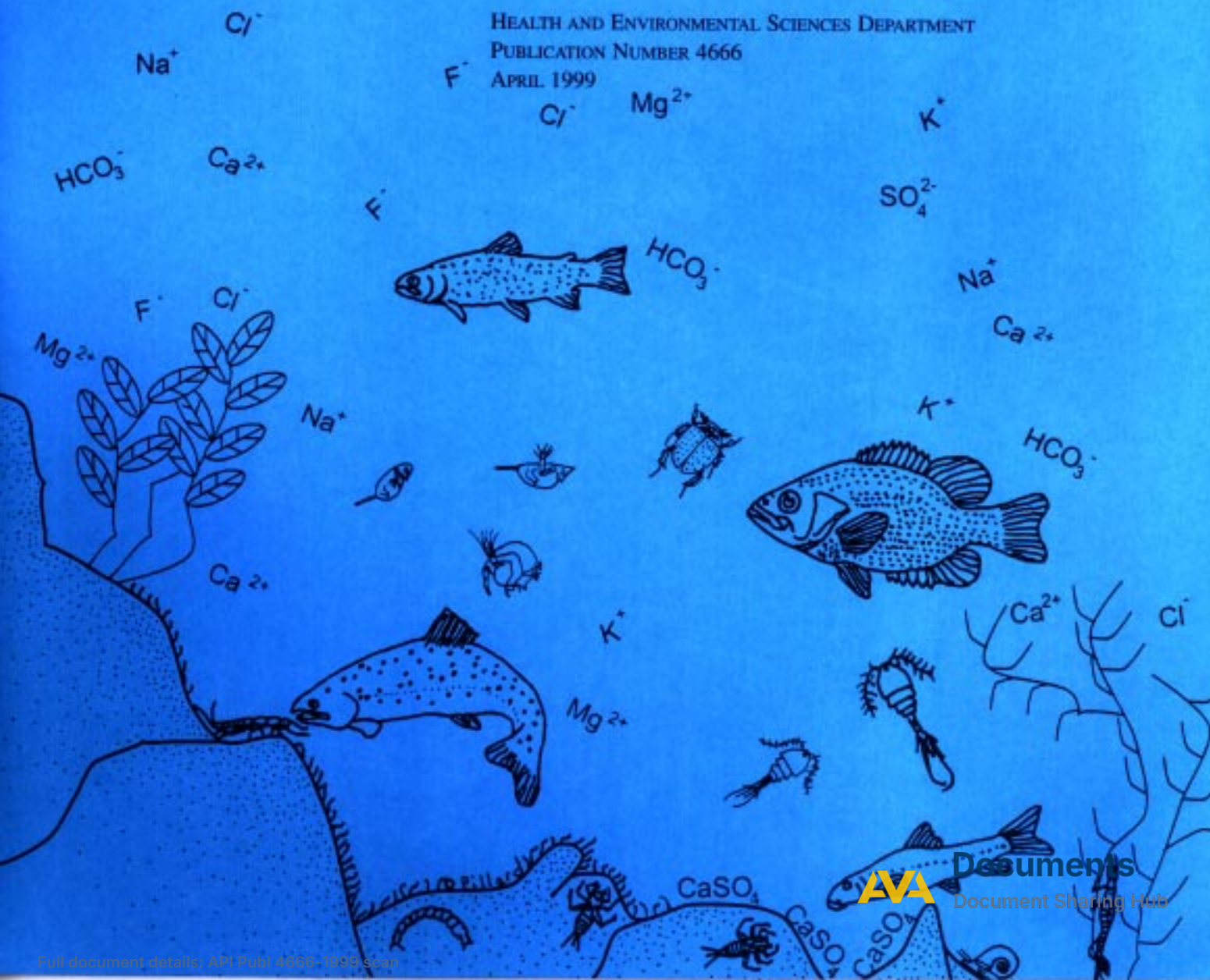


THE TOXICITY OF COMMON IONS TO FRESHWATER AND MARINE ORGANISMS

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT

PUBLICATION NUMBER 4666

APRIL 1999



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The Toxicity of Common Ions to Freshwater and Marine Organisms

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4666

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ABSTRACT

Whole effluent toxicity (WET) tests have become a common tool in the evaluation of effluent for discharge acceptability. The majority of toxicants identified in effluents are either inorganic trace metals (e.g., cadmium, copper, etc.) or organic compounds (e.g., diazinon, surfactants). Others, however, are inorganic ions that nearly always are present in most aquatic systems and, in most cases, are present at nontoxic concentrations. These ions include bicarbonate, calcium, chloride, magnesium, potassium, sodium, sulfate, and others. Recent investigations have indicated that, in certain effluents, deficiencies or excesses of these "common" ions can cause significant acute or chronic toxicity in WET tests. This report presents the results of a review of toxicological and physiological data on inorganic ions that have been implicated in causing significant toxicity.

The scientific literature was searched for freshwater and marine toxicity data on bicarbonate (HCO_3^-), borate ($\text{B}_4\text{O}_7^{2-}$), bromide (Br^-), calcium (Ca^{2+}), chloride (Cl^-), fluoride (F^-), magnesium (Mg^{2+}), potassium (K^+), strontium (Sr^{2+}), and sulfate (SO_4^{2-}). A review also was completed on the roles that several common ions play in normal physiological functions and the impacts of abnormal levels of these ions. All states and EPA regions were surveyed to determine what, if any, guidelines currently are in place to address the question of common ion toxicity.

The impact of aberrant levels of ions differs markedly with the ion in question as well as the organism being tested. Some ions, Ca^{2+} and K^+ for example, cause significant acute toxicity when they are deficient in the exposure media, while other ions appear to have demonstrable effects only at excess levels. Whole effluent toxicity due to the common ions can pose a problem for some dischargers who must identify and/or eliminate toxicity in their effluent. This problem arises because standard Toxicity Identification Evaluation (TIE) manipulations often are ineffective in separating ion toxicity from other potential candidates. However, techniques such as mock effluent studies and computer models can be used in conjunction with traditional TIE methods to provide definitive identification of ion toxicity.

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EXECUTIVE SUMMARY

This report presents and discusses the results of a review of the scientific literature pertaining to the toxicity of common inorganic ions (e.g., calcium, potassium, chloride) to freshwater and marine organisms. Also examined were 1) important physiological functions of the ions, 2) how these ions can affect whole effluent toxicity (WET) tests, and 3) what methods may be used to identify ion toxicity and discern it from toxicity due to other chemicals.

WET testing has become a common parameter evaluated as part of National Pollutant Discharge Elimination System (NPDES) permits. The use of WET tests brings such permits closer to the fulfillment of one of the major goals of the Clean Water Act, to prevent the discharge of toxic materials in toxic amounts. One of the problems that has arisen in the WET testing program has been associated with the confounding effects of ions typically associated with total dissolved solids (TDS). It is well known that elevated TDS or salinity will cause adverse effects to some species, and the salinity of an effluent (or of the receiving environment) will often dictate the test organisms used for WET testing. However, more recent data have shown that the individual ions that comprise TDS may have more influence on toxicity than can be estimated through gross measurements such as TDS, salinity, conductance, or even chloride concentration. In addition, toxicity caused by TDS ions often is difficult to identify through traditional techniques and thus may be difficult to separate from toxicity due to other materials.

