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Evaluation of Military Field-Water Quality

Volume 2. Constituents of Military Concern from Natural and Anthropogenic Sources

Part 3. Inorganic Chemicals and Physical Properties

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January 1988

Lawrence Livermore National Laboratory

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In this part of Volume 2 we identify those inorganic chemical constituents and physical properties of field-water supplies that can be present at levels that could degrade the performance of exposed military personnel. To identify these inorganic constituents and physical properties of most concern, we employed a screening methodology for comparing measured concentrations of inorganic chemicals in U.S. and foreign surface and ground waters against estimated threshold concentrations that might produce toxic and/or organoleptic effects in humans. In order to complement the results derived from the screening comparisons and identify the physical properties of most concern in field water we examined the occurrence, toxicity, and organoleptic (e.g., color, odor, taste) data contained in review literature addressing each substance of interest. This combination of screening and survey of the review literature revealed that only arsenic, chloride, cyanide, magnesium, sulfate, total dissolved solids (TDS), and

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turbidity and color are likely to be of concern to military personnel consuming field water. Thus, only the inorganic substances and physical properties of water with field drinking-water-quality standards in current versions of military manuals pose potential health risks of significance to exposed troops. Consequently, up-to-date criteria documents and recommendations for field drinking-water-quality standards need to be prepared for these inorganic constituents and physical properties. We also determined that, with the possible exception of cyanide, inorganic constituents of field water will not produce performance-degrading health effects in military personnel exposed externally as a result of swimming, showering, or bathing.

This report is the third part of the second volume of a nine-volume study entitled Evaluation of Military Field-Water Quality. The first and second parts of this volume address organic chemicals and pesticides, respectively. Titles of the other volumes are as follows: Vol. 1, Executive Summary; Vol. 3, Opportunity Poisons; Vol. 4, Health Criteria and Recommendations for Standards; Vol. 5, Infectious Organisms of Military Concern Associated with Consumption: Assessment of Health Risks, and Recommendations for Establishing Related Standards; Vol. 6, Infectious Organisms of Military Concern Associated with Nonconsumptive Exposure: Assessment of Health Risks, and Recommendations for Establishing Related Standards; Vol. 7, Performance Evaluation of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU): Reverse Osmosis (RO) Components; Vol. 8, Performance of Mobile Water Purification Unit (MWPU) and Pretreatment Components of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU) and Consideration of Reverse Osmosis (RO) Bypass, Potable-Water Disinfection, and Water-Quality Analysis Techniques; and Vol. 9, Data for Assessing Health Risks in Potential Theaters of Operation for U.S. Military Forces.

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FOREWORD

This report is the third part of the second volume of a nine-volume study entitled Evaluation of Military Field-Water Quality. The first and second parts of this volume address organic chemicals and pesticides, respectively. Titles of the other volumes are as follows: Vol. 1, Executive Summary; Vol. 3, Opportunity Poisons; Vol. 4, Health Criteria and Recommendations for Standards; Vol. 5, Infectious Organisms of Military Concern Associated with Consumption: Assessment of Health Risks, and Recommendations for Establishing Related Standards; Vol. 6, Infectious Organisms of Military Concern Associated with Nonconsumptive Exposure: Assessment of Health Risks, and Recommendations for Establishing Related Standards; Vol. 7, Performance Evaluation of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU): Reverse Osmosis (RO) Components; Vol. 8, Performance of Mobile Water Purification Unit (MWPU) and Pretreatment Components of the 600-GPH Reverse Osmosis Water Purification Unit (ROWPU) and Consideration of Reverse Osmosis (RO) Bypass, Potable-Water Disinfection, and Water-Quality Analysis Techniques; and Vol. 9, Data for Assessing Health Risks in Potential Theaters of Operation for U.S. Military Forces.

As indicated by the titles listed above, the nine volumes of this study contain a comprehensive assessment of the chemical, radiological, and biological constituents of field-water supplies that could pose health risks to military personnel as well as a detailed evaluation of the field-water-treatment capability of the U.S. Armed Forces. The scientific expertise for performing the analyses in this study came from the University of California Lawrence Livermore National Laboratory (LLNL) in Livermore, CA; the University of California campuses located in Berkeley (UCB) and Davis (UCD), CA; the University of Illinois campus in Champaign-Urbana, IL; and the consulting firms of IWG Corporation in San Diego, CA, and V.J. Ciccone & Associates (VJCA), Inc., in Woodbridge, VA. Additionally a Department of Defense (DoD) Multiservice Steering Group (MSG), consisting of both military and civilian representatives from the Armed Forces of the United States (Army, Navy, Air Force, and Marines), as well as representatives from the U.S. Department of Defense, and the U.S. Environmental Protection Agency provided guidance, and critical reviews to the researchers. The reports addressing chemical, radiological, and biological constituents of field-water supplies were also reviewed by scientists at Oak Ridge National Laboratory in Oak Ridge, TN, at the request of the U.S. Army. Furthermore, personnel at several research laboratories, military installations, and agencies of the U.S. Army and the other Armed Forces provided technical assistance and information to the researchers on topics related to field water and the U.S. military community.

ACKNOWLEDGMENTS

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Part 3. Inorganic Chemicals and Physical Properties

PREFACE

Water that may be used by military personnel in the field can contain many different organic and inorganic chemical constituents. These chemicals may exist in a dissolved or colloidal state or on suspended material, and they are present as a consequence of either natural geochemical and hydrological processes or the industrial, domestic, or agricultural activities of man.

The health risk to military personnel from a chemical constituent of field water is largely a function of the frequency with which it occurs at concentrations that are high enough to produce a toxic or organoleptic (e.g., detectable taste or odor) effect that leads directly or indirectly to the diminished ability of exposed military forces to perform assigned tasks. To minimize performance-related effects in military personnel using field-water supplies, the high-risk chemical constituents must be identified and analyzed. The potential health risks of the contaminants can then be managed by adopting field-water quality standards. The health effects that could occur when standards are exceeded can be addressed on a case-by-case basis.

The objective of this volume of Evaluation of Military Field-Water Quality is to indicate the chemical constituents of field water that are of possible military concern and to describe the screening methodology and supporting data that we used to identify them. Briefly, the screening methodology is separated into two phases. In both phases the general approach consists of comparing (1) the maximum likely concentration in field water of each possible chemical constituent with (2) a corresponding concentration we estimate to be the threshold above which toxic effects, including impaired performance, could occur. Our analyses are based on 70-kg military personnel consuming field water at a maximum rate of 15 L/d. Maximum likely concentrations in field water for each chemical are derived from our compilation of available U.S. and worldwide water-quality monitoring data. However, in the first phase of screening we make conservative assumptions to extrapolate the threshold concentration above which toxic effects could occur in military forces from either oral-mammalian LD50 (lethal dose to 50% of a population) data or Acceptable Daily Intake (ADI) values for humans. The result of this

screening procedure is to exclude from further consideration those chemical constituents that are not expected to be of military concern. Although the conservative assumptions incorporated into the initial screening exercise minimize the omission of substances that may actually be of concern, some substances may be identified incorrectly as high risk. Therefore, to refine the results of the initial screening effort, we reexamine the available monitoring data and review the published human-toxicity data more carefully for eachchemical indicated to be of possible military concern. Next, we use any more appropriate human-toxicity data (e.g., dose-response information from reported accidental poisonings, occupational exposures, or therapeutic administrations) we find and apply it in the second phase of screening. Then, as in the initial screening procedure, any ratio greater than unity between the maximum likely concentration for a chemical in field water and the concentration above which it could produce toxic or organoleptic effects in 70-kg military personnel consuming field water at a maximum rate of 15 L/d indicates that the chemical really could be of military concern. Because impaired performance can occur as a result of indirect health effects, especially from heat illnesses caused by dehydration resulting from reduced consumption of poor-tasting water, we also screen the initial list of chemicals by comparing maximum likely concentration data for each one with available data corresponding to the concentration of the substance that represents the taste- or odor-detection threshold in water.

To facilitate data acquisition, analysis, and review, as well as application of the screening methodology, we separated the potential chemical constituents of field water into three categories and divided Volume 2 into three corresponding parts. Part 1 covers organic solutes (except pesticides), Part 2 addresses pesticides, and Part 3 focuses on inorganic chemicals and physical properties.

ABSTRACT

In this part of Volume 2 we identify those inorganic chemical constituents and physical properties of field–water supplies that can be present at levels that could degrade the performance of exposed military personnel. To identify these inorganic constituents and physical properties of most concern, we employed a screening methodology for comparing measured concentrations of inorganic chemicals in U.S. and foreign surface and ground waters against estimated threshold concentrations that might produce toxic and/or organoleptic effects in humans. In order to complement the results derived from the screening comparisons and identify the physical properties of most concern in field water we examined the occurrence, toxicity, and organoleptic (e.g., color, odor, taste) data contained in review literature addressing each substance of interest. This combination of screening and survey of the review literature revealed that only arsenic, chloride, cyanide, magnesium, sulfate, total dissolved solids (TDS), and turbidity and color are likely to be of concern to military personnel consuming field water. Thus, only the inorganic substances and physical properties of water with field drinking–water–quality standards in current versions of military manuals pose potential health risks of significance to exposed troops. Consequently, up–to–date criteria documents and recommendations for field drinking–water–quality standards need to be prepared for these inorganic constituents and physical properties. We also determined that, with the possible exception of cyanide, inorganic constituents of field water will not produce performance–degrading health effects in military personnel exposed externally as a result of swimming, showering, or bathing.

INTRODUCTION

The objective of Vol. 2 of <u>Evaluation of Military Field-Water Quality</u> is to identify those organic substances, pesticides, and inorganic chemicals and physical properties that when present in field drinking-water supplies have potential for impairing troop performance. Key considerations in identifying the hazardous constituents are their occurrence in foreign water supplies, the concentrations measured, and importantly, their toxicity. Volume 2 is divided into three parts: Part 1 covers organic solutes (except pesticides);[1] Part 2 deals with pesticides exclusively,[2] and this part addresses inorganic chemical species and physical properties that can be constituents of field water.

Of particular concern are health effects that would directly affect an individual's ability to conduct a military mission. Indirect effects, such as heat illnesses caused by dehydration resulting from the reduced consumption of poor-tasting water, are also important. The health risk of any constituent of a drinking water is a function of its occurrence, expected concentrations, toxicity, and organoleptic properties. As an illustration, a substance that is toxic at low concentrations in water but is found rarely in surface and ground waters would not be considered a high-risk substance. Accordingly, a basic requirement of a screening methodology for field-water contaminants is that it capture those factors that directly influence risk; specifically, the risk of degraded performance of exposed military personnel. For example, this methodology must consider occurrence in different water sources, measured or predicted concentrations in water, and finally, concentrations that could cause adverse health responses. Another requirement is that the screening procedure should minimize omission of those inorganic solutes that are actually of concern. This means that the methodology should be based on conservative assumptions, even if some substances are incorrectly identified as high-risk during the initial phases of screening. In the following sections we review (1) the basic methodology for screening the inorganic solutes and physical properties, (2) the data and procedures used to estimate maximum-likely concentrations of these constituents, and (3) the data and procedures used to determine toxic- or organoleptic-threshold concentrations.

OVERVIEW OF THE SCREENING METHODOLOGY

In Part 1 of this volume[1] an easily applied screening procedure is described for excluding from further consideration those organic constituents of field water with a very small probability of reaching concentrations high enough to produce performance-degrading effects in 70-kg military personnel consuming up to 15 L/d of field water. Screening by this method involves comparing the maximum-likely concentration of

No effects level	No effects level	Odor/taste threshold	Solute concentration	Solute concentration
Odor/taste threshold	Solute concentration	Solute concentration	No effects level	Odor/taste threshold
Solute concentration	Odor/taste threshold	No effects level	Odor/taste threshold	·No effects level
A	B	C	D	E

Contaminant concentration →
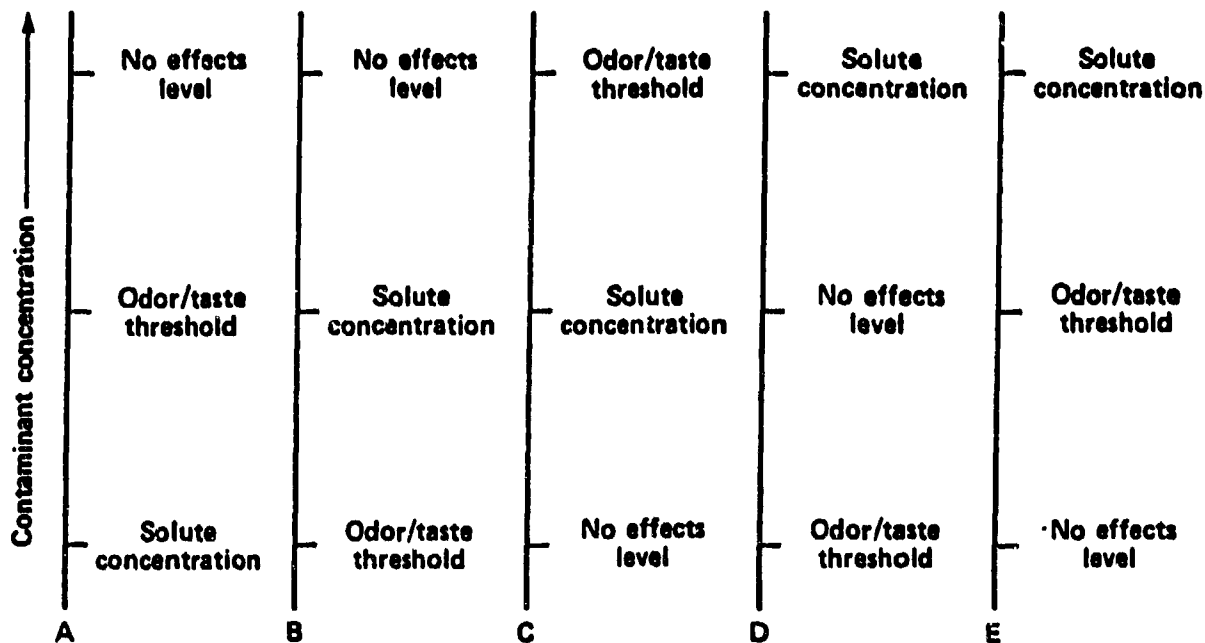
Figure 1. Possible comparisons between water concentrations and threshold concentrations for toxic and organoleptic responses (taken from Part 1 of this volume).[1]

a particular constituent in field water (determined by either measurement or prediction) with the highest concentration for the constituent determined to be a no-effect level (derived from easily accessible animal health-effects data and defined as the screening concentration). Figure 1 shows the various comparisons that can be made. For example, if the maximum-likely concentration for an inorganic constituent in water is below both the concentration determined to be a threshold for toxic effects and the concentration determined to be a threshold for an objectionable organoleptic response (comparison A), then the substance does not constitute a potential health risk. However, if the maximum concentration of the inorganic substance is greater than either the threshold for toxicity or the threshold for an organoleptic response (i.e., comparisons B through E), then the substance is considered a potential high-risk constituent. The highest potential health risk occurs when the odor or taste threshold is above the toxicity threshold; consequently, there is no organoleptic warning of possible danger (comparison E).

As discussed in Part 1,[1] one of the more difficult components of this screening methodology is the calculation of toxic- or organoleptic-threshold concentrations, above which there would be a high probability of an effect in exposed humans. Acquisition and analysis of toxicological data on each substance to define these thresholds are an expensive proposition. An alternative is to estimate the thresholds from the more widely available data on mammalian laboratory animals. The most frequently reported parameter

in this regard is the lethal dose (expressed in mg of chemical per kg of body weight) to 50% of a population of laboratory animals (i.e., an LD50). The LD50 of the species most sensitive to the substance of concern is then used to estimate human threshold concentrations. This value is multiplied by a fraction derived from a statistical analysis of the ratios of no-effect dose rates [in units of mg/(kg • d)] to LD50's for a set of chemicals. After this value is determined, an equivalent concentration in water (i.e., the screening concentration) is calculated, based on a 70-kg man consuming 15 L of water per day. The calculated threshold concentrations are then compared with observed or predicted concentrations in water to determine the inorganic constituents of field-water supplies that could be of most concern from a military perspective.

In addition to applying this screening procedure to the inorganic constituents of field water, we also survey the review literature concerned with the toxic and organoleptic (e.g., color, odor, or taste) properties of each of the potential inorganic constituents of field water. This data-base analysis complements the more automated screening effort in the following ways. First, it is required for validating that none of the inorganic constituents excluded from further consideration by the more automated screening procedure actually is of concern. Second, it is essential for determining if all of the inorganic substances listed by the screening procedure as being of high-risk are actually identified correctly, and if not, which ones among them are of genuine concern and are not an artifact of the conservatism incorporated into the more automated screening procedure. Third, it is necessary for indicating whether or not an inorganic substance has been shown to produce carcinogenic, mutagenic, and/or teratogenic effects, especially in humans. Finally, it is indispensable for verifying whether or not an inorganic substance could be of military concern from the perspective of dermal exposure as a consequence of showering, bathing, or swimming.

In summary, the focus of this report is to indicate the inorganic constituents and physical properties of field-water supplies that can be of military concern from the perspective of consumption or external exposure. Criteria and recommendations for field-water-quality standards will then be developed for these substances. Thus, the screening procedure and complementary data-base analysis are designed to be an expedient and cost-effective mechanism for determining what detailed studies need to be prepared.

IDENTIFICATION OF INORGANIC CHEMICAL SPECIES IN FIELD WATER

We begin by identifying the common and trace inorganic chemicals that could be present as constituents of field drinking-water supplies for military personnel. For each of the identified inorganic constituents, we state the typical valences (oxidation states)

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and chemical species ordinarily present naturally in fresh, ground, and surface waters. The maximum-likely concentration (MLC) values are estimated for each of these substances and then used for comparisons in both the screening procedure and data-base assessment phases of our approach for determining the inorganic constituents of possible concern.

The MLC values for inorganic substances in natural water* are of interest because, unlike sea water and other high-salinity water, natural water could be consumed as "pick-up" water by military personnel in the field. Pick-up water, by definition, will not be treated by a reverse osmosis water purification unit (ROWPU) prior to consumption; therefore, concentrations of inorganic constituents in the water would not be lowered to acceptable levels before the water was consumed. Moreover, the data bases we used to estimate MLC values are confined to analyses of natural water because they include the most likely sources of pick-up water. Furthermore, natural waters that obviously would not be consumed as pick-up water are rare and virtually always associated with hydrogeologically anomalous conditions (e.g., hot springs, volcanic fumaroles, or mine drainage) that are quite easily recognized geological phenomena. Finally, in the natural waters likely to be encountered most frequently, the physical characteristics determining the solubility of constituents occur within specific ranges; whereas, in those natural waters that are rare and therefore going to be encountered far less frequently, the values for these physical characteristics may exceed such ranges. The physical characteristics of importance to solubility are the oxidizing/reducing state and the acidity/alkalinity condition of the water. Ordinarily, natural waters have values for reduction/oxidation potential (Eh) between -0.4 V and +0.8 V and values for acidity/alkalinity between pH 5 and 9. Additionally, the total-dissolved-solids (TDS) content (typically ions of soluble salts) of most common natural waters usually is less than 2500 mg/L.

BASIS FOR IDENTIFICATION

To identify the common and trace inorganic chemicals that could be present as constituents of field drinking-water supplies, we surveyed two types of literature: reports reviewing the chemical composition of natural waters and reports concerning water-related priority pollutants. These references also provided information about the typical valences (or oxidation states) and chemical species of the inorganic substances that can be present in natural waters.

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*"Natural water" is water that occurs in a "real-world" environment, such as a lake, a stream, or a reservoir of ground water. Natural water is not necessarily unaffected by the activities of man.

BASIS FOR MLC ESTIMATES

Our quantitative estimates of the MLC for each of the potential inorganic constituents of military field-drinking-water supplies are based principally on water-quality monitoring data for U.S. surface waters, together with some U.S. groundwater-quality monitoring data. We consider these data to be indicative of worldwide water-quality data for the following reasons. First, the U.S. surface-water-quality data base is very complete, containing large numbers of measurements of both common constituents and trace elements. Second, a very large number of data points are digitized, and the data base covers the entire nation, including tropical (Hawaii and Puerto Rico) and arctic (Alaska) regions. The United States Geological Survey has selected representative subsets of these data of manageable size that can readily be used for statistical manipulation. Third, the U.S. is a large geographic region with many heterogeneous hydrologic environments that adequately represent the major environments in the world. The fact that the water chemistry of major U.S. rivers is not very different from that of other major rivers worldwide indicates that this assumption is reasonable.[3,4] For these reasons, we consider the surface-water-quality monitoring data of the U.S. to be reasonably indicative of worldwide water chemistry.

We did not include foreign water-quality data in our analysis primarily because the data we found were incomplete. Trace-element data, especially, are extremely rare. The data that are available are not in digitized form and it would require a great deal of time to reduce them to computer-readable form for statistical manipulation.

We also consider the U.S. water-quality data to be reasonably indicative of measurements likely to be reported for ground water. Actual groundwater data in usable form are virtually nonexistent; even for the U.S., groundwater data are only now being compiled.[5] However, we did include a small amount of groundwater data in our estimates of MLC values. We would expect that groundwater-quality data would not be dramatically different from the surface-water-quality data we used. Furthermore, our estimates of the MLC values for inorganic constituents in military field drinking-water supplies will be conservative ones that generally should account for MLC values for ground water as well.

Inorganic Chemical Species and Physical Properties and
Their Estimated MLC Values in Field Water

Our review of the water-quality monitoring data revealed 40 common and trace inorganic substances as potential constituents of field-water supplies. These substances are described in detail in Appendix A. Appendix A also contains discussions of the

total-dissolved-solids (TDS) content and the oxidizing/reducing (Eh) and acidity/alkalinity (pH) characteristics of typical natural waters. The discussions of the 40 possible inorganic constituents and TDS identify the typical chemical forms in water and explain the basis for the MLC estimate. Table 1 summarizes the contents of Appendix A.

The inorganic substances reviewed can be classified as common or trace constituents. The MLC estimates in Table 1 reflect the fact that the common constituents include the cations, sodium (Na^+), potassium (K^+), calcium (Ca^{+2}), and magnesium (Mg^{+2}), and the anions, chloride (Cl^-), sulfate (SO_4^{-2}), bicarbonate (HCO_3^-), and carbonate (CO_3^{-2}). These common inorganic constituents of natural water also collectively comprise the major portion of the TDS content. The trace inorganic constituents of natural water have MLC estimates substantially lower than those for the common constituents (see Table 1), and constitute most of the remaining TDS content of the water. Trace inorganic constituents include arsenic, cadmium, iron, manganese, copper, silver, bismuth, cesium, and uranium. The presence of trace inorganic substances in water is controlled by their availability, solubility, and interactions with other chemicals to form insoluble complexes in natural water, as well as by the Eh and pH characteristics of the water. For example, concentrations of arsenic or mercury much greater than their MLC's are not likely to occur at significant distances from natural geological deposits or industrial sources for one or more of the previously stated reasons. However, if sufficiently high cadmium concentrations become available to a water (e.g., as industrial effluent, etc.), then relatively high concentrations can remain in solution over a relatively wide adjoining area because the processes that reduce trace-element concentrations to low levels may not be effective with cadmium.

In the screening procedure and the complementary data-base assessment, which are described next, pH is assumed to be within the limits indicated to be typical of most natural waters. These typical limits for pH are used because they are regarded as tolerable in terms of palatability and potability. Additionally, data are not available for determining the possible health consequences or aesthetic impacts of chemical constituents and physical properties of natural water if the pH of the water is atypical. A temperature consistent with palatable, potable water also is assumed in performing the screening procedure and complementary data-base assessment. This assumption is made because natural water having a temperature that is outside limits for palatability and potability may be undesirable for consumption, independent of the level of any other chemicals or physical properties in the water, and reduced water consumption could lead to dehydration, and subsequent performance degradation.

Table 1. Estimated maximum likely concentration (MLC) for common and trace inorganic constituents of typical fresh water.[a]

Constituent	Typical aqueous valence (oxidation state) and species	Ref.	MLC (mg/L)	Basis for MLC	Ref.
Aluminum	Al^{+3} as $Al(OH)_3(s)$, which limits solubility of trivalent cation	6	0.5	>55th cumulative percentile for total aluminum	7
Ammonia	NH_4^+ as monovalent cation	6	0.6	>95th cumulative percentile	8
Antimony	$Sb(+3)$ as Sb_2O_3 in reducing waters and $Sb(+5)$, probably as Sb_2O_5 in oxidizing waters	9	0.004	From limited data	10
Arsenic	$As(+3)$ as $HAsO_3^{-2}$ divalent anion in reducing waters and $As(+5)$ as $HAsO_4^{-2}$, divalent anion in most oxidizing waters	6	0.02	>95th cumulative percentile for total arsenic	11
Barium	Ba^{+2} as divalent cation and $BaSO_4(s)$, which limits solubility of cation	6	0.2 1.0	>95th cumulative percentile for surface water From data for ground water	8
Beryllium	Be^{+2} usually as soluble complexes (e.g., organo-metallic fluoroberyllates), and $Be(OH)_2(s)$, which limits solubility of other species	6,12	0.000014	From limited data	13
Bismuth	$Bi(+3)$ usually as soluble complexes (e.g., $BiOCl$ and BiO^+ cation)	12	0.003	From limited data	10
Boron	$B(+3)$ as H_3BO_3 (undissociated)	6	1.15	>95th cumulative percentile	8
Cadmium	Cd^{+2} as divalent cation	14	0.01	>95th cumulative percentile for total dissolved cadmium	11
Calcium	Ca^{+2} as divalent cation	6	165	>95th cumulative percentile	8
Carbonate/ Bicarbonate	CO_3^{-2} as divalent carbonate anion at pH > 8.5, and HCO_3^- as monovalent bicarbonate anion at pH > 8.5	6	315	>95th cumulative percentile for bicarbonate	8

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Table 1. (Continued)

Constituent	Typical aqueous valence (oxidation state) and species	Ref.	MLC (mg/L)	Basis for MLC	Ref.
Cesium 16	Cs^+ as monovalent cation	6	0.00004	From limited data	15,
Chloride	Cl^- as monovalent anion	6	960	>95th cumulative percentile	8
Chromium	Cr^{+3} as trivalent cation and $Cr(+6)$ as the complex divalent anions CrO_4^{-2} and $Cr_2O_7^{-2}$	6	0.007	>95th cumulative percentile for total chromium	8
Cobalt	Co^{+2} as divalent cation	6	0.006	From limited data	17
Copper	Cu^{+2} usually as divalent cation	6	0.011	>95th cumulative percentile	8
Cyanide	CN^- anionic ligand usually as HCN, forms other complexes easily	18	0.04	From limited data	18
Fluoride	F^- as monovalent anion and $CaF_2(s)$ which limits solubility of anion	6	2.5	>95th cumulative percentile	7
Iodide	I^- as monovalent anion	6	0.04	From limited data	6
Iron	Fe^{+3} as $Fe(OH)_3(s)$, which limits solubility of trivalent cation, and Fe^{+2} as divalent cation in reducing waters	6	0.40 / 1.5	>95th cumulative percentile for total iron in surface water / From limited data for total iron in ground water	8 / 6
Lead	Pb^{+2} as divalent cation; and $PbCO_3(s)$ which limits solubility of cation	6	0.02	>95th cumulative percentile for total lead	8
Lithium	Li^+ as monovalent cation	6	0.05	>95th cumulative percentile	7

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Table 1. (Continued)

Constituent	Typical aqueous valence (oxidation state) and species	Ref.	MLC (mg/L)	Basis for MLC	Ref.
Magnesium	Mg^{+2} as divalent cation	6	50	>95th cumulative percentile	8
Manganese	Mn^{+2} as divalent cation in reducing to moderately oxidizing waters; $Mn(+4)$ as oxide, $MnO_2(s)$, in alkaline oxidizing waters	6	0.3	>95th cumulative percentile for total manganese	8
Mercury	Hg^{+2} as divalent cation (limited by solubility of oxide); Hg in reducing to moderately oxidizing waters	19	0.0032	From limited data	19
Molybdenum	$Mo(+6)$, usually as $MoO_4{}^{-2}$ divalent anion	6	0.01	>95th cumulative percentile	7
Nickel	Ni^{+2} as divalent cation	6	0.01	>95th cumulative percentile	8
Nitrate	$NO_3{}^-$ as monovalent anion	6	23	>95th cumulative percentile	8
Phosphate	$PO_4{}^{-3}$ as trivalent anion	6	1.5	>95th cumulative percentile	8
Potassium	K^+ as monovalent cation	6	16	>95th cumulative percentile	8
Selenium	$Se(+6)$ as $SeO_4{}^{-2}$ divalent anion in alkaline oxidizing waters; $Se(+4)$ as $SeO_3{}^{-2}$ monovalent anion in moderately oxidizing waters	20	0.007	>95th cumulative percentile for total selenium	21
Silver	Ag^+ as monovalent cation and AgCl, which limits solubility of cation	6	0.002	>95th cumulative percentile for total silver	8
Sodium	Na^+ as monovalent cation	6	500	>95th cumulative percentile	8
Strontium	Sr^{+2} as divalent cation	6	0.5	>95th cumulative percentile	7
Sulfate	$SO_4{}^{-2}$ as divalent anion	6	700	>95th cumulative percentile	8

Table 1. (Continued)

Constituent	Typical aqueous valence (oxidation state) and species	Ref.	MLC (mg/L)	Basis for MLC	Ref.
Thallium	Tl+ as monovalent cation	22	0.00002	From limited data	23
Tin	Sn+2 as divalent cation; and Sn(OH)2(s), which limits solubility of cation	17	0.002	From limited data	17
Uranium	U(+6) as UO2 +2 divalent cation in oxidizing waters	24	0.002	>95th cumulative percentile for total uranium	7
Vanadium	V(+5) as VO3 − monovalent anion	6	0.015	>95th cumulative percentile for total vanadium	7
Zinc	Zn+2 as divalent cation	6	0.2	>95th cumulative percentile	11
Total dissolved solids	TDS (salinity)	24	2100	>95th cumulative percentile	8

aFresh water has values of Eh (reduction–oxidation potential) between −0.4 V and +0.8 V, values of pH (acidity–alkalinity state) between 5 and 9, and total–dissolved–solids (TDS) concentrations usually less than 2500 mg/L.
bA reasonable estimate of the MLC for lognormally distributed data is the concentration with a greater than 95% probability of being equal to, or less than, any observed value.

