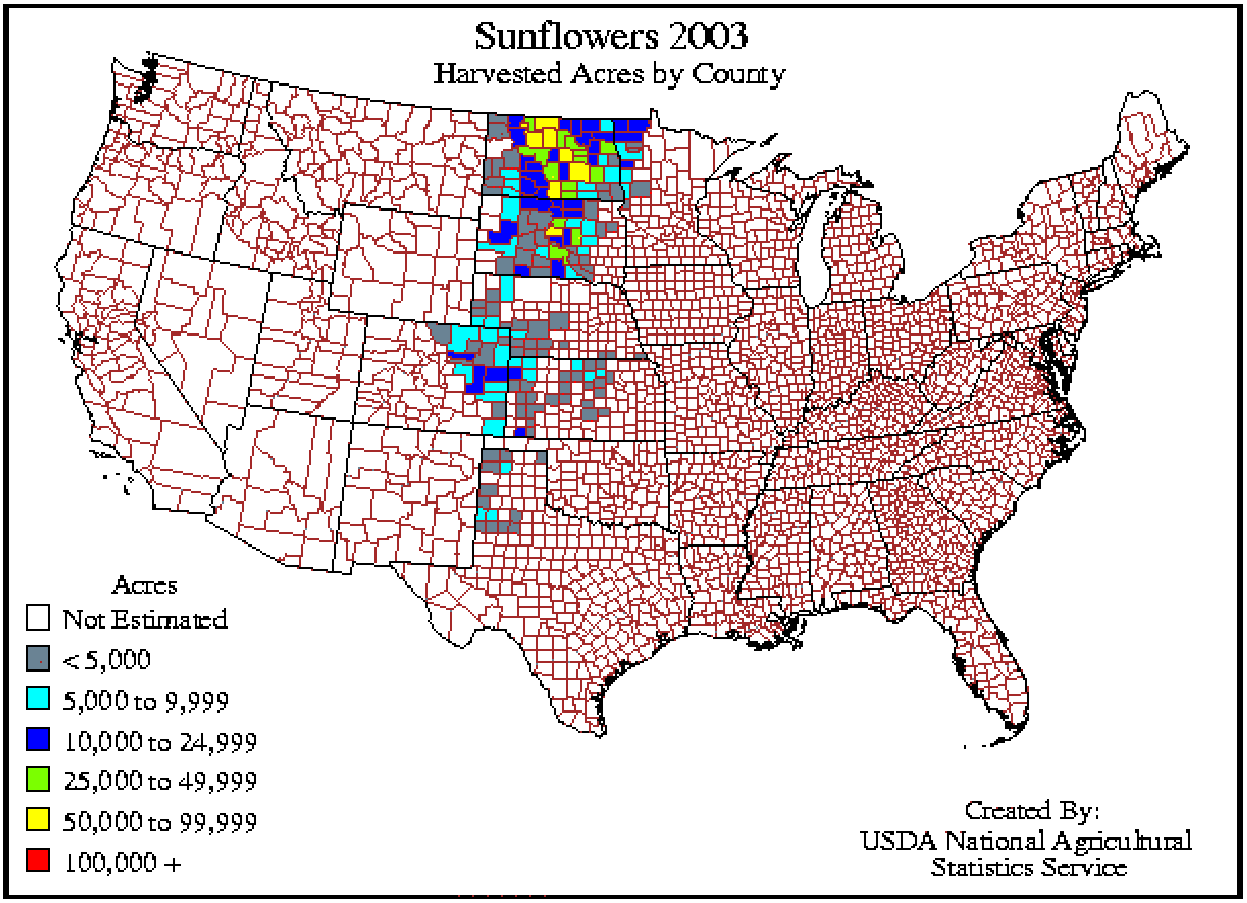


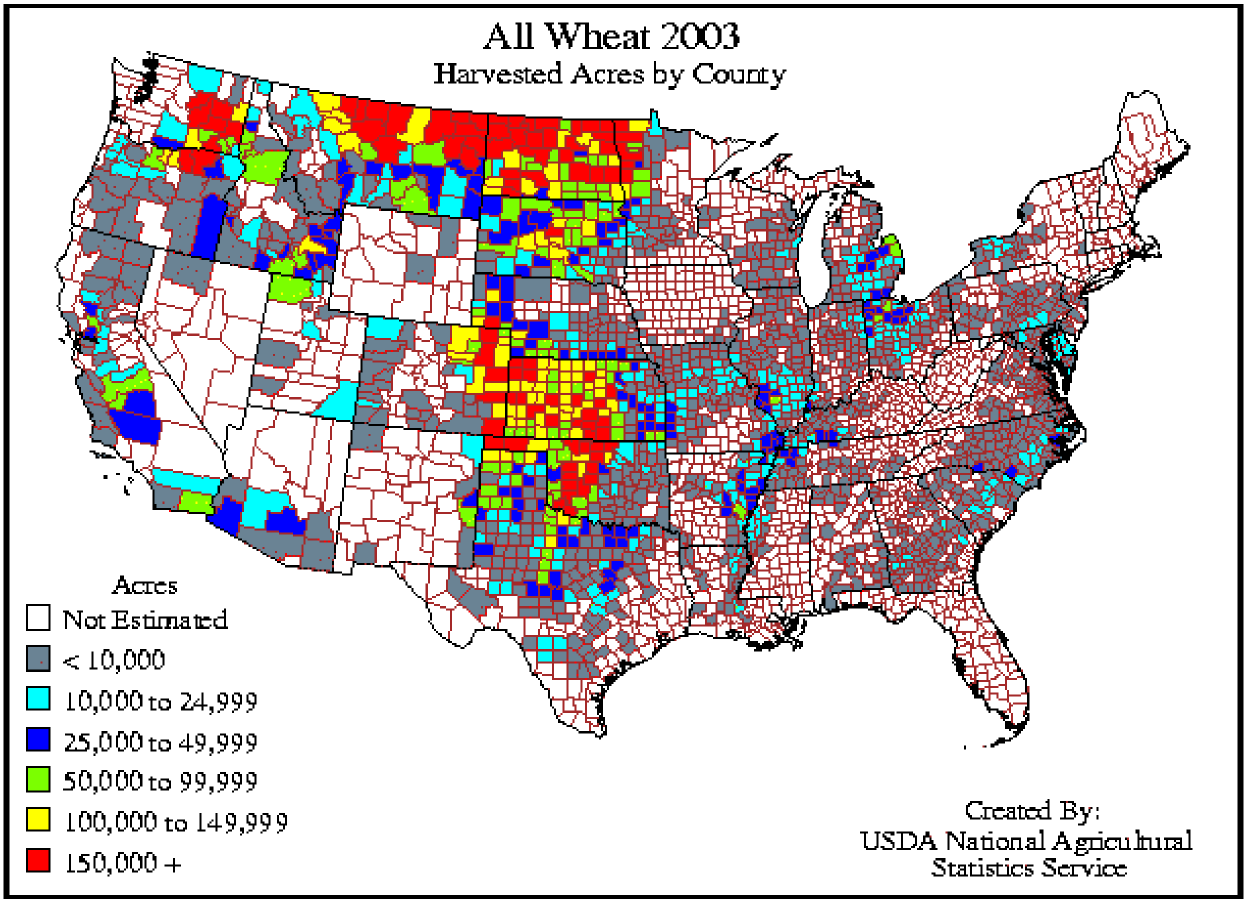
## Appendix C. Areas in the United States That Grow Selected Commodities on Which Sodium Chlorate Is Used


Upland Cotton 2003
Harvested Acres by County
Acres
Not Estimated
< 5,000
5,000 to 9,999
10,000 to 24,999
25,000 to 49,999
50,000 to 99,999
100,000 +
Created By:
USDA National Agricultural


Sorghum for Grain 2003
Harvested Acres by County
Acres
Not Estimated
< 2,000
2,000 to 4,999
5,000 to 9,999
10,000 to 24,999
25,000 to 49,999
50,000 +
Created By:
USDA National Agricultural
Statistics Service


Soybeans 2003
Harvested Acres by County
Acres
□ Not Estimated
< 10,000
10,000 to 24,999
25,000 to 49,999
50,000 to 99,999
100,000 to 149,999
150,000 +
Created By:
USDA National Agricultural
Statistics Service

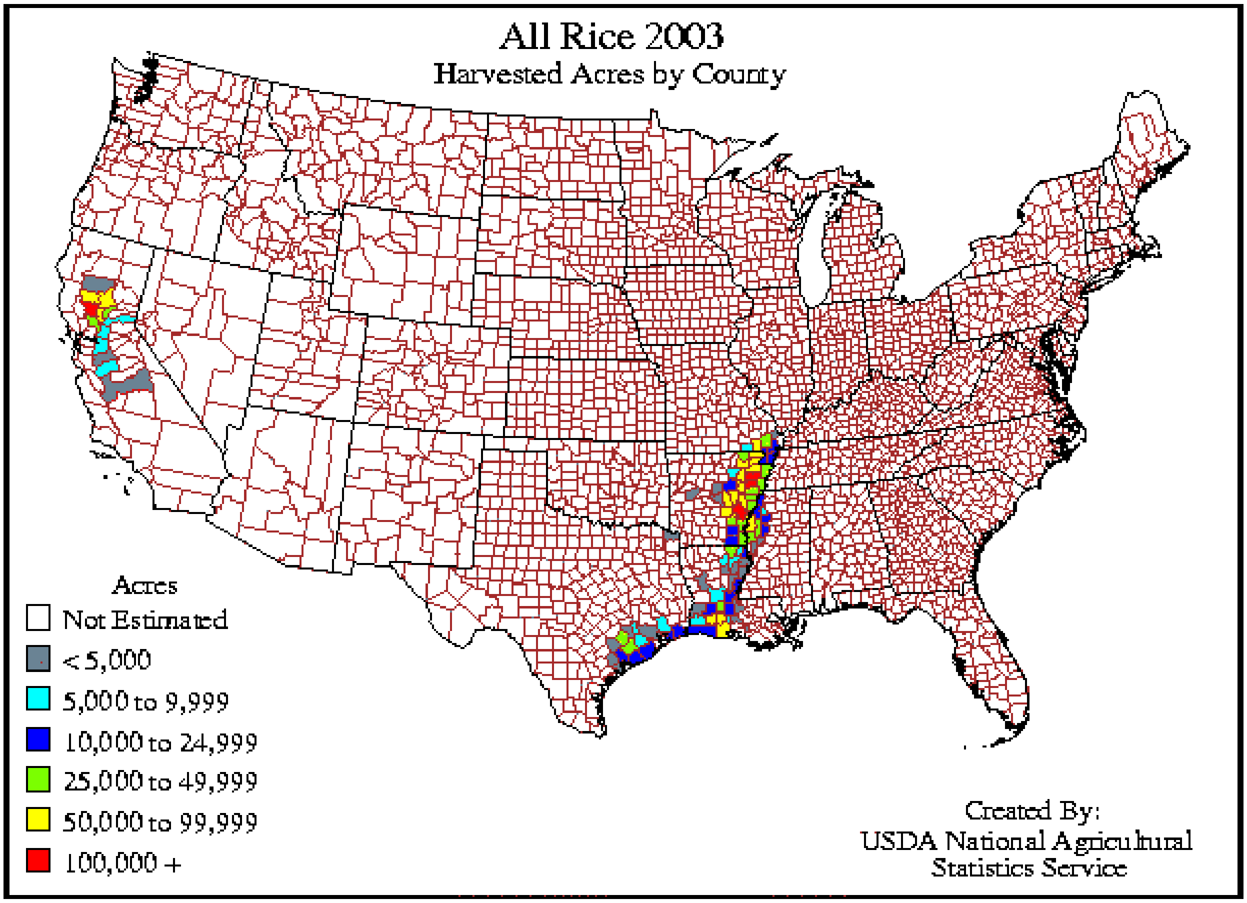

Sunflowers 2003
Harvested Acres by County
Acres
☐ Not Estimated
< 5,000
5,000 to 9,999
10,000 to 24,999
25,000 to 49,999
50,000 to 99,999
100,000 +
Created By:
USDA National Agricultural
Statistics Service