Several literature databases were searched to obtain information for this review, including AQUIRE, Enviroline, WATERNET, and others. Additional literature was collected through searches of specific journals, such as *Environmental Toxicology and Chemistry*, and by cross-referencing from in-hand articles. The physiology section of this report provides a review of how essential ions interact and affect functions in living organisms, primarily animals. The most current information is reviewed and discussed, recognizing that ongoing investigations into physiological aspects of ion toxicity may yield new information. Information on Toxicity Identification Evaluations (TIEs) was obtained through recent literature reviews and discussions with laboratory technicians and scientists currently involved in TIE studies where ion toxicity is suspected.

ION TOXICITY

Bicarbonate (HCO_3^-), borate ($\text{B}_4\text{O}_7^{2-}$), bromide (Br^-), calcium (Ca^{2+}), chloride (Cl^-), fluoride (F^-), magnesium (Mg^{2+}), potassium (K^+), strontium (Sr^{2+}), and sulfate (SO_4^{2-}) toxicity were evaluated. These ions have demonstrated substantially different toxicity to freshwater and marine organisms. There are also differences in sensitivity to a single ion among species. For example, to *Ceriodaphnia dubia* and *Mysidopsis bahia*, two common invertebrate organisms used in WET tests, the approximate relative acute toxicity (as measured by mass concentration) of some ions is:

C. dubia (More Toxic) $\text{K}^+ > \text{HCO}_3^- > \text{Mg}^{2+} > \text{Cl}^- > \text{SO}_4^{2-} > \text{Br}^-$ (Less Toxic)

M. bahia (More Toxic) $\text{F}^- > \text{B}_4\text{O}_7^{2-} > \text{K}^+ > \text{HCO}_3^- > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Br}^- > \text{SO}_4^{2-}$ (Less Toxic)

To freshwater organisms, Mg^{2+} , HCO_3^- , and K^+ were the most toxic, generally causing acute toxicity at less than 1,000 mg/L. While Br^- was one of the least acutely toxic ions to freshwater organisms, it had apparent chronic effects at much lower concentrations. To marine test organisms, HCO_3^- , K^+ , $\text{B}_4\text{O}_7^{2-}$, and F^- caused acute toxicity at lower concentrations than the other ions evaluated; Sr^{2+} may also cause toxicity to *Menidia beryllina* at approximately 200 mg/L.

As with many toxicants, the complexity of common ion toxicity is associated with the chemistry of effluents and the interactions of all the chemicals within that effluent. This relationship is especially true in waters of high ionic strength such as those discharged to marine environments. Because some ions may be near saturation and can form strong bonds with other materials, toxicity may be reduced through complexation and precipitation of salts. Toxicity, therefore, cannot always be defined in terms of the concentration of one or more ions, as measured in an analytical laboratory; rather, the chemistry of the whole effluent, including such modifying factors as temperature, atmospheric pressure, carbon dioxide concentration, and pH may be considered. Isolation of the causative toxicant(s) in an effluent may require investigations along several lines in a toxicity identification evaluation. In addition to comparing measured ion concentrations with historic literature, the use of synthetic or "mock" effluents and computer models can prove useful. Even these multiple lines of evidence may prove inconclusive in some cases where toxicity is associated with common ions and other organic or inorganic compounds.

PHYSIOLOGICAL ROLE OF COMMON IONS

Several of the ions reviewed in this report are essential to aquatic organisms in various metabolic activities, as well as to maintain a favorable intra- and extracellular environment in which those activities occur. Calcium, for example, in addition to being critical in building skeletal structures, also contributes significantly to the regulation of membrane permeability and control of the gating of Na⁺-fluxes in the nerve membrane, and is also an essential cofactor in blood clotting and for digestion. Because of the importance of Ca²⁺ and other ions to physiological processes, organisms have developed mechanisms for maintaining intra- and extracellular ion concentrations within the favorable ranges that individual species can tolerate. Mechanisms include active excretion or absorption of ions through gills or other structures and adjustments in the permeability of cellular tight junctions.

CONCLUSIONS

Common ions have been found to cause toxicity in effluents from several different sources, including gas and oil production, chemical manufacturing, refining, agriculture, and seawater desalination. In a large number of studies, the concentrations of ions that are likely to cause adverse effects on aquatic organisms have been identified. While most of these studies have addressed acute toxicity, chronic effects have also been investigated and may become increasingly important as the inclusion of short-term chronic studies becomes more commonplace in NPDES permits. Organisms that are commonly used in NPDES WET tests differ in their responses to these ions, with some, such as *Cyprinodon variegatus*, being much more tolerant to low and high ion concentrations than others.

While in many cases toxicity can be associated with specific ions, adverse effects often are difficult to quantify, particularly in high ionic strength solutions, due to the interactions that common ions have with each other and with other organic and inorganic constituents. The identification of ion toxicity, therefore, often involves using not only historical toxicity data but also traditional TIE methods and computer modeling to provide a weight of evidence approach to toxicity identification. Because many of these ions are essential nutrients to aquatic organisms and may normally be present in source and receiving water, it may be appropriate to evaluate the potential impacts of ion toxicity, as found in laboratory studies, in light of the ecology of the receiving environment.

Section 1

INTRODUCTION

It has long been recognized that some chemical constituents, when present in the aquatic environment above certain levels, may be toxic to organisms. Aquatic toxicology can, in fact, be defined as "the qualitative and quantitative study of the adverse or toxic effects of chemicals and other anthropogenic materials or xenobiotics on aquatic organisms" (Rand and Petrocelli, 1985). Typically, any reference to "toxic materials" usually is associated with complex synthetic chemicals or heavy metals. However, common constituents found in aquatic environments can also be toxic to aquatic organisms when present in sufficient quantities. Ions such as potassium, magnesium, and calcium are present naturally in water and are part of a group of elements that are essential to proper organism function. When concentrations of these common ions exceed a certain level or, in the case of some essential ions, are below a certain level, adverse effects can occur.

The issue of ion imbalance in effluents recently has been highlighted in a re-evaluation of EPA's whole effluent toxicity (WET) testing program. Waters with substantially elevated salinity or total dissolved solids (TDS) have been shown to be toxic when ionic constituents are not in the same proportions as in natural saline waters. High-TDS effluents from operations utilizing water conservation have also shown toxicity. Many processes in manufacturing plants result in a high-TDS effluent with disproportionate ionic ratios. Examples of effluent that may have ion imbalances include those from oil and gas production, water conservation or recycled process waters, and caustic/basic treatment processes using CaCO_3 neutralization. The process of increasing effluent salinity ("salting-up") to accommodate marine/estuarine organism tolerances also can result in toxicity.

SCOPE OF REVIEW

This review focuses on laboratory data regarding the effects of common cations and anions on both freshwater and marine organisms. While a given water can have a variety of constituents, only a few are considered to be common. The major cations are calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), and strontium (Sr^{2+}), and the major anions are bicarbonate (HCO_3^-), borate ($\text{B}_4\text{O}_7^{2-}$), bromide (Br^-), chloride (Cl^-), fluoride (F^-), and sulfate (SO_4^{2-}). This document provides a general summary of the results of toxicity studies on ions and explores the physiological effects of those ions on a tissue and cellular basis.

Section 1 describes some of the current regulatory schemes concerned about ion toxicity. Section 2 summarizes the ionic composition of natural waters in the world, both fresh and saline. A review of some of the sources of high TDS waters is provided in Section 3, along with a discussion of Toxicity Identification Methods (TIE) and what techniques are effective in separating toxicity related to common ions from toxicity due to other constituents. Section 4 is a review of the toxicological data for different ions. Section 5 explores the physiological function of ions and the various models of ion regulation that exist in different taxa. A summary is included in Section 6. References, a Glossary, and a Bibliography follow the summary.