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SCREENING PROCEDURE

Conceptually, a screening procedure can be considered analogous to a sieve. Like a sieve, it is a quick method for separating one type of substance from a collection of similar but not identical substances. The screening procedure we apply to the collection of inorganic substances identified as possible constituents of field-water supplies possesses such general attributes. Specifically, it is used to separate those inorganic substances with a very small probability of reaching concentrations that would produce toxic effects in 70-kg personnel consuming the water at the maximum rate of 15 L/d. The general nature of this screening procedure has been mentioned previously and is well described in Part 1.[1] A review of the most important details regarding its design and application to inorganic constituents of field water are discussed next, as are the results.

DESIGN

Ideally, we would calculate the equivalent screening concentration for toxicity as follows:

$$C_s = \frac{NOEL}{SF} \times \frac{W}{I} \tag{1}$$

where

C_s = screening concentrations for human toxicity, mg/L;

NOEL = maximum no-observed-effect level in rats, mg/(kg $\cdot$ d);

SF = safety factor for adjusting the animal data to compensate for intra- and interspecies variation, dimensionless;

W = reference body weight of military personnel, kg; and

I = maximum daily intake of water by military personnel, L/d.

Unfortunately, the no-observed-effect levels (NOEL) derived from laboratory-animal studies are available for only a relatively small number of substances. The data that best meet the criteria for availability are the oral LD50's for mammalian animal species. Alone, however, LD50's are not particularly useful for developing a screening dose or concentration because there is no direct way to relate this acute measure of animal toxicity (i.e., lethality) to a threshold for toxic effects in humans. To relate LD50 data to screening-concentration thresholds we adopted the strategy used by Layton et al. in Part 1;[1] the LD50 is used to define a lower-bound limit of toxicity, based on a statistical analysis of the relationship between LD50 values and subchronic (approximately 90-d)

NOEL's. McNamara,[25] in a study of the relationship between chronic and acute toxicities, computed the ratios of subchronic NOEL's to LD50's (oral administrations to rats) for 33 organic substances. We assume that if related data existed and were compiled similarly for the possible inorganic constituents of field water, then the statistical distribution of these ratios would be consistent with the lognormal distribution derived by Layton et al. in Part 1[1] from the 33 ratios for organic chemicals calculated by McNamara. The geometric mean of the lognormally distributed ratios was 0.03 d^{-1}, with a geometric standard deviation of 4.8. A conservative NOEL (i.e., a NOEL that has a high probability of being below a toxic threshold) can then be calculated from an LD50 by multiplying the median-lethal dose by a ratio that corresponds to a suitable cumulative percentile on the lognormal distribution. For the purposes of this screening exercise, we chose the ratio corresponding to the 10th cumulative percentile for the lognormal distribution, or 0.004 d^{-1} (i.e., $0.03/4.8^{1.3}$).

As discussed by Layton et al. in Part 1, the 90-d exposure period used typically for the NOEL is similar to a human exposure period of nearly ten years, based on the assumption that the ratios of the two periods to the lifespans of the respective species are approximately the same (i.e., 90 d/730 d = 9 y/75 y). By comparison, the assumed exposure period for consuming field-water supplies is one year, and so there is an implicit margin of safety in using the subchronic mammalian animal NOEL. Furthermore, we assume that the military population is predominantly male, ranges in age from 18 to 55 y, and is in good health. Thus, the military population collectively has a greater tolerance to toxic substances than the general population with its sensitive subgroups (e.g., infants, the elderly, and the chronically ill), and this assumption adds even more conservatism to the results of the screening procedure. Nevertheless, we also selected a safety factor of 100 to adjust the derived NOEL to one for human exposure because this factor has been widely used by regulators for the purpose of setting standards, and it is supported by data on intra- and interspecies variations (see Dourson and Stara[26]).

Consequently, to calculate the screening concentration (C_s), in mg/L, for inorganic substances from animal LD50's (mg/kg), we first assume that the reference body weight (W) for military personnel is 70 kg, and that the maximum intake of drinking water (I) by military personnel is 15 L/d. Then, we introduce into our calculation the value for the 10th cumulative percentile of the lognormal distribution of ratios of subchronic NOEL's to LD50's (i.e., 0.004 d^{-1}), and the safety factor of 100 mentioned previously, and solve the equation:

$$C_s = \frac{LD50 \cdot 0.004}{100} \times \frac{70}{15} \tag{2}$$

To simplify the computation of the screening concentrations for each inorganic chemical of interest, we actually multiply the LD50 values by 10^{-4} (i.e., the product of 0.004/100, and 70/15 , approximately). Moreover, we used the oral LD50 value for the most sensitive mammalian species; most of these LD50's were for rats. When oral LD50's were not listed in the 1983 supplement to the 1981-1982 edition of the <u>Registry of Toxic Effects of Chemical Substances</u>[27,28] (RTECS) (or in the 1981-1982 edition of the RTECS[29] itself), we used the lowest lethal dose (LDLo) produced by oral administration of the chemical that was listed.

Additionally, the chemical species of the inorganic substances that can be present in field water are not necessarily the chemical forms that were administered orally to laboratory animals to determine an LD50. This is because the vast majority of inorganic substances exist in water as the dissociated ions of dissolved salts, but animal LD50 determinations are made on the basis of the salts themselves or other compounds containing the inorganic chemical of interest. For this report we selected the LD50 for each of the inorganic substances identified as possible constituents of military field-water supplies based on surrogate compounds. For purposes of maintaining relative consistency between LD50 values, the following two criteria were used to select the surrogate compounds.

- A surrogate compound should have an oral mammalian animal LD50 recorded in the RTECS data base, and

- The surrogate compound should consist of the inorganic chemical of interest in combination with a relatively benign inorganic- chemical companion.

From a cursory analysis of toxicology data for the inorganic substances of interest in field drinking water, we concluded that for a military population the relatively benign inorganic-chemical companion substances include sodium (Na), potassium (K), chloride (Cl), and hydroxide (OH). Thus, we assume that the LD50 value associated with an appropriate surrogate inorganic-chemical compound is primarily a consequence of the effect of the inorganic substance of interest, and that any contributing effects from the inorganic-chemical companion substance are negligible.

Table 2 contains an alphabetical listing of the inorganic substances that are possible constituents of military field-water supplies. Presented along with each inorganic constituent in Table 2 are (1) its typical valence (oxidation state) in water; (2) the surrogate substance used as the basis for the LD50; (3) the molecular formula for the surrogate substance; (4) the Chemical Abstracts Service Registry Number (CASID) for the

surrogate substance; (5) the RTECS accession number, page, and volume for convenience in locating the data; and (6) the laboratory animal median-lethal-dose (LD50) data for the corresponding surrogate substance, including both the lowest LD50 value reported for oral administration to a mammalian laboratory animal and for comparison, the oral rat LD50 (if reported). In Table 2 most of the surrogate inorganic-chemical compounds used are composed of the inorganic substance of interest and either sodium or chloride. A few of the inorganic substances of interest were complemented by either potassium or hydroxide. Two inorganic substances, however, have complementing companion substances that differ from sodium, potassium, chloride, and hydroxide. One is the surrogate for molybdenum, molybdenum trioxide (MoO_3). The other one is the surrogate for silver, silver nitrate ($AgNO_3$). We assume that the trioxide and nitrate companion species are relatively benign toxicologically.

RESULTS OF SCREENING

Table 3 presents the comparisons between the MLC values summarized in Table 1 (and discussed in detail in Appendix A) and the screening concentrations for human toxicity (C_S) calculated using the lowest mammalian LD50 for oral administration for each inorganic chemical. The data in this table have been organized so that the constituents are divided into two categories: (1) those constituents, appearing first, with MLC values greater than C_S values and (2) those constituents, appearing second, with MLC values less than C_S values. Within each category, the constituents are listed alphabetically. Accompanying each entry are (1) the corresponding typical valence (oxidation state) in water, (2) the value for the MLC, (3) the lowest oral-mammalian LD50, (4) the screening concentration for human toxicity (C_S), (5) the MLC/C_S ratio, and (6) a qualitative indication as to whether or not the MLC is greater than the C_S value (i.e., "yes or no"). The magnitude of the difference between the MLC and C_S values is of no importance in these comparisons because conceptually, the possibility of harmful effects depends on whether or not the MLC is greater or less than the C_S value.

Our screening procedure separates out 13 inorganic constituents as probably being of no military concern in field-drinking water supplies: (1) antimony, (2) beryllium, (3) bismuth, (4) cesium, (5) iodide, (6) lead, (7) lithium, (8) molybdenum, (9) nickel, (10) silver, (11) thallium, (12) tin, and (13) vanadium. This is because the MLC is less than the C_S value for each of these substances. Accordingly, the remaining inorganic substances may be of concern because the MLC is greater than the C_S value. Interestingly, in Table 3, all of the inorganic substances for which military field drinking-water quality standards now exist are included among the substances that may be of military concern (i.e., MLC>C_S).

Table 2. Possible inorganic constituents of field water and corresponding LD50 values based on surrogate chemical species. [a]

Constituent	Typical valence (oxidation state) in water	Substance used as basis for LD50 estimate	Molecular formula	Chemical Abstracts Service Registry Number (CASID)	RTECS 1983-Sb Accession Number Page/Vol.		Laboratory mammal median lethal dose (LD50) (mg/kg; rte-animal)
Aluminum	Al(+3)	Aluminum chloride	AlCl3	7446-70-0	BD0525000	226/1	770 orl-mus
Ammonium	NH4+	Ammonium hydroxide	NH4OH	1336-21-6	BQ9625000	245/1	350 orl-rat
Antimony	Sb(+3,+5)	Antimony (III) chloride	SbCl3	10025-91-9	CC4900000	281/1	525 orl-rat
Arsenic	As(+3,+5)	Arsenic acid	AsH3O4	7778-39-4	CG0700000	289/1	48 orl-rat
Barium	Ba+2	Barium chloride	BaCl2	10361-37-2	CQ8750000	315/1	76 orl-gp (118 orl-rat)
Beryllium	Be+2	Beryllium chloride	BeCl2	7787-47-5	DS2625000	407/1	86 orl-rat
Bismuth	Bi(+3)	Bismuth oxychloride	BiOCl	7787-59-9	EB2700000	422/1	22,000 orl-rat
Boron	B(+3)	Boric acid	B(OH)3	10043-35-3	ED4550000	428/1	2,660 orl-rat
Cadmium	Cd+2	Cadmium chloride	CdCl2	10108-64-2	EV0175000	462/1	60 orl-mus (88 orl-rat)
Calcium	Ca+2	Calcium chloride	CaCl2	10043-52-4	EV9800000	466/1	1,000 orl-rat
Carbonate	HCO3-	Sodium bicarbonate	NaHCO3	144-55-8	VZ0950000	1374/2	4,220 orl-rat
Cesium	Cs+	Cesium hydroxide	CsOH	21351-79-1	FK9800000	502/1	570 orl-rat
Chloride	Cl-	Sodium chloride	NaCl	7647-14-5	VZ4725000	1375/2	3,000 orl-rat
Chromium	Cr(+3,+6)	Sodium dichromate	Na2Cr2O7	10588-01-9	HX7700000	626/1	50 orl-rat
Cobalt	Co+2	Cobalt chloride	CoCl2	7646-79-9	GF9800000	545/1	55 orl-gp (80 orl-rat)
Copper	Cu+2	Copper chloride	CuCl2	1344-67-8	GL7000000	553/1	31 orl-gp (140 orl-rat)
Cyanide	CN-	Sodium cyanide	NaCN	143-33-9	VZ7525000	1375/2	4 orl-dom (6.4 orl-rat)
Fluoride	F-	Sodium fluoride	NaF	7681-49-4	WB0356000	1376/2	80 orl-rat
Iodide	I-	Sodium iodide	NaI	7681-82-5	WB6475000	1377/2	4,340 orl-rat
Iron	Fe+3	Ferric chloride	FeCl3	7705-08-0	LJ9100000	756/1	1,278 orl-mus
Lead	Pb+2	Lead chloride	PbCl2	7758-95-4	OF9450000	905/2	1,500 orl-gp (LDLo)
Lithium	Li+	Lithium chloride	LiCl	7447-41-8	OJ5950000	912/2	526 orl-rat
Magnesium	Mg+2	Magnesium chloride	MgCl2	7786-30-3	OM2800000	922/2	2,800 orl-rat
Manganese	Mn+2	Manganese chloride	MnCl2	7773-01-5	OO9625000	927/2	1,715 orl-mus
Mercury	Hg+2	Mercuric chloride	HgCl2	7487-94-7	OV9100000	941/2	1 orl-rat
Molybdenum	Mo(+6)	Molybdenum trioxide	MoO3	1313-27-5	QA4725000	990/2	125 orl-rat

Table 2. (Continued)

Constituent	Typical valence (oxidation state) in water	Substance used as basis for LD50 estimate	Molecular formula	Chemical Abstracts Service Registry Number (CASID)	RTECS 1983-S[b] Accession Number	Page/Vol.	Laboratory mammal median lethal dose (LD50) (mg/kg; rte-animal)
Nickel	Ni+2	Nickel (II) chloride	NiCl2	7718-54-9	QR6475000	1031/2	105 orl-rat
Nitrate	NO3-	Potassium nitrate	KNO3	7757-79-1	TT3700006	1225/2	3,015 orl-rbt
Phosphate	PO4-3	Disodium phosphate heptahydrate	Na2HPO4 7H2O	7782-85-6	WC4600000	608/3[c]	12,930 orl-rat
Potassium	K+	Potassium hydroxide	KOH	1310-58-3	TT2100000	1224/2	365 orl-rat
Selenium	Se(+4,+6)	Sodium selenite	Na2SeO3	10102-18-8	VS7350000	1358/2	7 orl-rat
Silver	Ag+	Silver nitrate	AgNO3	7761-88-8	VW4725000	1370/2	50 orl-mus
Sodium	Na+	Sodium chloride	NaCl	7647-14-5	VZ4725000	1375/2	3,000 orl-rat
Strontium	Sr+2	Strontium chloride	SrCl2	10476-85-4	WK8400000	1408/2	2,250 orl-rat
Sulfate	SO4-2	Potassium bisulfate	KHSO4	7646-93-7	TS7200000	1223/2	2,340 orl-rat
Thallium	Tl+	Thallium chloride	TlCl	7791-12-0	XG4200000	1443/2	24 orl-mus
Tin	Sn+2	Tin (II) chloride	SnCl2	7772-99-8	XP8700000	1462/2	700 orl-rat
Vanadium	V(+5)	Vanadium trichloride	VCl3	7718-98-1	YW2800000	1552/2	350 orl-rat
Zinc	Zn+2	Zinc chloride	ZnCl2	7646-85-7	ZH1400000	1572/2	200 orl-gp (350 orl-rat)

[a] An oral-mammal LD50 for uranium species, total dissolved solids, or dissolved gases were not reported in the RTECS documents.[27-29]

[b] RTECS 1983 Supplement to the 1981-1982 Edition,[27,28] unless otherwise noted.

[c] RTECS 1981-1982 Edition, Volume 3, Part 6.[29]

Table 3. Results from application of the screening procedure.[a]

Constituent	Typical valence (oxidation state) in water	Maximum likely concentration (MLC) in water (mg/L)	Lowest oral-mammal median lethal dose (LD50) (mg/kg)	Screening concentration [LD50 • 1.0E-4] (C_s.mg/L)	MLC/C_s	MLC>C_s
Aluminum	Al(+3)	5.0E-01	7.70E+02	7.70E-02	6.49E+00	yes
Ammonium	NH4+	6.0E-01	3.50E+02	3.50E-02	1.71E+01	yes
Arsenic[b]	As(+3,+5)	2.0E-02	4.80E+01	4.80E-03	4.17E+00	yes
Barium	Ba+2	1.0E+00	7.60E+01	7.60E-03	1.32E+02	yes
Boron	B(+3)	1.1E+00	2.66E+03	2.66E-01	4.32E+00	yes
Cadmium	Cd+2	1.0E-02	6.00E+01	6.00E-03	1.67E+00	yes
Calcium	Ca+2	1.6E+02	1.00E+03	1.00E-01	1.65E+03	yes
Carbonate[b]	HCO3-	3.2E+02	4.22E+03	4.22E-01	7.46E+02	yes
Chloride[b]	Cl-	9.6E+02	3.00E+03	3.00E-01	3.20E+03	yes
Chromium	Cr(+3,+6)	7.0E-03	5.00E+01	5.00E-03	1.40E+00	yes
Cobalt	Co+2	6.0E-03	5.50E+01	5.50E-03	1.09E+00	yes
Copper	Cu+2	1.1E-02	3.10E+01	3.10E-03	3.55E+00	yes
Cyanide[b]	CN-	4.0E-02	4.00E+00	4.00E-04	1.00E+02	yes
Fluoride	F-	2.5E+00	8.00E+01	8.00E-03	3.13E+02	yes
Iron	Fe+3	1.5E+00	1.28E+03	1.28E-01	1.17E+01	yes
Magnesium[b]	Mg+2	5.0E+01	2.80E+03	2.80E-01	1.79E+02	yes
Manganese	Mn+2	3.0E-01	1.72E+03	1.72E-01	1.75E+00	yes
Mercury	Hg+2	3.2E-03	1.00E+00	1.00E-04	3.20E+01	yes
Nitrate	NO3-	2.3E+01	3.02E+03	3.01E-01	7.63E-01	yes
Phosphate	PO4-3	1.5E+00	1.29E+04	1.29E+00	1.16E+00	yes
Potassium	K+	1.6E+01	3.65E+02	3.65E-02	4.38E+02	yes
Selenium	Se(+4,+6)	7.0E-03	7.00E+00	7.00E-04	1.00E+01	yes
Sodium	Na+	5.0E+02	3.00E+03	3.00E-01	1.67E+03	yes
Strontium	Sr+2	5.0E-01	2.25E+03	2.25E-01	2.22E+00	yes
Sulfate[b]	SO4-2	7.0E+02	2.34E+03	2.34E-01	2.99E+03	yes
Zinc	Zn+2	2.0E-01	2.00E+02	2.00E-02	1.00E+01	yes

Table 3. (Continued).

Constituent	Typical valence (oxidation state) in water	Maximum likely concentration (MLC) in water (mg/L)	Lowest oral-mammal median lethal dose (LD50) (mg/kg)	Screening concentration [LD50 • 1.0E-4] (C_s, mg/L)	MLC/C_s	MLC>C_s
Antimony	Sb(+3,+5)	4.0E-03	5.25E+02	5.25E-02	7.62E-02	no
Beryllium	Be+2	1.4E-05	8.60E+01	8.60E-03	1.63E-03	no
Bismuth	Bi(+3)	3.0E-03	2.20E+04	2.20E+00	1.36E-03	no
Cesium	Cs+	4.0E-05	5.70E+02	5.70E-02	7.02E-04	no
Iodide	I-	4.0E-02	4.34E+03	4.34E-01	9.22E-02	no
Lead	Pb+2	2.0E-02	1.50E+03	1.50E-01	1.33E-01	no
Lithium	Li+	5.0E-02	5.26E+02	5.26E-02	9.51E-01	no
Molybdenum	Mo(+6)	1.0E-02	1.25E+02	1.25E-02	8.00E-01	no
Nickel	Ni+2	1.0E-02	1.05E+02	1.05E-02	9.52E-01	no
Silver	Ag+	2.0E-03	5.00E+01	5.00E-03	4.00E-01	no
Thallium	Tl+	2.0E-05	2.40E+01	2.40E-03	8.33E-03	no
Tin	Sn+2	2.0E-03	7.00E-02	7.00E-02	2.86E-02	no
Vanadium	V(+5)	1.5E-02	3.50E+02	3.50E-02	4.29E-01	no

[a] No oral-mammalian LD50 was reported for uranium species of interest, total dissolved solids, or dissolved gases in the RTECS[27-29] data; consequently, those constituents are not addressed by this screening procedure.

[b] Inorganic chemical constituents of field water for which field drinking-water quality standards exist.

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Next, we will survey the review literature addressing the toxic and organoleptic properties of each substance appearing in Table 3, as well as uranium, dissolved gases, and TDS (for which oral-mammalian LD50 toxicity data were not available in the RTECS[27-29] data base). The information from this assessment of data contained in the review literature is used to validate the results of the screening procedure.

COMPLEMENTARY DATA-BASE ASSESSMENT

As a consequence of the inherent conservatism of the screening procedure, some of the inorganic constituents listed as being of military concern are categorized incorrectly. Therefore, to identify these substances and to make certain that all of the ones categorized as not being of concern are listed correctly, we analyzed the toxicological data base presented in review literature for each inorganic chemical that was considered a possible constituent of field water (see Table 2). Specifically, the data-base assessment is used to (1) determine quantitatively or qualitatively whether the calculated toxic dose (based on an LD50) for a particular inorganic chemical of interest actually could degrade the performance of military personnel in the field, and (2) to decide whether the toxic dose actually could occur from the consumption of up to 15 L/d of field water containing the MLC for the substance. If the calculated toxic dose can degrade the performance of military personnel and military personnel can receive the toxic dose by consuming up to 15 L/d of water containing the MLC for the substance, then those inorganic chemicals are considered to be of military concern.

Our data-base assessment was also employed for three other very important purposes. First, it was necessary to use the data-base assessment to determine whether or not total dissolved solids (TDS), uranium, dissolved gases, and color and turbidity in field drinking-water supplies can be of military concern. These substances and physical characteristics of field water could not be addressed by the screening procedure because, as mentioned previously, some or all of the data needed to perform the screening calculations (e.g., lowest oral mammalian LD50) were not available. Second, the data-base assessment was essential for determining whether an inorganic substance could be of military concern based on any objectionable organoleptic properties (e.g., color, odor, and taste) in water. Such properties were not addressed by the screening procedure, and objectionable color, odor, or taste could make water unacceptable for consumption by military personnel. For example, personnel refusing to consume water based on objectionable color, odor, or taste could become susceptible to dehydration, which could lead to degraded performance. Finally, our data-base assessment was employed for the purpose of identifying those inorganic constituents of military field drinking-water

supplies for which carcinogenic, mutagenic, teratogenic, or reproductive toxicity have been reported, as well as for indicating those inorganic substances that are considered essential nutrients and that are readily absorbed from the gastrointestinal tract.

DESIGN OF DATA-BASE ASSESSMENT

The data-base assessment we performed was not intended to be a detailed analysis of the toxicity literature for the screened inorganic substances, and uranium, TDS, dissolved gases, color, and turbidity. Such an analysis could not be performed in an expedient, cost-effective manner and would defeat the purpose of a screening procedure entirely. Instead, we chose to survey the literature, particularly detailed review articles, that presented discussions about the toxic, organoleptic, and essential properties and pharmacokinetic behavior of the inorganic constituents of field water. Most of the reports we surveyed underwent comprehensive peer review before their publication. Therefore, we felt confident that the original research of others cited in these reports is presented accurately and precisely and can be used to complement the more automated screening methodology used first.

Much of the data concerned with human health are associated with therapeutic overdoses, poisonings, safe and adequate daily doses, and recommended daily allowances. Therefore, in most cases, we extrapolated from these data to doses per day for comparison with doses per day from the consumption of up to 15 L/d of field water containing the MLC. For the majority of inorganic chemicals examined, the daily dose from water is at least an order of magnitude lower than the reported toxic-effect dose or no-observed-effect level.

RESULTS OF DATA-BASE ASSESSMENT

Detailed summaries of the human health implications attributable to the presence of each of the inorganic substances in military field drinking-water supplies are presented in Appendix B. The inorganic chemicals discussed first in this appendix are those that were addressed by the more automated screening procedure (included among these is uranium), followed by discussions concerning TDS, dissolved gases, and color and turbidity. A summary of the information contained in Appendix B appears in Table 4.

According to the results of the data-base assessment, for the majority of the inorganic constituents of field water, the doses necessary to induce acute or chronic toxicity, which could degrade the performance of military personnel in the field, are not considered to be possible from the consumption of field water, even at a maximum

Table 4. Summary of health implications associated with the inorganic substances that are possible constituents of military field-water supplies and their indicated military importance.