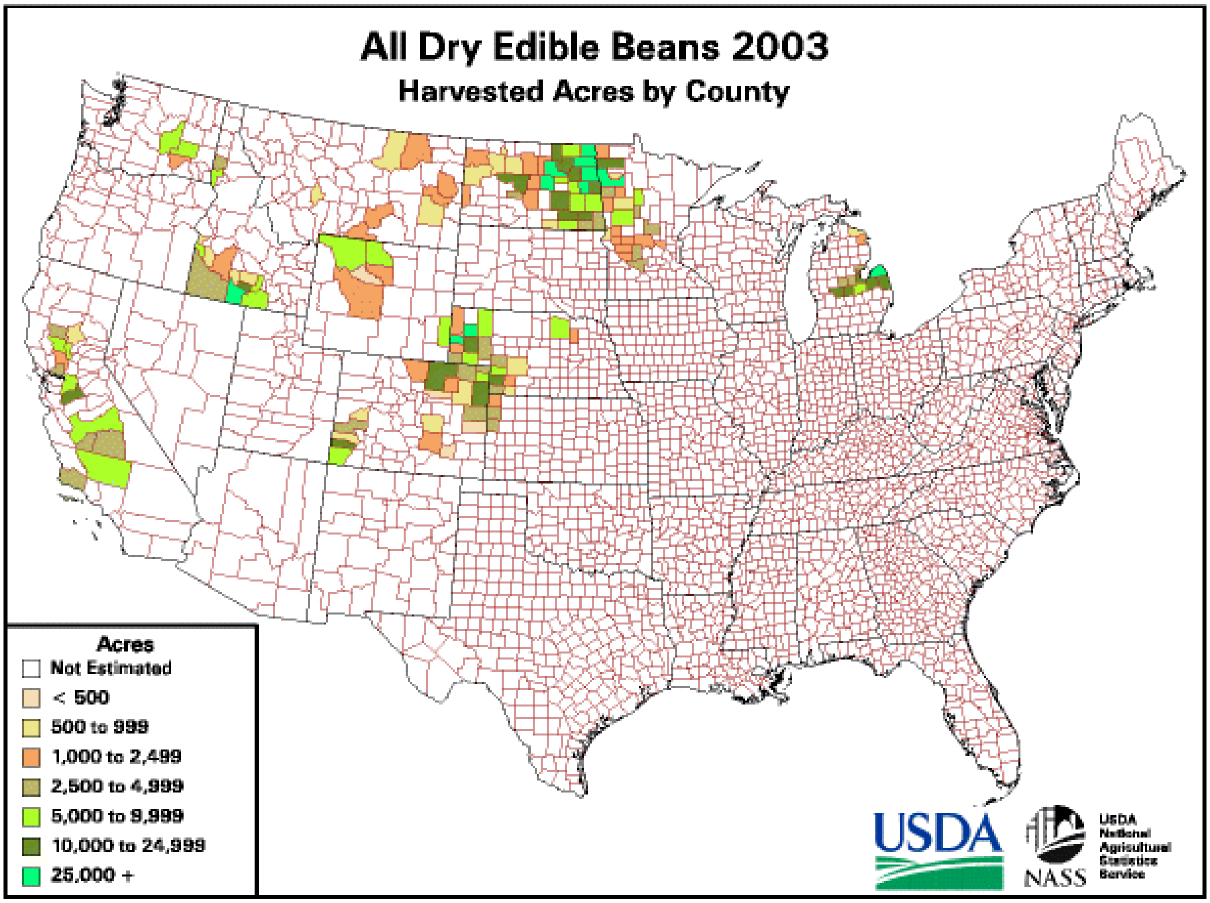


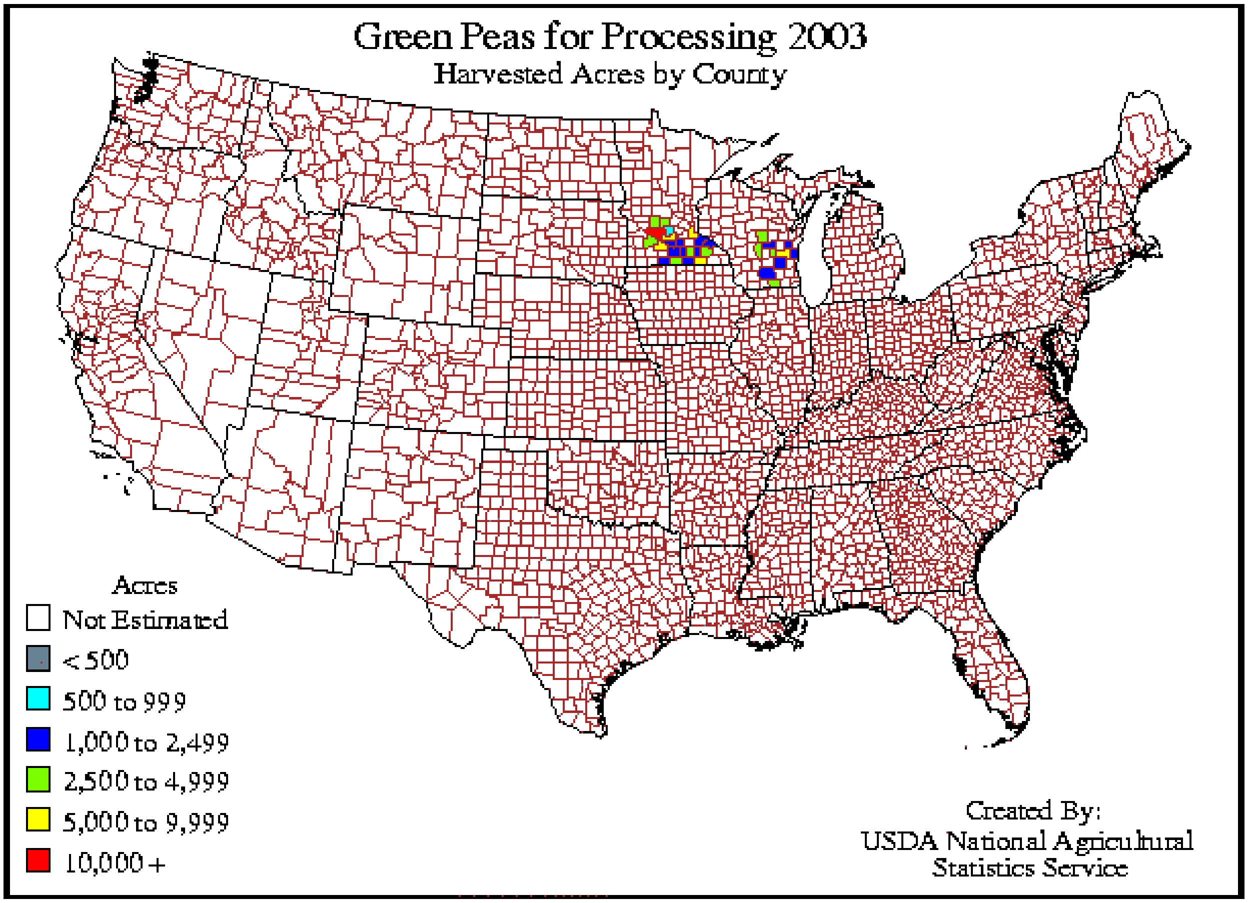
All Wheat 2003

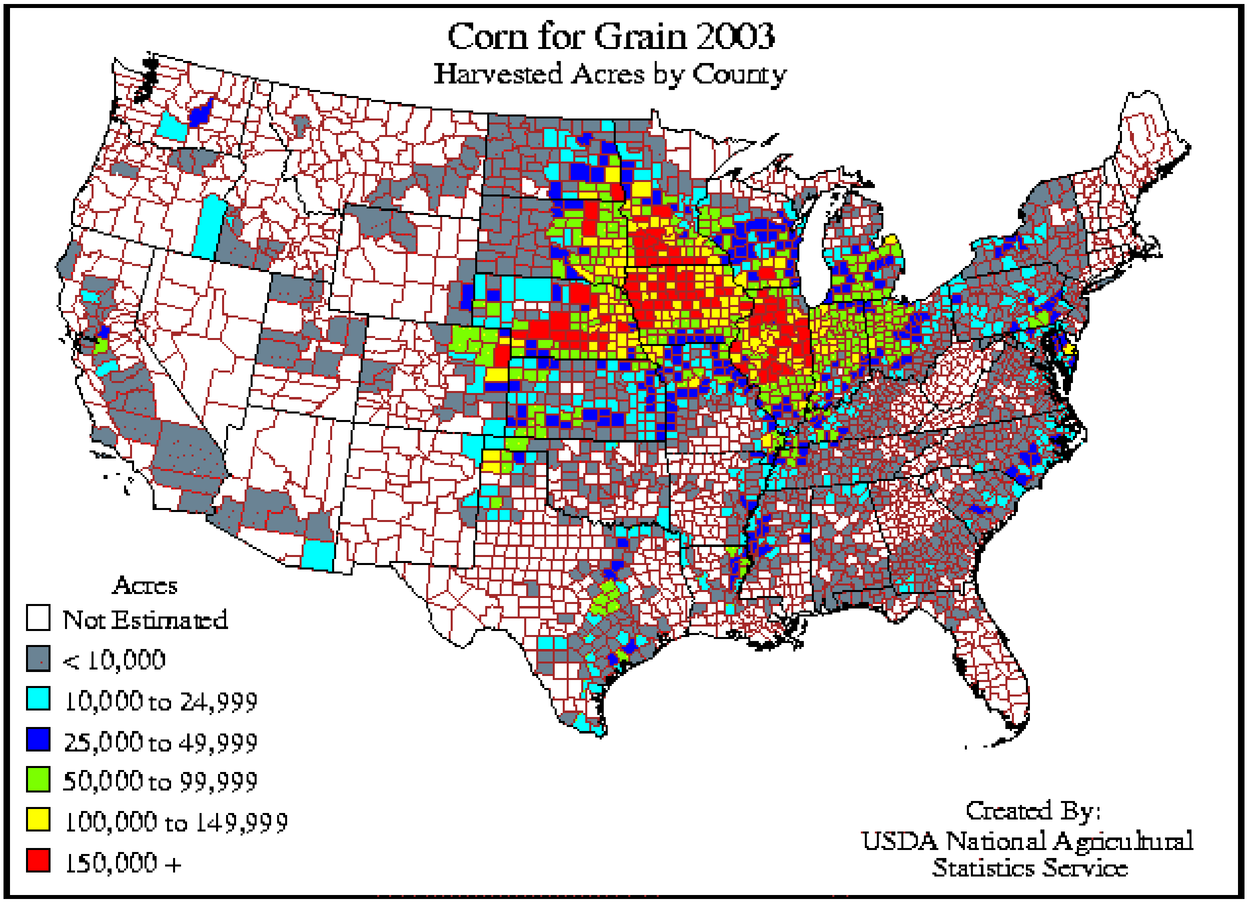
Harvested Acres by County

Created By:
USDA National Agricultural
Statistics Service


All Rice 2003
Harvested Acres by County
Acres
Not Estimated
< 5,000
5,000 to 9,999
10,000 to 24,999
25,000 to 49,999
50,000 to 99,999
100,000 +
Created By:
USDA National Agricultural
Statistics Service


All Dry Edible Beans 2003
Harvested Acres by County
Acres
Not Estimated
< 500
500 to 999
1,000 to 2,499
2,500 to 4,999
5,000 to 9,999
10,000 to 24,999
25,000 +
USDA
NASS
USDA National Agricultural Statistics Service


Green Peas for Processing 2003
Harvested Acres by County
Acres
Not Estimated
< 500
500 to 999
1,000 to 2,499
2,500 to 4,999
5,000 to 9,999
10,000 +
Created By:
USDA National Agricultural
Statistics Service


Corn for Grain 2003
Harvested Acres by County
Acres
☐ Not Estimated
< 10,000
10,000 to 24,999
25,000 to 49,999
50,000 to 99,999
100,000 to 149,999
150,000 +
Created By:
USDA National Agricultural
Statistics Service

## Appendix D. Percent of Irrigated Acres Estimated for Cotton

## Cotton

Sodium chlorate is used on cotton as a harvest aid (defoliant, desiccant, or both). Timing of use as a defoliant depends on: (a) Maturity of the crop; (b) Condition of the crop; (c) Prevailing weather conditions and (d) Harvest schedule. However, timing depends mainly on maturity of the bolls[53] and harvest schedule. Too late defoliation can increase the likehood of rot bolls and fiber damage. Lower temperatures as the Fall season progresses (i.e., below 60° F; < 16° C) may inhibit the activity of defoliant. In general, good conditions for defoliation are high temperature, high humidity, low wind velocity, and high to adequate soil moisture. Stressed cotton by drought or retarded growth from cold weather can result in unsatisfactory defoliation. Therefore, there is a temporal and spatial variability in the timing of application of sodium chlorate. Thus, this spatial and temporal variability reflects also on the environmental fate of chlorate (refer to the “Environmental Fate” section).

Cotton constitutes the crop of most extensive use of sodium chlorate, at about 90% of the total use of this chemical on agricultural commodities. However, not all of the harvested cotton may use sodium chlorate as a harvest aid. Table D-1 summarizes the number of harvested acres (in descending order of total harvested acreage) in the major cotton growing states. The Table also includes the percent of crops that is irrigated. Note that all Pima cotton is irrigated, but the percent of irrigated upland cotton varies with region. The lowest percent of irrigation is in some eastern and south eastern states (FL, VA, SC, TN, AL).

**Table D-1. Cotton Production (Harvest Acres) and Percent of Irrigated Acreage (Source; USDA, Census of Agriculture, 2002)**

| State | Upland Cotton, Acres Harvested | Upland Cotton, % Irrigated | Pima Cotton Acres Harvested | Pima Cotton % Irrigated |
|---|---|---|---|---|
| Texas | 4,638,240 | 40 | 18,789 | 100 |
| Georgia | 1,267,150 | 26 | None | None |
| Mississippi | 1,157,432 | 35 | None | None |
| North Carolina | 924,097 | 2.5 | None | None |
| Arkansas | 921,316 | 77 | None | None |
| Tennessee | 533,755 | 1.8 | None | None |
| Alabama | 523,123 | 6.2 | None | None |
| California | 495,943 | 100 | 198,710 | 100 |
| Louisiana | 474,784 | 32 | None | None |

---

[53] The maturity of the crop is measured in terms of the maturity of the bolls and depends on the time of the year when cotton was set. Boll maturity is determined by visual observation of bolls in the field intended for harvest

| State | Upland Cotton, Acres Harvested | Upland Cotton, % Irrigated | Pima Cotton Acres Harvested | Pima Cotton % Irrigated |
|---|---|---|---|---|
| Missouri | 395,880 | 52 | None | None |
| Arizona | 214,880 | 100 | 7,842 | 100 |
| South Carolina | 208,420 | 7 | None | None |
| Oklahoma | 172,228 | 39 | None | None |
| Florida | 101,766 | 8 | None | None |
| Virginia | 92,809 | 0.9 | None | None |
| Kansas | 55,953 | 45 | None | None |
| New Mexico | 45,994 | 100 | NM 7,051 | 100 |

## Appendix E.  Maximum Labeled Application Rates and Crops for all Agricultural End-Use Products

## Table E-1. Maximum Labeled Application Rates and Crops for all Agricultural End-Use Products

| Label | Crop | Application rate (lbs a.i./Acre) | Application method |
|---|---|---|---|