Information for this review was gathered in three ways. First, several computer databases were searched for information related to the toxicity of the common ions (listed above) to aquatic organisms. Those databases included AQUIRE, Biosis Previews®, Compendex®, Oceanic Abstracts, Aquatic Science Abstracts, CAB Abstracts, Inside Conferences, Wilson Applied Science and Technology Abstracts, Water Resources Abstracts, WATERNET™, GEOBASE™, IAC Newsletter DB™, Enviroline®, Pollution Abstracts, Environmental Bibliography, and SciSearch®. Second, a manual literature search was conducted to gather information that might not be found in the databases. Finally, there was direct communication with researchers involved in ion toxicity studies.

TOTAL DISSOLVED SOLIDS IN WET TESTS

Recent studies have shown that toxicity in effluents from many different sources can be attributed to major ions. Many of these ions occur naturally in receiving streams and do not pose the bioaccumulative risk that some other toxicants do. Elevated ion levels occur in some industry source waters and WET toxicity may therefore be artifactual and not a true reflection of effluent toxicity resulting from a manufacturing or treatment process. Nevertheless, there are few regulatory guidelines specifically designed to address TDS ion toxicity. Many states have limits on TDS or a few TDS ions (principally Cl^- and SO_4^{2-}). But compliance with existing water quality discharge criteria or state standards does not guarantee that an effluent will not be toxic. In addition, few permits require analysis of a full suite of ions. Measurement of limited parameters such as TDS, Cl^- , and SO_4^{2-} would be insufficient to determine if toxicity were due to an unmeasured single ion.

There is no national policy for addressing TDS toxicity issues. A survey conducted of all state and USEPA regions indicated that many states have not experienced problems with TDS, although unexplained episodes of toxicity might be attributable to TDS. Only three states and two USEPA regions were identified that have established some current or proposed procedural

guidance for dealing with TDS toxicity; those are described in the following sections. Table 1-1 provides a list of individuals who can provide information from states and EPA regions about TDS and toxicity related to TDS. Additional information on the role of TDS and ion imbalance in toxicity testing may be found in Goodfellow *et al.* (In Preparation).

USEPA Regions 9 and 10

USEPA Regions 9 and 10 recognized that TDS ions in effluent can cause toxicity and confound efforts to identify the causative toxicant(s). As a general guide, it is suggested that if conductivity exceeds 3,000 and 6,000 $\mu\text{mhos/cm}$ at the LC_{50} for *Ceriodaphnia dubia* and *Pimephales promelas* (fathead minnow), respectively, then TDS toxicity should be considered (USEPA, 1996). In order to quantify the impacts of TDS, an effluent sample should be thoroughly characterized relative to the ions in the sample. Once this characterization is completed, a computer model (the **GRI-FW STR™** program, Tietge *et al.*, 1994) can be used to predict toxicity. Mock effluent tests are also an important part of the confirmation process.

Colorado

The Colorado Department of Public Health and Environment (CDPHE) Water Quality Control Division (Division) has prepared a draft revision of its "Whole Effluent Toxicity Permit Implementation Guidance Document" that specifically addresses TDS as a toxicant. Although this document remains in draft form (as of this writing), permittees can follow the procedures to identify and address toxicity due to TDS ions. The guidelines state that, if a TIE rules out other toxicants, except TDS, then the permittee can provide the Division with 1) effluent analytical chemistry, 2) results of an effluent WET test, and 3) results of a mock effluent WET test. If acute toxicity is of concern, then the Division will use a computer program (the **GRI-FW STR™** program, Tietge *et al.*, 1994) to complement existing WET data. If the acute WET test is passed using *Daphnia magna* (which is more tolerant than *C. dubia* to TDS ions), then the permittee may request a permit amendment to change WET test species.

If *D. magna* cannot tolerate the elevated TDS, or if the required test is chronic, permittees may be required to conduct an Aquatic Impairment Study (AIS) of the receiving stream. A CDPHE AIS includes the collection of *in situ* biological, chemical, and physical data and incorporates some of the methods described in the USEPA's Rapid Bioassessment Protocols (Plafkin *et al.*, 1989). Following the AIS, WET tests may be modified to switch species or remove TDS (if possible). Additional mitigation measures also may be needed.

Table 1-1. State and Regional Contacts Regarding TDS Toxicity Questions.

State or Region	Name	Phone	Affiliation
AK	Madonna Narvaez	(206) 553-1774	USEPA Regional Office (Region 10) in Seattle
AL	Marion Bertolotti	(334) 260-2748	Alabama Department of Environmental Management
AR	Bernie Finch Nat Nehus	(501) 682-0744 (501) 682-0663	Arkansas Department of Pollution Control and Ecology, NPDES Branch Biomonitoring Branch
AZ	Linda Taunt	(602) 207-4665	Arizona Department of Environmental Quality, Water Permits
CA	Victor de Vlaming	(916) 657-0795	California State Water Resource Control Board, Division of Water Quality
Reg 1-	Bruce Gwynne	(707) 576-2661	California Regional Water Quality Control Board, North Coast Region
	William Rodriguez	(707) 576-2863	California Regional Water Quality Control Board, North Coast Region
	Tuck Vath	(707) 576-2699	California Regional Water Quality Control Board, North Coast Region
	Peter Otis	(707) 576-2662	California Regional Water Quality Control Board, North Coast Region
Reg 2-	Lila Tang	(510) 622-2300	California Regional Water Quality Control Board, San Francisco Bay Region
Reg 3-	Brad Hagemann	(805) 549-3697	California Regional Water Quality Control Board, Central Coast Region
Reg 4-	Dennis Dasker	(323) 266-7518	California Regional Water Quality Control Board, Los Angeles Region
Reg 5-	Valerie Connor	(916) 255-3111	California Regional Water Quality Control Board, Central Valley Region
Reg 6-	Bruce Warden	(530) 542-5416	California Regional Water Quality Control Board, Lahontan Region
Reg 7-	Orlando Gonzalez	(760) 776-8962	California Regional Water Quality Control Board, Colorado Basin
Reg 8-	Hope Smythe	(909) 782-4493	California Regional Water Quality Control Board, Santa Anna Region
Reg 9-	Bruce Posthumus	(619) 467-2964	California Regional Water Quality Control Board, San Diego Region
CO	Robert McConnell	(303) 692-3578	Colorado Department of Public Health and Environment
CT	Lee Dunbar	(860) 424-3731	Connecticut Department of Environmental Protection
DE	Rick Greene	(302) 739-4590	Delaware Department of Environmental Quality, Office of Water Resources
FL	Steve Wolfe	(850) 921-9830	Florida Department of Environmental Protection, Biology Section

Table 1-1. Continued.