Constituent	Typical valence (oxid. state) in water	Identified as an essential nutrient	Readily absorbed from GI tract	Acute toxicity		Chronic toxicity		Organoleptic threshold concentration likely in water	Identified carcinogenic (C), mutagenic (M), teratogenic (T), and/or reproductive (R) toxicity[a]	Indicated to be of possible military concern
				Degrades military performance	Possible from drinking field water	Degrades military performance	Possible from drinking field water			
Aluminum	Al(+3)	no	no	yes	no	no	no	no	no	no
Ammonia	NH$_4^+$	no	no	no	no	no	no	no	no	no
Antimony	Sb(+3,+5)	no	no	yes	no	no	no	no	no	no
Arsenic	As(+3,+5)	no	yes	yes	no	yes	no	no	C(H),T(A)	yes[b]
Barium	Ba^{+2}	no	no	yes	no	no	no	no	no	no
Beryllium	Be^{+2}	no	no	no	no	no	no	no	C(H)	no
Bismuth	Bi^{+3}	no	no	yes	no	no	no	no	no	no
Boron	B(+3)	no	yes	yes	no	yes	no	no	R(A)	no
Cadmium	Cd^{+2}	no	no	yes	no	no	no	no	C(A),T(A)	no
Calcium	Ca^{+2}	yes	yes	yes	no	yes	no	no	no	no
Carbonate	HCO$_3^-$	no	no	no	no	no	no	no	no	no
Cesium	Cs$^+$	no	no	yes	no	no	no	no	no	no
Chloride	Cl$^-$	yes	yes	yes	no	no	no	yes	no	yes
Chromium	Cr(+3,+6)	yes	yes	yes	no	no	no	no	C(A)	no
Cobalt	Co^{+2}	no	yes	yes	no	no	no	no	no	no
Copper	Cu^{+2}	yes	yes	yes	no	no	no	no	no	no
Cyanide	CN$^-$	no	yes	yes	no	no	no	no	no	yes[b]
Fluoride	F$^-$	yes	yes	yes	no	yes	no	no	no	no
Iodide	I$^-$	yes	yes	no	no	yes	no	no	no	no
Iron	Fe^{+3}	yes	no	no	no	yes	no	yes	no	no[c]
Lead	Pb^{+2}	no	no	no	yes	no	no	no	C(A),T(A)	no
Lithium	Li$^+$	no	yes	yes	no	no	no	no	T(A)	no
Magnesium	Mg^{+2}	yes	yes	no	no	yes	no	yes	no	yes
Manganese	Mn^{+2}	yes	yes	no	no	no	no	no	no	no
Mercury	Hg^{+2}	no	yes	no	no	yes	no	no	no	no
Molybdenum	Mo^{+6}	yes	yes	no	no	yes	no	no	no	no

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Table 4. (Continued)

Constituent	Typical valence (ox. state) in water	Identified as an essential nutrient	Readily absorbed from GI tract	Acute toxicity		Chronic toxicity		Organoleptic threshold concentration likely in water	Identified carcinogenic (C), mutagenic (M), teratogenic (T), and/or reproductive (R) toxicity?	Indicated to be of possible military concern
				Degrades military performance	Possible from drinking field water	Degrades military performance	Possible from drinking field water			
Nickel	Ni^{+2}	no	no	yes	no	no	no	no	no	no
Nitrate	NO_3^-	no	no	no	no	no	no	no	C(H)	no
Phosphate	PO_4^{-3}	yes	yes	yes	no	no	no	no	no	no
Potassium	K^+	yes	no	yes	no	no	no	no	no	no
Selenium	Se(+4,+6)	yes	yes	yes	no	no	no	no	T(H)	no
Silver	Ag^+	no	no	yes	no	no	no	no	no	no
Sodium	Na^+	yes	yes	yes	no	no	no	no	no	no
Strontium	Sr^{+2}	no	no	yes	no	no	no	no	T(A)	no
Sulfate	SO_4^{-2}	no	yes	yes	yes	no	no	yes	no	no
Thallium	Tl^+	no	yes	yes	no	yes	no	yes	T(H,A)	yes
Tin	Sn^{+2}	no	no	no	no	no	no	no	no	no
Uranium	U(+6)	no	no	yes	no	no	no	no	no	no
Vanadium	V(+5)	yes	no	yes	no	no	no	no	no	no
Zinc	Zn^{+2}	yes	no	yes	no	no	no	no	no	no
Total dissolved solids	—[d]	no	no	yes	yes	no	no	yes	NA[e]	yes
Dissolved gases	—[f]	no	no	no	no	no	no	yes	NA[e]	no[f]
Color and turbidity	—	no	no	no	no	no	no	yes	NA[e]	yes

[a] Not necessarily from oral ingestion. (A), laboratory animal data; (H), human data.

[b] Based on the severity of symptoms associated with acute toxicity and used historically as a threat agent for chemical warfare; otherwise, would not ordinarily be of military concern.

[c] Based on the conclusion that the organoleptic properties of iron species are more accurately addressed by considering them in terms of total dissolved solids, color, and turbidity.

[d] Primarily toxic species of inorganic chemicals.

[e] Not applicable.

[f] Only for hydrogen sulfide.

[g] Based on the fact that the aqueous solubility of hydrogen sulfide gas is reduced substantially by aeration and that water containing hydrogen sulfide can be avoided in favor of superior alternative supplies due to the easily recognizable odor (rotten eggs) of hydrogen sulfide gas.

consumption rate of 15 L/d. In fact, as shown in Table 4, chronic toxicity is not considered a likely consequence of drinking 15 L/d of natural water containing the MLC of any of the inorganic chemicals of interest. Moreover, acute toxicity seems to be associated with drinking 15 L/d of field water containing the MLC of only three of the inorganic constituents of interest (magnesium, sulfate, or TDS). Nevertheless, in addition to magnesium, sulfate, and TDS, the inorganic substances and characteristics that are of possible military concern and require further, more detailed analysis are arsenic, chloride, cyanide, and color and turbidity.

Magnesium, sulfate, and TDS are of possible military concern for both toxic and organoleptic reasons. Chloride, color and turbidity, are possibly of military concern strictly on the basis of organoleptic considerations. Our reasons for identifying arsenic and cyanide as being of possible military concern are not as straightforward. Typically, these inorganic substances do not appear in natural water at concentrations high enough to degrade the performance of military personnel, even if must to consume 15 L/d of field water. Furthermore, there is no organoleptic property that indicates these substances could be of possible military concern. However, both arsenic and cyanide are well-known for their lethal effects in humans, and under unusual circumstances, military personnel could encounter a field-water supply that might contain an elevated level of arsenic or cyanide sufficient to degrade their performance, especially if they must consume field water at the rate of 15 L/d. Additionally, there are standards for arsenic and cyanide in current versions of military field manuals, presumably because these two substances could be present at high concentrations as a consequence of chemical warfare activity and not necessarily industrial pollution. Thus, the combination of all of these factors (e.g., lethal toxicity, standards in current field manuals because of possible introduction of chemical warfare agents into field water, etc.) warranted identifying arsenic and cyanide as being of possible military concern. However, the possibility of these two chemicals being of concern probably is more remote than for the other substances included on this list.

We concluded from our data-base analysis that none of the other substances was indicated to be of possible military concern. For instance, iron was not identified as being of military concern, even though its organoleptic-detection threshold for taste can occur in water, because (1) the organoleptic-detection threshold is not a concentration that would degrade performance if consumed, and (2) the organoleptic-detection threshold would not necessarily discourage troops from consuming the water. Furthermore, iron is a constituent of TDS and, therefore, will be present with other constituents of TDS that possess organoleptic thresholds; consequently, all of the organoleptic properties can be addressed collectively by evaluating the TDS concentration, turbidity, and color.

Additionally, dissolved gases are not likely to constitute a problem for military personnel. To illustrate, hydrogen sulfide, which has a characteristic rotten-egg odor as a dissolved gas in water, can represent a nuisance, but is not indicated to be of possible military concern because it is easily dissipated by aerating the water before consumption. Although this may be a time-consuming process, it effectively alleviates the undesirable nuisance odor so that the water will be palatable.

The carcinogenic, mutagenic, teratogenic, and reproductive toxicity reported for each substance is included in Table 4 and mentioned in the discussions of each inorganic constituent addressed in Appendix B. Only arsenic is distinguished as being carcinogenic in humans and teratogenic in laboratory animals among the inorganic chemicals indicated to be of military concern. These adverse health consequences could only be qualitatively identified on the basis of data available in the review literature.

The results from the data-base assessment discussed in Appendix B validate those obtained from application of the more automated screening procedure in terms of excluding from further consideration those inorganic constituents that typically are of no military concern. However, the data-base analysis verified that the more automated screening procedure was too conservative because it incorrectly identified many substances that are not of military concern as being of potential concern.

Appendix C reviews the human health implications that can result from external exposure to the inorganic constituents possible in military field-water supplies. The information in Appendix C is summarized in Table 5. Only cyanide may be of military concern in relationship to external exposure from bathing, swimming, or showering.

SUMMARY AND RECOMMENDATIONS

Our screening procedure and data-base analysis indicate that arsenic, chloride, cyanide, magnesium, sulfate, TDS, color, and turbidity are the only constituents of field-water supplies that are of possible military concern from the standpoint of degrading troop performance. Although these inorganic substances and physical properties do have drinking-water standards in current versions of military manuals, we recommend that detailed analyses be performed concerning each of these substances so that updated water-quality criteria and recommendations for standards can be derived from such analyses. Furthermore, we conclude from our screening procedure and complementary data-base analysis that the organoleptic-detection threshold for the taste of iron is best addressed by criteria and recommended standards for TDS, turbidity, and color particularly, because (1) iron is a component of the TDS concentration, (2) it possesses a

Table 5. Summary of health implications associated with external exposure of military personnel to inorganic constituents of field-water supplies.

Constituent	Typical valence (oxid. state) external exposure	Health effects possibly of military concern	Indicated to be of possible military concern in water
Aluminum	$Al(+3)$	no	no
Ammonia	NH_4^+	yes	no
Antimony	$Sb(+3,+5)$	yes	no
Arsenic	$As(+3,+5)$	yes	no
Barium	Ba^{+2}	no	no
Beryllium	Be^{+2}	no	no
Bismuth	$Bi(+3)$	no	no
Boron	$B(+3)$	no	no
Cadmium	Cd^{+2}	no	no
Calcium	Ca^{+2}	no	no
Carbonate	HCO_3^-	no	no
Cesium	Cs^+	no	no
Chloride	Cl^-	no	no
Chromium	$Cr(+3,+6)$	yes	no
Cobalt	Co^{+2}	no	no
Copper	Cu^{+2}	no	no
Cyanide	CN^-	yes	yes
Fluoride	F^-	no	no
Iodide	I^-	yes	no
Iron	Fe^{+3}	no	no
Lead	Pb^{+2}	no	no
Lithium	Li^+	no	no
Magnesium	Mg^{+2}	no	no
Manganese	Mn^{+2}	no	no
Mercury	Hg^{+2}	yes	no
Molybdenum	Mo^{+6}	no	no
Nickel	Ni^{+2}	yes	no
Nitrate	NO_3^-	no	no

Table 5. (continued).

Constituent	Typical valence (oxid. state) external exposure	Health effects possibly of military concern	Indicated to be of possible military concern in water
Phosphate	PO_4^{-3}	no	no
Potassium	K^+	yes	no
Selenium	Se(+4,+6)	yes	no
Silver	Ag^+	yes	no
Sodium	Na^+	no	no
Strontium	Sr^{+2}	no	no
Sulfate	SO_4^{-2}	no	no
Thallium	Tl^+	yes	no
Tin	Sn^{+2}	no	no
Uranium	U(+6)	no	no
Vanadium	V(+5)	yes	no
Zinc	Zn^{+2}	yes	no

taste threshold in water that is not related directly to performance-degrading toxic effects, and (3) field troops may not be discouraged from consuming field water based on the taste-detection threshold.

Our comparisons between MLC and C_s values, in conjunction with the complementary data-base analysis, show that there is a very low probability that most inorganic constituents of field water will cause direct, debilitating health effects in troops. However, this assumes that troops follow existing doctrine regarding the placement of water-supply points. Siting a water-supply point directly below a sewage outfall on a stream or river, or in waters expected to have been sabotaged by opportunity poisons or chemical warfare agents, for example, greatly enhances the risk of health effects. Likewise, the use of a well that is in the immediate vicinity of actual or possible surface industrial contamination poses an increased health risk. Avoiding these obvious situations is a key precaution in the management of health risks from field-water contaminants.

APPPENDIX A

ESTIMATED MAXIMUM LIKELY CONCENTRATIONS (MLCs) FOR INORGANIC SUBSTANCES IDENTIFIED AS POSSIBLE CONSTITUENTS OF MILITARY FIELD-WATER SUPPLIES

We surveyed the literature concerning water-related priority pollutants and the chemical composition of natural waters to identify those inorganic substances that represent probable constituents of military field-water supplies. For each of the 40 individual inorganic substances that we identified and for the dissolved inorganic substances identified collectively as total dissolved solids (TDS), we estimated a maximum likely concentration (MLC) that could be present in fresh waters that normally occur in nature. These estimated MLC values are an integral part of our approach for determining the inorganic substances in field-water supplies that could be of military concern. The purpose of this appendix is (1) to explain the basis of our MLC estimates, (2) present the MLC estimate for each of the 40 inorganic substances and TDS, and (3) provide a brief review of the geochemistry of each substance in those fresh waters that normally occur in nature. We include the brief review of the geochemistry of each inorganic substance because the MLC for each of these substances in natural waters ultimately depends upon their geochemical behavior.

BASIS FOR MLC ESTIMATES

The basis of our MLC estimates for the 40 inorganic substances and TDS that we identified as the possible inorganic constituents of military field-water supplies is the published and computerized collections and compilations of surface-water-quality monitoring data for the United States. We used these sets of water-quality monitoring data primarily for the following reasons. First, only for U.S. surface waters are reliable concentration data available for the vast majority of both common inorganic constituents and trace elements. Second, these concentrations already appear in formats that make it possible to statistically analyze the data expediently and cost-effectively. Unfortunately, foreign ground- and surface-water-quality monitoring data could not be used because there is a paucity of these data. The small amount of reliable foreign water-quality monitoring data that does exist is incomplete chemically; only concentrations of common inorganic constituents are routinely reported, and trace-element concentration data virtually never appear. In fact, much of the existing U.S. groundwater-quality monitoring data could not be used because only a portion of these data has been reduced to formats

that would make it possible to statistically analyze the data expediently and cost-effectively. Finally, the U.S. surface-water-quality monitoring data can be considered to represent an approximation of water quality expected worldwide because surface waters from all regions of the United States are monitored, and the United States is a relatively large geographic area with heterogeneous climates, rock types, environments, and water quality. These data even include some measurements of the concentrations of inorganic substances in waters in Hawaii and Puerto Rico, where humid, tropical conditions exist.

Although we used only a limited amount of the available U.S. groundwater-quality monitoring data to estimate MLC's, we recognize that there will almost always be fairly small differences between the concentrations of inorganic chemicals in ground and surface waters. These differences can be attributed to very complex chemical reactions between chemical substances in ground water and the soil environment through which the ground water flows. For example, ground water may leach chemical constituents from the rock particles in the aquifers through which it moves, which would suggest that the chemical concentrations of slightly soluble substances often present in such rocks would be higher in ground water than in surface water. However, sorption effects that can remove elements from water in contact with rock particles are more efficient in ground water systems than in surface-water systems. Thus, it is very difficult to predict the potential additions and decreases of various substances in ground water relative to surface water, even in the same region. Nevertheless, a cautious generalization is possible: ground water may contain somewhat higher concentrations of the slightly soluble chemical constituents of the rocks comprising its aquifer than the surface water from which it arises. There are two companion reports that contain data reflecting this cautious generalization for the chemical differences between surface and ground waters. The first report is by Livingstone[3] and discusses the chemical properties of surface water. The other report, by White et al.,[30] describes the chemical characteristics of ground water.

Sources of Data for MLC Estimates

Most collections and compilations of water-quality monitoring data for waters in the United States have been prepared by the Water Resources Division of the U.S. Geological Survey (USGS). For example, Durfor and Becker[7] collected extensive chemical data on the public-water supplies of the 100 largest U.S. cities; a number of these water supplies are obtained from ground water. Later, when interest in the distribution of certain potentially toxic trace elements had intensified, and analytical techniques had improved, Durum et al.[11] obtained trace-element data from over 700 monitoring stations

located in surface waters across the United States. More recently, a continuing project to compile water-quality data for the United States was undertaken by the USGS; the data from several hundred thousand water-quality monitoring stations in the United States are being stored in a data base entitled WATSTORE. Smith and Alexander[8] extracted two subsets of the data contained in the WATSTORE data base for the years 1974 through 1981 and summarized some of this information. The summary of the smaller of the two data sets is entitled BENCHMARK; it was chosen to represent essentially undisturbed conditions for use as baseline measurements. The second data-set summary is entitled the National Stream Quality Assessment Network (NASQAN) and consists of data from over 300 monitoring stations chosen to represent the major surface-water features of the United States.

A few collections of water-quality monitoring data not assembled by the USGS also are available. One of these was prepared by Greathouse and Craun[10] as part of a study concerning the relationship between cardiovascular disease and water quality. This particular compilation of water-quality monitoring data is important because it contains concentration levels for some of the more unusual elements.

Each of the previously mentioned data bases has advantages and shortcomings for estimating MLC values. The NASQAN data have by far the most data points; however, the analytical techniques used to obtain the data were not always the most sensitive. For instance, the detection threshold for cadmium in the NASQAN data base is equal to the U.S. Drinking Water Standard. Nevertheless, we did use Smith and Alexander's[8] summary of the NASQAN data to estimate MLC values whenever more precise data were unavailable. The data compiled by Durum et al.[11] were collected using superior analytical techniques, and so, whenever possible, we used these data to estimate the MLC values. Unfortunately, a shortcoming of the data compiled by Durum et al.[11] is that common water-quality constituents were not included; therefore, no correlations can be made between trace-element concentrations and the concentrations of the more common chemical constituents of these monitored waters. However, for those elements of interest that were not included in the Smith and Alexander[8] summary of NASQAN data, we obtained MLC values using the data of Durfor and Becker[7] that were obtained using acceptably accurate analytical techniques. When none of the previously mentioned data bases contained needed information about a particular substance of interest, we used Greathouse and Craun[10] as a resource. Finally, in those cases where the data we needed were not contained in any of the references, we estimated the MLC from information obtained from a search of the geochemical literature.

Methodology for Estimating MLC's

Our methodology for estimating MLC'S began with statistical analysis of the data from the larger data bases. Generally, the concentration data for the inorganic substances of interest contained in these larger data bases were found to be lognormally distributed. We concluded that a reasonable estimate of the MLC for these lognormally distributed data would be the concentration with a probability less than or equal to 5% of being greater than any measured value. Accordingly, we chose as an MLC value for these substances as the concentration that corresponds to the 96th cumulative percentile. Consequently, the probability of the actual MLC being greater than this selected value is less than 5%. Durfor and Becker[7] used a similar technique to show that over 90% of the public water supplies that were monitored contained concentrations that were lower than a specific concentration selected for a particular constituent (i.e., <10% probability that concentrations would be greater than that selected for the constituent). When the MLC for a particular substance of interest could not be calculated in this manner because of insufficient data, we made the best possible estimate of the MLC from the data that were available.

MLC ESTIMATES

In this part, we present our estimates of the MLC's for the 40 inorganic substances and TDS identified as possible constituents of concern in natural waters. These estimates are accompanied by brief reviews of the geochemistry of each substance in natural waters. Before we present the MLC estimates, we describe the range of Eh (oxidation/reduction potential) and pH (acidity/alkalinity state) that defines typical natural water, and we indicate the chemical processes that can take place in such waters that can directly affect the concentration of dissolved inorganic substances.

Typical Natural Water and Related Eh, pH, and Chemical Processes

The vast majority of fresh waters that represent potential sources of military field-water supplies are typical natural waters. Generally, two important chemical characteristics of water are found within relatively restricted limits in typical natural water. The limits of these characteristics can be used to define such natural water. These are the oxidation/reduction potential (Eh) and the acidity/alkalinity state (pH). The oxidation/reduction potential of natural water is measured by Eh. This quantity is a measure of oxidation state, with a zero value indicating a neutral state. According to

Hem,[6] the Eh range of typical natural water is from +0.8 V (well oxidized) to -0.4 V (moderately reduced). Values of Eh seldom vary far from these bounds, even in unusual waters.[6] The acidity of water is measured by pH, the negative logarithm to the base 10 of the hydrogen-ion concentration. A pH value of 7 is neutral; a pH value less than 7 indicates acid water, while a pH value greater than 7 indicates alkaline water. Hem[6] states that the range of pH in natural water is from 5 to 9. We consider this to be a very conservative estimate because the NASQAN data base[8] shows that the vast majority of waters sampled had pH values between 6.4 and 8.5, which corresponds to an arithmetic mean pH value of 7.4. Thus, most natural waters have a near-neutral pH, with a slightly alkaline mean value. A more detailed discussion of Eh and pH in natural water is provided by Hem.[6]

The unusual natural waters, those with pH values occurring outside of the normal range, are often more acidic than typical natural waters (i.e., pH less than about 5). These waters occur in geologically unusual environments such as hot springs, volcanic fumaroles, steam emissions, and mine waters. At such low pH levels, many metals are far more soluble than they are in typical natural water and under such conditions they may reach toxic levels. However, a geological reconnaissance usually will indicate the presence of such unusual situations and these waters can be avoided.

Most trace elements are present only in low concentrations in natural water. There are several processes responsible for maintaining these concentrations. These processes are listed below.

1. Most Group II elements form slightly soluble compounds with sulfates, carbonates/bicarbonates, or hydroxides/oxides, all of which are common in natural waters. Most Group V or VI trace elements, usually as oxide complexes, form slightly soluble compounds with calcium, and sometimes, magnesium ions.

2. Sorption phenomena that physically or chemically bind many trace-element molecules to particulate matter can remove these elements from natural water.

3. Changes in pH and Eh affect the solubility of many trace elements. Elements particularly affected include arsenic, cadmium, iron, manganese, selenium, and uranium.

4. The formation of complexes of trace elements and either organic or inorganic matter present in water affect solubility. The complexes formed will have different chemical characteristics from those of the components. These characteristics usually include greater solubility but lower toxicity than the uncomplexed trace elements.

5.   Low concentrations of many trace elements are a function of the rarity of the element.   For example, silver, bismuth, cesium, and thallium are almost never present at saturation levels in natural water.   Other elements, for example selenium, are rare in some regions and concentrated in others.

The effectiveness of the removal processes in extracting large fractions of trace elements from natural water can be dramatic. For example, the mercury concentration in river water downstream from a natural mercury deposit was found to decrease from 0.135 mg/L to 0.00004 mg/L in a 50-km (30-mile) reach of the river.[19]

Many of the previously discussed processes are affected by salinity. In estuaries, where fresh water mixes with sea water, many elements that have been sorbed on particulate matter in fresh water will desorb and display higher concentrations. In seawater, concentrations of most trace elements are stable, and therefore the chemical composition of seawater is not very different in most environments. Table A-1 shows concentrations of a number of trace elements in seawater.

While most trace elements are present only in small quantities in natural water, several potentially toxic elements can be present at relatively high levels. Among these are arsenic, selenium, and cadmium. However, toxic amounts of arsenic are unlikely in natural waters except very near natural deposits or sources of pollution. Selenium is rare in many regions, but present in potentially troublesome quantities in others. Selenium is both soluble and stable in oxidized, slightly alkaline natural water, and if there is a supply of selenium from a natural source, then relatively large concentrations of the element are possible in natural waters. Furthermore, cadmium is rare in many areas, but surprising concentrations are found in natural waters over wide geographic regions. For example, all the stations sampled by Durum et al.[11] in the state of Alabama had cadmium concentrations higher than the U.S. standard. The solubility of cadmium carbonates, sulfates, and hydroxides are relatively high, and sorption and complexation are not that effective in lowering concentrations of cadmium. If an effluent from a pollution source such as a metal plating shop were to enter natural water, it is possible that amounts sufficient to be acutely toxic could be present. It would seem to be a prudent practice to be aware of this possibility when operating in unexplored industrialized regions, especially near cities in underdeveloped countries.

Aluminum

The MLC for aluminum in natural water is 0.5 mg/L as dissolved aluminum. This MLC estimate is based on the 96th cumulative percentile of aluminum concentrations

Table A-1. Concentrations of inorganic substances in seawater.[a]

Constituent	Typical dissolved species	Concentration in seawater (mg/L)
Aluminum	--	1.0E-03
Antimony	--	3.0E-04
Arsenic	$HAsO_4^{-2}$; $H_2AsO_4^-$	2.6E-03
Barium	Ba^{+2}	2.0E-02
Beryllium	--	6.0E-07
Bismuth	--	2.0E-05
Boron	$B(OH)_3$; $B(OH)_4^-$	4.5E+00
Cadmium	Cd^{+2}	1.0E-04
Calcium	Ca^{+2}	4.1E+02
Carbonate/bicarbonate	HCO_3^-; CO_3^{-2}	2.8E+01
Cesium	Cs^+	3.0E-04
Chloride	Cl^-	1.9E+04
Chromium	CrO_4^{-2}; Cr^{+3}	5.0E-04
Cobalt	Co^{+2}	4.0E-04
Copper	Cu^{+2}	3.0E-03
Fluoride	F^-	1.3E+00
Iodide	IO_3^-; I	6.0E-02
Iron	--	3.0E-03
Lead	$PbCl_3^-$; $PbCl^+$; Pb^{+2}	3.0E-05
Lithium	Li^+	1.7E-01
Magnesium	Mg^{+2}	1.3E+03
Manganese	Mn^{+2}	2.0E-03
Mercury	$HgCl_4^{-2}$; $HgCl_2^0$	2.0E-04
Molybdenum	MoO_4^{-2}	1.0E-02

Table A-1. (continued)

Constituent	Typical dissolved species	Concentration in seawater (mg/L)
Nickel	Ni^{+2}	7.0E-03
Nitrate	NO_3^{-}	6.7E-01
Phosphate	HPO_4^{-2}; $H_2PO_4^{-}$; PO_4^{-3}	9.0E-02
Potassium	K^{+}	3.9E+02
Selenium	SeO_4^{-2}	9.0E-05
Silver	$AgCl_2^{-}$	3.0E-04
Sodium	Na^{+}	1.1E+04
Strontium	Sr^{+2}	8.0E+00
Sulfate	SO_4^{-2}	9.0E+02
Thallium	Tl^{+}	<1.0E-04
Tin	--	8.0E-04
Uranium	$UO_2(CO_3)_3^{-4}$	3.0E-03
Vanadium	$VO_2(OH)_3^{-2}$	2.0E-03
Zinc	Zn^{+2}	1.0E-02

[a] Adapted from Goldberg et al.[31]

reported by Durfor and Becker.[7] More recent data from the NASQAN data base could not be used to estimate the MLC because the detection threshold for aluminum was so high in this data base that relatively few data points were recorded. The concentration of dissolved aluminum may be artificially elevated in some of the measurements because of the presence of submicron particles of aluminum oxide, which pass through the filters used to prepare water for analysis of aluminum. This matter is discussed later in this section.

Although aluminum is the third most abundant element in the earth's outer crust, it seldom appears in natural waters in concentrations as high as 1 mg/L; the exceptions are

waters of abnormally low pH. Aluminum is a major component of virtually all rock-forming minerals, which basically are aluminum silicates with varying amounts of other elements.

The geochemistry of aluminum is complex. There is an excellent discussion of this complex geochemistry by Hem,[6] and much of this summary is derived from it. Aluminum is a hydrosolic metal with an insoluble hydroxide, $Al(OH)_3(s)$, that forms a sol (a colloidal suspension of low viscosity) in natural waters with pH between 5 and 9.[32] The maximum solubility of aluminum is a little less than 0.001 mg/L in water with a pH near 6.0, a low dissolved-solids content, and less than 0.01 mg/L of fluoride.[6] Higher concentrations of fluoride increase the solubility of aluminum, at least in part, by forming strong complexes of aluminum and fluoride (AlF^{+2} and AlF_2^+). These complexes have different chemical characteristics from those of either parent element.

A problem in measuring dissolved aluminum (Al^{+3}) correctly in natural water is the presence of insoluble colloidal aluminum hydroxide. This inert material may pass through the filters normally used in preparing water samples for analysis. Consequently, the analytical techniques typically used will include this inert material in the results for Al^{+3}. The presence of dissolved aluminum-fluoride complexes in the water can also contribute to the amount of Al^{+3} measured, even though the complexes are different chemically from the dissolved metal. These factors may result in measurements of dissolved-aluminum concentrations as high as 1 mg/L, when the actual concentration of Al^{+3} is much less.

Water with pH less than 4.0 may contain several hundreds of milligrams per liter of aluminum in true solution, and the cation Al^{+3} predominates in many such solutions.[6] Such waters occur in mine drainage and in some springs. One of the more unusual aspects of the acid-rain problem is the mobilization of aluminum from rock-forming minerals in lakes containing low-pH waters. Such lakes are most commonly found in granitic terrain where the water is unbuffered by the presence of carbonate and bicarbonate ions. However, once such water leaves the low-pH environment of the lake, the unusual levels of dissolved aluminum would be expected to decrease.

Ammonia

The estimated MLC of ammonia in natural water, based on the 96th cumulative percentile of ammonia concentrations reported in the NASQAN data base, is 0.6 mg/L as ammonium ion (NH_4^+).[8]

Ammonia can be generated by volcanic activity, but most commonly it is introduced into water as the product of natural biological activity or from use as a fertilizer. Ammonia and the ammonium ion are reduced forms of nitrogen that are not very stable in water and eventually oxidize to nitrates.

Antimony

The estimated MLC of antimony in natural water is 0.004 mg/L. This estimate is based on limited data in Greathouse and Craun.[10] Other data are very sparse, and dissolved-antimony measurements were not available from the other information sources used.

The chemistry of antimony resembles that of arsenic. While some compounds of antimony, such as antimony chloride, are very soluble in aqueous solution, the oxides usually occur in natural water, with the trivalent form, Sb(+3), occurring as Sb_2O_3, and the pentavalent form, Sb(+5), occurring as Sb_2O_5.[9] Presumably, the trivalent antimonous ion is stable in moderately reducing environments with pH levels between 5 and 9, while the pentavalent antimonic ion is stable in oxidizing environments, as is the case for the corresponding arsenic ions.