| Helena 2 lb. Sodium chlorate defoliant-desiccant | Cotton | 5 | Aerial or ground<br>Second application may be required for cotton |
| | Grain | 6 | |
| Helena 3 lb. Sodium chlorate defoliant-desiccant | Chili Peppers | 7.5 | Aerial or ground |
| | Corn, beans, flas, grain sorghum, guar beans, rice, safflowers, southern peas, soybeans, sunflower | 6 | |
| | Cotton | 4.5 | |
| Helena 6 lb sodium chlorate defoliant desiccant | Dry beans, guar beans, flax, corn, rice, safflower, soybeans, sunflower | 6 | Aerial or ground |
| | Chili peppers | 7.5 | |
| | Cotton, grain sorghum | 4.5 | |
| Leafex 2 defoliant-desiccant | Cotton | 5.3 (Arizona)<br>4.7 (all other states) | Allows no more than two applications (re-application interval not specified) |
| Leafex 3 defoliant-desiccant | Cotton | 5.25 (Arizona)<br>4 (all other states) | Allows no more than two applications (re-application interval not specified) |
| | Grain sorghum, corn, rice, soybean, sunflower | 6 | Maximum number of applications not specified |
| Shed-a-leaf "L" | Cotton | 3.75 | Ground or aerial |
| | Rice (MS only) | 4.5 | |
| | Soybean (MS only), | 6 | |
| Riverside sodium chlorate | Corn | 6 | Aerial |
| | Cotton | 3.75 | Ground or aerial |
| | Dry beans, grain sorghum, safflower, southern peas, soybeans, sunflower | 6 | Ground or aerial |

| **Table E-1. Maximum Labeled Application Rates and Crops for all Agricultural End-Use Products** | | | |
|---|---|---|---|
| **Label** | **Crop** | **Application rate (lbs a.i./Acre)** | **Application method** |
| | Rice | 6 | Aerial |
| Sodium chlorate 6 | Dry beans, grain sorghum, guar beans, safflower, southern peas, soybeans, sunflower | 6 | Ground or aerial |
| | Corn, flax, rice | 6 | Aerial |
| | Cotton | 4.5 | Ground or aerial |
| | Chili peppers | 7.5 | Ground or aerial |
| D-Leaf-M cotton defoliant | Cotton | 4 | Ground or aerial |
| Britz cotton defoliant concentrate | Cotton | 4.58 | Ground or aerial |
| First choice cotton defoliant concentrate | Cotton | 5.52 | Ground or aerial |
| | Chili peppers | 9.2 | Ground or aerial |
| | Grain sorghum | 4.97 | Ground or aerial |
| Drexel Defol | Chili peppers | 7.5 | Ground or aerial |
| | Corn, rice | 6 | Aerial |
| | Cotton | 4.5 | Ground or aerial |
| | Dry beans, flas, grain sorghum, guar beans, potatoes, safflower, southern peas, soybeans, sunflower | 6 | Ground or aerial |
| | Ornamental gourds | 6 | Georgia only<br>Ground or aerial |
| Drexel Defol 6 | Chili peppers | 7.5 | Ground or aerial |
| | Corn, rice | 6 | Aerial |
| | Cotton | 4.5 | Ground or aerial |

| **Table E-1. Maximum Labeled Application Rates and Crops for all Agricultural End-Use Products** | | | |
|---|---|---|---|
| **Label** | **Crop** | **Application rate (lbs a.i./Acre)** | **Application method** |
| | Dry beans, flax, cucurbits, grain sorghum, guar beans, potatoes, safflower, southern peas, soybeans, sunflower | 6 | Ground or aerial |
| Drexel Defol 6W | Chili peppers | 7.5 | Ground or aerial |
| | Corn, rice | 6 | Aerial |
| | Cotton | 4.5 | Ground or aerial |
| | Dry beans, flax, cucurbits, grain sorghum, guar beans, potatoes, safflower, southern peas, soybeans, sunflower, fallow ground | 6 | Ground or aerial |
| Drexel defol 5 | Chili peppers | 7.5 | Ground or aerial |
| | Corn, rice | 6 | Aerial |
| | Cotton | 4.5 | Ground or aerial |
| | Dry beans, flax, cucurbits, grain sorghum, guar beans, potatoes, safflower, southern peas, soybeans, sunflower | 6 | Ground or aerial |
| Drexel defol 750 | Chili peppers | 7.5 | Ground or aerial |
| | Corn, rice | 6 | Aerial |
| | Cotton | 4.5 | Ground or aerial |
| | Dry beans, flax, cucurbits, grain sorghum, guar beans, potatoes, safflower, southern peas, soybeans, sunflower | 6 | Ground or aerial |
| Clean crop sodium chlorate | Cotton | 4.5 | Ground or aerial |

| Table E-1. Maximum Labeled Application Rates and Crops for all Agricultural End-Use Products | | | |
|---|---|---|---|
| **Label** | **Crop** | **Application rate (lbs a.i./Acre)** | **Application method** |
| | Grain sorghum, safflower, soybeans, sunflower, rice | 6 | Ground or aerial (except rice - aerial only)<br>California restriction on safflower, soybeans, sunflower |
| MAPCO brand poly foliant | Cotton | 5.76 | Ground or aerial |
| Moore AG Brand Poly-Foliant | Dry beans, guar beans, cotton, flax, grain sorghum, corn, rice, safflower, soybean, sunflower, southern peas | 7.5 | Ground or aerial |
| | Chili peppers, potatoes | 12.5 | Ground or aerial |
| | Flax, corn, rice | 7.5 | Aerial |
| Pick-Mor | Cotton | 4.7 | Ground or aerial |