State or Region	Name	Phone	Affiliation
GA	Susan Salter	(404) 362-2680	Georgia Environmental Protection Division
HI	Alec Wong	(808) 586-4309	Hawaii Department of Health, Environmental Management Division, Clean Water Branch
IA	Charles Furrey Steve Williams	(515) 281-4067 (515) 281-8884	Iowa Department of Natural Resources, Municipal Permits Industrial Permits
ID	Rick Huddleston	(208) 373-0502	Idaho Department of Environmental Quality
IL	Bob Mosher Mike Henebry	(217) 782-3362	Illinois Environmental Protection Agency, Planning Division
IN	Catherine Hess Steve Roush	(317) 232-8704 (317) 232-8706	Indiana Department of Environmental Management, Office of Water
KS	Mike Tate	(785) 296-5504	Kansas Department of Health and Environment, Division of Environment, Bureau of Water
KY	Charlie Roth	(502) 564-3410	Kentucky Department of Environmental Protection, Division of Water
LA	Ronnie Bean	(504) 765-2779	Louisiana Department of Environmental Quality
MA	Arthur Johnson	(508) 767-2873	Massachusetts Department of Environmental Protection, Office of Watershed Management
MD	Melvin Knott	(410) 631-3906	Maryland Department of the Environment
ME	Dennis Merrill	(207) 287-7788	Maine Department of Environmental Protection, Bureau of Land and Water Quality
MI	Phil Diamond	(517) 323-0880 F (517) 323-9084	Michigan Department of Environmental Quality, Great Lakes and Environmental Section, Surface Water Quality Division,
MN	Gary Kimball	(612) 297-8221	Minnesota Pollution Control Agency
MO	Ranall Crawford	(573) 526-3353	Missouri Department of Natural Resources
MS	Phil Bass	(601) 961-5143	Mississippi Department of Environmental Quality, Office of Pollution Control
MT	Mike Pasichnyk	(406) 444-5326	Montana Department of Environmental Quality, Water Protection Bureau
NC	Matt Matthews	(919) 733 2136	North Carolina Department of Environment and Natural Resources
ND	Gary Bracht	(701) 328-5227	North Dakota Health Department, Division of Water Quality
NE	Ron Asch	(402) 471-2188	Nebraska Department of Environmental Quality
NH	Jeff Andrews	(603) 271-3503	New Hampshire Department of Environmental Services, Surface Water Quality Bureau
NJ	Betty Boros-Russo	(609) 292-3950	New Jersey Department of Environmental Protection
NM	Glenn Saumes	(505) 827-0596	New Mexico Environment Department, Surface Water Quality Bureau

Table 1-1. Continued.

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OH	Eric Nygaard	(614) 644-2024	Ohio Environmental Protection Agency, Division of Surface Water
OK	Mike Moe	(405) 702-8100	Oklahoma Department of Environmental Quality, Water Quality Division
OR	Judy Johndohl	(503) 229-6896	Oregon Department of Environmental Quality
PA	R. La Roue Wyrick	(717) 787-8184	Pennsylvania Department of Environmental Protection, Bureau of Water Quality Protection
RI	Bob Richardson	(401) 222-7400 x 7240	Rhode Island Department of Environmental Management, Water Resources
SC	Andy Yasinsac Vernon Beaty	(803) 734-5246 (803) 734-5396	South Carolina Department of Health and Environmental Control, Industrial Wastewater Permitting Section Aquatic Biology Section
SD	Stacy Reed	(605) 773-3351	South Dakota Department of Environment and Natural Resources
TN	Saya Ann Qualls	(615) 532-0652	Tennessee Department of Environment and Conservation
TX	Faith Hambleton	(512) 239-4600	Texas Natural Resources Conservation Commission, Research and Environmental Assessment Division
UT	Don Hilden Mike Herkimer	(801) 538-6146	Utah Department of Environmental Quality, Division of Water Quality
VA	Deborah DeBiasi	(804) 698-4028	Virginia Department of Environmental Quality, Permits Section
VT	Doug Burnham	(802) 241-3777	Vermont Department of Environmental Conservation, Water Quality Division
WA	Randall Marshall	(360) 407-6445	Washington Department of Ecology
WI	Diane Drinkman	(608) 264-8950	Wisconsin Department of Natural Resources
WV	Dave Montali	(304) 558-4086	West Virginia Department of Environmental Protection, Office of Water Resources
WY	Leah Krafft	(307) 777-7093	Wyoming Department of Environmental Protection
EPA Region 1	Bill Beckwirth	(617) 918-1544	Environmental Protection Agency, Region 1
EPA Region 2	Phil Sweeney	(212) 637-3873	Environmental Protection Agency, Region 2
EPA Region 3	Kristine Matzko	(215) 814-5719	Environmental Protection Agency, Region 3
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EPA Region 7	John Dunn	(913) 551-7594	Environmental Protection Agency, Region 7
EPA Region 8	Debbie Thomas Glenn Rodriguez	(303) 312-6373 (303) 312-6832	Environmental Protection Agency, Region 8
EPA Region 9	Debra Denton	(415) 744-1919	Environmental Protection Agency, Region 9
EPA Region 10	Madonna Narvaez	(206) 553-1774	Environmental Protection Agency, Region 10

Note: The telephone numbers and affiliations in this table were determined to the best of the authors' abilities at the time of publication. Errors in this information may exist.

Florida

Some drinking water facilities in Florida incorporate membrane technology in the production of drinking water. The membrane concentrate (reject water) from these facilities typically has common seawater ions present at proportions dissimilar to actual seawater. Because many of the concentrates failed toxicity tests under the National Pollutant Discharge Elimination System (NPDES) program, the Florida Department of Environmental Protection (FDEP) developed a series of protocols designed to address major seawater ion toxicity in membrane effluents (FDEP, 1995). The protocols are a result of studies conducted from December 1994 through June 1995. The protocols consist of nine tests, including:

Test 1 - Initial test on unaltered concentrate.

If Test 1 indicates the concentrate is nontoxic, no additional tests are needed.

Test 2 - Baseline test on unaltered concentrate.

If the concentrate in Test 2 is not toxic, no further tests are necessary. This might occur if the toxicant from Test 1 was labile and degraded during the period (typically < 24 hours) between Tests 1 and 2.

Test 3 - Mock concentrate tests.

Test 4 - Ion-adjusted concentrate.

Chemical salts are added to the concentrate sample to balance the major seawater ions to seawater proportions. The balancing is controlled by the concentrate ion that is in the highest proportion relative to seawater.

Test 4a - Ion-adjusted concentrate tests where major seawater ions are incompletely adjusted.

Major seawater ions present in concentrations below that of 35‰ (salinity symbol; equivalent to g/L or parts per thousand of dissolved solids in laboratory-prepared artificial seawater) are adjusted up to 35‰ seawater concentrations. Major seawater ions present in concentrations greater than that of 35‰ seawater are left unaltered.

Test 4b - Ion-adjusted concentrate tests where major seawater ions are completely adjusted then diluted to 35‰.

After adjustment of all ions to seawater proportions, the concentrate is then diluted with deionized water to 35‰ salinity.

Test 5 - Ion-adjusted concentrate (diluted with mock concentrate).

This is the same as Test 4, except the diluent is mock, ion-adjusted concentrate. Therefore, as test concentrations are prepared, the major seawater ions will remain the same in all concentrations; however, the concentration of any other toxicant(s) will change.

Test 5a - Ion-adjusted concentrate tests where major seawater ions are incompletely adjusted (diluted with mock concentrate).

This is the same as Test 4a, except the diluent is mock, ion-adjusted concentrate.

Test 5b - Ion-adjusted concentrate tests where major seawater ions are completely adjusted then diluted to 35‰ (diluted with mock concentrate).

This is the same as Test 4b, except the diluent is mock, ion-adjusted concentrate.

Texas

If a permittee can demonstrate that effluent toxicity is caused by dissolved salts, then the permittee may be exempt from the Total Toxicity provisions of the Texas Surface Water Quality Standards (TSWQS). The exemption applies to 1) 100% end-of-pipe acute toxicity (24-hour acutes) and 2) 48-hour and chronic tests when dissolved salts originate in a permittee's source water. To demonstrate that effluent toxicity (24-hour acute tests) is due to TDS ions, the Texas Natural Resources Conservation Commission (TNRCC) requires one set of TIE/TRE characterization tests, including an ion-exchange procedure. If the TIE/TRE tests indicate TDS ions are a cause of toxicity, the permittee must then prove that these ions are the primary cause of acute toxicity, using a combination of the following techniques (TNRCC, 1995):

- 1) toxicity tests using a more TDS-tolerant species (e.g., *D. magna* vs. *C. dubia*),
- 2) side-by-side toxicity tests of the effluent and a mock effluent,
- 3) analytical verification of major ion concentrations,
- 4) computer models to predict acute toxicity of saline waters, or
- 5) effluent toxicity tests using salts that are formulated to correct ion imbalance.