Antimony is not a common element, but is found in sulfide ore deposits as the sulfide. It finds wide use in electronic equipment and therefore may be included in the effluents of facilities manufacturing such equipment.

Arsenic

The estimated MLC of arsenic in natural water is 0.02 mg/L. This value corresponds to the 96th cumulative percentile of total-dissolved-arsenic concentrations reported by Durum et al.[11] These data were used in preference to those reported in the NASQAN data base because more sensitive measurement techniques were employed. The levels in natural water near arsenic-bearing mineral deposits can be considerably higher than the MLC; such localities can be identified by their geologic characteristics.

Arsenic is commonly found as the sulfide in mineral deposits, and is sometimes found dispersed as arsenopyrite (FeAsS) in rocks where pyrite might normally be found.[6] Some parts of the United States, such as Arkansas and southern Missouri, have slightly elevated values for arsenic, presumably from dispersed arsenopyrite in the region.

Discussions of the aqueous geochemistry of arsenic are presented by Faust and Aly[20] and Hem.[6] At pH values between 5 and 9, which are characteristic of natural water, and under mildly reducing conditions, the trivalent form of arsenic, As(+3), is stable as the

anion $HAsO_3^{-2}$. Under the more oxidizing conditions characteristic of aerated natural water, the pentavalent form of arsenic, As(+5), is stable as the anion, $HAsO_4^{-2}$. Because the trivalent form is more toxic, the mildly reducing conditions are more critical. In the pH range of natural water (i.e., pH between 5 and 9), several tens of milligrams per liter of total arsenic may be in solution; ultimately, the concentration is controlled by the solubility of calcium or magnesium arsenate. Some minor metal ions, such as Cu^{+2} at concentrations of a few tens of micrograms per liter, will limit the solubility of arsenic to a few tenths of a milligram per liter. Another factor that can limit the concentration of arsenic in natural water is sorption of arsenate ion on surface-active ferric hydroxide or other particulates. Arsenic also complexes with humic and fluvic material, and these complexes are also bound to particulate matter.[33]

Barium

Barium is widely used in industry and is a fairly common element in igneous rocks; it is also found in sedimentary rocks, frequently as the sulfate, barite ($BaSO_4$). The estimated MLC of barium in natural surface water is 0.2 mg/L, based on the 96th cumulative percentile of occurrences both in NASQAN[8] and from Durfor and Becker.[7] The concentration of barium as Ba^{+2} in water is limited by the low solubility of barium sulfate when sulfate is present in the water. Many ground waters contain little sulfate, and therefore such ground water is estimated to have an MLC of 1 mg/L of barium in solution.

Beryllium

The estimated MLC of beryllium in natural water is very low. Very few measurements are available. Using special techniques, Burba et al.[13] made several analyses of German river waters; the MLC of dissolved beryllium based on these data is 0.000014 mg/L. Burba et al.[13] comment that because of the toxicity of dissolved beryllium (Be^{+2}) in water, a standard of 0.0001 mg/L has been suggested in Germany, although nowhere has a beryllium standard been established.

Beryllium is found widely dispersed in rock-forming minerals. Its solubility in natural water is very low. While beryllium sulfate and beryllium chloride are very soluble, they hydrolyze quickly to the insoluble beryllium hydroxide in the pH range (5 to 9) of typical natural water.[17]

Uncomplexed beryllium, usually as the insoluble hydroxide, is easily fixed on finely dispersed particles that will pass through a 0.45-micron filter. These insoluble particles

are inert chemically, but it is possible that they may be measured together with dissolved beryllium. Beryllium is known to form strong complexes with fluoride, and Wedepohl[12] suggests that some beryllium transport may take place in natural waters with beryllium in the form of organometallic fluoroberyllates.

Bismuth

The estimated MLC of bismuth in natural waters is 0.003 mg/L. This value is estimated from data presented by Greathouse and Craun.[10] Bismuth was reported at 1.4% of their sampling stations. Apart from this single reference, documented measurements of bismuth in natural waters are very sparse. The MLC in seawater is 0.00004 mg/L, according to Wedepohl.[12]

Bismuth is usually found as a minor constituent of various ore minerals. Trivalent bismuth, Bi(+3), is the characteristic oxidation state in water, and Vinogradov, as cited by Wedepohl,[12] expects that bismuth would occur in seawater as cationic BiO^+ or as $BiOCl$.

Boron

The estimated MLC of boron in natural water is 1.15 mg/L, based on the 96th cumulative percentile of the occurrences in the NASQAN data base.[8]

Volcanic rocks are the most common sources of boron. In some areas, notably in eastern California and adjacent Nevada, high concentrations of boron accumulate in some of the internal drainage-basin lakes characteristic of the region. Boron complexes have been found in the evaporitic salts characteristic of these high-salinity lakes.[6]

The chemistry of boron, B(+3), in aqueous solution is intricate and not very well known. The simplest assumption is that orthoboric acid (H_3BO_3) species are the most likely to be found in natural water systems. Calculations indicate that the acid is undissociated in the pH range of typical natural water (i.e., pH between 5 and 9).

Cadmium

The estimated MLC of cadmium in natural water is 0.010 mg/L, based on the 96th cumulative percentile of total-dissolved-cadmium occurrences reported by Durum et al.[11] These data were chosen rather than those presented in NASQAN because of the more sensitive analytical technique that was employed in monitoring for cadmium.

Cadmium is commonly found in zinc minerals and is commercially produced as a by-product of refining zinc and copper.[14] The metal is much rarer than zinc; the ratio

between cadmium and zinc in the outer crust of the earth is approximately 1:1000.[14] Waters near mineral deposits containing cadmium tend to contain concentrations of cadmium considerably higher than the MLC that we estimate. Such waters can usually be recognized by their geological characteristics.

Cadmium is commonly used in industry, in electrical equipment, and in plating shops. Larger amounts of cadmium might be expected in water bodies near the entry point of effluents from such industrial sources, and indeed a number of reports describe such occurrences, for example, Shephard et al.[34] Even in underdeveloped regions, such relatively low-technology facilities as plating shops are common sources of cadmium effluents, especially because pollution-control techniques are less likely to be used in these underdeveloped countries. Many plumbing fixtures are cadmium-plated, and data for drinking-water samples from these fixtures tend in many cases to show slightly higher levels of cadmium than the raw water.

Until recent years, the measurement of small but potentially toxic quantities of cadmium in natural water was difficult; the detection threshold for the most commonly used technique was 0.01 mg/L -- a concentration that is equivalent to the U.S. standard and the MLC estimated here. Durum et al.[11] used atomic absorption spectroscopy, which has a sensitivity of 0.001 mg/L for cadmium in water. Whereas earlier studies tended to show no cadmium in most water supplies, Durum et al.[11] detected concentrations of more than 0.001 mg/L in 46% of the sources monitored.

The geochemistry of cadmium has been the subject of relatively intensive study in recent years, and a reasonably clear understanding of its complex behavior in natural water has emerged. Hem,[14] in a discussion of the data collected by Durum et al.,[11] calculated solubilities of various inorganic compounds of cadmium and summarized the Eh-pH relationships of these compounds. Over a relatively wide range of pH (from approximately 5 to 8) and at oxidizing Eh values, the dominant form is divalent cadmium, Cd^{+2}, which is relatively soluble. At higher pH and the same Eh values, insoluble cadmium carbonate occurs. Under reducing conditions, with Eh less than +0.2 V, and over the entire range of pH in natural water, the stable state is cadmium sulfide, which is very insoluble.[14]

In fresh water with pH less than 8, cadmium concentrations usually are far lower than the maximum concentration compatible with the solubility product of the carbonate, which probably is the least soluble salt in oxidizing natural waters.[14,35] It is likely, according to Gardiner,[35] that adsorption on solids and complexation are major factors influencing the distribution of cadmium between aqueous and solid phases. Gardiner concludes from a series of laboratory experiments that the adsorption of cadmium on mud solids from rivers and lakes is probably of major importance in controlling the

concentration of cadmium in fresh water, and that the major component of mud responsible for adsorption -- or complexation in some cases -- is humic material included in the mud. Other substances are also involved in adsorption, including such surface-active materials as iron and manganese hydroxide particles.[6] Gardiner[35] states that when sediments carrying adsorbed cadmium are brought into an anaerobic environment, such as that beneath the surface of bottom sediment in streams or reservoirs, the cadmium probably forms highly insoluble cadmium sulfide and is thus fixed.

Even with adsorption and complexation, the most insoluble cadmium salts are sufficiently soluble to permit concentrations of cadmium (Cd^{+2}) in natural waters to reach levels that can exceed the U.S. standard of 0.01 mg/L.

There is a reasonably strong pattern of regionality in the distribution of cadmium in natural waters in the United States. Water sources with relatively high levels of cadmium are found in the eastern U.S.; the western states appear to have generally lower concentrations. For example, the data stations reported by Durum et al.[11] for the entire state of Alabama exceed the U.S. standard for cadmium. Durum et al.[11] and Hem[14] conclude that much of the cadmium in natural waters is derived from rainout or adjacent pollution sources.

Calcium

The estimated MLC of calcium, a common constituent of natural water, is 165 mg/L, based on the 96th cumulative percentile of the data in the NASQAN data base for U.S. surface waters.[8] Somewhat higher concentrations are probable in those high-salinity drinking waters in many desert areas of the world that are used for lack of better water. The ultimate maximum solubility of calcium is limited by the solubility of calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), and dolomite [$CaMg(CO_3)_2$]. The usual dissolved form of calcium in natural water is the divalent cation Ca^{2+}. Calcium does form complexes with both organic and inorganic substances, but under most conditions these are seldom present in major amounts. The ion pair (a complex), $CaSO_4(aq)$, can have a noticeable effect on the solubility of calcium salts when the sulfate concentration in the water is high.

Calcium is the dominant cation in natural waters. Although some calcium salts enter water as a result of leaching from igneous rocks, this process is relatively slow. Most of the calcium salts found in natural water are probably the result of leaching from slightly soluble carbonate rocks, where calcium makes up part of calcite and aragonite

(both $CaCO_3$ but with different crystal structure), and dolomite $[CaMg(CO_3)_2]$. Additionally, much of the cement that binds sedimentary rocks, such as sandstone, is composed of calcium carbonates, and this too contributes to the calcium content of natural water.

Carbonate/Bicarbonate

The estimated MLC of this common constituent in natural waters is 315 mg/L as bicarbonate (HCO_3^-), based on the 96th cumulative percentile of NASQAN data.[8] Bicarbonate concentrations were converted from measurements of total alkalinity as $CaCO_3$ reported by Smith and Alexander,[8] by multiplying by the factor, 1.219.[6] There are potable waters that are supersaturated with carbon dioxide and thus saturated with carbonate/bicarbonate ion. For most natural waters at normal pH, the bicarbonate ion predominates. Undissociated carbonic acid occurs at pH less than 5, while carbonate ion increases at a pH greater than about 8.0.[6]

The primary source of bicarbonate ion in water is dissolved carbon dioxide, and usually large amounts are present in waters that have been in contact with slightly soluble carbonate rocks. The concentration of carbonate/bicarbonate is ultimately limited by the solubility of calcium carbonate and calcium-magnesium carbonate (dolomite). However, waters low in calcium and magnesium may contain as much as 1100 mg/L of carbonate/bicarbonate ion.[6]

Cesium

Cesium is found in small quantities in some rock-forming minerals. It is one of the alkali metals, which include sodium, potassium, and lithium. Cesium is present in water as the cation Cs^+. However, cesium is not routinely measured in water analyses, and only a few data have been located. These were reported in papers by Kharkar et al.[15] and Sreekumaran et al.[16] Based on these data, the estimated MLC of cesium dissolved in natural water is 0.00004 mg/L. Cesium is found in small quantities in some rock-forming minerals.

While there have been few papers discussing the chemistry of cesium in natural waters, the radioisotope, cesium-137, is an important fission product of nuclear reactors and weapons tests. Cesium-137 has a moderately long half-life and emits relatively high levels of ionizing radiation. For this reason, the behavior of ^{137}Cs in the aqueous environment has been studied in great detail. Cesium-137 is quite readily sorbed on particulate matter, most of it soon after it has been introduced into water. This is

especially true of ground water, where the water and its dissolved constituents are brought into intimate contact with rock particles. Most surface waters, however, contain sufficient suspended particulate matter to sorb large amounts of dissolved cesium. It is not unreasonable to suppose that the stable isotope of cesium resembles the radioisotope ^{137}Cs with regard to sorption. Thus, most cesium that finds its way into water is probably sorbed very quickly onto particulate matter.

Chloride

The estimated MLC of the chloride anion (Cl⁻) in typical natural waters, based on the 96th cumulative percentile of the concentrations reported in the NASQAN data base,[8] is 960 mg/L. However, much higher concentrations of chloride ions are possible, particularly in highly concentrated brines that can contain concentrations of chloride exceeding 100,000 mg/L. Such elevated chloride concentrations are even greater than the average amount in seawater, which is 19,000 mg/L.[6]

Furthermore, three-quarters of the chlorine known to be present in the outer 18 km of the earth's crust is to be found dissolved as chloride in the oceans. The general consensus of papers discussing how chlorine reached the ocean is that, owing to its volatility, the elemental chlorine separated from the rocks of the crust at an early stage of the earth's development.[6]

The geochemistry of the chloride ion is relatively simple. Generally, chloride ions do not enter into redox reactions, do not form low-solubility salts, are not significantly sorbed, and play few vital biochemical roles.[6]

Chromium

The estimated MLC of total chromium in natural water is 0.007 mg/L. This estimate is based on the 96th cumulative percentile (Cr^{+3}) of occurrences reported in the NASQAN data base.[8] Because trivalent chromium is not toxic, special efforts have been made to measure concentration of the more toxic hexavalent chromium, Cr(+6), that usually is present as the chromate anions CrO_4^{-2} or $Cr_2O_7^{-2}$. Durum et al.[11] present data that indicates the MLC of hexavalent chromium is 0.003 mg/L in natural waters; this estimate is based on the 96th cumulative percentile of occurrences reported in their data base.

Chromium occurs naturally in many igneous rocks, especially basalt and other silica-deficient types. Normally, the chromium is trivalent. The hexavalent state does occur in nature and is relatively stable; however, it is usually present in small amounts. If

moderately large amounts are present, usually it is the result of pollution. Plating shops, which are common even in underdeveloped countries, are among the major sources of chromate anions in natural water.

Cobalt

The estimated MLC of cobalt, as the divalent cation (Co^{+2}), in natural water is 0.006 mg/L. Cobalt concentration is limited by the low solubility of cobalt carbonate.[17] However, cobalt does form many complexes that may increase its concentration. Other factors controlling cobalt concentration include sorption on surface-active particulate matter, such as ferric hydroxide and manganese oxide colloidal particles.

Cobalt is found largely in igneous rocks, mostly in those deficient in silica. It is used widely in industry as an alloying element in steels.

Copper

An estimated MLC of copper in natural water could be 0.10 mg/L, based on the 96th cumulative percentile of measurements by Durfor and Becker.[7] These measurements are considerably higher than the 96th cumulative percentile of copper concentrations reported in NASQAN, which is 0.011 mg/L.[8] However, we think that the NASQAN data are more representative and consider 0.011 mg/L of copper to be a better estimate of the MLC of copper in natural waters. Both data sets indicate that copper is widely distributed in natural water, but at relatively low concentrations. The cation Cu^{+2} is most common in natural water.

Copper is commonly found disseminated in igneous rocks. Most commercial deposits are found in hydrothermal mineral deposits.

Hem[6] comments that the higher levels in natural waters reported by Durfor and Becker[7] may be related to the fact that these occurrences were measured in public water supplies. Copper is often added to such water for a variety of reasons, including control of algal growth in reservoirs and lakes used for storage. Additionally, low-carbonate water in copper plumbing may leach some copper from the pipes, and as a result, tap water can have higher concentrations of copper than the raw water entering the distribution system. Hem[6] noted that ordinarily the solubilities of cupric oxide or hydroxycarbonate minerals would tend to limit concentrations of copper to a few tens of micrograms per liter. However, higher naturally occurring concentrations of copper may occur near ore bodies.

Cyanide

Cyanide ion (CN^-) virtually never occurs in water naturally and is usually a result of industrial pollution. Routine analyses of natural water very seldom include measurements of cyanide. Scofield et al.[18] prepared a summary table of the existent monitoring data, and their table shows that only a few tens of micrograms of cyanide per liter of water may be encountered in water that is not in the immediate vicinity of the source of the pollution. Based on such data, the MLC is 0.04 mg/L in natural water not adjacent to a pollutant source.

Scofield et al.[18] point out that two factors tend to decrease the concentration of cyanide in natural water over time: (1) hydrogen cyanide (HCN) is volatile and evaporates from water, and (2) the cyanide ion tends to recomplex strongly with sulfur and with various metals, often forming much less toxic substances [e.g., the thiocyanate ion (CNS^-)].

Fluoride

The MLC of fluoride, usually present as the anion F^-, in natural waters is estimated to be 2.5 mg/L, based on data from Durfor and Becker.[7]

Igneous rocks, especially some recent volcanics, are an important source of fluoride, as are sedimentary rocks containing fluorite, CaF_2. The solubility of calcium fluoride is relatively low and limits the concentration of fluoride in most waters to a few milligrams per liter. The higher concentrations of fluoride in water are usually found when the calcium concentration is low.[6]

The fluoride ion tends to form complexes with a number of substances. Among those stable in natural water are the complexes of aluminum and ferric iron. Such complexes may be more soluble than the simple fluoride ion but also have different chemical properties.

Iodide

Iodide is not normally measured in analyses of fresh waters because the amounts are usually very small. The limited measurement data that are available, primarily from Konovalov in 1959 (cited by Hem[6]) indicate that concentrations up to a few tens of micrograms per liter exist in Russian rivers. Based on these data, the estimated MLC for iodide is 0.04 mg/L as the anion I^-.

Iron

The estimated MLC of dissolved iron in natural surface water with typical pH (5 to 9) is 0.4 mg/L, based on the 96th cumulative percentile of total-dissolved-iron measurements in the NASQAN data base.[8] However, considerable ferrous iron (Fe^{+2}) may be dissolved in anoxic waters, primarily ground water. The MLC of ferrous iron in such ground water is estimated to be 1.5 mg/L, based on a relatively small amount of data presented by Hem.[6]

The geochemistry of iron is quite complex. There is some question whether all such iron is truly dissolved or uncomplexed. A comprehensive discussion concerning the geochemistry of iron, as presented by Hem[6], is summarized here.

Ferric iron is stable in acidic water (pH less than about 4.8) as Fe^{+3} under strongly oxidizing conditions, but at pH values characteristic of typical natural water (pH 5 to 9), the solubility of ferric iron is less than 0.01 mg/L. In this range of pH and over a relatively wide range of oxidizing conditions (Eh greater than +0.2 V), the stable state of iron is the insoluble ferric hydroxide $Fe(OH)_3$, which forms a colloidal suspension (a sol) in such water. Some of these insoluble particles are of submicron size and may even pass through filters that are normally used in the preparation of water for chemical analysis. Thus, it is possible that some of this inert colloidal material may be measured as if it were dissolved iron when, in fact, it is not. Also, ferric iron forms complexes with both organic matter and inorganic substances. Hem[6] states, however, that such inorganic complexes are not significant in typical natural water. The chemistry of the organic complexes is often quite complex and sometimes not well understood, but it is known that the chemical characteristics of the organo-iron complexes are not necessarily the same as those of dissolved uncomplexed iron. Thus, the significance of the potential for incorrect measurement of the colloidal particles and complexes as dissolved iron lies in the fact that the chemical properties of these different forms of iron are not the same. Consequently, if nontoxic substances are included in measurements of the dissolved substances, false positives for toxic levels of iron are conceivable.

Ferrous iron (Fe^{+2}) is stable under reducing conditions at pH values characteristic of typical natural water. Under strongly reducing conditions, insoluble ferrous sulfide (FeS_2, pyrite) is stable. A considerable concentration of ferrous iron can be in solution when the pH is between 5 and 9 and the Eh is between +0.2 V to -0.1 V. Ultimately, the concentration of ferrous iron is limited by the solubility of ferrous carbonate, but under these conditions a few tens of milligrams per liter of ferrous iron can be stable, although concentrations usually are less than 10 mg/L.

Changes between the states of iron are relatively rapid. Thus, when insoluble pyrite (FeS_2) is exposed to oxygenated water, or when insoluble ferric hydroxide is mixed with reducing material such as organic matter, iron will tend to go into solution rather quickly. When anoxic ground water containing dissolved ferrous iron is exposed to air and oxygen dissolves in the water, the ferrous iron oxidizes and insoluble ferric hydroxide forms and then precipitates, largely as a colloidal suspension. Similarly, anoxic well water that contains substantial amounts of dissolved ferrous iron will quickly oxidize when exposed to air, and the ferrous iron will be converted to the form of iron that is characteristic of oxygenated surface water, namely insoluble ferric hydroxide.

Lead

The estimated MLC of lead in natural water is 0.02 mg/L, based on the 96th cumulative percentile of occurrences in the NASQAN data base.[8] The data of Durum et al.[11] give a similar result. The Pb^{+2} oxidation state of lead is at equilibrium over most of the water-stability region,[6] and the most likely control of solubility in oxidizing systems is the carbonate ($PbCO_3$), cerussite. Lead sulfate ($PbSO_4$) is also relatively insoluble and could also control the concentration of lead in oxidizing systems. Under reducing conditions and with reduced sulfur species, the lead sulfide, galena (PbS), which has a very low solubility, is stable. There is a high probability that lead concentrations in natural water would be limited mainly by these solubility restrictions.[6]

Lead is found in nature both in igneous and sedimentary rocks, although the most common commercial sources are lead ores associated with carbonate sedimentary rocks. Lead is also found in the environment through anthropogenic activity. The use of leaded gasoline began some 60 years ago, and lead from the exhausts of automotive vehicles has subsequently been entering the air in finely dispersed form. However, the effect of this lead on natural water has not yet been determined.

When low-pH, low-TDS natural waters stand in lead pipes, which were used in older distribution systems, objectionable amounts of lead can be dissolved from the pipes to the water. Additionally, lead concentrations are frequently higher near mineral deposits containing the element.

Lithium

The estimated MLC of lithium as Li^+ in natural water is 0.05 mg/L, based on the 96th cumulative percentile of lithium concentration reported by Durfor and Becker.[7] The element is relatively rare, but shows evidence of localized geographical distribution.

Colorado River water contains unusual amounts of the substance,[16] and many enclosed drainage basins like those located in the Basin and Range region of the intermountain western U.S. also contain unusually high concentrations of lithium.[36]

Igneous rocks are the primary source of lithium: hot springs in volcanic areas also often contain unusually large amounts of the element. The chemistry of lithium in natural water is not especially complex; it resembles that of sodium and potassium. The major limit on concentration appears to be availability, because lithium is a rare element.

Magnesium

The estimated MLC of magnesium, a common constituent of natural water, is 50 mg/L, based on the 96th cumulative percentile of occurrences in NASQAN data.[8] In some areas of the world, such as Iran, where the only available water is rather saline, higher concentrations of magnesium are found in water used for drinking. Such high concentrations are often associated with waters that have been in contact with slightly soluble magnesium-bearing rocks. Magnesium occurs in water as the divalent cation Mg^{+2}.

The geochemistry of magnesium is relatively simple until extremely high salinity is reached. However, one major complication at lower salinities is the precipitation of dolomite, which is calcium-magnesium carbonate $[CaMg(CO_3)_2]$. This relationship has been the subject of much research and has only recently become well understood. Usually less magnesium is present in natural water than calcium; the exceptions occur when the waters have been in contact with rocks containing unusual amounts of magnesium, or when calcium has been removed from the water by the precipitation of calcium carbonates.

Magnesium is a constituent of many major rock-forming minerals, although much has been dissolved in water and precipitated in such sedimentary rocks as magnesite ($MgCO_3$) and the previously mentioned dolomite. In industry, the metal has wide uses in structures where a high strength/weight ratio is necessary. Magnesite is used in the manufacture of refractories (heat-resistant ceramic material).

Manganese

The estimated MLC of manganese in natural waters is 0.3 mg/L, based on the 96th cumulative percentile of occurrences in NASQAN data.[8] Although manganese geochemistry is somewhat similar to that of iron, there are important differences. As is the case with iron, the geochemistry of manganese is complex. The topic is discussed in detail by Hem,[6] and the following review is excerpted largely from that discussion.

The range of stability of divalent manganese (Mn^{+2}) extends over more of the range of conditions of natural water than does the corresponding divalent (ferrous) iron (Fe^{+2}). Manganese concentrations in the range of 1 mg/L are relatively stable in oxygenated water unless the pH is high (greater than 7). Although manganese forms complexes with many kinds of organic material, the divalent manganese ion (Mn^{+2}) is relatively stable in uncomplexed form under conditions likely to be found in river water.[6] Ultimately, the concentration is limited by the solubility of manganese oxides and carbonates, especially at higher pH values.

Manganese oxides, for example MnO_2, which are stable in water at relatively high pH (7 to 9) and oxidizing conditions (Eh greater than about +0.20 V), precipitate as colloidal suspensions. The rate of the reaction is increased as pH increases and as the surface area of the manganese oxide increases. These oxides tend to adsorb other metallic cations very strongly, and thus the naturally occurring oxides usually have many impurities. The manganese oxides have a strong tendency to form surface-active crusts on the rocks and particles in stream beds. As noted elsewhere, these surface-active crusts play an important part in controlling the concentration of several other substances in natural water.

Manganese is essential in plant metabolism and can be removed from water by vegetation. For example, leaves and aquatic plants are known to accumulate relatively large amounts of manganese. Additionally, manganese forms complexes with many types of organic matter.

The redox reactions of manganese are perceptibly slower than those of iron. For example, aeration of water is sufficient to oxidize ferrous iron to insoluble colloidal ferric hydroxide; however, simple aeration is not sufficient to remove soluble manganous ions from water unless the pH is quite high (above 7 and preferably nearer 9). Similarly, when both soluble iron and soluble manganese are introduced into a stream as pollutants, the iron is oxidized, relatively quickly precipitated, and removed from solution. The manganese persists in solution for a longer time.

Manganese is present in many rock-forming minerals. Much of the manganese normally encountered has been leached from the rocks into water and later precipitated as one of the manganese oxides. Manganese carbonate, $MnCO_3$ (rhodochrosite), is a fairly common manganese-bearing mineral. Manganese is used in industry as an alloying element in steels.

Mercury

The estimated MLC of dissolved mercury, usually as Hg^{+2}, in natural water is 0.0032 mg/L, based on data from Wershaw as cited in USGS Prof. Paper 713.[19] Mercury tends to sorb readily onto a variety of clay minerals, suspended particulate matter, and bottom sediments of rivers. In general, such sediments are likely to contain much greater concentrations of mercury than the water itself.

Although normal stream water, at pH 5 to 9, may have a mercury solubility of as much as 0.025 mg/L, concentrations downstream from a mercury source are likely to be much lower as the result of a number of factors, including dilution, vaporization of volatile metallic mercury, precipitation of insoluble mercury hydroxides, sorption, and chemical reactions (Summary, USGS Prof. Paper 713[19]). Mercury entering water from industrial sources is apparently removed from solution in large part by adsorption on clayey sediments and suspended particles of hydrous oxides of iron and manganese, as well as by sorption by algae and plankton.

Mercuric-ion compounds hydrolyze readily to form mercury hydroxides in water. These have a relatively low solubility. While the methyl-mercury complex is toxic, Hem, in the USGS Prof. Paper 713[19] states that it is not thermodynamically stable under normal conditions in natural waters and thus cannot be expected to be present for long periods of time.

Mercury is found in nature near volcanic vents and in altered rock-forming minerals deficient in silica. There are several regions in Northern California where mercury is a fairly common substance, primarily near geothermal-steam fields and recent volcanic fields. It is geographically restricted in distribution and in many regions is virtually absent.

Molybdenum

The estimated MLC of molybdenum in natural water is 0.01 mg/L, based on the 96th cumulative percentile of concentrations recorded by Durfor and Becker.[7]

The geochemistry of molybdenum is quite complicated. The substance has multiple oxidation states and polymeric hydroxide anion species. Hexavalent molybdenum, Mo(+6), as the anionic molybdate form, MoO_4^{-2}, seems to predominate in natural water.[6]

The concentrations in water are related more to the amount of molybdenum available than to its solubility. For example, concentrations are generally low except in regions where molybdenum ore deposits are known to be present, such as in Colorado.