# Appendix F. Estimated Average Percent Crop Treated for Sodium Chlorate on Selected Crops

Estimate of Average Percent Crop Treated (PCT) for Sodlium Chlorate on Selected Crops

Alan Halvorson, BEAD/EAB, 10/26/04

| | Avg PCT | | Data Source |
|---|---|---|---|
| Beans, Lima, Fresh | <1% | | Source (1): 1998 & 2000 |
| Beans, Lima, Process | 2% | | Source (1): 2000 |
| Beans, Snap | <1% | | Source (1): 1998, 2000 & 2002, and source (3) |
| Beans/Peas, Dry | <1% | | Source (3) |
| Corn, Field | <1% | | Source (2): 1998 - 2003, and source (3) |
| Corn, Sweet | <1% | | Source (1): 1998, 2000 & 2002, and source (3) |
| Cotton | 5% | | SLUA with data for 1998 - 2002, and source (2): 2003 |
| Flax | <1% | | Source (3) |
| Guar | - | | No data available |
| Peas, Green | <1% | | Source (1): 1998, 2000 & 2002, and source (3) |
| Peppers, Non-Bell | <1% | | Source (1): 1998, 2000 & 2002, and source (3) |
| Potatoes | <1% | | SLUA with data for 1998 - 2002 and source (2): 2003 |
| Rice | <1% | | SLUA with data 1998 - 2002 |
| Safflower | 2% | | Source (4) |
| Sorghum | <1% | | Source (2): 1998 & 2003, and source (3) |
| Soybeans | <1% | | Source (2): 1998 & 2003 |
| Sunflower | <1% | | Source (2): 1999, and source (3) |
| Wheat | <1% | | Source (2): 1998, 2000 & 2002, and source (3) |

Data Sources:
(1) USDA/NASS Agricultural Chemical Usage: Vegetables
(2) USDA/NASS Agricultural Chemical Usage: Field Crops
(3) EPA proprietary usage data, 1998 - 2003
(4) CA DPR, California Use Reports, 2000 - 2002

# Appendix G: Description of the Risk Quotient Method

The Risk Quotient Method is the means used by EFED to integrate the results of exposure and ecotoxicity data. For this method, risk quotients (RQs) are calculated by dividing exposure estimates by ecotoxicity values (i.e., RQ = EXPOSURE/TOXICITY), both acute and chronic. These RQs are then compared to OPP's levels of concern (LOCs). These LOCs are criteria used by OPP to indicate potential risk to non-target organisms and the need to consider regulatory action. EFED has defined LOCs for acute risk, potential restricted use classification, and for endangered species.

The criteria indicate that a pesticide used as directed has the potential to cause adverse effects on nontarget organisms. LOCs currently address the following risk presumption categories:

(1) acute - there is a potential for acute risk; regulatory action may be warranted in addition to restricted use classification;
(2) acute restricted use - the potential for acute risk is high, but this may be mitigated through restricted use classification
(3) acute endangered species - the potential for acute risk to endangered species is high, regulatory action may be warranted, and
(4) chronic risk - the potential for chronic risk is high, regulatory action may be warranted.

Currently, EFED does not perform assessments for chronic risk to plants, acute or chronic risks to non-target insects, or chronic risk from granular/bait formulations to mammalian or avian species.

The ecotoxicity test values (i.e., measurement endpoints) used in the acute and chronic risk quotients are derived from required studies. Examples of ecotoxicity values derived from short-term laboratory studies that assess acute effects are: (1) $LC_{50}$ (fish and birds), (2) $LD_{50}$ (birds and mammals), (3) $EC_{50}$ (aquatic plants and aquatic invertebrates), and (4) $EC_{25}$ (terrestrial plants). Examples of toxicity test effect levels derived from the results of long-term laboratory studies that assess chronic effects are: (1) LOAEL (birds, fish, and aquatic invertebrates), and (2) NOAEL (birds, fish and aquatic invertebrates). The NOAEL is generally used as the ecotoxicity test value in assessing chronic effects.

Risk presumptions, along with the corresponding RQs and LOCs are summarized in Table G-1.

## Table G-1: Risk Presumptions and LOCs

| Risk Presumption | RQ | LOC |
|---|---|---|
| Birds[1] | | |
| Acute Risk | EEC/LC$_{50}$ or LD$_{50}$/sqft or LD$_{50}$/day | 0.5 |
| Acute Restricted Use | EEC/LC$_{50}$ or LD$_{50}$/sqft or LD$_{50}$/day (or LD$_{50}$ < 50 mg/kg) | 0.2 |
| Acute Endangered Species | EEC/LC$_{50}$ or LD$_{50}$/sqft or LD$_{50}$/day | 0.1 |
| Chronic Risk | EEC/NOAEC | 1 |
| Wild Mammals[1] | | |
| Acute Risk | EEC/LC$_{50}$ or LD$_{50}$/sqft or LD$_{50}$/day | 0.5 |
| Acute Restricted Use | EEC/LC$_{50}$ or LD$_{50}$/sqft or LD$_{50}$/day (or LD$_{50}$ < 50 mg/kg) | 0.2 |
| Acute Endangered Species | EEC/LC$_{50}$ or LD$_{50}$/sqft or LD$_{50}$/day | 0.1 |
| Chronic Risk | EEC/NOAEC | 1 |
| Aquatic Animals[2] | | |
| Acute Risk | EEC/LC$_{50}$ or EC$_{50}$ | 0.5 |
| Acute Restricted Use | EEC/LC$_{50}$ or EC$_{50}$ | 0.1 |
| Acute Endangered Species | EEC/LC$_{50}$ or EC$_{50}$ | 0.05 |
| Chronic Risk | EEC/NOAEC | 1 |
| Terrestrial and Semi-Aquatic Plants | | |
| Acute Risk | EEC/EC$_{25}$ | 1 |
| Acute Endangered Species | EEC/EC$_{05}$ or NOAEC | 1 |
| Aquatic Plants[2] | | |
| Acute Risk | EEC/EC$_{50}$ | 1 |
| Acute Endangered Species | EEC/EC$_{05}$ or NOAEC | 1 |

[1] LD$_{50}$/sqft = (mg/sqft) / (LD$_{50}$ * wt. of animal)
LD$_{50}$/day = (mg of toxicant consumed/day) / (LD$_{50}$ * wt. of animal)

[2] EEC = (ppm or ppb) in water

# Appendix H. Discussion of Waived Environmental Fate Data

Hydrolysis (161-1) (Abiotic Hydrolysis)
The chemistry of chlorate in water is dominated by redox reactions that require the presence of reductants (inorganic and/or organic). Because the 161-1 Hydrolysis study is conducted in abiotic media and in types of buffer solutions that are not likely to act as reductants, this study was waived as it was concluded that the study was not going provide any useful or very limited information, unless known environmental reductants were included in the aqueous media. Moreover, the redox chemistry of chlorate in water is extensively documented in the chemical literature.

Photodegradation in water (161-2) (Direct Photolysis)
The 161-2 study is conducted in the absence of chemical photosensitizers. That is, this study is designed to address the role of direct photolysis in aqueous media. A necessary, but not sufficient, condition for direct photolysis in environmentally significant aqueous media is that the chemical must absorb energy (photon) in the sunlight wavelength range. Chlorate does not absorb energy in this range. Therefore, the 161-2 study was waived because it does not the necessary condition for direct photolysis..

Photodegradation on soil (161-3)
This study was waived because the combined soil sterilization and variability in nature and concentration of reductants in soil are not likely to provide data that can identify that photolysis on soil contributes to the degradation of chlorate.

Note: Photoreactions induced by transfer of energy from photosensitizers in natural water and soils may contribute to the transformation of chlorate in the environment (that is, indirect photolysis contribution). Many chemical reductants present in natural environments may also behave as photoreductants.

Anaerobic/aerobic aquatic metabolism (162-3/162-4) and Aerobic/Anaerobic soil metabolism (162-1/-2)
These studies would not likely produce useful information due to sodium chlorate antimicrobial properties that destroy the microbial populations in soil and water-sediment systems. If the microbial population is destroyed, the study cannot adequately address the role of microorganisms in the degradation of chlorate.

Mobility in soil (163-1)
Sodium chlorate is fully ionized in water. The chlorate anion is not likely to adsorb onto soils or sediments. Therefore, high mobility was anticipated. Guideline studies would not provide additional information.

Bioaccumulation in fish (165-4)
The estimated log *n*-octanol water partition coefficient is -7 (i.e., it is a highly hydrophilic chemical) Therefore, the *n*-octanol water partition coefficient does not trigger the need for a 165-4 study.

### Aquatic field dissipation (164-2)

There are no direct applications of sodium chlorate to water bodies (aquatic field). Therefore, this study is not required[54].

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[54] There are no direct applications to water bodies for uses as an herbicide. However, sodium chlorate can be used to generate chlorine dioxide *in situ*, which is used as an antimicrobial agent in drinking water disinfection and in microorganism control in water cooling systems. The focus of the present ecological risk assessment is solely for the terrestrial field uses of sodium chlorate. Aquatic uses are regulated under the jurisdiction of the Antimicrobial Division and Office of Water.

# Appendix I. Impact of sodium from sodium chlorate on soil quality (soil dispersion).

The analysis was designed to assess the sodium adsorption ratio (SAR) in acid-near neutral and alkaline soils. These conditions were selected because they represent two different soil chemical equilibrium conditions for Ca and Mg, major competing cations on soil adsorption sites. Under the acid-near neutral soil conditions, the Ca and Mg activities in soil solution are likely controlled simple cation exchange. These activities are described in chemical equilibrium terms as soil-Ca and soil-Mg. Under alkaline conditions, the Ca and Mg activities in soil solution are expected to be controlled by calcite ($CaCO_3$) and dolomite ($MgCO_3$) (Lindsay, 1978). The sodium activity in soil solution (under ideal conditions) was assumed to be controlled by the sodium chlorate application rate.