If these or other acceptable techniques fail to confirm toxicity due to common TDS ions, the permittee must continue with the TIE/TRE process to address toxicity. If the techniques do show that the primary cause of toxicity is TDS ions, the TNRCC will evaluate, or require the permittee to evaluate, the use of an alternative test species or modified test protocol.

If a permittee believes that effluent toxicity in a 48-hour acute or chronic test is due to dissolved salts, then a permittee may use the same techniques to confirm TDS as the cause of toxicity. If TDS is not coming from source water, the permittee may conduct a biological study to evaluate instream impacts. The evaluation should follow USEPA's Rapid Bioassessment Protocols (Plafkin *et al.*, 1989).

The *in situ* evaluation of aquatic communities via impairment studies can be important because laboratory WET caused by TDS ions does not necessarily reflect adverse impacts in receiving waters. Because of the rapid dilution that can occur in receiving water bodies, ion imbalances may be eliminated quickly, although the ratio of effluent to receiving stream (Instream Waste Concentration, IWC) must be considered. Laboratory manipulation of effluent also can affect ion concentrations and thus result in artifactual toxicity, which can complicate efforts to identify real effluent toxicity (Douglas *et al.*, 1996).

In summary, toxicity in WET tests due to TDS ions has proven to be a concern for some effluents from certain industries. Ion toxicity also is something that can appear occasionally in many effluents, including municipal discharges. Although adverse effects to laboratory test organisms due to TDS are a concern and must be addressed, there are considerations that should be taken into account both in the potential for ecological impacts as well as in the identification of toxicants. Many of these TDS ions are essential for long- and short-term survival and general health. Rapid dilution with receiving waters can often correct ion imbalances quickly and, although organisms certainly accumulate many of these ions (e.g., Ca^{2+} in skeletal structures), most species have also evolved elaborate mechanisms for transporting and storing common TDS ions. Therefore, they generally do not bioaccumulate in the same, potentially deleterious, manner as other chemicals. The following sections detail many of these issues.

Section 2

IONIC COMPOSITION OF WATER

SALINITY

Salinity originally was intended to be a measure of the mass of dissolved salts in a given volume of solution. An accurate measure of the salinity of a natural water would, therefore, require a complete analysis of all ions in solution, which would be time-consuming, expensive, and ultimately impractical. It became apparent to early researchers that the ratios of ions in seawater were very constant. Therefore, measurement of a single major parameter would allow calculation of the remaining ion concentrations. Chloride was chosen early on as this single parameter. However, the measurement of chloride, though not difficult, included the addition of AgNO_3 , which also precipitates bromide (Br^-) and iodide (I^-) (Pytkowicz, 1983). Therefore, chlorinity was introduced as a chloride equivalent and is currently defined as the weight of silver needed to precipitate all of the Cl^- , Br^- , and I^- in 0.32867 kg of seawater (Pytkowicz, 1983).

Although chlorinity is still used, salinity is usually considered a unitless measure in which a physical property of a solution (conductivity, density, refractive index, or sound speed) is used to represent salinity (APHA, 1989). Typically, conductivity (presented as micromhos per centimeter [$\mu\text{mhos/cm}$] or millisiemens per meter [mS/m]) is used as a measure of salinity, with a conductivity ratio (R), representing the ratio between the conductivity of the seawater sample being tested and the conductivity of a standard KCl solution (Brown *et al.*, 1995). The resulting number is unitless, although sometimes referred to as *practical salinity units* (p.s.u.).

While there are difficulties in accurately quantifying the salinity of natural waters, it is relatively easy to determine salinity as a mass measurement in solutions prepared in the laboratory. To prepare the solutions, reagent-grade compounds are added to deionized water in known amounts. With careful measurements, nominal concentrations can be quite accurate, and samples can be analyzed to verify concentrations. In these artificial solutions, therefore, salinity can be accurately described as mg/L of solutes, although more traditionally salinity is referred to as g/L (or parts per thousand [ppt]). In this document salinity will generally be considered a true measure of the concentration of dissolved material in solution, with the units being g/L or ppt (often designated by the symbol ‰). A salinity value not accompanied by units should be considered a unitless value determined indirectly through the measurement of some physical property of the water (such as refractive index), although somewhat representative of the concentration of dissolved materials.

Salinity is often considered roughly equivalent to the TDS of a solution, TDS being the material remaining in a sample of water after it is passed through a membrane filter (e.g., 1.2 μm glass fiber) and dried at 180°C (APHA, 1989). TDS, however, is generally reported in mg/L rather than g/L. Although TDS is not always equal to salinity, because most studies use laboratory-prepared solutions, TDS will be considered roughly equivalent to salinity, with the exception of the units in which each term is presented (i.e., 100,000 mg/L TDS = 100‰ salinity). Other terms that are typically used in toxicological discussions are defined in the Glossary.

IONS IN FRESHWATER

There is a great deal of variation in the ionic composition of the freshwater systems of the world. The salinity of a water body depends upon the geological and biological composition of the watershed, atmospheric sources of ions, precipitation, evaporation, and exchange with sediments within the water body. The average salinity of the world's river water is 120 mg/L (Wetzel, 1983), however, the actual ion concentrations in individual lotic systems vary with location and time of year. Table 2-1 lists the concentrations of some common ions from several rivers from around the world. Sodium concentration, for example, ranges from 2.5 mg/L in the Wisconsin to over 800 mg/L in the Powder (after addition of oil-field produced water).

Chemistry will fluctuate with the seasons as patterns of precipitation, sunshine, vegetation, etc. change. Spring snowmelt, for example, often significantly alters water chemistry via dilution and transport of materials accumulated over the winter. Manmade structures, such as dams, also affect downstream water chemistry through deposition of certain minerals (e.g., silica). This effect, in turn, can have dramatic impacts on biological communities (e.g., diatoms). Lake chemistry is often more stable than that of rivers, although seasonal changes and watershed activities can impact lake chemistry as well.

Freshwater bodies are greatly influenced by precipitation and the materials provided from the watershed by the resulting runoff. Precipitation contains dissolved constituents due to 1) droplet formation and 2) particles flushed from the atmosphere by the physical and chemical action of precipitation. Rain and snow droplets form around nuclei, which are primarily soil and dust particles, combustion products, and sea salts (Berner and Berner, 1987). The nuclei may contain any number of ions, depending upon their source. Ions such as Ca^{2+} , Mg^{2+} , and K^{+} originate commonly from soil dust, but also are generated anthropogenically and via sea salt aerosols. The ocean can contribute significantly to precipitation-forming nuclei, although the relative importance of the ocean as a source of ions in inland precipitation varies with distance from the coast (Berner and Berner, 1987).

Table 2-1. Major Dissolved Ion Concentrations in Selected Rivers of the World.