Nickel

The MLC of dissolved nickel as Ni^{+2} in natural water is 0.01 mg/L, based on the 96th cumulative percentile of occurrences reported in the NASQAN data base. Data from Durfor and Becker[7] and Greathouse and Craun[10] confirm this value. The chemistry of nickel resembles that of cobalt, but generally the concentrations of nickel in water are slightly larger. In a discussion of the limits on concentration of nickel in water, Hem[6] points out that nickel probably is strongly sorbed on iron and manganese oxides, and that concentrations are also limited by the solubility of the hydroxide, $Ni(OH)_2$. This differs from cobalt, the concentration of which is limited primarily by the solubility of its carbonate.

Nickel is found associated with silica-deficient rock-forming minerals. It is used in industry for plating and as an alloying agent.

Nitrate

The MLC of nitrate (NO_3^-) in natural waters is 23 mg/L, based on the 96th cumulative percentile of occurrences in the NASQAN data base[8] and the data presented by Durfor and Becker.[7] With the exception of extremely arid regions, most high concentrations of nitrate in natural water are the result of contamination of the water by fertilizers or by sewage.

In the arid southwestern states, moderately high levels of nitrate are found in some ground waters in unpopulated areas where pollution is unlikely. Although studies of such nitrate occurrences are few, it appears that the nitrate is found in oxidized waters -- both surface and ground waters -- where there is little reducing material available. In some areas of the world, such as the extremely arid Chilean coastal region, nitrates are widespread and are locally concentrated by cycling in playas characteristic of the region.[37]

As implied above, most natural nitrates are found primarily in saline deposits in arid regions. Most nitrate used today is synthesized from ammonia, produced in turn from natural gas by a catalytic process, and is used widely in fertilizers. Another major source, as mentioned above, is pollution from sewage. The chemistry of nitrogen in natural waters is relatively simple; most salts are soluble.

Phosphate

The estimated MLC of phosphate as PO_4^{-3} in natural water is 1.5 mg/L, based on the 96th cumulative percentile of concentrations reported in the NASQAN data.[8]

Phosphate in water is a biological nutrient, and Hem[6] speculates that much of it is taken up by aquatic organisms. The geochemistry of phosphate in water is relatively complex, and it seems unlikely that the concentration of phosphate in natural water is limited by the presence of a sparingly soluble compound.[6] Hem[6] thinks that it is more likely that the limited amount of phosphate in natural water is the result of biological uptake and sorption on metal hydroxides, rather than being the result of the limited solubility of phosphates.

Phosphate is found in nature largely in phosphatic shales deposited in unusual, relatively reducing marine environments. It is used widely as a fertilizer. In recent years, phosphates have become a major component of detergents, and because these are disposed of into sewage water, the level of phosphate in sewage effluent has increased sharply in many regions.

Potassium

The estimated MLC of potassium, K^+, in natural waters is 16 mg/L, based on the 96th cumulative percentile of occurrences in NASQAN data.[8] Basically, the chemistry of potassium is relatively similar to that of sodium, but there are some fairly significant differences. Perhaps the most important is that concentrations of potassium in natural water are virtually always significantly less than those of sodium, even though the amount of potassium in rocks is roughly equal to that of sodium. The small concentration of potassium present in water is thought to be related to the resistance to solution of potassium feldspars at normal temperatures. Another factor is the apparent preferential incorporation of potassium into insoluble mica and clay mineral structures.[6]

Selenium

The estimated MLC of selenium in natural surface waters is 0.007 mg/L, based on the 96th cumulative percentile of concentrations reported in WATSTORE data acquired directly from King[21] and processed on LLNL computers. Data from Greathouse and Craun[10] and in Volume 1 of Drinking Water and Health[17] suggest that the MLC may be slightly lower (about 0.005 mg/L).

Selenium concentrations in natural waters are strongly localized. In certain regions, such as the San Joaquin Valley in California, the Colorado Plateau of Utah and Colorado, and the U.S. high plains from northeastern Colorado to North Dakota, selenium levels may be as high as 1 mg/L in surface and ground waters.[6,21] In other regions, selenium may be virtually absent in natural waters.

When soluble, selenium can be toxic; the maximum contaminant level (MLC) for selenium in U.S. drinking-water supplies is 0.01 mg/L.[38] Nevertheless, a small amount of selenium may have to be added to the diet of animals for proper nutrition in selenium-deficient areas. Thus, one of the uses of selenium in agriculture is as a feed supplement for livestock in selenium-deficient regions.[20]

While not simple, the geochemistry of selenium is reasonably straightforward. The solubility of the substance depends primarily upon the oxidation potential (Eh) and acidity/alkalinity (pH) of the water. The following summary is based on a comprehensive discussion in Faust and Aly.[20] Selenium has several oxidation states: Se(-2), Se^0, Se(+4), and Se(+6). Under reducing conditions, and all pH values found in typical natural waters (pH 5 to 9), selenium is present as the insoluble selenide, e.g., FeSe. Native selenium, $Se^0(s)$, is stable in the Eh range from +0.3 V to -0.3 V and at pH 5 to 9; however, this form is insoluble, inert, and not a toxicity problem. Biselenite ion ($HSeO_3^-$) is stable at moderately oxidizing conditions in the pH range from 5 to 9. Most biselenite/selenite salts are slightly soluble; however, ferric selenite, probably the most common, is virtually insoluble. Moreover, selenites form stable adsorption complexes with ferric oxides and hydroxides that are even more insoluble than ferric selenite.

Compounds of the selenate ion, SeO_4^{-2}, are generally more soluble than those of the selenite/biselenite ion. If present in sufficiently high concentration, selenate compounds could constitute a toxicity hazard. Selenate is stable in oxidizing, alkaline waters (Eh $\geq$ +0.5 V; pH greater than about 7.0). These conditions are common in well-oxygenated waters -- the mean pH of natural water according to NASQAN data is 7.4[8] -- so that if there is a supply of selenium available to the water, significant amounts may be present.

Silver

The estimated MLC of silver (Ag^+) in natural water is 0.002 mg/L, based on the 96th cumulative percentile of occurrences recorded in the NASQAN data.[8] Silver is a rather rare element. Although it was reported both in NASQAN and by Durfor and Becker,[7] only a few stations in either data set had measurable amounts of the metal in water. In a brief discussion of the geochemistry of silver, Hem[6] points out that metallic silver is stable over most of the ranges of Eh and pH characteristic of natural water. Silver chloride has a low enough solubility to exert a major control over silver concentrations in waters where

chloride concentrations exceed 35 mg/L; this includes most natural water. However, the major factor controling silver concentration in most waters remains the scarcity of silver, not the solubility limits of silver compounds.

Silver is often found in nature as a constituent of lead ores.

Sodium

The estimated MLC of sodium, a common constituent of natural water is 500 mg/L, based on the 96th cumulative percentile of occurrences recorded in the NASQAN data base.[8] Sodium chloride is an extremely soluble compound, and highly concentrated brines are found in nature.

The geochemistry of sodium is quite simple. Most sodium compounds are reasonably soluble, and it forms few complexes. The element is present as the cation Na^+.[6]

The major source of sodium is rock-forming minerals, from which it is leached over a period of time. Much of the sodium at the surface of the earth is found in the oceans as sodium chloride. Other sodium salts are common and are also easily soluble in natural waters.

Strontium

The estimated MLC of strontium (Sr^{+2}) in natural waters is 0.5 mg/L, based on the 96th cumulative percentile of occurrences reported by Durfor and Becker.[7]

The geochemistry of strontium is analogous to that of calcium. The concentration of strontium in water is probably controlled by the solubilities of the carbonate and the sulfate. Another important factor in controlling strontium concentrations is sorption on surface-active particulates.[6] This is indicated by the behavior of the radioisotope strontium-90, which is known to sorb onto particulate matter relatively strongly. In general, the strontium concentration in most water does not approach the solubility of either strontium carbonate or sulfate. Probably the ultimate controling factors for the strontium concentration in most aquatic environments is the relative scarcity of the substance.[6]

Sulfate

The estimated MLC of sulfate, another common constituent in natural water, is 700 mg/L, based on the 96th cumulative percentile of concentrations reported in the

NASQAN data base.[8] However, some water used for drinking in arid regions, for example Iran, or where gypsum or anhydrite are exposed at the surface, contain even higher concentrations of sulfate.

The following summary of sulfur geochemistry is based on a comprehensive discussion by Hem.[6] Sulfur has several oxidation states: S(-2), S(0), S(+4), and S(+6). Hexavalent sulfur is present in oxygenated aqueous solutions at all pH values of natural water and virtually always as the sulfate ion, SO_4^{-2}. Sulfate ion is present in the rainfall over most continents; although some is derived from pollutants released to the atmosphere, more is derived from such terrestrial sources as volcanic emissions and as a result of bacterial metabolism that releases sulfur compounds to the atmosphere, usually as H_2S. Sulfate is also derived from the dissolution of sulfides (most commonly pyrite, FeS_2) by oxygenated water. Although pyrite is widely disseminated in many rocks, it is present usually in small quantities. Consequently, most waters with high sulfate content have been in contact with rocks containing gypsum (hydrated $CaSO_4$) or anhydrite (anhydrous $CaSO_4$); both these minerals are somewhat soluble in low-salinity water. Such rock sources include evaporite deposits, gypsum-bearing limestones and dolomites, and gypsum-containing carbonate cements in particulate rocks such as sandstone.

Sulfate concentrations are often low in ground water. Many ground waters are anoxic; chemical reduction and bacterial action in the aquifers reduces sulfate entering such anoxic aquifers to insoluble sulfides. Oxygenated ground waters can contain sulfates, and shallow ground waters in contact with gypsum or anhydrite would be expected to contain some level of sulfate concentration.

Sulfate concentrations are frequently higher in waters in arid or semiarid regions because the products of rock leaching, which include sulfate, are not carried away as effectively as in humid regions where high rainfall provides more water. In much of the American West, which is arid or semiarid, white efflorescent deposits are common where water has evaporated; many of these crusts are composed of sodium sulfate.

Over most of the Eh-pH field for oxidizing natural waters, sulfate ion (SO_4^{-2}) is in equilibrium. The sulfate ion is already a complex ion, and tends to form further complex ions of the type known as "ion pairs", which have different chemical properties from the sulfate ion itself. The most common of these ion pairs is $NaSO_4^-$ and $CaSO_4^0$. These ion pairs have little effect on most aspects of sulfate geochemistry, but are of considerable importance in determining the solubility of solids such as gypsum and anhydrite.[6] Thus, they also affect the concentration of sulfate that can be in equilibrium in natural waters.

Under reducing conditions (negative Eh values) the stable forms of sulfur are undissociated, such that H_2S exists at pH less than 7 and HS^- is present at pH greater than

7. As noted above, many ground waters contain little sulfate because they are anoxic and thus have negative Eh values. The sulfides stable under reducing conditions in normal natural water have very low solubilities.

Thallium

Thallium is a rare element and is not commonly measured in routine analyses. Greathouse and Craun[10] analyzed for thallium but found it in fewer than 1% of their samples and give no concentration data. Batley and Florence,[23] in a paper describing special techniques for the measurements of thallium, include a few data about the concentrations measured in fresh water in Australia. Based on these data, the MLC in fresh water is to be 0.00002 mg/L. Thallium occurs as the cation Tl^+.[22]

Thallium sulfate was used as a rodenticide in some regions, and elevated concentrations might be expected near plants where the material was manufactured and areas where it was used. However, thallium is known to sorb readily onto particulate matter, and probably most of the thallium entering the soil near such facilities and places of use would be bound on particles close to the point of entry to the environment.

Tin

The MLC of tin in natural water is estimated to be 0.002 mg/L, based on the limited data reported in Volume 1 of Drinking Water and Health.[17] This source reports serious reservations about the analytical techniques normally used to measure tin concentrations at the low levels present in natural waters. This problem undoubtedly accounts for the very limited amount of monitoring data available generally.

Tin occurs in a number of rock–forming minerals. There are no commercial deposits in the United States, and it is a relatively rare metal elsewhere.

The concentration of tin in natural waters is probably limited by its relative scarcity; however, in areas where tin is plentiful, the concentration is probably controlled by the solubility of stannous hydroxide, $Sn(OH)_2$, to about 1.6 mg/L. Tin usually occurs as the cation Sn^{+2} in natural waters. In addition to inorganic compounds, tin is known to form organo–tin complexes with organic matter.[17] Little is reported about the chemistry of these complexes.

Uranium

The estimated MLC of uranium in natural waters is 0.002 mg/L, based on the 96th cumulative percentile of concentrations reported in Durfor and Becker.[7]

The geochemistry of uranium is very complex; the element is multivalent, and its solubility is strongly affected by the oxidation potential of the aqueous solution, as well as the presence of vanadium. The most soluble form is hexavalent uranium, U(+6), as the uranyl ion (UO_2^{+2}), which is stable under oxidizing conditions.[6] Sedimentary deposits of uranium are found where the uranium, which dissolved in oxidizing ground waters, was deposited after the waters became reducing.[24] In some of the aquifers that carry uranium in oxidizing ground waters, such as in the Grants mining district of New Mexico, concentrations exceeding 10 mg/L have been measured.[39]

Uranium also forms soluble complexes with many inorganic substances, including fluorides, sulfates, phosphates, and carbonates.[24] The solubility of uranium is sensitive to the presence of vanadium in the aqueous solution. If 0.1 mg/L of vanadium is present, uranium becomes insoluble over a wide range of Eh at normal pH (4.5 to 8). The mineral carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$, forms under these conditions.[24]

Uranium is found in igneous rocks, both disseminated and in more concentrated ore deposits of pitchblende. A major source of uranium is in sedimentary deposits; uranium is leached from deposits in the igneous rocks and carried in soluble form in aquifers to regions in which water in the aquifer is reduced. Because the reduced forms of uranium are insoluble, the substance is concentrated in these regions.

Vanadium

The MLC of vanadium in natural water is estimated to be 0.015 mg/L, based on the 96th cumulative percentile of occurrences reported in the data presented by Durfor and Becker.[7]

Vanadium is a multivalent element, with both cationic and anionic forms having oxidation states of +3, +4, and +5. The pentavalent forms are anionic (VO_3^-) and generally of higher solubility.[6] It would appear that vanadium would be most soluble in surface water or well-oxygenated ground water. Vanadium also forms covalent bonds with organic molecules; these organometallic compounds are very important in the transport of vanadium in aqueous solution. Crude petroleum often contains relatively large amounts of vanadium, probably in the form of vanadium complexes. Soluble vanadium compounds in water are known to sorb readily onto clays and to precipitate with organic matter, indicating that the mobility of soluble vanadate compounds is probably low.[40]

As noted in the comments about uranium, the presence of moderate amounts of vanadium in aqueous solution (0.1 mg/L) has a profound effect on the solubility of uranium.[24]

Zinc

The estimated MLC of zinc (Zn^{+2}) in natural waters is 0.2 mg/L, based on the 96th cumulative percentile of data presented by Durum et al.[11] Near zinc deposits, the concentrations can be much higher. Zinc is relatively ubiquitous in natural water, but usually at relatively low concentrations.

The concentration of zinc is ultimately limited by the solubility of zinc hydroxide, $Zn(OH)_2$, and zinc carbonate, $ZnCO_3$. Nevertheless, these compounds do not limit the concentration of zinc to an extremely low level unless unusually high concentrations of dissolved carbon dioxide species are present.[6] However, the solubility of the zinc silicate, willemite, $2ZnO \cdot SiO_2$, is quite low, and in river waters containing approximately 6 mg/L of dissolved silica the calculated solubility of the zinc silicate is between 0.07 and 0.15 mg/L. Hem[6] thinks that zinc silicate may well be an effective control of the solubility of zinc in natural waters.

Zinc is frequently found in combination with lead in the mineral deposits of carbonate rocks, usually in considerably smaller amounts than the lead. Zinc is used widely in industry as a plating metal, in die-casting small parts, and in galvanizing steel sheet and fencing wire. Zinc-plated and galvanized articles are widely distributed in agricultural areas, and zinc may enter water as the result of leaching from this material.

Total Dissolved Solids

The estimated MLC of total dissolved solids (TDS) is 2100 mg/L, based on the 96th cumulative percentile of all data points recorded in the NASQAN data base.[8]

Total dissolved solids is a simple concept; it is the total of all the dissolved substances in a water sample, without differentiation. However, the ions of mineral salts are the principal constituents of TDS. The measurement is relatively simple to make; most often the water is evaporated and the dehydrated residue weighed, but it can be made more quickly and conveniently by measuring the electrical conductivity of a water sample with a conductivity meter. The TDS measurement is a good approximation of the potability of water because saline water has an objectionable taste for most individuals. Since the measurement is quick and inexpensive to conduct, it is the only measurement made in many cases where the major interest is to determine the potability of water.

In most waters (except those with very high sulfate-ion concentration), the chloride-ion concentration is somewhat more than half the TDS, and the total-dissolved-solids measurement can be used to approximate the chloride-ion content. The cases where sulfate-ion concentration is high are apparent from the geology and hydrology of a region; most of the high-sulfate waters frequently occur in arid environments or where the rocks contain exposed gypsum or anhydrite.

Dissolved Gases

The dissolved gases to be found most often in natural water are oxygen (O_2), nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and methane (CH_4).[20] Contact between surface water and the atmosphere; between ground water and soil gases; and between ground water and the products of biogeochemical processes accounts for the presence of these and other dissolved gases in natural waters. Among the other dissolved gases that have been reported in ground water in minute amounts are radon-222 (a decay product of radioactive uranium and thorium, which are present in some rocks and soils) and argon, helium, krypton, and xenon.[41]

Among the dissolved gases only H_2S constitutes a potential problem from the standpoint of drinking-water quality. This gas has a characteristic objectionable odor (rotten-egg smell) and concentrations of H_2S greater than 1 mg/L can make water unfit for consumption.[41] However, the solubility of this gas is lowered as the water becomes aerated.[20] Therefore, the potability of water containing H_2S is easily improved by the simple process of aeration.

APPENDIX B

COMPLEMENTARY HEALTH-EFFECTS DATA-BASE ASSESSMENT TO DETERMINE WHICH OF THE POSSIBLE INORGANIC CONSTITUENTS OF MILITARY FIELD-WATER SUPPLIES COULD BE OF MILITARY CONCERN FROM THE PERSPECTIVE OF FIELD-WATER CONSUMPTION

In this appendix, we determine which of the possible inorganic constituents of field-water supplies could be of military concern from the perspective of field-water consumption. This assessment is based on whether or not the toxic and organoleptic (e.g., color, odor, and taste) properties reported in the literature for each of these inorganic substances could degrade military performance in 70-kg personnel consuming up to 15 L/d of field water containing the maximum likely concentration (MLC) of a particular inorganic substance. The human health-effects data base for this assessment was compiled from a survey of the literature, particularly those detailed review articles that described the essential, toxic, and organoleptic attributes of the inorganic substances that are of interest with respect to field drinking water. For each of the inorganic substances discussed in this appendix, we also state whether the chemical has been implicated as a carcinogenic, mutagenic, or teratogenic agent. However, discussions concerning the organoleptic properties and reproductive toxicity associated with each substance are included only if such effects were identified in the review literature. The health-effects assessments of the possible inorganic constituents of typical natural waters are presented alphabetically, followed by discussions addressing total dissolved solids (TDS), dissolved hydrogen sulfide gas, color, and turbidity.

Comparison of the results from this data-base assessment with those from the application of the screening methodology reveals that the most conservative screening procedure (based on animal LD50 data) did not exclude from further consideration any inorganic substance that actually might be of concern in military field drinking-water sources. Furthermore, the details about acute and chronic human health implications for the inorganic constituents addressed in this appendix were used to determine whether a substance selected by the screening procedure for further consideration is of practical importance to military personnel in the battlefield.

Most of the assessments performed in this appendix were based on human health effects reported in the review literature. Unfortunately, these human health effects in most cases are associated with therapeutic overdoses, poisonings, safe and adequate daily doses, and recommended daily allowances. Consequently, we extrapolated such information to dose per day for purposes of comparison with dose per day from 15 L/d of

field water containing the MLC for the substance. In some cases, the human health effects and corresponding doses were not quantified for acute toxicity, and so we incorporated available animal data into our assessment, along with a 100-fold safety factor to account for the uncertainty in the extrapolation between animal and man. The 100-fold safety factor was employed in accordance with guidelines established for its use that are described in Volume 1 of Drinking Water and Health.[17] Finally, there are some substances that could only be evaluated qualitatively because of the paucity of data. Nevertheless, our analysis of the data available in the review literature indicates that only arsenic, chloride, cyanide, magnesium, sulfate, TDS, color, and turbidity are likely to be of military concern in field drinking-water supplies.

Aluminum

Although controversial experimental data suggest that aluminum might have a biological function in mammalian systems,[42] there is no definitive evidence that adverse health effects can be caused by inadequate amounts of aluminum in the diet.[43] One reason for this absence of data may be that it is virtually impossible to obtain a diet that is naturally deficient in this metal, and such a diet is required to demonstrate that physiological effects can be produced by a biological deficiency of aluminum.[42]

The trivalent form of aluminum, Al(+3), and its related compounds are the most prevalent forms of aluminum in surface waters and in most foods.[44] Typical concentrations of these forms of aluminum in food and water are considered to be nontoxic to humans when orally ingested.[45] In man, aluminum is poorly absorbed and rapidly excreted, which is probably the reason for its low level of toxicity. Nevertheless, extremely high doses of aluminum can produce adverse human health effects that are of military significance. However, it is unlikely that military field-water supplies will contain aluminum at concentrations high enough to produce a toxic dose, even if military personnel consume water at a maximum daily consumption rate of 15 L/d.

Acute toxicity. According to our survey of the toxicity literature, only massive oral doses of aluminum can produce symptoms[45] that can be considered performance-degrading by military standards. These symptoms include gastrointestinal disturbances, skin lesions, and nervous afflictions. These symptoms occur because the phosphate absorption from the digestive tract is inhibited as a result of the transformation of trivalent aluminum compounds into insoluble aluminum phosphate salts.[46] Biochemically, this inhibition of phosphate leads to a negative phosphate balance, which adversely alters phosphorylation

reactions in the tissues.[47] Extreme cases of phosphorus imbalance can even lead to the onset of rickets, a crippling disease that is characterized by an excessive proliferation of bone tissue.[48]

It is unlikely that military personnel will encounter concentrations of aluminum in field water capable of delivering a massive dose, even if consumption of 15 L/d were maintained over a prolonged period. This conclusion is based on the following reasoning. First, evidence in the literature indicates that ingestion of 16 g/d of aluminum hydroxide, $Al(OH)_3$, over a six-month period does not cause either acute or chronic adverse human health effects.[46] Consequently this dose corresponds to a no-observed-effect level of 5.53 g/d of aluminum. Second, the maximum likely daily dose of trivalent aluminum from field-water supplies is calculated to be 7.5 mg, based on an MLC of 0.5 mg/L and a 15-L/d maximum consumption rate for military personnel. Comparison of these values reveals that the maximum likely daily dose of aluminum from field water is almost three orders of magnitude smaller than the no-observed-effect level indicated in the literature. Therefore, a wide margin of safety should exist between the maximum likely daily dose from field water and the massive oral dose reported to induce performance-degrading health effects.

Chronic toxicity. Aluminum has been implicated as the etiologic agent in two slowly progressive chronic neuropathies: "dialysis dementia" and Alzheimer's disease.[38] "Dialysis dementia" is a progressive form of mental deterioration that is observed exclusively in chronic renal-dialysis patients, a population of no immediate military concern. Alzheimer's disease is a slowly progressive and fatal senile dementia occurring usually in people beyond the age of 40, a population not likely to represent a significant fraction of field personnel. Additionally, aluminum has been linked only circumstantially to Alzheimer's disease, and before symptoms of the disease can be considered important from a military perspective, more definitive data are needed about its association with aluminum and its effects during its early stages.

Carcinogenicity, Mutagenicity, and Teratogenicity. There is no evidence in the review literature indicating that orally ingested aluminum or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. The most prevalent forms of aluminum in foods and natural waters are the trivalent compounds. These forms of aluminum are not likely to occur in natural waters at a concentration that would be high enough to cause a massive oral dose, even if the water consumption rate is at a maximum of 15 L/d. Therefore, acute health effects

that are reported to result from a massive oral dose of aluminum should not occur. The relationship between aluminum ingestion and possible chronic effects is not well-defined and, according to currently available data, appears to be of no military significance. Therefore, there is no need to develop specific criteria and recommendations for standards concerning aluminum in military field-water supplies.

Ammonia

Ammonia exists as two forms in natural waters, molecular ammonia (NH_3) and the ammonium ion (NH_4^+). The percentage of ammonium ion in aqueous solutions depends upon pH and temperature. At a pH less than 8.0 and temperatures less than 25°C, characteristics commonly associated with natural water, the ammonium ion (NH_4^+) is the predominant species.[49] The ammonium ion is neither readily absorbed from the gastrointestinal tract nor accumulated within the human body. It is not essential for human metabolism.

Our survey, of the review literature revealed that cases of human toxicity due to the ingestion of elevated ammonia levels in drinking waters are unknown. The absence of such reported cases indicates that ammonia toxicity is not a significant public health problem in drinking-water supplies. In fact, most available ammonia toxicity data related to water are concerned with adverse effects produced in various species of freshwater fish. For instance, molecular ammonia (NH_3) is a well-known toxicant to fish and is lethal at concentrations above 0.2 mg/L.[49]

Acute Toxicity. There is no evidence in the review literature to indicate that the presence of ammonia in natural waters, even at our estimated MLC of 0.6 mg/L, could produce performance-degrading acute toxic effects in military personnel consuming up to 15 L/d of such waters.

Chronic Toxicity. There is no evidence in the review literature to indicate that the presence of ammonia in natural waters, even at our estimated MLC of 0.6 mg/L, could produce performance-degrading chronic toxic effects in military personnel consuming up to 15 L/d of such waters.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested ammonia or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. In summary, at a pH less than 8.0 and temperatures less than 25°C, the ammonium ion (NH_4^+) is the most prevalent species.[49] In water, this form of ammonia, as well as any other form that can occur, are considered essentially nontoxic to human systems, even at our estimated MLC. This can probably be attributed to the poor gastrointestinal absorption and retention of ammonia within the human body. Consequently, we conclude that the presence of ammonia in military field-water supplies poses no acute or chronic performance-degrading health threat to field personnel.

Antimony

Antimony (Sb) is not identified in the literature as an element essential for human metabolism. The trivalent, Sb(+3), and the pentavalent, Sb(+5), forms of antimony and their related compounds are the most prevalent forms in natural waters. These forms exhibit a very low order of toxicity in human systems, probably because of poor absorption from the gastrointestinal tract.[47] However, an extremely high therapeutic dose of a trivalent antimony compound has been reported to produce adverse health effects that are of military significance.[50] Nevertheless, it is unlikely that compounds of antimony will occur in field waters at concentrations high enough to correspond to a therapeutic dose of trivalent antimony, even if military personnel consume water at a maximum rate of 15 L/d.

Acute Toxicity. Our survey of the toxicity literature found one documented case of acute trivalent antimony poisoning. This case involved a 10-year-old African child who received a therapeutic overdose of sodium antimony gluconate as treatment for schistosomiasis.[50] The symptoms of acute toxicity experienced by the youngster included severe vomiting, convulsions, and heart-related complications. The toxic dose in this case was 300 mg of sodium antimony gluconate ($C_6H_8NaO_7Sb$) administered each day for a period of six days. This corresponds to an accumulated oral toxic dose of 650 mg of trivalent antimony over 6 d (i.e., 108 mg/d x 6 d). Although the reported symptoms are considered to be performance-degrading from a military perspective, it is highly unlikely that antimony in field waters will reach levels high enough to correspond to a therapeutic overdose. The calculated maximum likely daily dose of antimony for military personnel from the ingestion of field waters is 0.06 mg, which corresponds to an accumulated oral dose of only 0.42 mg over 7 d. This dose is based on our estimation of the MLC for antimony in natural waters of 0.004 mg/L and a 15-L/d maximum consumption rate. Thus, the dose accumulated by military personnel over 7 d from a maximum likely daily dose of 0.06 mg from field water is over three orders of magnitude lower than the accumulated dose (650 mg) considered necessary to produce debilitating health effects.