**Predicted Na Concentration in soil solution**

*Assumption*:

A soil bulk density of 1.3 g/cc, 20% field capacity-- the Na concentration in soil solution = 6.74 mg/L=2.933E-4 moles/L= 0.29 moles/$m^3$

*Predicted Ca Concentration in Soil Solution*:

<u>Acidic and Near-Neutral Soil</u>= Soil-Ca-Ca (log K=-2.5)= Ca activity=0.003 moles/L= 3 moles/$m^3$

<u>Alkaline</u> Soil (Assuming $CaCO_3$ equilibria)= $CaCO_3$ + 2H+-$Ca^{2+}$ + $C0_2$(g) +$H_20$ (Log K=9.74) (log $Ca^{2+}$ =9.74 - 2pH -log $CO_2$(g))

At $CO_2$(g) =0.0003 atm and pH=8.5 = Ca activity=0.00018 moles/liters=0.18197 moles/$m^3$

At $CO_2$(g)=0.003 atm and pH=8.5= Ca activity= 0.000018 moles/liter=0.018197 moles/$m^3$

*Predicted Mg Concentration in Soil Solution*

<u>Acidic and Neutral Soil</u>= Soil-Mg-Mg (log K=-3.00)= Mg activity= 0.001 moles/liter= 1 mole/$m^3$

<u>Alkaline Conditions</u> (Assume equilibrium with calcite and dolomite) $MgCa(CO_3)$ + 2H+-$Mg^{2+}$ + $CO_2$(g) + $H_2O$ + $CaCO_3$ (Log K=8.72)
(log $Mg^{2+}$=8.72-log$C0_2$(g)-2pH)

At $CO_2$(g)=0.0003 atm and pH 8.5 = 1.7 x 10-5 mole/L=0.01737 moles/$m^3$
At $CO_2$(g)=0.003 atm and pH 8.5 =1.7X 10- 6 moles/L=0.001737 moles/$m^3$

*Predicted Na concentration in Soil Solution*

Using the SAR equation= Na/(Ca+Mg)^1/2 (Sposito,1989)

Acid-Near Neutral Soil Conditions SAR (acid/neutral soils)= 0.29/(3+1)^1/2= 0.145
Alkaline Soils (pH 8.5) and $CO_2$(g)=0.0003 SAR (alkaline, pC02=3.52)= 0.29/(0.18197+0.01737)^1/2= 0.29/0.44= 0.6590
Alkaline Soils (pH 8.5) and $CO_2$(g)=0.003 SAR (alkaline, pCO2=2.52)= 0.29/ 0.018197 +0.001737)^1/2=0.29/0.14= 2.07

# Appendix J. Discussion on Chlorate Redox Chemistry as it Relates to Exposure to Aquatic Organisms in the Environment

Although there are some models[55] available that are used in water chlorination, they are not suitable for uses that have a direct application to a terrestrial environment (i.e., environmental conditions for chlorination in water treatment plants are markedly different than those found in terrestrial environments).

Because the chlorate chemistry is highly dependent on pH-pE (redox) conditions in the environment, these factors need to be considered in modeling the environmental fate and transport of chlorate. One problem is that environmental fate and transport models for pesticides (GENEEC, SCI-GROW, FIRST, PRZM) do not have the capability to quantitatively assess the impact of environmental redox potentials (pH-pE) on chemical speciation. Although the EXAMS component of PRZM-EXAMS has the capability to use redox potential as an input parameter with specific chemical species, it also needs kinetics data (which is difficult to obtain for redox systems such as the chlorine)[56] . Moreover, even if the kinetics data were available, the nature and predominance (relative concentrations) of reduction products cannot be obtained using EXAMS.

Further refinement of the exposure assessment was conducted to investigate the impact of redox conditions on the distribution of chemical speciation of chlorine including: (1)) Chlorate, $ClO_3^-$; Cl(V); (2) Chlorite, $ClO_2^-$; Cl (III); Hypochlorite,$ClO^-$ ; Cl (I); and Chloride, $ClO^-$; Cl (-I).

A chemical equilibrium modeling approach was used as a first approximation on the distribution of chemical species of chlorine as function redox potential. This approach, however, does not consider reaction kinetics. Reaction kinetics have been shown to be an important consideration in determining the stability of chlorate ($ClO_3^-$) in soil and aquatic environments (see reference). As discussed in 3.1.1, reaction kinetics of the chlorine system is extremely complex and most of data comes from study conditions that are not relevant to conditions found in the environment. However, thermodynamic data is readily available and was obtained from peer-reviewed data included in publications widely used as reference (see Appendix **A**)[57]

A mole fraction diagram for chlorate and redox species for the reactions was constructed to show the relative predominance of chlorine species as function of redox potential (Figure 1). This exercise demonstrated that chlorate ($ClO_3^-$) and chlorite ($Cl0_2^-$) **under equilibrium conditions** are not expected to be predominant Cl species under normal environmental redox potentials (pe+pH<17). Hypochlorite was the predominant Cl species pe+pH > ~17, which is outside the environmentally significant pe + pH range. As expected, the chloride ion ($Cl^-$) was the

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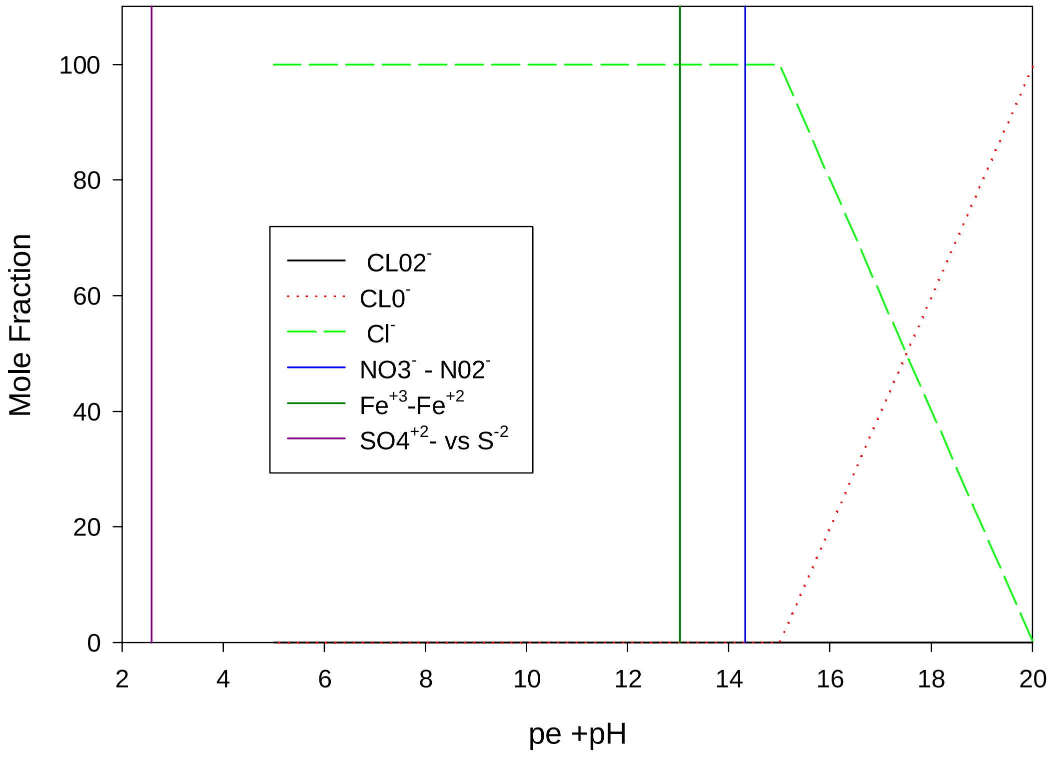
[55] See “Water Chlorination: Chemistry, Environmental Impact and Health Effects”, Volume 5. Edited by Jolley, R.L., et al. Lewis Publishers, 1985.

[56] See http://www.epa.gov/oppefed1/models/water/index.htm

[57] “Standard Potentials in Aqueous Solutions”, Edited by A.J. Bard, R. Parsons, and J. Jordan for the International Union of Pure and Applied Chemistry, Physical and Analytical Chemistry Divisions, Commissions on Electrochemistry and Electroanalytical Chemistry. Published by Marcel Dekker, New York, 1985.

predominant Cl species under normal environmental redox potentials (pe+pH < 17) These data suggest that chlorate and chlorite are not expected to be stable under normal environmental redox conditions in surface water. This assessment, however, assumes the kinetics of reactions do not control the rates of reduction and oxidation of the various chloride species. As previously discussed, the nature and concentration of redox species in natural water should also be taken into account. However, given the extensive spatial and temporal variability of redox species in natural water, a quantitative assessment cannot be performed.

Both the mole fraction and the activity fraction diagrams (Appendix B-2) showed that, at thermodynamic equilibrium, chloride is the predominant chlorine chemical species under environmental conditions. The fraction diagram is illustrated in Figure J-1 below.



# Appendix K. Terrestrial EECs for the Maximum Labeled Application Rates for all of Sodium Chlorate's Current End-Use Products

| Table K. Calculated EECs (mg ai/kg-food item) for Terrestrial Animal Risk Assessment (Non-agricultural Uses) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Use** | **Application rate (lbs a.i./Acre)** | **Predicted 90th Percentile Residue Levels (ppm)** | | | | **Predicted Mean Residue Levels (ppm)** | | | |
| | | **short grass** | **tall grass** | **broadleaf forage, small insects** | **fruit, pods, seeds, small insects** | **short grass** | **tall grass** | **broadleaf forage, small insects** | **fruit, pods, seeds, small insects** |
| Industrial sites such as driveways, paths, brick walks, cobble gutters, tennis courts | 52 | 12500 | 5700 | 7000 | 780 | 4400 | 1900 | 2300 | 360 |
| Driveways, parking lots, walks, around fences, curbs, similar areas. Not for use on lawns. | 140 | 33600 | 15400 | 18900 | 2100 | 11900 | 5040 | 6300 | 980 |
| Fence rows, rights-of-ways and similar areas;<br>Around buildings, storage areas, fences, recreational areas, guard rails, highway medians, industrial sites;<br>Around buildings, storage areas, fences, pumps, machinery, fuel tanks, recreational areas, roadways, guard rails, airports, rights of ways. | 160 | 38400 | 17600 | 21600 | 2400 | 13600 | 5760 | 7200 | 1120 |
| Driveways, walks, patios, tennis courts, curbs, garages, etc. | 220 | 52800 | 24200 | 29700 | 3300 | 18700 | 7920 | 9900 | 1540 |

| **Table K. Calculated EECs (mg ai/kg-food item) for Terrestrial Animal Risk Assessment (Non-agricultural Uses)** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Industrial sites, rights of way, lumberyards, petroleum tank farms, around farm buildings, along fence lines, and similar areas;<br>Bleachers, fence lines, fire hydrants, helo pads, parking lots, runways, vacant lots. | 240 | 57600 | 26400 | 32400 | 3600 | 20400 | 8640 | 10800 | 1680 |
| Brick walks, patios, parking areas, along fences, curbs, gutters, around building, graveled pathways, driveways, under asphalt paving | 330 | 79200 | 36300 | 44550 | 4950 | 28050 | 11880 | 14850 | 2310 |
| Bleachers, bridge abutments, buildings, guard rails, helo pads, under asphalt, concrete, gravel, driveways, sidewalks, wood decks. | 390 | 93600 | 42900 | 52650 | 5850 | 33150 | 14040 | 17550 | 2730 |
| Parking lots, under asphalt paving, fence lines, building perimeters, ditch banks, picnic areas, vacant lots, wood decks, bleachers, cemeteries, fuel tanks, runways, helo pads, etc.;<br>Bleachers, fence lines, fire hydrants, guard rails, parking lots, under driveways, sidewalks, asphalt | 520 | 125000 | 57000 | 70000 | 7800 | 44000 | 19000 | 23000 | 3600 |
| Pre-paving | 650 | 157000 | 72000 | 88000 | 9800 | 56000 | 24000 | 29000 | 4600 |