River	Concentration (mg/L)									Reference
	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	SiO ₂	TDS	
Colorado	83	24	95	5.0	82	270	135	9.3	703	Meybeck, 1979
Yukon	31	5.5	2.7	1.4	0.7	22	104	6.4	174	Meybeck, 1979
Mississippi ^a	39	10.7	17	2.8	19.3	50.3	118	7.6	265	Meybeck, 1979
Rio Grande	109	24	117	6.7	171	238	183	30	881	Livingstone, 1963
Clark Fork (MT) ^b	65.7	14.1	15.4	4.0	6	79.5	185	NM	298	ENSR, 1996
Powder (WY) ^c	146	60	176	5	78	275	224	NM	NM	Boelter <i>et al.</i> , 1992
Powder (WY) ^{c,d}	49	36	801	9	689	228	568	NM	NM	Boelter <i>et al.</i> , 1992
San Joaquin (CA)	88	40	236	NM	253	316	215	NM	1160	Saiki <i>et al.</i> , 1992
Pecos (NM)	394	93	333 ^e	333 ^e	538	1150	157	17	2610	Hem, 1985
Wisconsin (WI)	18	8.5	2.5	2.4	1.5	9.5	90	42	106	Hem, 1985
Nile	25	7.0	17	4.0	7.7	9	134	21	225	Meybeck, 1979
Ganges	24.5	5.0	4.9	3.1	3.4	8.5	105	12.8	167	Meybeck, 1979

^a Data from 1965 to 1967.

^b Mean of data from four seasons, 1994-1995.

^c Mean of high-, medium-, and low-flow concentrations in 1988.

^d Downstream of confluence with tributary containing oil-field produced water.

^e Combined sodium and potassium measurement.

TDS in rainwater averages approximately 5 mg/L, while TDS in river water is approximately 100 mg/L. While evaporation tends to concentrate rainwater, much of this increase in TDS is due to contributions from watershed soils and rocks during weathering. Ca²⁺ and HCO₃⁻ are the dominant ions in the world's rivers, and are primarily the product of limestone weathering (Berner and Berner, 1987). The relative contribution of other ions varies with location. In Australia, for example, Ca²⁺ concentrations tend to be lower than Na⁺ and Mg²⁺, while in other parts of the world, Ca²⁺ tends to be higher (Williams and Wan, 1972).

IONS IN SALTWATER

Unlike freshwater, seawater tends to be consistent in its salinity and ionic composition, regardless of location on the planet. The surface water salinity of the open oceans is within the range of 33 to 37‰, although the average salinity is approximately 35‰ (Brown *et al.*, 1995). Na⁺ and Cl⁻ are the most abundant ions in seawater, making up approximately 11 and 19 g/L, respectively (Table 2-2). However, in estuarine areas that experience significant tidal influence as well as freshwater input, salinity can decrease substantially. Brackish water found in

estuaries generally has a salinity of less than 25, although tides and river discharge rate play an important role in the actual salinity at any particular time.

Table 2-2. Average Concentrations of the Major Ions in Seawater.

Ion	Conc. (mg/L)	Molarity (moles/L)
Cl ⁻	18,980	0.535
SO ₄ ²⁻	2,649	0.028
HCO ₃ ⁻	140	2.3 x 10 ⁻³
Br ⁻	65	8.1 x 10 ⁻⁴
H ₂ BO ₃ ⁻	26	4.3 x 10 ⁻⁴
F ⁻	1	5.3 x 10 ⁻⁵
Na ⁺	10,556	0.459
Mg ²⁺	1,272	0.052
Ca ²⁺	400	0.010
K ⁺	380	9.7 x 10 ⁻³
Sr ²⁺	13	1.5 x 10 ⁻⁴
Total Salinity	34.482‰	

Source: Brown *et al.* (1995)
Note: HCO₃⁻ includes carbonate, CO₃²⁻

At the extreme end of the salinity spectrum are inland saline lakes containing hypersaline water with a salinity in excess of approximately 40‰. Typically, these saline lakes exist in relatively arid regions and are closed basins, having no outflow. Ions, accumulated from the drainage basin, are therefore trapped in the water and sediments (due to the precipitation of minerals). Because of the accumulation of salts in saline lakes, a characteristic feature is the presence of relatively high concentrations of some unusual minerals, such as glauberite [Na₂Ca-(SO₄)₂], trona [Na₂(CO₃)•Na(HCO₃)•2H₂O], pirssonite [Na₂Ca-(CO₃)₂•2H₂O], and sepiolite [Mg₄(Si₂O₅)₃-(OH)₂•6H₂O] (Berner and Berner, 1987). The only loss of ions occurs through wind deflation during periods of drought and exposure of the sediments (Wetzel, 1983). The Great Salt Lake in the United States and the Dead Sea in Israel have salinities near 200‰.

Section 3

ION IMBALANCE IN EFFLUENTS

There are several industries that produce effluent that is ionically imbalanced, such that the ratios or concentrations of ions deviate significantly from what is typical in either freshwater or seawater, depending upon where the effluent will be discharged. This imbalance may be due to an excess or deficiency of ions, or to an overall imbalance of the ionic composition. Ionically-imbalanced effluents may originate as a result of 1) high-salinity source water, 2) addition of salts during a treatment process in a production stream, or 3) manipulation of the water via a chemical or physical process (e.g., evaporation). Effluents from different sources may all exhibit toxicity associated with ion imbalance, yet the processes that formed the effluents, and the ion composition of the effluents, can be vastly different. Subsequently, the methods required to ameliorate the toxicity also may be markedly dissimilar.

The purpose of this section is to describe some of the more common sources of effluents that exhibit ion-related toxicity and to identify procedures and techniques developed by regulatory agencies to address ion toxicity. Also included is a discussion of the application of Toxicity Identification Evaluation (TIE) methods that can be employed to help isolate ion toxicity.

SOURCES AND CHARACTERISTICS OF HIGH TDS WATERS

Produced Water

The production of oil and gas typically results in the concurrent production of water that shares the pore space in reservoir rocks. More often than not, the water that is produced along with the hydrocarbons tends to be saline, although the salinity varies regionally. The oil and gas industry produces approximately 14 billion barrels of saline water annually, the majority of which is associated with the oil industry (Daly *et al.*, 1995). The TDS of the produced water ranges from relatively fresh to several times that of seawater. TDS of 100,000 mg/L are not uncommon and some effluents may reach 200,000 mg/L or more (Tibbetts *et al.*, 1992).

Typically, the predominant cation in produced water is Na^+ and the predominant anion is Cl^- . However, produced waters can vary in composition depending upon the type of production operation, geologic source of the water, and the treatment of the water once it is brought to the surface. For example, HCO_3^- (>9,000 mg/L), rather than Cl^- , was reported as the dominant anion in coalbed methane-produced water from Colorado (Simmons, 1992). In the United States some of the more saline gas production-related waters are obtained at operations in East Texas and the Arkansas/Louisiana area, with TDS concentrations in the range of 150,000 mg/L (Daly *et al.*, 1995). Produced water from the Rocky Mountain and Appalachian regions, on the other hand, tend to have low TDS concentrations, in some cases less than 5,000 mg/L.

Reverse Osmosis Membrane (Desalination Water)

Ever-increasing human population densities have strained freshwater drinking supplies in many areas. In coastal areas, infiltration of saline water into formerly freshwater supply wells has further reduced available drinking water. In response to the need for drinking water, desalination plants have been developed in coastal areas which use reverse-osmosis (RO) and membrane technology to reduce TDS in water to a level that is sufficient for drinking water. In the United States these plants are especially predominant in Florida. The concentrate (or "reject" water) from desalination plants typically contains elevated levels of common ions that may be in different proportions than are found in natural seawater (FDEP, 1995). Generally, the salinity of the membrane concentrates is lower than that of seawater.