Chronic Toxicity. Chronic toxicity due to prolonged ingestion of antimony or its compounds has not been substantiated in humans. However, long-term feeding of antimony compounds to rats resulted in albuminuria (i.e., the presence of albumin in the urine), jaundice, and damage to heart, liver, and kidney tissues.[40,46] These symptoms are not considered to be of military concern because in the rats these symptoms were not accompanied by lethality and the effects can not be translated to performance-degrading effects for military personnel.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested antimony or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Taste and Odor. The Safe Drinking Water Committee of the National Research Council[45] cites a 1964 report by Arzamastev indicating that 0.6 mg/L is the accepted taste threshold for antimony in potable waters. Concentrations above this threshold presumably give waters an unpleasant taste, although reference was not made to the actual palatability of waters containing such high concentrations of antimony. Nevertheless, we assume that antimony concentrations greater than or equal to 0.6 mg/L will impart an undesirable taste to military field waters. This undesirable taste could cause decreased consumption of field water and increased susceptibility to the performance-degrading effects of dehydration. However, we estimated the MLC of antimony in natural waters to be 0.004 mg/L, and this concentration is 150 times smaller than the reported taste threshold. Thus, it seems highly unlikely that naturally occurring concentrations of antimony in field waters will make the taste of field waters objectionable to military personnel.

Recommendation. In summary, antimony compounds exhibit a very low order of toxicity in human systems after ingestion, probably because of poor absorption from the gastrointestinal tract. In fact, adverse health effects in humans following the ingestion of antimony compounds have been reported only for one therapeutic overdose. Comparison between the maximum likely daily dose of antimony for military personnel from the ingestion of field waters and the therapeutic dose necessary to cause performance-degrading effects reveals that a toxic dose of antimony from drinking field water is highly unlikely, even if the water is consumed at a 15-L/d maximum rate over a prolonged period. Additionally, comparison between the MLC of antimony in natural waters and the reported taste threshold indicates that concentrations of antimony will not be high enough to impart an objectionable taste to the water that can lead to decreased

water consumption among military personnel. Consequently, we conclude that there is no need to establish criteria and make recommendations for standards for antimony in military field-water supplies.

Arsenic

The most common arsenic species in natural waters are the trivalent, As(+3), and pentavalent, As(+5) forms. "Total arsenic," which includes both the trivalent and pentavalent forms, typically is reported from analyses of water quality. However, trivalent arsenic, As(+3), is the most prevalent, as well as the most toxic, species in natural waters.[17] Gastrointestinal absorption of this form is rapid and complete. Primary excretion occurs via the kidneys, with lesser amounts lost through the bile.[47] Absorbed arsenic typically accumulates in the liver, kidney, spleen, lung, and intestinal wall.[17] The average human body burden of arsenic has been reported to be between 3 and 4 mg.[40] Although evidence has suggested that trace amounts of arsenic may be essential for the nutrition of certain laboratory animals, this essentiality has not been substantiated for humans.[40]

Considerable information exists concerning arsenic poisoning in humans. Comparison of our best estimate of the maximum likely daily dose of arsenic from drinking field water, with the dose necessary to produce acute or chronic performance-degrading effects, reveals that there is less than a 5% probability that arsenic concentrations naturally occurring in military field waters will be high enough to correspond to a toxic dose. This probability holds true even if military personnel find it necessary to consume water at a maximum rate of 15 L/d over a prolonged period. However, the toxic properties of arsenic, combined with its incorporation into Lewisite threat agents used for chemical warfare, make it a candidate for criteria and recommendations for standards for field water.

Acute Toxicity. Scofield and Hsieh[51] cite a 1956 report by Mizuta et al. to show that daily ingestion of contaminated soy sauce containing approximately 3 mg of total inorganic arsenic over a period of two to three weeks produced acute debilitating symptoms in several individuals. The toxic symptoms experienced by these individuals included vomiting, nausea, diarrhea, and deterioration of nervous-system and circulatory functions. In contrast, military personnel deployed in the field may consume up to 0.30 mg of arsenic per day. This is based on an estimated MLC of arsenic in natural waters of 0.02 mg/L and a 15-L/d maximum daily consumption rate. Therefore, the maximum daily arsenic dose likely for military personnel from drinking water is approximately 10 times

lower than the dose necessary to produce toxic effects. Thus, it seems highly unlikely that typical arsenic concentrations in field waters will reach levels high enough to pose a health threat of military significance.

A 1943 report by Goudey cited by Scofield and Hsieh[51] states that daily ingestion of drinking water containing an arsenic concentration of 0.05 to 1.0 mg/L produced no noticeable acute debilitating health effects in consumers, even after several months of exposure. These concentrations equate to a daily arsenic dose of 0.1 to 2.0 mg/d, based on an average consumption rate of 2 L/d of water. Thus, we consider this to be an adequate estimation of a no-observed-effect range. In comparison, our calculated maximum likely daily arsenic dose for troops falls well within the no-observed-effect range. This further supports our conclusion that there is a wide margin of safety between the dose necessary to produce acute debilitating effects and the maximum dose likely to be delivered to military personnel from the ingestion of field water.

Chronic Toxicity. A case of chronic arsenic poisoning is described in Drinking Water and Health, Volume 3.[40] This case involved the therapeutic oral administration of arsenic trioxide to treat asthma in an adult. Approximately 6.69 mg of arsenic per day (as arsenic trioxide) was administered over a period of nine months, followed by administration of 3.5 mg of arsenic per day for an additional 19 months. This corresponds to an average daily dose of approximately 4.5 mg of arsenic over a total exposure period of 2.3 years. Debilitating health effects were first noticed after thirteen months of exposure. Symptoms included cramps, nausea, diarrhea, increased freckling, and darkening of the nipples. Other disorders, including hyperkeratosis (i.e., thickening of the skin) of the palms and soles and edema of the eye region, were detected after approximately 1.5 years. Neurological symptoms, including paresthesia (e.g., numbness) and weakness of the hands, became evident after 2.5 years. Most of these chronic symptoms were alleviated after arsenic treatment was withdrawn. Although these symptoms are considered potentially performance-degrading from a military perspective, they probably will not interfere with performance in the field because of the long latency period. Furthermore, the estimated toxic dose and exposure period necessary to produce such debilitating chronic effects probably is 4.5 mg of arsenic per day for 13 months. In contrast, personnel in the field may be exposed to an MLC of arsenic of 0.02 mg/L for a maximum of one year. Therefore, it is highly unlikely that personnel will be exposed to arsenic concentrations in field waters sufficient to induce chronic performance-degrading effects of military concern.

Controversial epidemiological evidence also exists associating chronic arsenic exposure with vascular and pulmonary diseases. For instance, a three to four times higher

rate of blackfoot disease (i.e., a peripheral vascular disorder resulting in gangrene of the extremities) was reported in Taiwanese people who consumed well water containing at least 0.6 mg/L of arsenic; however, this effect did not occur in those individuals in Taiwan consuming well water with 0.29 mg/L or less of arsenic.[40] Chilean populations consuming well water containing 0.8 mg/L arsenic have also been reported to experience abnormal skin pigmentation, as well as increased incidence of bronchial and pulmonary diseases and skin cancers.[40] Unfortunately, duration of exposure was not indicated for either the Taiwanese or Chilean population. Although these symptoms may be potentially performance-degrading, they are of no immediate concern to field personnel because our estimation of the MLC of arsenic in natural waters of 0.02 mg/L is at least 10 times lower than the concentrations reported to produce these chronic effects.

Carcinogenicity, Mutagenicity, Teratogenicity. The ingestion of arsenic compounds has been associated with human carcinogenesis. Unfortunately, neither an exact exposure period nor a quantitative dose-response relationship has been established for carcinogenic effects. In fact,, our survey of the review literature revealed only one study in which any type of oral dose-response data was presented. This study conducted by Tseng et al. in 1968 and reported in Volume 1 of Drinking Water and Health,[17] took place in an area in the southwest corner of Taiwan that presumably was supplied for more than 45 years with water from artesian wells containing approximately 0.5 mg/L of arsenic. The data indicated that the rate of skin cancer among the inhabitants of the area varied directly with the arsenic content of the well water. Additionally, a 1976 follow-up study conducted by Tseng, and also reported in Volume 1 of Drinking Water and Health,[17] confirmed his previous finding that the prevalence of skin cancer among the population increased as the arsenic content of the well water increased. However, arsenic has not been universally accepted as a carcinogen because of the inability to produce arsenic-induced cancers in laboratory animals.[40]

In contrast, teratogenicity has been demonstrated in laboratory animals, but has not been demonstrated in humans. Volume 1 of Drinking Water and Health[17] reports that a single intravenous administration of 15 to 20 mg/kg of sodium arsenate can produce anencephaly (i.e., absence of a brain and spinal cord), rib malformations, exencephaly (i.e., protrusion of the brain through a cranial fissure), and genitourinary malformations in mice and hamsters. However, there is no evidence in the review literature indicating that orally ingested arsenic or its compounds are teratogenic or mutagenic in humans or laboratory animals.

Recommendation. Our assessment of the review literature indicates that arsenic typically does not occur in natural waters at concentrations that could be associated with acute or chronic toxicity in military personnel consuming up to 15 L/d of water. However, there are unusual waters, particularly ground waters, that may contain arsenic at extraordinarily high levels that could be toxic. For this reason and because arsenic is a component of Lewisite threat agent, arsenic exposure in field drinking waters requires special attention. Therefore, a document addressing criteria and recommending standards should be prepared for arsenic in field-water supplies.

Barium

Barium is not identified in the literature as an element essential for human metabolism. The most prevalent forms of barium in natural waters are the divalent cation (Ba^{+2}) and its related compounds. The review literature indicates that ingestion of water-soluble forms of barium can be toxic in humans. However, the chemical properties of barium cause it to exist in natural waters primarily as insoluble barium sulfate ($BaSO_4$). Such insoluble forms of barium are not considered to be toxic to humans, and their formation precludes the presence of the more toxic soluble forms in significant quantities.[17] In addition, gastrointestinal absorption of naturally occurring barium in foods is quite limited.[46]

Acute Toxicity. Our survey of the review literature revealed no evidence that elevated barium levels in drinking waters induced acute debilitating toxic effects among human populations. However, accidental therapeutic overdoses of barium salts have been reported to cause adverse health effects of military concern such as vomiting, colic, violent diarrhea, tremors, muscular paralysis, and paralysis of the central nervous system.[46] The mechanism for acute barium toxicity involves a prolonged stimulant action on all muscles.[46] Unfortunately, quantification of a dose-response relationship for these effects has not been established. The only quantification of an acute toxic dose found during our review of the toxicity data is that of a human lethal dose of barium chloride ($BaCl_2$), which is reported to be 800 to 900 mg.[17] This dose corresponds to 530 to 600 mg of barium.[52] Because this is a reported lethal dose, we can assume that a sublethal toxic dose of barium lies somewhere below 530 mg. In contrast, the maximum likely daily dose of barium that military personnel can receive from the ingestion of field waters is 15 mg/d. This is based on our estimated MLC of barium in natural waters of 1.0 mg/L and a 15-L/d maximum drinking-water consumption rate for field troops. Thus, the lowest reported lethal dose of barium is about 35 times larger than the maximum likely daily dose

from water for military personnel. Based on this comparison, we conclude that it is highly unlikely that field personnel will be exposed to barium concentrations high enough to be lethal or to induce acute performance-degrading effects, even if the troops maintain a 15-L/d consumption rate over a prolonged period.

According to the Safe Drinking Water Committee of the National Research Council,[17] a barium concentration of about 2.0 mg/L for drinking waters was calculated as a safe intake level for a healthy adult human population based on the TLV (i.e., Threshold Limit Value) for barium in industrial air established by the American Conference of Governmental Industrial Hygienists (ACGIH). This value corresponds to a no-observed-effect level, and therefore indicates that exposure to a barium concentration greater than 2.0 mg/L is necessary to induce adverse health effects. Because this value is two times greater than our estimated MLC for barium in natural waters, this further supports our conclusion that the presence of barium in military field-water supplies is of no toxicological concern to field personnel.

Chronic Toxicity. There is no evidence in the review literature indicating that elevated levels of ingested barium compounds induce debilitating symptoms of chronic toxicity among healthy human populations. Consequently, we do not consider chronic barium toxicity as a performance-degrading health threat to military personnel deployed in the field.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested barium or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. In summary, the most prevalent forms of barium in natural waters are the divalent form (Ba^{+2}) and its related compounds. Our review of the toxicity literature concerning barium compounds indicates that they are poorly absorbed from the gastrointestinal tract of humans. Additionally, the chemical properties of barium cause it to exist primarily as insoluble barium sulfate ($BaSO_4$) in natural waters. Finally, comparison between the maximum likely daily dose of barium from the ingestion of field waters and the dose necessary to produce debilitating health effects reveals that naturally occurring barium concentrations in field waters will not be high enough to deliver a toxic dose, even if troops consume water at a maximum rate of 15 L/d. Consequently, we conclude that there is no need to establish criteria and make recommendations for standards for barium in military field-water supplies.

Beryllium

Beryllium is not identified in the literature as an element essential for human metabolism. The most prevalent forms of beryllium in natural waters are the divalent form (Be^{+2}) and its related compounds. Beryllium, at a pH between 7 and 8 (common for many natural waters), forms beryllium oxides and hydroxides that are relatively insoluble in these waters and tend to sorb onto soil particles.[17] This process reduces the availability of the more toxic, soluble forms of beryllium in drinking waters. In addition, beryllium compounds exhibit very poor gastrointestinal absorption, and the little beryllium that is absorbed undergoes rapid elimination via the kidney.[53]

Acute Toxicity. According to our survey of the review literature, the only reported acute adverse effects of beryllium are the result of industrial inhalation exposure to beryllium dusts and fumes. Symptoms of this acute inhalation toxicity include skin and eye ulcers and inflammation of nose, throat, and mucous membranes of the lungs.[46] Although these symptoms may become performance-degrading in extreme cases, they are not considered to be a performance-degrading health threat to military personnel from the perspective of beryllium in field drinking-water supplies.

Chronic Toxicity. As in the case of acute toxicity, the only reported chronic adverse health effects associated with beryllium exposure are the result of industrial inhalation of beryllium dusts and fumes. Symptoms of chronic beryllium toxicity from inhalation include pneumonitis, pulmonary dysfunction, cyanosis (i.e., bluish or gray discoloration of the skin), congestive heart failure, enlargement of the liver and spleen, and cellular infiltration of the interstices of various organs and tissues.[46] All of these symptoms appear initially as clinical manifestations and do not fully express themselves as physiological debilitation until several years after exposure.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested beryllium or its related compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals. However, reported cases of lung cancer among workers in beryllium refineries and related industries have been attributed to inhalation of beryllium dusts and fumes.[46]

Recommendation. In summary, the divalent form of beryllium (Be^{+2}) and its related compounds are the most prevalent forms in natural waters. According to the review literature, these forms undergo poor gastrointestinal absorption and are present in drinking

waters as the insoluble oxides and hydroxides. The only reported adverse health effects of beryllium exposure are the results of inhalation of beryllium dusts or fumes. Consequently, we conclude that the presence of beryllium in military field-water supplies does not pose a debilitating acute or chronic health threat to military populations deployed in the field and does not require further attention.

Bismuth

Bismuth is not identified in the literature as an element essential for human metabolism. In fact, depending on exposure pathway and absorption, some bismuth compounds are considered to be quite toxic to humans. However, the trivalent species of bismuth (Bi^{+3}) and its related compounds, which are the prevalent forms of bismuth in natural waters, are not likely to be toxic to man if ingested.[46]

Acute Toxicity. Although human acute toxicity data concerning bismuth are limited, there is evidence[47] that ingestion of the strongly acidic bismuth salts, such as bismuth trinitrate, can induce health effects that would be considered performance-degrading from a military perspective. For example, vomiting, diarrhea, and gastrointestinal ...... have been attributed to the ingestion and subsequent caustic effects of these substances. However, these substances are not likely to be encountered in military field-water supplies in concentrations high enough to induce these effects. This is because of the low aqueous solubility of bismuth and because less reactive bismuth salts are the more prevalent species in water. In addition, most ingested bismuth salts, particularly trivalent ones, are converted in the gastrointestinal tract of man into sparingly soluble and poorly absorbed monohydroxy compounds.[47] This process has been observed clinically after therapeutic ingestion of trivalent bismuth salts which are frequently administered to control diarrhea and other types of gastrointestinal disturbances.[47]

Chronic Toxicity. Evidence in the review literature indicates that long-term therapeutic exposure to bismuth compounds can result in chronic toxicity. The symptoms of this chronic toxicity include renal dysfunction, rheumatic pain, dermatitis, diarrhea, and fever.[47] Although these symptoms can be considered performance-degrading to military personnel, such adverse health effects have only been reported to be associated with accidental therapeutic overdoses of orally administered bismuth compounds. Such doses are not likely to arise from the oral ingestion of field-water supplies by military personnel.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested bismuth or its compounds are carcinogenic, mutagenic, or teratogenic in humans or animals.

Recommendation. In summary, bismuth is slightly soluble in water; the most prevalent forms in natural waters are the trivalent species (Bi^{+3}) and its compounds; and ingested trivalent bismuth species are converted to sparingly soluble and poorly absorbed compounds in the gastrointestinal tract. Furthermore, the scientific evidence we reviewed indicates that bismuth will be encountered at low concentrations in military field-water supplies. Consequently, we conclude that there is no need to establish criteria and make recommendations for standards for bismuth in military field-water supplies.

Boron

Boron is not identified in the literature as an element essential for human metabolism. The most prevalent forms in natural waters are the trivalent species, B(+3), and related compounds. Although absorption of these forms from the gastrointestinal tract of humans is rapid and complete, they exhibit a very low order of toxicity in human systems due to almost total elimination via the kidney.[47] Our survey of the review literature reveals that boron concentrations present in natural waters are not likely to be high enough to induce performance-degrading effects of military concern among military personnel deployed in the field.

Acute Toxicity. Although human acute toxicity data concerning boron are limited, there is evidence[54] that boron compounds can induce acute health effects that would be considered performance-degrading from a military perspective. For example, severe vomiting, diarrhea, abdominal pain, damage to the central nervous system, depression of circulation, shock, and coma have been attributed to th; ingest c... of these compounds. Unfortunately, the dose necessary to produce these perform nce-degrading effects has not been quantified. However, the human fatal dose of ingested boric acid (i.e., H_3BO_3) has been reported as ranging between 15 and 20 g.[54] This corresponds to approximately 2.6 to 3.5 g of boron. Thus, we can assume that the acute toxic dose lies somewhere below 2.6 g of boron. In contrast, military personnel could be exposed to a maximum daily boron dose of approximately 17.3 mg. This dose is based on a MLC of boron in natural waters of 1.15 mg/L and a 15-L/d maximum field-water consumption. Consequently, the maximum possible daily boron dose from water is about 150 times less than the lowest reported

human lethal dose. We consider this to be a substantial margin of safety and conclude that concentrations of boron in military field waters will not produce acute debilitating health effects in field personnel.

Chronic Toxicity. Our survey of the review literature found no evidence that long-term exposure to ingested boron or its compounds induces chronic performance-degrading effects of military significance.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested boron or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Reproductive Toxicity. Investigators have reported that oral doses of borax (sodium tetraborate, $Na_2B_4O_7$) at 1170 mg/L (equivalent to approximately 250 mg/L of boron) in drinking water produced sterility among test animals.[55] However, these same investigators demonstrated that borax ($Na_2B_4O_7$) or boric acid (H_3BO_3) doses of up to 350 mg boron/L in the diet produced no adverse effects on reproductive function. In another study, Dixon et al.[54] exposed treatment groups of male rats to 0.3, 1.0, and 6.0 mg boron/L in the form of borax in drinking water. The animals were exposed for a total period of 90 days, with observations of randomly selected groups occurring after 30, 60, and 90 days of treatment. No significant effects of reproductive toxicity were observed at any of the sampling intervals. There is no direct evidence in the review literature associating adverse reproductive effects in humans with the ingestion of boron or its compounds, and such effects in animals are controversial at this time.

Recommendation. Our survey of the review literature indicates that ingested trivalent boron species, B(+3), and related compounds (i.e., the most prevalent forms in natural waters) exhibit a very low order of toxicity in human systems. This can probably be attributed to rapid and efficient elimination via the kidney. Comparison between the maximum daily boron dose likely for military personnel from the ingestion of field waters and the lowest reported lethal dose indicate that boron concentrations will not produce lethal effects and will most likely never produce acute toxic effects, even if military personnel consume water at 15 L/d over a prolonged period. Chronic effects due to elevated levels of boron have not been demonstrated in human systems and are, therefore, of no concern from a military perspective. Consequently, we conclude that there is no need to investigate further the possible consequences of the presence of boron in military field-water supplies.

Cadmium

Cadmium is not considered to be an element essential for human metabolism. The most prevalent forms of cadmium in natural waters are the divalent cation (Cd^{+2}) and its related compounds. Gastrointestinal absorption is limited, thereby decreasing the toxic potential of cadmium in human systems. Excretion is slow and occurs primarily via the urine with lesser amounts lost through the feces.[46]

Our survey of the toxicity literature indicates that it is highly unlikely that military field-water supplies will contain concentrations of cadmium high enough to induce acute or chronic performance-degrading effects among military personnel, even at 15-L/d maximum field-water consumption.

Acute Toxicity. Acute cadmium toxicity in humans usually results from the ingestion of food or beverages that contain a high concentration of cadmium from contamination during storage in cadmium-plated containers.[45] Acute debilitating symptoms include vomiting, diarrhea, severe nausea, muscle cramps, and salivation. In extreme cases, these symptoms may be followed by death within 24 hours to 14 days. Lethality in such cases results from related shock and coma or from acute renal failure coupled with cardiopulmonary depression.[45]

Estimates of acute oral cadmium toxicity in humans have been reported by several investigators. These are summarized in Table B-1. According to information in the table, the emetic threshold range is 3 to 90 mg of cadmium. This implies that 3 mg is the lowest dose at which emetic effects were exhibited. Any dose below 3 mg of cadmium should not produce any toxic symptoms after ingestion. Based on this assumption, any dose below 3 mg per day of cadmium should be tolerated without performance-degrading effects. In comparison, the maximum daily dose of cadmium likely for military personnel from the ingestion of natural waters is 0.15 mg of cadmium. This dose is based on the MLC for cadmium of 0.01 mg/L in natural waters and maximum field-water consumption of 15 L/d. This estimated daily dose of 0.15 mg of cadmium is 20 times less than the dose necessary to produce performance-degrading effects. Thus, it is highly unlikely for military personnel deployed in the field to receive an acute toxic dose from the daily consumption of typical field waters.

Chronic Toxicity. Chronic cadmium toxicity due to oral exposure is rare and, in most cases, limited to industrial inhalation exposure.[47] The critical target organ in chronic cadmium poisoning, independent of route of exposure, is the kidney. Adverse effects in

Table B-1. Dose-response relationships for ingestion of cadmium by humans.

Acute dose	Acute health effects	Reference
3 to 90 mg	Emetic threshold	49
15 mg	Experimentally induced vomiting	46
10 to 326 mg	Severe toxic symptoms of vomiting, diarrhea, nausea	15,49
350 to 3500 mg	Lethality	49

the kidney are noted at lower exposure levels than for other organs and systems. This is not, however, necessarily due to hypersensitivity of the kidney but may be attributed to rapid rate of accumulation.

Rowe et al.[56] report that an annual intake of 0.9 to 1.7 mg/L of cadmium administered orally to humans over a 30-year exposure period can induce noncarcinogenic chronic poisoning involving renal toxicity which is characterized by proteinuria (i.e., excess protein in the urine). Itai-Itai disease syndrome may also result from this type of exposure, coupled with other predisposing factors. Itai-Itai is a cadmium-induced disease that has occurred among the general population of Japan and inhabitants of the Jintsu River Valley as a result of long-term daily intake of cadmium-contaminated rice. Multigravid, postmenopausal women were the most severely affected with symptoms of this disease. The symptoms in these women included proteinuria, glycosuria, osteomalacia (i.e., softening of the bones), and spontaneous, multiple bone fractures.[40] Such chronic symptoms are not considered performance-degrading by military standards because of their long latency period.

Rowe et al.[56] also report that a cadmium concentration that ranges between 0.01 and 0.1 mg/L in water can be considered a no-effect level, based on human dose-response relationships reported in the literature. This estimated level correlates directly with the well-documented no-observed-effect level established for cadmium intake by other investigators. Our estimated MLC of cadmium in natural waters of 0.01 mg/L is well within the range of this no-observed-effect level. Therefore, we can conclude that the trace amounts of cadmium typical in natural waters pose no debilitating health threat to military field personnel.

<u>Carcinogenicity, Mutagenicity, Teratogenicity</u>. There is evidence in the review literature suggesting that cadmium exposure may cause cancer in laboratory animals. For instance, according to 1963 and 1967 reports by Gunn <u>et al</u>. that are cited in <u>Drinking Water and Health Volume 3</u>,[40] subcutaneous injections of 0.03 mmol/kg of cadmium chloride ($CdCl_2$) have resulted in sarcomas at the site of injection, as well as testicular tumors in rats and mice. However, <u>Drinking Water and Health Volume 3</u>[40] also cites a 1965 publication by Schroeder <u>et al</u>., which reported that a concentration of 5 mg/L in drinking water fed to mice throughout their lifetime produced no carcinogenic effects of any kind. Human epidemiological surveys have implied that cadmium workers exhibit an increased incidence of prostate cancer in relation to the general population. However, age variability and concurrent exposure to other environmental contaminants were not taken into consideration in these surveys. Consequently, human carcinogenicity due to ingested cadmium is not likely to be of military concern.

Teratogenic effects, including spina bifida, cleft palate, clubfoot, malformation of the ribs, skull, vertebrae, and an increase in fetal deaths, have been shown to occur in laboratory rats, mice, and hamsters following parenteral injection of 4 to 12 mg/kg of cadmium chloride.[40] However, there is no evidence in the review literature that cadmium-induced teratogenic effects have ever occurred in humans. Furthermore, there is no evidence in the review literature indicating that ingested cadmium or its compounds are mutagenic in humans or laboratory animals.

<u>Recommendation</u>. Our survey of the review literature reveals that performance-degrading effects are not likely to occur among military personnel as a result of exposure to cadmium compounds from the ingestion of field drinking water. Comparison between the maximum likely daily dose of cadmium for military personnel and the dose necessary to cause acute or chronic effects indicates that the trace amounts of cadmium in field waters will not reach toxic concentrations under normal conditions. In addition, gastrointestinal absorption of the most prevalent form of cadmium occurring in field waters (i.e., Cd^{+2}) is quite limited, thereby reducing the toxic potential of cadmium in human systems. Consequently, we conclude that there is no need to establish criteria and make recommendations for standards for cadmium in military field-water supplies.

<u>Calcium</u>

Calcium is identified in the literature as an element essential for human metabolism. Calcium plays a vital role in regulating the excitability of peripheral nerves and muscle.[57] It is also necessary for bone formation, blood coagulation, membrane

permeability, enzyme catalysts, myocardial function, muscle contractibility, and for the integrity of intracellular components.[46,57] Calcium deficiency results in muscle weakness, bone demineralization, stunted growth, hyperirritability, parathyroid hyperplasia, tetany, and death in some cases.[46] A recommended allowance of 800 mg of calcium per day has been established as adequate to meet physiological requirements in adults. An additional allowance of 400 mg/d has been recommended for women during gestation and lactation.[57]

The most prevalent forms of calcium in natural waters are the divalent cation (Ca^{+2}) and its related compounds. Gastrointestinal absorption and excretion are presumably regulated by an efficient homeostatic mechanism involving glycolysis and sodium, potassium, magnesium, and hydrogen exchange.[46] According to the review literature, ingested calcium and its related salts are generally considered to be nontoxic except at very high doses. Our calculations and comparisons of the daily calcium dose for military personnel and the dose necessary to produce adverse health effects reveal that it is highly unlikely that military personnel will be exposed to toxic calcium concentrations from the ingestion of field waters, even if they found it necessary to consume water at a 15-L/d maximum rate over a prolonged period.