## Appendix L. Summary of Publically Available Data in EPA's ECOTOX Database

# Fish

| Common Name | Endpoint | Test Duration | Duration Units | Ref # | LC50 (ug/L) |
|---|---|---|---|---|---|
| Brown trout | LC50 | 48 | h | 448 | LC50: 7,300 |
| Cherry salmon, yamame trout | LC50* | 96 | h | 6034 | LC50: 1,100,000 |
| Cherry salmon, yamame trout | LC50* | 48 | h | 6034 | LC50: 3,300,000 |
| Cherry salmon, yamame trout | LC50* | 24 | h | 6034 | LC50: 4,000,000 |
| Cherry salmon, yamame trout | NR-ZERO | 4 | d | 8138 | NR |
| Cherry salmon, yamame trout | NR | 2 | d | 8138 | NR |
| Cherry salmon, yamame trout | NR | 1 | d | 8138 | NR |
| Fathead minnow | LC50 | 96 | h | 6051 | LC50: 13,500,000 |
| Fathead minnow | LC50 | 96 | h | 6051 | LC50: 13,600,000 |
| Fathead minnow | LC50 | 96 | h | 6051 | LC50: 13,800,000 |
| Goldfish | NR | 4 | d | 916 | Endpoint Not Reported: 1,000,000 |
| Harlequinfish, red rasbora | LC50* | 24 | h | 542 | LC50: 8,600,000 |
| Hasu fish | LC50 | 96 | h | 12402 | LC50: 2,340,000 |
| Japanese barbel | LC50* | 10 | d | 6034 | LC50: 2,000,000 |
| Japanese barbel | LC50* | 96 | h | 6034 | LC50: 3,300,000 |
| Japanese barbel | LC50* | 48 | h | 6034 | LC50: 3,800,000 |
| Japanese barbel | LC50* | 48 | h | 6034 | LC50: 3,800,000 |
| Japanese barbel | LC50* | 96 | h | 6034 | LC50: 3,800,000 |
| Japanese barbel | LC50* | 24 | h | 6034 | LC50: 4,000,000 |
| Japanese barbel | LC50* | 24 | h | 6034 | LC50: 4,200,000 |
| Japanese barbel | LC50* | 12 | h | 6034 | LC50: 4,700,000 |
| Japanese barbel | LC50* | 6 | h | 6034 | LC50: 4,900,000 |
| Minnow | LC50 | 96 | h | 12402 | LC50: 2,340,000 |
| Rainbow trout,donaldson trout | LC50 | 48 | h | 344 | LC50: <1,100,000 |
| Rainbow trout,donaldson trout | NR | NR | wk | 8139 | Endpoint Not reported: No effects at 60,000 |
| Hasu fish | LC50 | 96 | h | 12402 | LC50: 2,340,000 |

## Fungi

| Scientific Name | Endpoint | Test Duration | Ref # | Concentration (mM) |
|---|---|---|---|---|
| Penicillium verrucosum | NOEC | 48 hr | 19279 | >= 7.48 |
| Trichoderma hamatum | NOEC | 48 hr | 19279 | >= 7.48 |

## Aquatic Invertebrates, Laboratory Studies

| Scientific Name | Common Name | Test Duration | Duration Units | Ref # | Concentration (ug/L, except where noted) |
|---|---|---|---|---|---|
| Asellus hilgendorfi | Aquatic sowbug | 96 | h | 6034 | LC50: 2,100,000 |
| Asellus hilgendorfi | Aquatic sowbug | 96 | h | 6034 | LC50: 2,800,000 |
| Asellus hilgendorfi | Aquatic sowbug | 48 | h | 6034 | LC50: 3,100,000 |
| Asellus hilgendorfi | Aquatic sowbug | 48 | h | 6034 | LC50: 3,400,000 |
| Asellus hilgendorfi | Aquatic sowbug | 24 | h | 6034 | LC50: 4,100,000 |
| Haliplus sp. | Beetle | 10 | d | 6696 | NOEC: 105,500 |
| Stenopsyche griseipennis | Caddisfly | 96 | h | 6034 | LC50: 2,700,000 |
| Stenopsyche griseipennis | Caddisfly | 24 | h | 6034 | LC50: 3,100,000 |
| Stenopsyche griseipennis | Caddisfly | 48 | h | 6034 | LC50: 3,100,000 |
| Cloeon dipterum | Mayfly | 24 | h | 6954 | LD50: >40,000 |
| Cloeon dipterum | Mayfly | 3 | h | 6954 | LD50: >40,000 |
| Cloeon dipterum | Mayfly | 48 | h | 6954 | LD50: >40,000 |
| Cloeon dipterum | Mayfly | 6 | h | 6954 | LD50: >40,000 |
| Baetis tricaudatus | Mayfly | 10 | d | 6696 | NOEC: 104,000 |
| Tricorythodes minutus | Mayfly | 10 | d | 6696 | NOEC: 109,000 |
| Polycelis nigra | Planarian | 48 | h | 10013 | LT50: 0.15 (M) |
| Rutilus rutilus | Roach | 96 | h | 12402 | LC50: 2,340,000 |
| Petromyzon marinus | Sea lamprey | 24 | h | 638 | Endpoint Not Reported: 5,000 |
| Isoperla longiseta | Stonefly | 10 | d | 6696 | NOEC: 52,000 |
| Isoperla transmarina | Stonefly | 10 | d | 6696 | NOEC: 104,000 |
| Daphnia magna | Water flea | 48 | h | 6696 | LC50: 3,162,000 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| Daphnia magna | Water flea | 48 | h | 2130 | Lethal concentration: 4,240,000 |
| Daphnia magna | Water flea | 48 | h | 607 | NOEC: 1,000,000 |
| Dasycorixa hybrida |  | 10 | d | 6696 | NOEC 107,000 |
| Table Notes. |  |  |  |  |  |

## Aquatic Invertebrates, Field Studies

| Scientific Name | Common Name | Effect | Trend | Test Duration | Duration Units | Ref # | Exposure Concentration (ug/L) | Application Rate (kg/ha) | Application Frequency | Application Date |
|---|---|---|---|---|---|---|---|---|---|---|
| Not Specified |  | POP | CHG | NR | wk | 8139 | <= 60,000 | NR | NR | NR |
| Not Specified |  | POP | DEC | 7 | h | 8139 | 20,000 - 60,000 | NR | NR | NR |
| Not Specified |  | POP | CHG | NR | d | 8138 | 0 - 57,000 | 200 | 1 X | 10/13/69 |
| Not Specified |  | POP | CHG | NR | d | 8138 | 0 - 57,000 | 200 | 1 X | 10/13/69 |
| Not Specified |  | POP | CHG | 4 | d | 8138 | 0 - 57,000 | 200 | 1 X | 10/13/69 |
| Ephemera japonica | Mayfly | MOR | DEC | 4 | d | 8138 | 800 - 57,000 | 200 | 1 X | 10/13/69 |
| Gammarus sp. | Scud, Amphipod | MOR | DEC | 4 | d | 8138 | 800 - 57,000 | 200 | 1 X | 10/13/69 |
| Note: Significance of Effects were not indicated |  |  |  |  |  |  |  |  |  |  |

## Aquatic Plants

| Scientific Name | Common Name | Test Duration | Ref # | Concentration | Units |
|---|---|---|---|---|---|
| Nostoc calcicola | Blue-green algae | 14 days | 19279 | NOEC: 3.74 | mM |
| Nostoc calcicola | Blue-green algae | 14 days | 19279 | NOEC: 3.74 | mM |
| Ectocarpus variabilis | Brown algae | 14 days | 19279 | NOEC: <0.005 | mM |
| Ectocarpus variabilis | Brown algae | 14 days | 19279 | LOEC: 0.005 | mM |
| Ectocarpus variabilis | Brown algae | 14 days | 19279 | EC50: 0.012 | mM |
| Ectocarpus variabilis | Brown algae | 14 days | 19279 | LOEC: 0.04 | mM |
| Ectocarpus variabilis | Brown algae | 14 days | 19279 | NOEC: 0.04 | mM |
| Ectocarpus variabilis | Brown algae | 14 days | 19279 | EC50: 0.14 | mM |
| Phaeodactylum | Diatom | 72 hours | 19369 | NOEC: 50 | mg/L |

| Scientific Name | Common Name | Test Duration | Ref # | Concentration | Units |
|---|---|---|---|---|---|
| tricornutum | | | | | |
| Phaeodactylum tricornutum | Diatom | 72 hours | 19369 | LOEC: 100 | mg/L |
| Phaeodactylum tricornutum | Diatom | 72 hours | 19369 | NOEC: 100 | mg/L |
| Phaeodactylum tricornutum | Diatom | 72 hours | 19369 | LOEC: 200 | mg/L |
| Phaeodactylum tricornutum | Diatom | 72 hours | 19369 | EC50: 298 | mg/L |
| Phaeodactylum tricornutum | Diatom | 72 hours | 19369 | EC50: 444 | mg/L |
| Lemna perpusilla | Duckweed | 7 days | 15281 | Endpoint Not Reported: 1000000 | ug/L |
| Selenastrum capricornutum | Green algae | 96 hours | 19279 | NOEC: 0.75 | mM |
| Selenastrum capricornutum | Green algae | 96 hours | 19279 | NOEC: >=0.93 | mM |
| Selenastrum capricornutum | Green algae | 96 hours | 19279 | LOEC: 0.93 | mM |
| Selenastrum capricornutum | Green algae | 5 days | 344 | EC50: 133 | ppm |
| Scenedesmus quadricauda | Green algae | 96 hours | 17729 | NOEC: >=784 | ug/L |
| Scenedesmus subspicatus | Green algae | NR | 19370 | NOEC: 1569 | mg/L |
| Scenedesmus subspicatus | Green algae | NR | 19370 | NOEC: 1569 | mg/L |
| Scenedesmus quadricauda | Green algae | 4 days | 607 | Endpoint Not reported: 3000 | ug/L |
| Scenedesmus subspicatus | Green algae | 72 hours | 19370 | LOEC: >3137 | mg/L |
| Scenedesmus subspicatus | Green algae | 72 hours | 19370 | LOEC: >3137 | mg/L |
| Scenedesmus subspicatus | Green algae | NR | 19370 | LOEC: 3137 | mg/L |
| Scenedesmus subspicatus | Green algae | NR | 19370 | LOEC: 3137 | mg/L |
| Scenedesmus subspicatus | Green algae | 72 hours | 19370 | NOEC: 3137 | mg/L |
| Scenedesmus subspicatus | Green algae | 72 hours | 19370 | NOEC: 3137 | mg/L |

# Appendix M.  Summary of Key Toxicity Studies for This Assessment

# Fish

**MRID 418872-03**
Rainbow trout (20/concentration) were exposed to sodium chlorate at 150, 240, 380, 600, and 1000 mg/L for 96 hours under flow-through conditions. Dissolved oxygen was 9.0 to 9.8 mg/L, pH was 6.8 to 7.3, and the temperature was 11.0 to 11.6°C. The NOAEC was 600 mg/L (1/20 fish died at 1000 mg/L). There was evidence that the chlorate concentrations were lower at the end of the study as indicated by a decline in conductivity between days 3 and 4 of the study. Conductivity is directly related to chlorate concentration. Therefore, this study is classified as **supplemental**.