Hydrostatic Water

State and federal laws require natural gas companies to maintain the integrity of transport pipelines. The primary purpose of this maintenance is to ensure public safety by preventing ruptures or failure of the pipelines. The integrity of pipelines is usually verified with a hydrostatic test of the pipeline using water. The test is performed by sealing the pipe and providing a fill location for water as well as air venting locations. Water is pumped into the pipe and the pressure is slowly increased until the desired pressure is achieved and then held for a predetermined time, typically eight hours (GRI, 1989). When the test is complete, the water is released and frequently is discharged to surface waters. State or federal regulations may require an NPDES discharge permit before the hydrostatic test water can be released.

The constituents of hydrostatic test water will vary with several factors, including the age of the pipe, composition of material transported, and test source water. Hydrostatic test waters may contain elevated levels of oil and grease as well as some metals that are flushed out of the pipe. Test waters can also contain elevated levels of TDS. Concentrations of TDS are highly variable and can range from under 1,000 to over 13,000 mg/L (GRI, 1989). The concentration of TDS in hydrostatic discharge water is controlled primarily by the salinity of the source water; for example, freshwater would produce a low-TDS effluent.

Agricultural Irrigation Drainwater

Agriculture in arid regions of the western United States is highly dependent upon intensive irrigation to sustain production. Evaporation and sparse rainfall often result in the concentration of ions from mineralized groundwater. Saiki *et al.* (1992) reported TDS concentrations in excess of 20,000 mg/L in tile drainwater collected from the Westlands Water District in Fresno County, California. In the same sample the SO_4^{2-} concentration was 13,300 mg/L and the Cl^- concentration was 1,240 mg/L (geometric means). Ingersoll *et al.* (1992) measured salinity of

23 g/L (23,000 mg TDS/L), and SO_4^{2-} and Cl^- concentrations of 2,660 and 11,200 mg/L, respectively, from the Stillwater Wildlife Management Area in Nevada, which receives irrigation drain water. Such high concentrations of salts can have adverse effects on organisms living in the aquatic systems that receive and accumulate irrigation waters.

Mining/Metals Industry

Obtaining and processing metals can result in high-TDS effluent at various points in the process stream. Groundwater used in mining operations may be naturally high in some ions and may also acquire ions during leaching or other processes. Toler (1980) found that, in a survey of streams in surface-mined areas of Illinois, SO_4^{2-} was the major mineral constituent from all sites, with concentrations ranging from 25 to 4,100 mg/L. Smelting operations can also result in effluents with elevated TDS ion levels, along with trace metals (e.g., cadmium, chromium, copper, lead, zinc). Hemens and Warwick (1972), for example, reported F^- concentrations of 40 to 60 mg/L in effluent from an aluminum smelting plant.

Other Water

Effluents from several other sources may potentially be high in TDS. Municipal as well as industrial effluents have been found to have TDS concentrations high enough to cause toxicity to test organisms. The causative agent of ion toxicity varies with the effluent source and may be associated with other toxicants. Mining effluents, as indicated, have been found to have toxicity due to common ions (e.g., SO_4^{2-}). However, these effluents also may have toxicity associated with metals such as copper, cadmium, or zinc. Fortunately, metals can generally be removed during TIE procedures through the use of sodium thiosulfate or ethylenediaminetetraacetic acid (EDTA).

TDS toxicity can be seasonal or associated with precipitation which, by flushing materials into a stream or runoff collection system, can cause concentrations of TDS and TSS (Total Suspended Solids) to increase. Toxicants other than TDS can also be flushed from the watershed. Municipal effluents, for example, which normally do not display WET, may demonstrate toxicity in the spring (April through June) due to increased levels of pesticides. Source water can also impact the toxicity of an effluent. Water used for cleaning, flushing, cooling, or other activities may start out with elevated levels of TDS if, for example, it is taken from a saline surface water lake or impoundment. Therefore, if ion-associated toxicity is discovered in an effluent, it may be important to test the source water to determine if toxicity exists prior to its use for a specific activity.

METHODS FOR IDENTIFYING ION TOXICITY

The presence of toxicity in an effluent regulated under the NPDES often triggers the need for a TIE. Although guidance for conducting TIEs has been established (USEPA 1989, 1991a, 1991b, and 1993), methods do not specifically target toxicity due to salinity or ion imbalance. Nevertheless, traditional TIE methods can be coupled with other tools to identify TDS toxicity.

The typical Phase I TIE characterization pattern for samples containing TDS toxicity is the failure of any of the manipulations to markedly reduce or remove effluent toxicity (Table 3-1). This characterization pattern is the first indication that TDS may be responsible for the observed toxicity. However, this pattern is also indicative of other toxicants (e.g., anionic metals such as hexavalent chromium). If Phase I manipulations do not reduce toxicity, and the conductivity and/or salinity measurements of the sample are consistent with toxicity due to TDS (e.g., conductivity measurements of 2,000 $\mu\text{mhos/cm}$ or higher in fresh waters), additional studies must be conducted to determine if TDS is, in fact, the cause of toxicity.

If an effluent sample demonstrates toxicity in a baseline study and Phase I manipulations are ineffective in characterizing the toxicant, then a series of steps may be employed if TDS or ion imbalance toxicity is suspected (Figure 3-1). Toxicity may be due to excessive quantities of one or more ions, a deficiency of ions, or an overall imbalance of ions. Mathematical models can be used to analyze ion concentrations to determine if they approach or exceed those found to be toxic to test organisms (Pillard *et al.*, 1996; Douglas and Horne, 1997, Mount *et al.*, 1997; Pillard *et al.*, 1998a). Although toxicity typically is considered as reflecting an excess of a chemical, some saltwater species are adversely affected by both an excess and a deficiency of some ions, particularly Ca^{2+} and K^+ (Douglas and Horne, 1997; Pillard *et al.*, 1998a). Even if ion concentrations fall within an acceptable range for organism survival, overall ion imbalance may still trigger significant reductions in survival or sublethal effects (Tucker *et al.*, 1997).

As described in Section 1, protocols developed to supplement and enhance traditional TIE techniques depend heavily on ion balancing and mock effluent studies. In both cases reagent-grade salts are added to either the effluent (for ion balancing) or deionized water (for mock effluent studies); both often are very effective in identifying ion toxicity.

Tietge *et al.* (1997) used mock effluents and computer models to analyze the toxicity of six produced waters collected at various sites in the United States. They found that the toxicity of mock effluents, in which the concentrations of major ions (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , HCO_3^- , and SO_4^{2-}) matched that of the effluents, was very similar to the toxicity of the actual effluent for four of the six effluents for *D. magna*, *C. dubia*, and *P. promelas*. In addition, for the latter two