Acute Toxicity. According to our survey of the review literature, ingested calcium compounds exhibit a very low order of oral toxicity in human systems. This probably is due to the efficient homeostatic mechanism that maintains calcium levels within adequate physiological levels, except in cases of extreme overloads. Nevertheless, some calcium salts, such as calcium chloride ($CaCl_2$), act as gastric irritants and can induce acute performance-degrading effects, including vomiting and diarrhea.[46] Unfortunately, the toxic dose necessary to produce these effects has not been firmly defined. However, the average daily calcium intake for U.S. populations is reported to range between 500 and 1000 mg.[40] Because doses of up to 1000 mg of calcium per day can be consumed by an average adult with no apparent ill effects, this can be considered an adequate estimate of a no-observed-effect level. In contrast, troops in the field may consume 471 to 2475 mg of calcium per day. This range is based on an average calcium concentration in natural waters of 31.4 mg/L,[34] our estimation of an MLC of 165 mg/L, and a maximum field-water consumption of 15 L/d. Comparison of these values reveals that consumption of waters containing average calcium concentrations will result in a calcium dose that does not exceed the maximum estimated no-observed-effect level of 1000 mg/d, while consumption of 15 liters of water containing the estimated MLC for calcium will result in an exposure exceeding the no-observed-effect level. However, a survey of worldwide

surface waters reported in <u>Drinking Water and Health, Volume 3</u>[40] indicates that waters rarely exceed average levels under normal conditions. Consequently, we do not consider the presence of calcium in military field-water supplies to be an acute debilitating health threat.

<u>Chronic Toxicity</u>. There is no evidence in the review literature associating long-term exposure to calcium or its related compounds in drinking water with the induction of chronic performance-degrading health effects in humans. However, a 1975 study by Peach cited in <u>Drinking Water and Health, Volume 3</u>[40] indicated that long-term calcium intakes in excess of 1000 mg/d may raise serum calcium to levels high enough for the induction of hypercalcemia. Symptoms of this affliction include renal dysfunction, lethargy, and possible dehydration due to vomiting and diarrhea.[40,46] However, Venugopal and Luckey[46] report that hypercalcemia may be caused by hyperthyroidism or excess vitamin D intake rather than by calcium toxicity or excess dietary calcium intake. Additionally, a 1957 report by Hegsted is reported in <u>Drinking Water and Health, Volume 3</u>[40] to have shown that high calcium intakes have been associated with the formation of kidney stones in humans. Unfortunately, a definitive dose-response relationship was never established for the chronic toxicity of calcium. Thus, the relationship between ingested calcium and chronic debilitating health effects is not clearly defined. Consequently, there is not enough evidence at this time to indicate that chronic calcium toxicity will be of immediate concern to military field personnel.

<u>Carcinogenicity, Mutagenicity, Teratogenicity</u>. There is no evidence in the review literature indicating that ingested calcium or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

<u>Recommendation</u>. In summary, the divalent cation of calcium (Ca^{+2}) and its related compounds are the most prevalent forms in natural waters. These forms exhibit a very low order of oral toxicity in humans, probably because of an efficient homeostatic mechanism that functions to maintain calcium levels within physiological requirements. Comparing the maximum likely daily calcium dose for military personnel and the estimated no-observed-effect dose revealed that military personnel will not be exposed to calcium levels high enough to correspond to an acute toxic dose, even if individuals maintained 15-L/d field-water consumption over a prolonged period of time. Additionally, chronic toxicity due to long-term ingestion of calcium or its compounds has not been

firmly substantiated in human systems and is, therefore, not considered to be of military concern. Consequently, we conclude that there is no need to establish criteria or make recommendations for standards for the presence of calcium in military field-water supplies.

Carbonates

Carbonates are components of natural waters that play an active role in determining the total alkalinity of the water.[20] The most prevalent forms in natural waters are the bicarbonate anion (HCO_3^-) and related compounds. Carbonates are neither essential for human metabolism nor readily absorbed from the human gastrointestinal tract.[17] Our survey of the review literature indicates that carbonates exhibit a very low order of toxicity in human systems.

Acute Toxicity. Our survey of the review literature revealed no reported cases of acute human toxicity due to high carbonate levels in drinking waters. In fact, the Safe Drinking Water Committee of the National Research Council states in Volume 1 of Drinking Water and Health[17] that "alkalinity resulting from naturally occurring materials such as carbonate and bicarbonate is not considered a health hazard in drinking waters, per se, and naturally occurring levels up to approximately 400 mg/L as calcium carbonate ($CaCO_3$) are not considered a problem to human health." According to the conversion procedure explained by Hem,[6] a total alkalinity measurement of 400 mg/L as $CaCO_3$ corresponds to a bicarbonate concentration of 488 mg/L. We assume that 488 mg/L of bicarbonate is an adequate estimation of a no-observed-effect level. In contrast, our best estimation of the MLC of carbonate in natural water is 315 mg/L. Comparison between these values reveals that naturally occurring carbonate levels, even at the estimated maximum likely concentration, should not pose a health threat to military personnel deployed in the field.

Chronic Toxicity. There is no evidence in the review literature indicating that ingested carbonates can potentially induce chronic performance-degrading effects in exposed military personnel. Instead, carbonates may exhibit a protective effect against the manifestation or intensification of cardiovascular disease.[15]

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that orally ingested carbonates are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that ingested carbonate compounds pose a significant acute or chronic performance-degrading health threat to humans. Consequently, we conclude that there is no need to establish criteria or make recommendations for standards for the presence of calcium in military field-water supplies.

Cesium

Cesium is not identified in the literature as an element essential for human metabolism. The most prevalent forms in natural waters are the monovalent cation (Cs^+) and its related compounds. Most ingested cesium compounds are readily absorbed from the gastrointestinal tract of mammals. Elimination is rapid and complete and occurs primarily via the kidney.[46] Although human studies concerning absorption and excretion of cesium compounds have not been reported in the literature, it is assumed that the processes are similar to those observed in laboratory animals.

Our survey of the toxicity review literature reveals that reported cases of human toxicity due to the ingestion of elevated cesium levels in drinking waters are virtually nonexistent. Additionally, there are no reported cases of human toxicity as a result of therapeutic overdoses or industrial exposures of any type. Unfortunately, the only data available at present involve laboratory rat- and mouse-feeding studies. This paucity of human toxicity data indicates that elevated cesium levels in the environment are not a significant public-health problem. Consequently, we do not regard the presence of cesium or its compounds in field-water supplies to be of concern to military personnel.

Acute Toxicity. Our survey of review literature revealed no animal toxicity studies quantifying the cesium dose required to produce acute toxic effects. However, the oral rat LD50 (i.e., lethal dose necessary to produce fatalities among 50% of the experimental test animals) has been reported to be 1026 mg/kg body weight for cesium hydroxide (CsOH). This is equivalent to a dose of 910 mg/kg body weight for cesium.[46] This also corresponds to a single oral human lethal dose of 718 mg of cesium hydroxide and 636 mg of cesium, based on a 70-kg adult and the use of a 100-fold safety factor. In comparison, the maximum likely daily dose of cesium for military personnel from the ingestion of field waters is 6×10^{-4} mg/d. This calculation is based on our estimated MLC for cesium in natural waters of 4.0×10^{-5} mg/L and a 15-L/d maximum water-consumption rate for military personnel. Thus, the maximum daily dose of cesium for military personnel from the ingestion of field waters is six orders of magnitude lower than the extrapolated human lethal dose for cesium. Although an acute toxic dose of cesium will be lower than the

estimated lethal dose, these calculations suggest that it is highly unlikely that cesium concentrations in military field-water supplies will cause performance-degrading acute health effects.

Chronic Toxicity. Chronic effects in rats due to long-term cesium ingestion have been reported, although quantification of a dose-response relationship has yet to be established. The symptoms of excessive chronic cesium intake in rats include liver disorder, neuroendocrine disturbances, and neuromuscular toxicity. However, these symptoms cannot be translated to performance-degrading effects that are considered to be of military concern. Performance-degrading effects, such as vomiting and diarrhea, were not evidenced at any time throughout the exposure period.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested cesium or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. In summary, the most prevalent forms of cesium in natural waters are the monovalent cation and related compounds. Acute or chronic toxicity due to the ingestion of these forms has not been evidenced in humans. Calculations and assumptions based on acute and chronic rat-feeding studies indicate that concentrations of cesium in field waters will not be high enough to induce acute or chronic performance-degrading effects among military personnel consuming the water, even at a 15-L/d maximum consumption rate maintained over a prolonged period. Consequently, we conclude that there is no need to establish criteria or make recommendations for standards for cesium in military field-water supplies.

Chloride

The most prevalent forms of chloride in natural waters are the chloride anion (Cl⁻) and its related compounds. The chloride anion is considered to be an essential element for human metabolism and is involved in a number of physiological reactions.[57] For example, chloride plays an important role in the maintenance of fluid and electrolyte balance. It is also a necessary component of gastric juice and aids in the conservation of potassium.[57]

According to the National Research Council Committee on Dietary Allowances,[57] the daily dietary intake of chloride is almost entirely through the ingestion of sodium chloride (NaCl). Furthermore, chloride and sodium levels within the body generally parallel each other. For instance, chloride levels in the urine and tissues drop when

sodium chloride intake is restricted or when sodium is lost through excessive sweating or prolonged diarrhea. Extreme chloride losses have been reported to result in hypochloremic metabolic alkalosis (i.e., a condition in which the alkalinity of the body tends to increase above normal). Conversely, increased amounts of chlorides taken into the body result in a higher urine chloride concentration, along with an increase in the volume of urine produced per day. However, this latter condition is not possible without a simultaneous increase in water intake.[58] The National Research Council Committee on Dietary Allowances[57] reports that 1700 to 5100 mg is an estimated adequate and safe daily dietary chloride intake for the maintenance of normal metabolism in adult humans.

In general, ingested chloride compounds exhibit a very low order of toxicity in human systems. This probably can be attributed to an efficient homeostatic mechanism that maintains chloride levels within physiological requirements. Our survey of the review literature concerning chloride toxicity reveals that chloride concentrations normally found in military field-water supplies will not pose a performance-degrading health threat to troops. However, certain chloride concentrations have been reported to impart unpleasant taste to drinking water. This may be potentially debilitating from a military perspective because undesirable taste can increase troop susceptibility to dehydration by causing decreased water consumption.

Acute Toxicity. According to the review literature, the only acute toxic effects due to ingestion of elevated chloride levels are laxative effects. However, our calculations indicate that chloride concentrations in natural waters will not be high enough to produce such adverse effects. For instance, Cass[59] reports that consumption of 0.5 L of water containing 7.4 g/L of sodium chloride (NaCl) can induce a laxative effect in man. This corresponds to a single toxic dose of approximately 2.2 g of the chloride anion. However, our best estimation of the MLC of chloride in natural ground and surface waters is 960 mg/L. Cass et al.[58] state that a chloride concentration of up to 1500 mg/L can be consumed over a short period of time with no onset of laxative or other performance-degrading effects, provided there is no restriction of normal daily water intake. Unfortunately, the exposure period necessary to induce laxative effects was not mentioned. Nevertheless, we consider 1500 mg/L of chloride to be an adequate estimation of a no-observed-effect level. This no-observed-effect level is approximately 1.5 times greater than our estimated MLC for chloride in natural waters. This further supports our conclusion that acute debilitating effects resulting from consumption of elevated chloride levels are very unlikely to occur among n.iitary personnel stationed in the field.

Finally, it is important to recognize that individuals can adjust physiologically to high chloride content in waters with time. Such acclimation with time can be used to eliminate susceptibility to laxative effects.

Chronic Toxicity. Kurtz and Morris,[60] suggest that dietary chloride intake in association with sodium in the form of sodium chloride (NaCl) may induce or intensify hypertension in humans. However, military populations would have to consume extremely high levels of sodium chloride in field waters over periods exceeding the maximum one-year deployment, and experience minimal sweat loss during the exposure period, to suffer from any debilitating health effects related to hypertension.

Carcinogenicity, Teratogenicity, Mutagenicity. Chlorinated hydrocarbons, by-products of the chlorination process widely used in the purification of drinking waters, have been associated with increased incidences of cancer mortality in humans. For instance, one report indicated a 15% higher cancer mortality rate among white males who drank water high in chlorinated hydrocarbons than among white males who drank untreated well waters.[61] However, further definitive evidence is necessary to establish this cause-effect relationship because critical factors such as smoking, diet, alcohol consumption, and air pollution were not taken into consideration in this particular study due to lack of available data.

There is no evidence in the review literature indicating that the chloride anion or related inorganic compounds are teratogenic or mutagenic in humans or laboratory animals.

Taste and Odor. Various concentrations of the chloride anion (Cl^-) in drinking waters have been reported to impart a taste that is considered objectionable to certain consumers. Thus, water may be rejected on the basis of its chloride content. This is an important consideration from a military perspective because rejection of field waters may result in a susceptibility to performance-degrading effects associated with dehydration. The Safe Drinking Water Committee of the National Research Council[40] cites a 1955 report by Lockhart et al. indicating that the taste threshold for the chloride anion ranges between 210 and 310 mg/L. Unfortunately, the investigators did not indicate whether these chloride concentrations produced a taste that was objectionable enough to decrease water consumption among consumers. However, to be conservative, we consider 210 mg/L to be an adequate estimation of the lowest chloride concentration that can potentially cause decreased water consumption due to unpleasant taste. In contrast, our best estimation of the MLC of chloride in fresh waters is 960 mg/L. Comparison between these values reveals that the lowest reported adverse taste threshold is over four times less than the

estimated MLC. Thus, the unpleasant taste produced by elevated levels of chloride in drinking water could cause some military personnel to avoid drinking the water and to thereby become susceptible to the debilitating effects of dehydration.

Recommendation. Our calculations indicate that performance-degrading acute or chronic physiological effects are not likely to occur among military personnel deployed in the field as a result of any form of chloride in field-water supplies. However, chloride at its MLC in field waters (i.e., 960 mg/L), may cause the taste of water to be undesirable to military personnel. This could result in decreased water consumption by exposed troops, thereby increasing their susceptibility to dehydration. Therefore, we conclude that the potential organoleptic properties of chloride in field waters should be addressed by establishing criteria and making recommendations for standards.

Chromium

Typically, chromium occurs in four oxidation states: Cr(0), Cr(+2), Cr(+3), and Cr(+6).[20] Although only trivalent chromium has been identified to be an essential trace element for human metabolism, both the trivalent and the hexavalent states are considered to be biologically active. The essentiality of chromium in man was based initially on the fact that trivalent chromium functions in the maintenance of normal glucose metabolism in experimental animals by acting as a cofactor for insulin. Subsequent studies showed that marginal chromium deficiency in man can result in disruption of glucose metabolism, and this served to confirm the essentiality of chromium in human systems.[57] A dietary intake of 200 mg of chromium per day has been recommended as the best assurance of an adequate and safe chromium intake level for human metabolism.[57]

The most prevalent forms of chromium in natural waters are the trivalent cation (Cr+3) and the anions of hexavalent chromium, chromate (CrO_4^{-2}) and dichromate $(Cr_2O_7^{-2})$.[20] According to the National Research Council Committee on Biological Effects of Atmospheric Pollutants,[62] trivalent chromium compounds are poorly absorbed from the gastrointestinal tract and exhibit no oral toxicity in human systems. In addition, no obvious adverse systemic health effects are known to occur as a result of inhalation exposure or dermal contact with trivalent chromium compounds.[62]

In contrast, hexavalent chromium species are reported to be more toxic than the trivalent forms. Hexavalent chromium is much more soluble in natural waters than trivalent species and is rapidly absorbed from the gastrointestinal tract following ingestion. However, extremely large quantities of hexavalent chromium must be ingested

to induce debilitating health effects. Such large quantifies are needed because gastrointestinal absorption is limited by the reduction of hexavalent chromium to the insoluble trivalent form within the highly acidic regions of the gut.[40] Our survey of the review literature indicates that hexavalent chromium concentrations in field waters will not be high enough to produce performance-degrading effects among military personnel consuming these waters, even if they need to consume water at a rate of 15 L/d. Additionally, elevated levels of hexavalent chromium have been reported to impart an adverse taste and color to drinking waters. However, our findings indicate that naturally occurring chromium levels in field-water supplies are not high enough to exceed the lowest reported color and taste thresholds.

Acute Toxicity. Ingested chromium compounds are generally considered to be nontoxic to humans because of the reduction of the toxic hexavalent forms to the insoluble, nontoxic trivalent forms within the gastrointestinal tract.[17] Nevertheless, extremely high therapeutic oral overdoses of hexavalent chromium compounds have resulted in effects that can be considered performance-degrading. These effects include vomiting, nausea, and diarrhea.[17] Unfortunately, the dose necessary to produce acute adverse health effects has yet to be quantified. However, it is highly unlikely that military personnel will encounter concentrations of chromium in field-water supplies capable of delivering a toxic dose, even if consumption of 15 L/d were maintained over a prolonged period of time. For instance, the estimated adequate and safe intake level of chromium for human metabolism has been set at 0.2 mg/d.[57] We consider this to be an adequate estimation of a no-observed-effect level. In contrast, the maximum likely daily dose of chromium for military personnel from the ingestion of field-water supplies is 0.1 mg/d, based on an MLC of total chromium in natural waters of 0.007 mg/L and a 15-L/d maximum consumption rate. Comparison between these values reveals that the maximum likely daily dose of chromium for field troops is one-half of the adequate and safe intake level (i.e., no-observed-effect level). These calculations indicate that it is highly unlikely that military personnel will receive a dose of chromium high enough to produce acute debilitating effects from the consumption of field waters.

Chronic Toxicity. There is no evidence presented in the review literature that associates chronic debilitating health effects with long-term oral exposure to chromium compounds. In fact, much of the knowledge available at present concerning chronic toxicity due to hexavalent chromium compounds is based on industrial inhalation exposure.[62] Symptoms of chronic inhalation toxicity include ulceration and perforation of the nasal septum, irritation of mucous membranes, pulmonary disease, and generalized bronchiospasm.[62] In

addition, ulceration of the skin, knuckles, eyelids, and roots of fingernails are the major results of direct contact with hexavalent chromium compounds in the workplace. Although these symptoms may become performance-degrading in extreme cases, they are not considered to be important from the perspective of chromium in military field drinking-water supplies because the route of exposure is not related to water consumption. Consequently, chronic toxicity due to the ingestion of chromium compounds is not considered to be a health threat to field personnel.

Carcinogenicity, Mutagenicity, Teratogenicity. According to the review literature, chronic inhalation of hexavalent chromium compounds causes cancers of the nasal mucosa and the respiratory tract in humans and laboratory animals.[62,63] The Environmental Protection Agency's 1980 Ambient Water Quality Criteria for Chromium[63] mentions a 1956 report by Bidstrup and Case that indicates that long-term inhalation of approximately 0.74 mg CrO_3/m^3 causes a higher incidence of lung cancers among industrial workers. Additionally, Langard and Norseth[64] report that industrial inhalation of chromium air levels of 0.5 to 0.9 mg/m^3 over a period of 6 to 9 years resulted in an increased incidence of pulmonary and nasal cancers among workers. However, there is no evidence indicating that ingested chromium compounds are carcinogenic in humans or laboratory animals. Furthermore, there is no evidence that ingested chromium compounds exhibit mutagenicity or teratogenicity in humans or laboratory animals.[62,63]

Taste and Odor. The U.S. Public Health Service Drinking Water Standards[65] cites a 1957 report by Cass and Foldes that indicates 1.4 mg/L to be the lowest accepted color- and taste-threshold level for hexavalent chromium in potable waters. Concentrations above this level presumably impart an unpleasant color and taste to drinking waters. We therefore made the conservative assumption that hexavalent chromium concentrations above this threshold have sufficient organoleptic effects to cause military personnel to decrease consumption of these waters. This decrease in consumption could, in turn, increase their susceptibility to the performance-degrading effects of dehydration. In comparison, our estimate of the MLC of total chromium in natural waters is over two orders of magnitude less than the reported taste and color threshold. Thus, it seems highly unlikely that naturally occurring concentrations of chromium in field waters will produce organoleptic properties that could make the water objectionable.

Recommendation. In summary, the most prevalent forms of chromium in natural waters are the trivalent cation and the anions of hexavalent chromium. However, only the hexavalent compounds are reported to be toxic. This is because trivalent forms of

chromium are poorly absorbed from the human gastrointestinal tract.[63] Therapeutic overdoses of hexavalent chromium compounds administered orally have been shown to cause acute effects that could be performance-degrading in military personnel. However, our calculations and comparisons between the maximum likely daily dose of chromium from the ingestion of field waters and the therapeutic dose necessary to cause acute debilitating effects indicates that it is highly unlikely for military personnel to be exposed to a toxic dose, even if they consume field waters at a maximum consumption rate of 15 L/d. Primarily, this is because hexavalent chromium is rapidly oxidized to the nontoxic and poorly absorbed trivalent species by the acids of the gastrointestinal tract of humans. Chronic toxicity due to the ingestion of chromium compounds has never been documented for human systems and therefore is considered of no significance to military populations deployed in the field. Additionally, comparison between the MLC of chromium in natural waters and the threshold concentration reported to produce organoleptic effects indicates that typical chromium concentrations will not be high enough to impart an undesirable color or taste to the water sufficient to lead to decreased water consumption among military personnel deployed in the field. Consequently, we conclude that there is no need to establish criteria or make recommendations for standards for chromium in military field-water supplies.

Cobalt

The most prevalent forms of cobalt in natural waters are the divalent cation (Co^{+2}) and its related compounds. Cobalt is not identified as an essential element for human metabolism, although it is a component of vitamin B_{12}, which is required for the prevention of anemia.[47] Absorption of ingested cobalt compounds from the gastrointestinal tract of humans is rapid and complete, but cobalt exhibits a relatively low order of oral toxicity in humans because of rapid and almost complete elimination via the kidney.[47]

Our survey of the review literature indicates that toxicity due to the ingestion of elevated cobalt levels in drinking waters rarely occurs. In fact, the only reported adverse health effects of military significance have resulted from therapeutic overdoses.

Acute Toxicity. Our survey of the review literature revealed that the only reported cases of acute toxicity were the result of accidental therapeutic overdoses. The debilitating health effects of military significance that are associated with a therapeutic overdose include vomiting, nausea, and diarrhea. Unfortunately, the dose necessary to induce these performance-degrading health effects was never quantified. However, cobalt sulfate

($CoSO_4$) has been used therapeutically at up to 300 mg/d without any symptoms of adverse health effects.[17] Thus, we consider 300 mg/d of cobalt sulfate an adequate estimation of a no-observed-effect level. This corresponds to a no-observed-effect dose of approximately 114 mg of cobalt. In contrast, military personnel could conceivably be exposed to a maximum likely daily cobalt dose of 0.09 mg/d. This calculation is based on an MLC of cobalt in natural waters of 0.006 mg/L and a 15-L/d maximum field water consumption rate. Thus, a wide margin of safety (i.e., over three orders of magnitude) exists between the maximum likely daily cobalt dose expected from the ingestion of field waters and the estimated no-observed-effect level. Therefore, it appears highly unlikely that cobalt concentrations in military field waters will reach concentrations high enough to induce acute performance-degrading effects among military personnel.

Chronic Toxicity. Symptoms of chronic toxicity as a result of long-term oral exposure to cobalt or its compounds have not been demonstrated in human adults.[17] However, chronic toxicity was manifest in children between the ages of three months and 12 years as a result of the administration of a commercially prepared cobalt compound to correct anemia.[17] Symptoms included development of goiter, decreased thyroid function, and increased cardiac and respiration rate. The dosages of cobalt at which these conditions were observed ranged between 1 and 6 mg/kg body weight per day. These values correspond to single oral doses ranging between 20 and 120 mg/d (based on a weight of 20 kg for a child[27]). Comparison of these values with the previously mentioned no-observed-effect level of cobalt for adults (i.e., 114 mg cobalt) suggests that cobalt exhibits a higher order of toxicity in children than in adults. This difference in toxic potential can probably be attributed to differences in gastrointestinal absorption and excretion of cobalt following ingestion. Therefore, we do not consider that this type of exposure is of concern to adult military populations. In addition, symptoms resulting from this type of exposure are better defined as clinical diagnoses (i.e., result of the study of the signs and symptoms of a disease in an institutional environment) rather than chronic performance-degrading effects of military significance.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested cobalt or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. The divalent cation of cobalt (Co^{+2}) and its related compounds are the most prevalent forms in natural waters. These forms exhibit a very low order of toxicity in adult human systems following ingestion, probably because of rapid and complete

elimination via the kidneys. Our survey of the review literature revealed that cobalt concentrations in drinking waters are not considered to be a public health threat. In fact, the only reported adverse health effects due to cobalt exposure are the result of accidental therapeutic overdoses. Comparison between the maximum likely daily cobalt dose for military personnel from the ingestion of field waters and the dose necessary to produce performance-degrading effects indicates that cobalt concentrations in military field-water supplies will not be high enough to correspond to toxic doses, even if a maximum consumption rate of 15 L/d were maintained over a prolonged period. Furthermore, chronic effects due to long-term oral cobalt exposure have not been evidenced in adult humans and are, therefore of no concern to the military. Consequently, we conclude that there is no need to establish criteria or make recommendations for standards for cobalt in military field-water supplies.

Copper

Copper is considered to be an essential element in human metabolism and is involved in enzymatic functions associated with iron metabolism and the rate of cell synthesis in the bone marrow.[17] It is also essential for connective-tissue formation and pigmentation.[46] Copper deficiency is characterized by anemia, reduced growth, loss of arterial elasticity, defective connective tissue, and loss of hair pigment.[17,46] A Recommended Daily Allowance has not been established for copper, but the National Academy of Sciences in a 1980 publication cited in Drinking Water and Health, Volume 3[40] has estimated an adequate and safe intake level of 2 to 3 mg/d. However, another source indicates that the average daily dietary copper intake by adults can be approximately 4 to 5 mg with no onset of ill effects.

The most prevalent forms of copper in natural waters are the divalent cation (Cu^{+2}) and its related compounds. Absorption and excretion of copper is regulated by an efficient homeostatic mechanism. Initial gastrointestinal absorption is about 30% of that ingested, with a net absorption of about 5 to 10% after major elimination via the bile. Absorbed copper is stored primarily in the liver and bone marrow.[46,47]

Toxicity due to the oral ingestion of copper compounds is rare. Our survey of the review literature indicates that copper concentrations in field-water supplies are probably not high enough to induce acute, chronic, or organoleptic effects that are of military concern for personnel deployed in the field.

Acute Toxicity. According to our survey of the review literature, only very large doses of ingested copper or its compounds will produce acute effects that can be considered

performance-degrading in military personnel. For instance, 500 mg of copper sulfate ($CuSO_4$) has been used therapeutically as an emetic for adults. This corresponds to a single oral dose of 199 mg of copper. In contrast, the maximum likely daily dose of copper for military personnel from the ingestion of field water is 0.17 mg/d. This dose is based on our estimate of an MLC for copper in natural waters of 0.011 mg/L and a maximum water-consumption rate of 15 L/d. Therefore, the estimated maximum likely daily dose of copper for military personnel is over three orders of magnitude less than the dose necessary to cause emetic effects.

Acute toxic symptoms due to nontherapeutic exposures to copper are rare. However, gastrointestinal disturbances have been reported in humans after ingestion of 40 to 50 mg of copper that leached into carbonated beverages from the copper containers in which the beverages were stored.[17] This toxic dose range is still well above the estimated maximum likely daily dose of copper military personnel may receive from the ingestion of field-water. This further supports our observation that there exists a wide margin of safety between the dose obtained from the ingestion of military field-water supplies and the dose necessary to cause acute performance-degrading health effects.

Chronic Toxicity. Based on available evidence surveyed by the U.S. Food and Drug Administration in a 1975 report cited in Volume 1 of Drinking Water and Health,[17] we determined that long-term oral intake by average adults of copper concentrations less than 1 mg/L does not result in the onset of any chronic debilitating health effects. Consequently, we consider this dose to be an adequate estimation of a no-observed-effect level. In comparison, this no-observed-effect level is approximately 90 times greater than our estimated MLC of 0.011 mg/L. This indicates that it is highly unlikely that military personnel will be exposed to toxic concentrations of copper from the ingestion of field water. Furthermore, daily intakes of dietary copper of up to 5 mg appear to pose little, if any, health hazard to the general population.[17] The only population adversely affected by small or normal amounts of copper in the diet are those with Wilson's disease, an inherited autosomal recessive trait involving degeneration of copper metabolism.[17] Symptoms of this disease involve hepatic cirrhosis, necrosis and sclerosis of the brain, and neurological disturbances including tremors, psychosis, and slurring of speech. This condition, however, is of no concern to the military because individuals with Wilson's disease are not likely to be a part of the military population.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no conclusive evidence in the review literature indicating that ingested copper or its compounds carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Taste and Odor. Copper has been known to impart an astringent taste to drinking waters. The National Secondary Drinking Water Regulations[66] for copper cite the findings of Cohen in 1960 which indicate that the taste threshold for copper ranges from 1 to 5 mg/L, based on variation among individual taste perceptions. The interim copper limit for drinking water has thus been established at 1 mg/L, based on consideration of taste rather than toxicity.[17] Offensive taste can pose a health threat to troops in the field by increasing susceptibility to dehydration as a result of decreased field-water consumption. However, this is highly unlikely to occur because the estimated MLC of copper in fresh waters of 0.011 mg/L is 90 times less than the organoleptic threshold of 1 mg/L.