**MRID 418872-02**
Bluegill (20/concentration) were exposed to sodium chlorate at 140, 240, 380, 600, and 1000 mg/L for 96 hours under flow-through conditions. Dissolved oxygen was 8.3 to 9.4 mg/L, pH was 8.0 to 8.7, and the temperature was 21.1 to 22.9°C. The NOAEC was 1000 mg/L. Chlorate concentrations were not analytically confirmed. Also, variability in some of the water quality parameters were observed. This variability, however, did not likely affect the results of this study, and submission of a new study in bluegill would not likely affect the conclusions of this risk assessment. As discussed in Section 3 of this assessment, this study was previously considered invalid by the Agency. Submission of a confirmatory study in daphnids was submitted, which allows this fish study to be upgraded from invalid to supplemental. Therefore, this study is classified as **supplemental**.

**MRID 418872-07**
Sheepshead Minnows (20/concentration) were exposed to sodium chlorate at 140, 240, 380, 600, and 1000 mg/L for 96 hours under flow-through conditions. The NOAEC was 1000 mg/L. Chlorate concentrations were not analytically confirmed. As discussed in this assessment, this study was previously considered invalid by the Agency. Submission of a confirmatory study in daphnids was submitted, which allows this fish study to be upgraded from invalid to supplemental. Therefore, this study is classified as **supplemental**.

# Aquatic Invertebrates

**MRID 418872-04**
Daphnids (20/concentration) were exposed to sodium chlorate at 150, 240, 380, 600, and 1000 mg/L for 48 hours under flow-through conditions. Temperature was 19.5-20.9°C. Dissolved oxygen was 8.5-9.0 mg/L, and pH was 7.3-7.7. The NOAEC was 1000 mg/L. Chlorate concentrations were not analytically confirmed. As discussed in this assessment, this study was previously considered invalid by the Agency. Submission of a confirmatory study in daphnids was submitted, which allows this fish study to be upgraded from invalid to supplemental. Therefore, this study is classified as **supplemental**.

**MRID 438748-01**
The 48-hour acute toxicity of sodium chlorate to the water flea was studied under static conditions. Daphnids (20/concentration) were exposed to the test material at mean measured concentrations of 0, 52, 103, 208, 405, and 1019 mg/L. The EC50 was 920 mg/L, and the NOAEC was 405 mg/L based on 55% mortality at 1019 mg/L. This study is classified as **supplemental** because the pH and water hardness were outside the range recommended by EPA guidelines. pH could affect the toxicity of chlorate because a reduction product (chlorite) is particularly toxic to daphnids.

**MRID 418872-06**
The 96-hour acute toxicity of sodium chlorate to mysid shrimp was studied under flow-through conditions. Mysid shrimp (20/concentration) were exposed to sodium chlorate at nominal concentrations of 0, 130, 220, 360, 590, and 1000 mg/L. Dissolved oxygen was 7.4 to 8.9 mg/L, pH was 7.6 to 7.8, and the temperature was 21.4 to 23.0*C. 2/20 mysids died at 1000 mg/L, and 1/20 died at 590 mg/L. No other mortalities or signs of toxicity were

noted. This study is classified as **supplemental** because the test substance concentratins were not analytcally confirmed. This study was previously assigned a classification of invalid; however, as discussed in this assessment, submission of a confirmatory study in daphnids was submitted, which allows this fish study to be upgraded from invalid to supplemental.

**MRID 418872-05**

Eastern oysters (20/concentration) were exposed to sodium chlorate at nominal concentrations of 0, 70, 120, 250, 500, and 1000 mg/L for 96 hours under flow-through conditions. Temperature was 20-23*C, dissolved oxygen was 7.2-7.5, pH was 7.7-8.0, and salinity was 21-24 ppt (parts per thousand). EC50 was >1000 mg/L. No treatment related mortalities occurred. Shell growth at 250, 500, and 1000 mg/L was 10%, 15%, and 30% lower than controls, respectively. Shell growth at all other concentrations were equivalent to or greater than controls. Chlorate concentrations were not analytically confirmed. As discussed in this assessment, submission of a confirmatory study in daphnids was submitted, which allows this fish study to be upgraded from invalid to supplemental. Therefore, this study is classified as **supplemental**.

## Aquatic Plants

### MRID 418872-01

Green algae were exposed to sodium chlorate at nominal concentrations of 0, 62.5, 125, 250, 500, and 1000 mg/L (nominal) for 96 hours under flow-through conditions. Temperature was 23.5-25.5°C and pH was 7.2-7.6. The EC50 was 133 mg/L and the NOAEC was 62.5 mg/L. This study is classified as **Core**.

### Van Wijk, Kroon, and Irmgard. 1998. Toxicity of chlorate and chlorite to selected species of algae, bacteria, and fungi. Ecotoxicology and Environmental Safety. 40: 206-211.

Green algae, brown algae, and blue-green algae were exposed to unreported chlorate concentrations for 14 days (brown and blue-green algae) or 96 hours (green algae). Initial cell density was not reported. Temperature was 22 to 24°C and pH was maintained at 7.8 to 9. EC50 values were estimated by linear regression. Organisms were grown using either ammonium or nitrate as the sole nitrogen source. The EC50 for brown algae was 0.012 mM to 0.14 mM depending on the nitrogen source. A NOEC was not observed (effects were observed at the lowest concentrations tested, 0.04 to 0.005 mM). EC50s were not estimated for green algae or blue-green algae. The NOEC and LOEC for green algae was 0.75 mM and 0.93 mM, respectively. No effects were observed in blue-green algae at concentrations up to 3.74 mM.

## Terrestrial Plants

### MRID 463008-01

Vegetative vigor was studied on 10 plant species after application of Sodium chlorate at 348 lb a.i./A. Test species included buckwheat, corn, cucumber, mustard, oats, onion, radish, sorghum, soybean, and tomato. The 348 lb a.i./A treatment group percent inhibitions exceeded 25% for the mean fresh weights of all test species. For all test species, almost all plants were dead by 11 days and the phytotoxic effects included chlorosis, necrosis and stunting in the 348 lb a.i./A treatment group. Cucumber exhibited the greatest reduction for a dicot, with 95.4% mean fresh weight inhibition and sorghum exhibited the greatest reduction for a monocot, with 83.1% mean fresh weight inhibition. The $EC_{25}$ and NOEC were <348 lb a.i./A for all test species. A Tier II study is recommended. **This study is classified as Core for a Tier I vegetative vigor study**.

### MRID 463008-02

Seed germination and seedling emergence were studied on 10 plant species after application of sodium chlorate at 348 lb a.i./A. Test species included buckwheat, corn, cucumber, mustard, oats, onion, radish, sorghum, soybean, and tomato. By 5 days in the petri dish bioassay, the 348 lb a.i./A treatment groups had failed to germinate for all test species compared to the controls. By 14 days, the percent inhibitions for emergence were 10, 3, 97, 81, 5, 0, 27, 21, 8, and 82% for buckwheat, corn, cucumber, mustard, oats, onion, radish, sorghum, soybean, and tomato, respectively, compared to the control. The 348 lb a.i./A treatment group percent inhibitions exceeded 25% for the mean fresh weights of all test species. For all test species, the phytotoxic effects included chlorosis, necrosis, stunting, and distortion in the 348 lb a.i./A treatment group. Cucumber exhibited the greatest reduction for a dicot, with 98% mean fresh weight inhibition and corn exhibited the greatest reduction for a monocot, with 90% mean fresh weight inhibition. The $EC_{25}$ and NOEC for this study was <348 lb a.i./A for all test species. A Tier II study is recommended. **This study is classified as Core for a Tier I seedling emergence study**.

## Sodium Chlorite

Two toxicity studies using sodium chlorite on non-target plants were submitted. These studies were not considered in this assessment on sodium chlorate because non-target plant exposure to chlorite from use of sodium chlorate is uncertain, and the relative toxicity of chlorite to chlorate is uncertain. Also, the maximum concentration used in these studies was equivalent to 7.0 lbs ai./Acre. Chlorate is used at up to 12.5 lbs a.i./Acre. Nonetheless, a summary of these studies are presented below.

**MRID 419485-01**
Seed germination (% germination and radicle length) and seedling emergence (% emergence and fresh weight) were studied on 10 plant species after application of Sodium Chlorite at 3.5 ppm (7.0 lb a.i./A). Test species included buckwheat, corn, cucumber, mustard, oats, onion, radish, sorghum, soybean, and tomato. Buckwheat was the only species which exhibited >25% inhibition, based on reductions in radicle length. In addition to this negative effect, oat and onion radicle length were also significantly reduced in the treatment group (however, reductions did not exceed 25% for these species). No other species was significantly affected by treatment for radicle length, % emergence, or fresh weight endpoints. The $EC_{25}$ and NOEC for buckwheat radicle length were <7 lb a.i./A. Based on the sensitivity of buckwheat radicle length (i.e., >25% reduction), a Tier II study with this species is suggested.

**This study is classified as Supplemental**. However, this study cannot fulfill the guideline requirements for a vegetative vigor study for sodium chlorate (Subdivision J, §122-1 (TIER I)) because the test substance was not sodium chlorate. Also, missing information needs to be provided to ensure that the study is scientifically sound. Additional water was applied to the soil surface immediately after application in the emergence test (reportedly to ensure contact of the test chemical with the seed). Chlorite is expected to be very soluble in water and very mobile in soil. Therefore, this watering may have resulted in decreased exposure to chlorite.