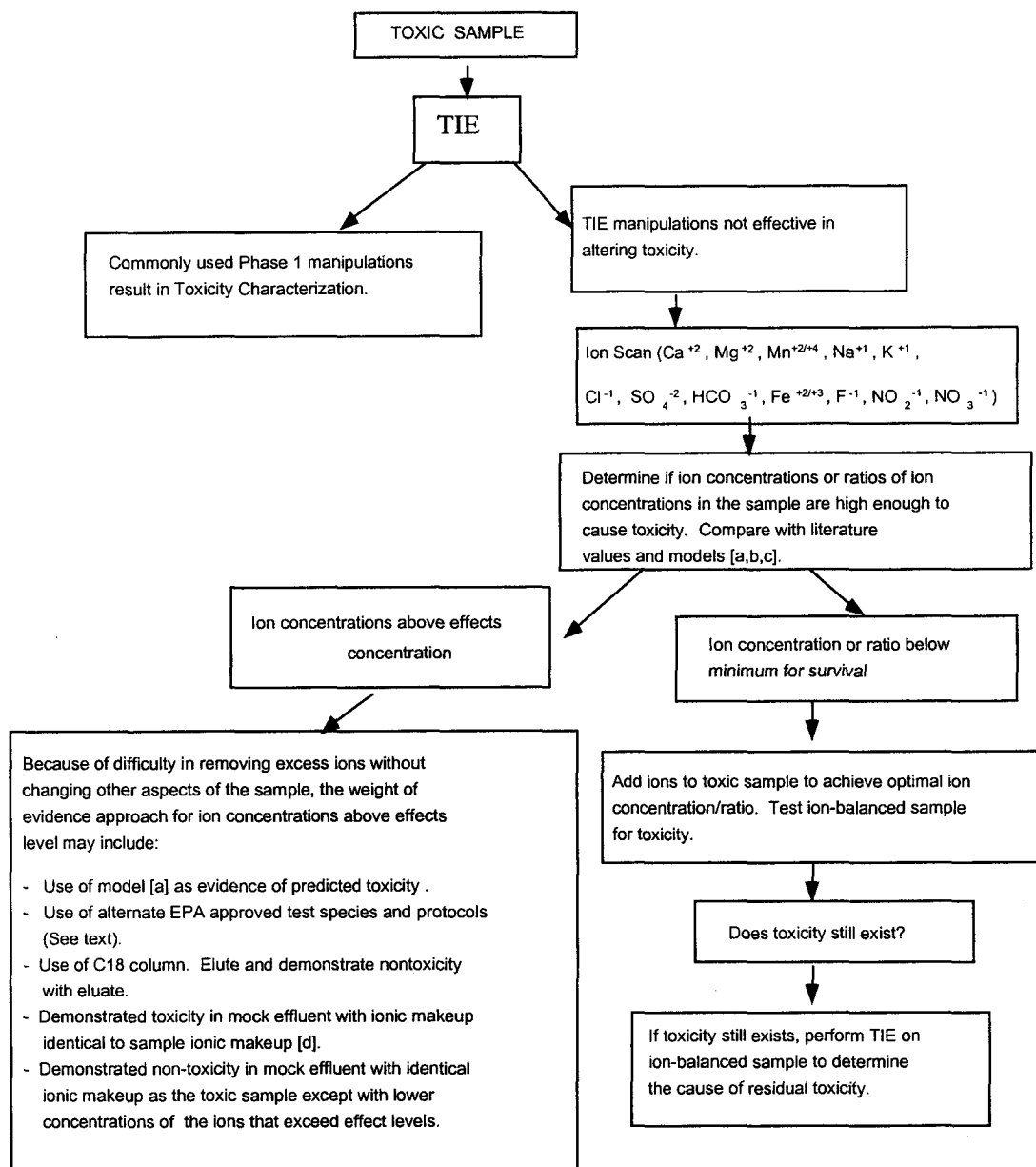
Table 3-1. Results of Acute Phase I Toxicity Characterization of an Industrial Effluent Using *D. magna* Where TDS Toxicity is Suspected.

Phase I Toxicity Characterization Test	48-Hour LC ₅₀ (%)
Baseline Toxicity (Unaltered Effluent)	40
pH 3 Adjustment	40
pH 3 Filtration	59
pH 3 Aeration	55
pH 3 SPE	62
Ambient pH Filtration	42
Ambient pH Aeration	35
Ambient pH SPE	55
pH 11 Adjustment	35
pH 11 Aeration	35
pH 11 Filtration	40
pH 9 SPE	42
Oxidant Reduction	40
EDTA Addition	35
Graduated pH	20

Source: Hockett and Mount (1993)

species, the actual and mock effluent study results correlated well with predictions made using a computer model (Tietge *et al.*, 1994). Toxicity in two of the produced water effluents was attributed to constituents other than ions. McCulloch and Smith (1994) used synthetic effluents to evaluate ion requirements of *Mysidopsis bahia* and found that combinations of ions could be added to effluents to offset the effects of ion imbalance.

For chronic TIE studies, mock effluent studies may be used to identify TDS toxicity. Results of a chronic Phase I Toxicity Characterization using *C. dubia* are provided in Table 3-2 (Hockett and Mount, 1993). None of the Phase I manipulations markedly reduced sample toxicity and TDS toxicity was suspected due to relatively high conductivity (2,420 $\mu\text{S}/\text{cm}$). The effluent sample was analyzed for TDS ions and a mock sample was then prepared and analyzed.



References: [a] Mount *et al.*, 1997
 [b] Tietge *et al.*, 1997
 [c] Douglas and Horne, 1997
 [d] McCulloch *et al.*, 1993

Figure 3-1. Framework for Isolating Ion Toxicity in a Toxic Sample.

Source: Ho and Caudle (1997)

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toxicity test with *C. dubia* was conducted (Figure 3-2). The toxicity of each of these solutions was very similar (IC_{25} [concentration at which there is a 25% reduction in organism performance] values were within 1% of one another). Based on the results of the Phase I TIE and Phase II TIE mock solution studies, common ions were judged responsible for the toxicity observed in this sample.

Identifying Ion-Specific TDS Toxicity

As illustrated in the examples presented above, mock effluents can be used to confirm TDS ion toxicity in effluents. Other manipulations can be used to identify and eliminate ion-specific toxicity. These methods take advantage of the fact that ions differ substantially in their toxicity to test organisms. The sensitivities of three common freshwater organisms are (Mount *et al.*, 1997):

<i>C. dubia</i>	(More Toxic) $K^+ > HCO_3^- > Mg^{2+} > Cl^- > SO_4^{2-}$ (Less Toxic)
<i>D. magna</i>	(More Toxic) $K^+ > Mg^{2+} > HCO_3^- > Cl^- > SO_4^{2-}$ (Less Toxic)
<i>P. promelas</i>	(More Toxic) $K^+ > Mg^{2+} > HCO_3^- > Cl^- > SO_4^{2-}$ (Less Toxic)

All three organisms are most sensitive to K^+ and least sensitive to SO_4^{2-} . Na^+ and Ca^{2+} do not appear to be directly toxic to freshwater species but are important to measure to ensure proper charge balance (i.e., they provide a quality assurance check during ion analysis). Ca^{2+} is, however, a significant toxicant in saltwater effluents. Pillard *et al.* (1998a; 1998b) studied the effects of several ions on marine species using 48-hour acute tests. They found that marine organisms are highly sensitive not only to excess quantities of certain ions but also to deficiencies. In addition, the interactions that occur in high ionic strength solutions seriously complicates efforts to identify a single cause of toxicity. Nevertheless, some generalizations can be made about the toxicity of ions (in excess) to marine species. The toxicity of ions (determined as unequilibrated mass concentration) to three common marine organisms are (Pillard *et al.*, 1998a):

<i>M. bahia</i>	(More Toxic) $B_4O_7^{2-} > K^+ > HCO_3^- > Ca^{2+} > Mg^{2+} > Br^- > SO_4^{2-}$ (Less Toxic)
<i>Cyprinodon variegatus</i>	(More Toxic) $B_4O_7^{2-} > K^+ > HCO_3^- > Ca^{2+} > Mg^{2+}$ (Less Toxic)
<i>Menidia beryllina</i>	(More Toxic) $Sr^{2+} > B_4O_7^{2-} > HCO_3^- > K^+ > Mg^{2+} > Ca^{2+} > Br^- > SO_4^{2-}$ (LT)