**MRID 419485-02**
Vegetative vigor (fresh weight) was studied on 10 plant species after application of Sodium Chlorite at 3.5 ppm (7.0 lb a.i./A). Test species included buckwheat, corn, cucumber, mustard, oats, onion, radish, sorghum, soybean, and tomato. The 7.0 lb a.i./A treatment group percent inhibitions were <25% for the mean fresh weights of all test species. No mortalities occurred throughout the duration of the test. Chlorosis was observed in three replicates of oats, new leaf-distortion was observed in all tomatoes. These observations were observed in treated and control plants. These symptoms were manifested throughout the course of the test for oats and tomatoes. Corn experienced symptoms of nitrogen deficiency during the first week of testing, but these symptoms were not present at the conclusion of the test. The EC25 and NOEC were >7.0 lb a.i./A for all test species.

This study is classified as **Supplemental**. This study cannot fulfill the guideline requirements for a vegetative vigor study for sodium chlorate (Subdivision J, §122-1 (TIER I)) because the test substance was not sodium chlorate. Also, this study did not evaluate some toxicological parameters including dry weight and plant height. In addition, overhead watering used in this study on two occasions could have facilitated chlorite's dissipation and reduced exposure time.

# Birds

**MRID 421494-01**
Mallard ducks (10/dose) were administered a single acute oral dose via gavage at 398, 631, 1000, 1590, or 2510 mg/kg-bw. No mortality or signs of toxicity were observed at any dose. This study is classified as **acceptable**.

**MRID 418199-07**
Bobwhite quail (10/dose) were maintained on a diet supplemented with sodium chlorate at measured concentrations of 562, 1000, 1780, 3160, or 5620 ppm for 5 days. No mortality or signs of toxicity were observed at any concentration. This study is classified as **acceptable**.

**MRID 418199-08**
Mallard ducks (10/dose) were maintained on a diet supplemented with sodium chlorate at measured concentrations of 562, 1000, 1780, 3160, or 5620 ppm for 5 days. No mortality or signs of toxicity were observed at any concentration. This study is classified as **acceptable**.

# Mammals

## *Acute exposures*

In an acute oral toxicity study (MRID 41819901), groups of fasted, young adult Sprague Dawley albino rats (5/sex) were given a single oral dose of sodium chlorate crystal (100 % a.i., batch/lot DL-1) in 50% w/w solution of distilled water at doses of 2 or 5 g/kg bw and observed for 14 days. These doses were based on a range finding study of 1 rat/sex dosed at 0.3, 0.6, 1.25, 2.5, or 5.0 g/kg bw, where there no mortalities observed. Oral $LD_{50}$ is equal or greater than 5000 mg/kg bw (both sexes). Sodium chlorate is of SLIGHT oral Toxicity based on the oral $LD_{50}$ in males and females (Toxicity Category IV). All animals in the 2 g/kg group survived with only transient hunched posture in one male 2-4 hours post-dosing. In the 5g/kg dose, one female died one day after dosing. Several other animals appeared lethargic and had hunched posture shortly after exposure that lasted for the first 24 hours. Necropsy findings of the dead female showed green discoloration of the intestine, a light green fluid on the stomach, pink liquid in the abdominal cavity and dark red lung discoloration. Necropsy findings of the survivors were unremarkable. This acute oral toxicity study is classified acceptable/guideline. This study satisfies does satisfy the guideline requirement for an acute oral toxicity study on the technical material (OPPTS 870.1100; OECD 401) in the rat. Other acute studies are summarized in Table M-1 below.

## Table M-1. Acute Toxicity Profile in Mammals

| Guideline No./ Study Type | Study Type - Species | MRID No. | Results |
|---|---|---|---|
| 870.1100 | Acute oral -Rats | 41819901 | 5000 mg/kg (rat) |
| 870.1200 | Acute dermal - Rabbits | 41819902<br>42497601 | $LD_{50}$ = > 2000 mg/kg (dry crystal)<br>$LD_{50}$ = > 2000 mg/kg (moistened) |
| 870.2400 | Acute eye irritation - Rabbit | 00085090;<br>00102998<br>41819904 | mildly irritating<br>mildly irritating |
| 870.2500 | Acute dermal irritation - Rabbit | 41819905<br>42497602 | non-irritating (dry crystal)<br>minimally irritating (moistened) |

## Table M-2. Summary of Selected Repeated-Dose Toxicity Studies Using Sodium Chlorate in Laboratory Animals[a]

| Guideline No./ Study Type | MRID No. (year)/ Classification /Doses | Results |
|---|---|---|
| 870.3100<br>90-Day oral toxicity (Sprague-Dawley Rats) | 40444801(1997)<br>Acceptable/guideline<br>0, 10, 40, 100 or 1000 mg/kg/day, oral gavage | **NOAEL** = 100 mg/kg/day<br>**LOAEL** = 1000 mg/kg/day based on hematological effects (hemoglobin concentration, hematocrit, RBC counts were statistically significantly decreased, and reticulocyte count was statistically significantly increased in females. In males, only the hematocrit was statistically significantly decreased. The adrenal weight was depressed in both males and females. |
| Non-Guideline<br>90-Day oral toxicity (Sprague-Dawley Rats) | McCauley *et al*, 1995<br>SD rats (10/sex/group)<br>$NaClO_3$ in the drinking water 3.0, 12.0, or 48 mM for 90 days<br>M: 30, 100 and 512 mg/kg/day<br>F: 42, 158, and 800 mg/kg/day | **NOAEL** = 30 and 42 mg/kg/day in males and females.<br>**LOAEL** = 100 mg/kg/day in males and 150 mg/kg/day in females, based on the pituitary effects (vacuolization) and thyroid gland effects (colloid depletion), the body weight decrease and organ weight changes and reduction in erythrocyte counts and hemoglobin content. |
| Non-Guideline<br>90-Day oral toxicity (F344 rats and B6C3F1 mice) | Hooth *et al*, 2001<br>$NaClO_3$ in drinking water at 0, 0.125, 0.25, 1.0 or 2 g/L for 21 days or 90 days in rats and mice<br>M: 14, 28, 112, 225 mg/kg/day<br>F: 20, 40, 160 mg/kg/day at 0, 0.5, 1.0, 2.0, 4.0, or 6 g/L | **NOAEL** = 0.25 g/L ( 28 & 40 mg/kg/day for males and females, respectively)<br>**LOAEL** = 1.0 g/L based on colloid depletion and follicular cell hyperplasia, (112 & 160 mg/kg/day for males and females, respectively)<br>Total serum triiodothyronine ($T_3$) and thyroxine ($T_4$) concentrations were decreased significantly and TSH levels increased significantly in male and female rats after 4 days of treatment with 1.0 or 2.0 g/L and after 21 days of treatment with 2.0 g/L. TSH levels also increased significantly in male rats after 21 days of treatment with 1.0 g/L. Serum $T_3$ and $T_4$ levels were comparable to controls in male and female rats after 90 days of treatment, but TSH levels were increased in both sexes.<br>Follicular cell hyperplasia was not present in male or female mice. |

## Table M-2. Summary of Selected Repeated-Dose Toxicity Studies Using Sodium Chlorate in Laboratory Animals[a]

| Guideline No./ Study Type | MRID No. (year)/ Classification /Doses | Results |
|---|---|---|
| 870.3150<br>90-Day oral toxicity (Beagle Dogs) | MRID 40460402 (1987)<br>Acceptable/Guideline<br>oral gavage 0, 30, 60 or 360 mg/kg/day for 90 d | **NOAEL** = 360 mg/kg/day (HDT)<br>**LOAEL** = greater than 360 mg/kg/day based on lack of detectable adverse effects. Higher dose levels were not possible due to occurrence of emesis at higher doses.Non-Guideline<br>subacute study in dogsHeywood *et al*, 1972<br>doses of 200 to 326 mg/kg/day of sodium chlorate administered daily by intubation as 50 ml of 6% solution to 8 dogs for 5 days<br>sodium chlorate caused reduction of packed cell volume, hemoglobin and red blood cells. A consistent increase in plasma urea concentration was also observed. Two animals that received 308 or 326 mg/kg/day suffered appetite loss, body weight decline and appearance of blood in their urine or feces. One of the animals died after 4 days of exposure. Postmortem examination of both animals revealed typical signs of chlorate poisoning, including cyanotic kidney surface and evidence of necrosis and hemolysis in the kidney. Five of the 8 animals displayed tissue pathology indicative of hemolysis such as Kupffer cells containing brown pigment. |
| Non-Guideline<br>21 day oral toxicity study (B6C3F1 mice) | NTP Study (1999a)<br>10/sex/dose: 0, 125, 500, 1000 or 2000 mg/L<br>M: 22, 43, 173 or 348 mg/kg/day 0, 20, 44,<br>F: 94, 192 or 363 mg/kg/day | Sodium chlorate had no effect on survival, body weights, clinical signs, water consumption, hematology parameters, methemoglobin concentration, or organ weights of either sex. There were no gross or microscopic lesions that were considered to be due to sodium chlorate treatment. |
| Non-Guideline<br>21 day oral toxicity study (Fisher 344 rats) | NTP Study (1999b)<br>10/sex/dose: 0, 125, 500, 1000 or 2000 mg/L<br>M: 0, 20, 36, 77 or 170 mg/kg/day<br>F: 0, 21, 38, 73, 152 or 338 mg/kg/day | Sodium chlorate had no effect on survival, body weights, clinical signs or water consumption. A moderate to severe neutropenia was observed in both sexes on day 4 and 22. Very mild decreases in erythrocyte counts, hemoglobin, and hematocrit were considered not to be biologically significant. The only gross or microscopic lesion that was considered to be treatment related was a minimal to mild follicular cell hyperplasia of the thyroid gland seen in males at 500 mg/L or greater and in females at 250 mg/L or greater. |
| 870.3700a<br>Prenatal developmental (rats) | MRID 40460401(1987)<br>Acceptable/Guideline<br>oral gavage<br>0, 10, 100 or 1000 mg/kg/d on GD 6-15 | **Maternal NOAEL** = 1000 mg/kg/day (HDT)<br>**LOAEL** = >1000 mg/kg/day.<br>**Developmental NOAEL** = 1000 mg/kg/day (HDT)<br>**LOAEL** = >1000 mg/kg/day based on lack of effects |

## Table M-2. Summary of Selected Repeated-Dose Toxicity Studies Using Sodium Chlorate in Laboratory Animals[a]

| Guideline No./ Study Type | MRID No. (year)/ Classification /Doses | Results |
|---|---|---|
| 870.3700b<br>Prenatal developmental (Rabbits) | NTP (2002)<br>Acceptable/Guideline<br>0, 100, 250, or 475 mg/kg/d on GD 6-29.<br>Range finding study: 0, 100, 250, 500, 750 or 1000 mg/kg/d | **Materna**l **NOAEL** = 475 mg/kg/day (HDT)<br>**LOAEL** = 500 mg/kg/day based on mortality in range finding study.<br>**Developmenta**l **NOAEL** = 475 mg/kg/day (HDT)<br>**LOAEL** = >475 mg/kg/day |

[a] Data compiled by the Health Effects Division of EPA.