Recommendation. In summary, copper is identified in the literature as an element essential for human metabolism. The most prevalent forms of copper in natural waters are the divalent cation (Cu^{+2}) and its related compounds. Absorption and excretion of copper are regulated by a homeostatic mechanism. Comparison between the maximum likely daily dose of copper for military field personnel and the dose necessary to produce acute, chronic, and organoleptic performance-degrading effects reveals that individuals will not receive toxic concentrations of copper from the ingestion of field water, even at a 15-L/d maximum consumption rate. Consequently, we conclude that there is no need to establish criteria or make recommendations for standards for copper in military field-water supplies.

Cyanide

Most of the inorganic cyanide salts (e.g., sodium cyanide, potassium cyanide, calcium cyanide) that occur in natural waters are quite soluble and hydrolyze to release free cyanide ions.[18] In most natural waters, these free cyanide ions (CN^-) quickly form the toxic hydrogen cyanide (HCN) molecule.[52] Although hydrogen cyanide is considered to be the most toxic form of cyanide in natural waters, toxic concentrations rarely occur because it tends to volatilize and be lost to the atmosphere. For example, cyanide salts occur in natural waters primarily as a result of industrial pollution; however, literature concerning water quality indicates that routine analyses of waters very seldom include cyanide measurements because of extremely low naturally occurring concentrations. Nevertheless, cyanide is of interest because of its potential use as a threat agent (e.g., prussic acid) in chemical warfare.

According to a 1980 report by Rumack and Peterson cited by Scofield et al.,[18] cyanide is generally considered to be a potent, fast-acting human toxin. This can be attributed to rapid and complete absorption from the gastrointestinal tract. The

mechanism by which cyanide functions toxicologically is through the binding of cyanide ions to cytochrome oxidase. This decreases the ability of the enzyme to catalyze and use oxygen in the electron–transport chain, thereby restricting aerobic metabolism. Respiratory arrest is the typical cause of death following exposure to lethal concentrations of cyanide.

The 1959 report of Williams cited by Scofield et al.[16] indicated that cyanide toxicity in human systems is regulated by an efficient detoxification mechanism involving the liver. Cyanide is enzymatically converted by the liver to the nontoxic thiocyanate, which is subsequently excreted via the urine. Toxic concentrations of cyanide rarely accumulate within the human body except in situations when the cyanide overwhelms the detoxification mechanism. Our survey of the review literature indicates that naturally occurring cyanide concentrations in military field–water supplies are of no toxicological concern to personnel deployed in the field. Therefore, only cyanide introduced as a threat agent constitutes a concern for military personnel consuming field water.

Acute Toxicity. A 1982 report by Hartung cited in Scofield et al.[18] indicates that acute toxic symptoms of cyanide poisoning manifest themselves almost immediately after ingestion. Symptoms include headache, nausea, breathlessness, weakness, cardiac palpitation, giddiness, and tremors. Convulsions, paralysis, and coma have also been reported as nonfatal symptoms of acute toxicity according to a 1980 publication by Rumack and Peterson that was also noted by Scofield et al.[18] The lowest lethal oral dose of hydrogen cyanide for an adult human is reported to be approximately 40 mg.[28] This corresponds to a single oral dose of approximately 38 mg of cyanide. Additionally, according to Scofield et al.,[18] Hartung reported in 1982 that ingestion of 50 to 100 mg of sodium or potassium cyanide can cause an individual to collapse and then suffer respiratory arrest. This is equivalent to 20 to 53 mg of cyanide. Fatalities were not reported after ingestion of these doses. Therefore, we consider 20 mg to be an adequate estimation of the lowest toxic dose of cyanide necessary to produce acute debilitating symptoms. Based on our best estimation of the MLC for cyanide in natural waters (i.e., 0.04 mg/L) and a maximum 15-L/d field–water consumption rate, military personnel may consume up to 0.60 mg of cyanide per day. Thus, the maximum likely daily cyanide dose for military personnel is approximately 33 times less than the lowest reported acute toxic dose. Consequently, it is highly unlikely that naturally occurring cyanide concentrations in field waters will be high enough to induce acute performance–degrading effects among military personnel consuming the water.

Chronic Toxicity. Chronic symptoms of long-term ingestion of cyanide compounds include goiter, diabetes, and neuropathies.[17] High rates of these afflictions are reported to occur in certain regions of Africa and the Caribbean where the cyanide-containing cassava root is consumed in large quantities. However, many contributing factors are involved in the development of these conditions, and the role of cyanide is not clearly understood. Additionally, a quantitative dose-response relationship for this form of ingested cyanide has never been established. However, Volume 1 of Drinking Water and Health[17] reports that long-term consumption of 5 mg/d or less of cyanide produces no adverse health effects in humans. Thus, we consider this to be an adequate estimation of a chronic no-observed-effect level. In comparison, our calculations indicate that the maximum cyanide dose for military field personnel is approximately one-eighth of this no-observed-effect level. Therefore, we conclude that naturally occurring cyanide levels in military field waters are not likely to induce chronic performance-degrading effects of military significance.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested cyanide or its related compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Taste and Odor. According to Scofield et al.,[18] cyanide is commonly known to have a characteristic "burnt almond" odor. However, an organoleptic threshold for this odor has not been defined. Additionally, according to a 1961 report published by Glout cited by Scofield et al.,[18] only sensitive individuals are capable of detecting cyanide odor, and between 20 and 40% of the U.S. population are unable to detect cyanide by odor. Consequently, it is highly unlikely that military field personnel will react to, or detect, cyanide odor to a degree that would decrease water consumption.

Recommendation. In summary, cyanide, particularly HCN, is a potent, fast-acting human toxin that is rapidly absorbed from the gastrointestinal tract of humans. However, consumption of relatively large oral doses of cyanide are necessary to induce acute or chronic performance-degrading effects because of an efficient detoxification mechanism in humans involving the liver and kidneys. Our survey of the review literature revealed that naturally occurring cyanide concentrations in military field waters will not be high enough to induce acute or chronic debilitating health effects, even if individuals needed to drink water at 15 L/d over a long period. Consequently, we conclude that the presence of cyanide in field-water supplies ordinarily poses no toxicological threat to troops. However, cyanide can be used as a threat agent (e.g., prussic acid) in chemical warfare or

as an opportunity poison to sabotage military field-water supplies. Cyanide is also a component of tear gas (cyanogen chloride), which can directly debilitate troops through contact with the eyes and skin, and can also indirectly affect troops by concentrating in field waters used for consumption. Therefore, cyanide introduced into field drinking-water sources indirectly during military conflicts could be of importance from a military health perspective. For this reason, the health implications of exposure to elevated cyanide levels in military field-water supplies should be investigated, criteria should be established, and recommended standards should be developed.

Fluoride

Fluoride is considered to be an essential element for human metabolism due to its proven beneficial effects on dental health. The National Research Committee on Dietary Allowances[57] cites a 1965 report by Sognnaes indicating that incorporation of the fluoride ion into the crystalline structure of hydroxyapatite in the enamel of teeth results in an increased resistance of teeth to the development of dental caries. Although fluoride protection is evidenced mainly in the preeruptive phase of the teeth, circumstantial evidence cited by the National Research Committee on Dietary Allowances[57] from a 1971 article by Beap suggests that fluoride may exhibit a protective effect against diseases of the elderly such as osteoporosis and periodontal disease. A recommended adequate and safe intake level of 1.5 to 4.0 mg/d for adults has been set by the Food and Nutrition Board of the National Research Council.[57]

The most prevalent forms of fluoride in natural waters are the monovalent anion (F^-) and its related compounds. Although gastrointestinal absorption is rapid and complete,[17] available evidence indicates that fluoride exhibits a relatively low order of toxicity when ingested by humans.

Acute Toxicity. Cases of acute toxicity due to the ingestion of high levels of fluoride in drinking waters are virtually unknown. However, rare cases of fluoride toxicity do occur principally as a result of suicide or accidental poisoning. Acute effects, including irritation of the gastrointestinal mucosa, vomiting, diarrhea, and abdominal pain followed by paresthesia (i.e., abnormal sensation without objective cause, such as numbness), hyperactive reflexes, and convulsive twitching of the muscles have been reported. In extreme cases death from respiratory paralysis or cardiac failure may result.[67] The lowest lethal dose of sodium fluoride has been reported in two references as being around 71 mg per kg of body weight, or about 5 g based on a 70-kg man.[17,27] This represents a lethal dose of 2.3 g of fluoride. Additionally, the lowest oral dose of fluoride ion reported

to produce toxic effects in humans, including convulsions, respiratory changes, and liver dysfunction, is 3 mg/kg of body weight.[27] This dose is equivalent to a single oral dose of 210 mg for a 70-kg adult. The no-observed-effect dose is assumed to be lower. In contrast to these levels, the maximum likely daily intake of fluoride for troops deployed in the field is 37.5 mg/d. This daily dose is based on our estimate of the MLC of fluoride in natural waters of 2.5 mg/L and a maximum consumption rate of 15 L/d. Comparison of these values reveals that the maximum likely daily dose of fluoride for troops from the consumption of field waters is five times smaller than the 210-mg value for a toxic effect. Therefore, the presence of fluoride in natural waters is not considered to pose a militarily significant health threat.

Chronic Toxicity. Two types of chronic effects are attributed to the excess intake of fluorides over a long period of time: dental fluorosis and crippling skeletal fluorosis.[17] Dental fluorosis is a mottled discoloration of teeth enamel resulting from ingestion of excessive amounts of fluoride during tooth development. This condition, however, is not considered to be performance-degrading for military personnel and will not be discussed in further detail. Skeletal fluorosis results from a gradual retention of fluoride in the skeleton after years of chronic exposure. Initial stages of toxicity appear as symptoms of mild rheumatism. Crippling effects, which usually manifest themselves after 10 to 30 years of exposure, include stiffness of the spine, rigidity of the thorax, and excessive degeneration and contractures of connective tissues of the joints.[17] The mechanism by which skeletal fluorosis occurs is dependent on the antagonistic relationship between the amount of fluoride and calcium in the body. Calcium is an essential element in the formation of bone and is utilized in its cationic form. Excessive fluoride forms complex salts with the calcium cation and thus reduces or prevents the absorption of calcium into the human skeleton, which culminates in skeletal fluorosis.[68]

Although crippling skeletal fluorosis can be considered a debilitating health effect for military personnel, its symptoms are manifest only after years of exposure to high fluoride levels. This disease has a very long latent period which far exceeds the maximum one-year field deployment of military personnel. As cited in Drinking Water and Health, Volume 3,[40] Roholm in 1937 estimated that crippling skeletal fluorosis results after daily ingestion of 20 to 80 mg of fluoride for 10 to 20 years. Our survey of the review literature indicates that this is the widely accepted dose-response relationship for fluoride and skeletal fluorosis. Basing chronic toxicity on this information, it is highly unlikely that military personnel will suffer from skeletal fluorosis after exposure to 37.5 mg of fluoride per day (based on an MLC of fluoride in natural waters of 2.5 mg/L and a 15-L/d consumption rate) during a one-year field deployment.

<u>Carcinogenicity, Mutagenicity, and Teratogenicity.</u> The review literature contains information suggesting an association between fluoridation of water and increased cancer rates. However, in considering the available evidence concerning the possible carcinogenic effects of fluorides, the National Cancer Institute found that many investigators failed to take into account age distributions and various demographic factors that can affect cancer rates.[17] Thus, there has been no confirmation that fluoride causes cancer in humans. In fact, epidemiological studies conducted by British investigators showed that cities practicing fluoridation had either the same or a lower cancer incidence rate than cities without water fluoridation.[17]

There is evidence in the review literature indicating that fluoride, in the form of hydrogen fluoride (HF), might be mutagenic in various species of plants and in certain strains of <u>Drosophila</u>.[17] However, there are no available data in the review literature suggesting that ingested fluorides exhibit mutagenic tendencies in humans. Teratogenicity, as a result of oral exposure to the fluoride ion (F^-) or its compounds, has not been reported in humans nor clearly demonstrated to occur in laboratory animals.[17]

<u>Recommendation.</u> The predominant forms of fluoride in natural waters are the monovalent anion (F^-) and its related compounds. Performance-degrading physiological effects are not likely to result from exposure to these forms of fluoride in field drinking-water supplies. The review literature indicates that induction of acute debilitating effects requires ingestion of extremely high levels of fluoride. Our calculations reveal that these levels will not be encountered in military field-water supplies as a result of natural geochemical processes or industrial activities. Skeletal fluorosis is not considered to be of military concern because it is typically associated with very long-term exposure to elevated fluoride levels. Consequently, we conclude that there is no need to develop specific criteria and recommendations for standards concerning the presence of fluoride in military field-water supplies.

Iodine

Dietary iodine, which is converted to iodide (I^-) in the gastrointestinal tract, is considered to be an essential trace element for human metabolism and is involved in the synthesis of thyroxine, an iodized, hormonally active amino acid located in the thyroid gland.[40,68] Iodine deficiency results in low levels of thyroxine that, through negative feedback, induces increased production of the thyroid-stimulating hormone (TSH) in the

blood. This culminates in an abnormal growth of the thyroid gland commonly referred to as goiter.[68] The recommended daily allowance for iodine has been established as 0.15 mg/d. The adequate and safe intake range for adults has been set at 0.05 to 1.00 mg/d.[57]

The monovalent iodide anion (I^-) usually occurs in natural waters. Many food sources contain appreciable amounts of iodine compounds, which are converted to iodides in the gastrointestinal tract and then rapidly and completely absorbed. Even though absorption is rapid and complete, iodides are known to exhibit a very low order of toxicity in human systems. This is attributed largely to a high rate of excretion via the renal system that occurs almost immediately following ingestion.[40] Due to this high turnover rate, only large oral doses of iodide (or iodine from foods) are capable of producing acute or chronic debilitating health effects in humans. According to our survey of the review literature, large oral doses such as these are not likely to be encountered by military personnel consuming field-water supplies, even at a maximum rate of 15 L/d.

Acute Toxicity. Acute poisoning due to the ingestion of iodide present in drinking-water supplies is not common. In fact, adverse health effects in humans following oral exposure to iodide compounds have been reported only for therapeutic overdoses. For instance, Block et al.[9] report that therapeutic oral administration of approximately 300 mg of potassium iodide (KI) four times per day exhibits an expectorant effect in most adults without inducing any symptoms of acute toxicity. This amount of KI corresponds to a single oral dose of 917 mg of iodide. Other acute adverse reactions have occasionally been exhibited within a short period of time following iodine administration, although quantification of the dose necessary to produce these effects has not been established.[34] The most frequent of these effects is referred to as "iodide mumps," and involves a swelling of the salivary glands along with fever and headaches. Clinical diagnoses of lymphoadenopathy, eosinophilia, and erythema have also occurred, but these are not considered to be performance-degrading from a military perspective. An oral dose of 2 to 3 g of iodine (I_2) has been estimated to be lethal to humans; however, full recovery has been reported in humans even after ingestion of 10 g of iodine.[40]

Our survey of the previously mentioned toxicity data concerning therapeutic iodide administration indicates that a single oral iodide dose must exceed 917 mg in order to produce acute debilitating health effects in most individuals.[40] Using 917 mg of iodide as a no-observed-effect level, it appears highly unlikely that military personnel stationed in the field will be exposed to a toxic dose from ingestion of natural waters. For instance, the maximum daily iodide dose for a soldier is 0.60 mg/d, based on our estimate of the MLC in field waters of 0.04 mg/L of iodide and a maximum 15-L/d water-consumption

rate. This is approximately three orders of magnitude less than the assumed no-observed-effect level, which indicates that there is a wide margin of safety between daily iodide intake from field waters and the dose necessary to produce acute debilitating toxic effects. This dose, even with the addition of iodine contributed by foods, should not reach toxic levels under normal conditions since dietary iodine deficiency occurs much more frequently worldwide than does detrimental iodine excess.[40,68]

Chronic Toxicity. Chronic effects of excessive iodide intake include congestion of nasal passages, severe headache, sneezing, gastrointestinal irritation, gingivitis (i.e., inflammation of the gums), and a burning sensation of the oral mucosa.[40] Such effects can be performance-degrading in extreme cases, but the dose necessary to produce these symptoms is not well-defined. For example, one investigator has suggested that long-term intake of 2.0 mg/d of iodide is potentially harmful, although iodide intake levels in some areas of Japan have reached 50 to 80 mg/d without apparent toxic effects.[40] However, none of these daily doses is likely from field-water supplies containing an MLC of 0.04 mg/L, even if such water is consumed at a maximum rate of 15 L/d.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested iodide or iodine is carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Taste and Odor. A taste threshold for the iodide ion and all other forms that may be present in natural waters has been reported to be 0.147 to 0.204 mg/L.[40] The MLC of iodide in natural waters is estimated to be 0.04 mg/L, significantly lower than this taste-threshold range. This indicates that organoleptic effects related to iodide in water should not increase troop susceptibility to dehydration. Additionally, no confirmation was made as to whether or not the taste resulting from this threshold range was sufficiently unpleasant to cause decreased water consumption among the taste panelists. Therefore, adverse taste due to the presence of iodide in military field-water supplies is not considered to be of concern for field troops.

Recommendation. In summary, the most prevalent forms of iodide in natural waters are the monovalent anion (I^-) and its related compounds. Although gastrointestinal absorption is rapid and complete, excretion of much of the absorbed iodide occurs almost immediately after ingestion, thus reducing the toxic potential of this element. Comparison of the maximum likely daily dose of iodide from the consumption of field-water supplies and the levels required to produce acute, chronic, and organoleptic

performance-degrading effects reveals that military personnel will not be exposed to toxic iodide concentrations, even at a 15-L/d water consumption rate. We conclude that there is no need to establish criteria and make recommendations for standards concerning iodide in military field-water supplies.

Iron

Iron is considered to be an essential element for human metabolism and is involved in a number of physiological reactions.[57] The primary function of iron is to contribute to the production of hemoglobin and myoglobin, both of which are involved in oxygen transport and storage.[69] Iron is also a cofactor in heme enzymes, including catalase and cytochrome C, and in nonheme enzymes, such as tryptophan oxygenase and aldolase.[46] Iron deficiency results in anemia, stunted growth, susceptibility to infection, and lassitude.[46] The actual daily requirement for absorbed iron has been established as 1.0 mg for adult males and 1.5 mg for adult females; the greater requirement for women is attributed to blood loss during menorrhea.[40] However, due to inefficient absorption of iron by the gastrointestinal tract, 10 to 20 times these quantities must be ingested to meet daily needs. The recommended daily allowance for iron has thus been set at 10 mg for adult males and 18 mg for females of reproductive age to assure adequate intake for the majority of the population.[40]

In humans, iron levels are regulated by a homeostatic mechanism. Actual absorption of iron compounds is controlled by the adequacy of iron stored in the body. For instance, in normal adults 8 to 10% of the iron ingested is absorbed, but in iron-deficient individuals this rises to about 10 to 15% of the amount ingested.[46] Iron ingested after physiological requirements have been achieved is eliminated primarily via the feces. However, extreme excesses above physiological requirements may be excreted in the urine.[47] Although the presence of high iron concentrations in the urine may be significant clinically, this is not important toxicologically to field personnel because this condition is not associated with performance-degrading effects.

The chemistry of iron in natural waters is complicated. Insoluble ferric hydroxide, $Fe(OH_3)$, is the most stable form of iron in surface waters and aerated ground waters. However, low-pH natural waters containing small concentrations of carbonate can contain ferrous iron (Fe^{+2}) in concentrations high enough to impart adverse taste. Although the toxicity data presented here do not distinguish between species of iron, the data indicate that iron is not likely to be toxic to man if ingested. However, there is evidence that iron

can affect the appearance and taste of water. The correspondence between iron species and organoleptic effect has not been well-defined, but insoluble ferric iron probably affects color, and dissolved ferrous iron probably affects taste.

Acute Toxicity. Our survey of the review literature revealed no evidence that the ingestion of iron at naturally occurring concentrations in food or water can produce acute toxic health effects in adults. In fact, adverse health effects following the ingestion of iron compounds have been reported only for therapeutic overdoses. Unfortunately, quantification of the dose-response relationship for such therapeutic overdoses has not been established, but the acute symptoms are reported to include vomiting, diarrhea, gastrointestinal bleeding, lethargy, and a rapid increase in respiration and pulse rate. Gray cyanosis (i.e., gray discoloration of the skin and mucous membranes) followed by pneumonitis, shock, coma, and death may result in extreme cases.[46,47]

The usual therapeutic daily dose of iron is 120 to 180 mg administered orally.[9] This dose normally produces no symptoms of acute adverse effects in the average individual.[69] Consequently, we consider this dose range to be an adequate estimation of a no-observed-effect range. In comparison, the National Research Council[69] cites Crotty in 1971 as reporting that the average human lethal dose of iron ranges between 200 to 250 mg/kg body weight, which corresponds to 14 to 15 g of elemental iron for a 70-kg adult male. The minimum lethal dose is probably much lower, because fatalities have occurred following ingestion of 7 g of iron.[46] In contrast to these figures, the maximum likely dose military personnel could ingest daily from field-water supplies is 22.5 mg. This dose is based on our estimation of an MLC of iron in water of 1.5 mg/L and a 15-L/d maximum water-consumption rate by military personnel. Thus, the maximum daily dose of iron for military personnel from water is 5.3 to 8.0 times less than our estimated no-observed-effect level and more than two orders of magnitude less than the minimum lethal dose. These calculations indicate that it is unlikely that iron concentrations in military field-water supplies will cause performance-degrading acute health effects.

Chronic toxicity. Chronic effects due to long-term therapeutic iron ingestion have been reported, although quantification of the dose necessary to produce chronic toxicity in man has yet to be established. The symptoms of excessive chronic iron intake may consist of the onset of hemosiderosis or hemochromatosis. Hemosiderosis is characterized by an increased iron content in body tissues, in particular the liver and the reticuloendothelial system. Hemochromatosis involves hemosiderosis in conjunction with diffused fibrotic

changes of the affected organ.[47] Both of these chronic health effects are important clinically, but do not appear to be associated with chronic health problems that could be considered performance-degrading to military personnel.

Carcinogenicity, Mutagenicity, and Teratogenicity. The review literature contains information suggesting that some iron compounds may act as co-carcinogens in laboratory rats after parenteral injection.[46] Nevertheless, carcinogenicity, mutagenicity, and teratogenicity have not been associated with the ingestion of iron compounds by humans or laboratory animals.

Taste and Odor. Iron may impart a brown or rusty color to water at concentrations above 0.05 mg/L, and a bitter or astringent taste may be detected by some individuals in water containing between 0.1 and 1.0 mg/L of iron.[66] The present recommended limit for iron in U.S. water supplies of 0.3 mg/L is based on minimizing these aesthetic effects and is not based on any toxicological data.[40]

Recommendation. Performance-degrading physiological effects are not likely to occur in military personnel as a result of any form of iron in field-water supplies. However, iron, particularly at its MLC in field-water supplies (i.e., 1.5 mg/L), may cause the taste and appearance of such waters to be undesirable aesthetically. These organoleptic conditions could cause some personnel to avoid drinking the water and to become susceptible to the performance-degrading effects of dehydration. Unfortunately, it is not possible to develop specific criteria and recommendations for standards for this dose-response relationship from the limited data available. Nevertheless, quantitative dose-response relationships can be derived to describe the general response of a population to the appearance or taste of drinking water resulting from the collective effect of all of the constituents of the water. Therefore, potential organoleptic consequences of iron species in these waters can be addressed indirectly by criteria and recommendations for standards for color, turbidity, and total dissolved solids.

Lead

Lead is not identified in the literature as an element essential for human metabolism. The predominant forms of lead in natural waters are the divalent cation (Pb^{+2}) and its related compounds. However, lead concentrations are not found at high levels in natural waters under normal circumstances because lead usually occurs as the insoluble carbonate ($PbCO_3$), sulfate ($PbSO_4$), and sulfide (PbS).

Gastrointestinal absorption of lead is quite variable. Approximately 5 to 10% of ingested lead is absorbed into the bloodstream of an average adult. Some studies, however, have reported almost 70% absorption of ingested lead among particular individuals.[70] Children exhibit a fivefold increase in gastrointestinal absorption of lead in comparison to adults. These differences in absorption rates have been attributed to factors including metabolic differences associated with age, physiological status of the individual, composition of the diet, and form of lead ingested.[47] Excretion is rapid and occurs primarily by way of urine and bile.[47]

Our survey of the review literature indicates that naturally occurring concentrations of lead in field waters are not high enough to produce acute or chronic performance-degrading effects of military significance even at a 15-L/d maximum consumption rate.

Acute Toxicity. Our survey of the available toxicity data revealed that reports of acute poisoning due to the ingestion of lead are limited. In fact, acute oral lead poisoning rarely occurs at all in the general population. Infants and small children are reported to be much more susceptible than adults to oral exposure to lead compounds. This is due to a more rapid and complete absorption from the gastrointestinal tract.[45] Acute symptoms in children include vomiting, lassitude, convulsions, and loss of appetite followed by coma and death in extreme cases. Unfortunately, the dose necessary to cause toxic effects has not been quantified. However, according to a 1970 report by Klein et al., cited in Volume 1 of Drinking Water and Health,[17] one child is known to have died as a result of consuming a dose of 1 g/d of lead over a period of 35 days; the lead was consumed during the ingestion of canned fruit juice. Therefore, 1 g/d of lead consumed per day over a period of 35 days can be considered an adequate estimation of a lethal dose for a child. If a child can tolerate 1 g of lead per day for a period of 35 days before death occurs, it seems reasonable to assume that an adult system would be capable of handling an even higher daily ingestion rate for a longer time before fatality occurs.

Although it is difficult to assess acute oral lead toxicity in adults due to the paucity of relevant data, this lack of data suggests that ingestion of lead is not ordinarily a major problem among the general adult population. Consequently, we conclude that our calculated MLC of lead in natural waters of 0.02 mg/L, which is less than one-half of the present drinking-water standard of 0.05 mg/L,[17] will not produce debilitating health effects among military personnel consuming field waters at 15 L/d.

Chronic Toxicity. The Safe Drinking Water Committee of the National Research Council[17] cites a 1972 report by Beattie et al. stating that cases of adult chronic lead poisoning have been associated with long-term consumption of soft well water from the

acidic moorlands of Scotland and Northern England. The lead concentration of tap water in these cases ranged between 0.57 and 3.1 mg/L as a result of leaching from lead pipes and lead-lined cisterns used for storage. According to a report by Harris and Elsea in 1967 cited in Volume 1 of <u>Drinking Water and Health</u>,[17] consumption of approximately 2 mg of lead per day for 1.5 y resulted in an onset of plumbism (lead poisoning) in one individual. Chronic symptoms of plumbism include renal malfunction, liver cirrhosis, and afflictions of the central and peripheral nervous systems.[17] Ingestion of elevated levels of lead apparently does not cause immediate gastrointestinal disturbances such as diarrhea and vomiting in adults, probably due to poor gastrointestinal absorption of ingested lead compounds.[17]

In contrast to the reported chronic toxic dose of 2 mg/d of lead for 1.5 y, the maximum possible daily dose of lead for military personnel consuming field waters is 0.30 mg. This dose, which is based on a calculated MLC of lead in natural waters of 0.02 mg/L and a maximum 15-L/d water-consumption rate, is less than one-sixth of the toxic dose. This comparison implies that exposure to this dose for the maximum field-deployment period (1 y) will not induce the chronic effects of plumbism. In addition, normal concentrations of lead in waters not associated with lead piping seldom reach levels exceeding the established U.S. drinking-water standard of 0.05 mg/L.[70]

<u>Carcinogenicity, Mutagenicity, Teratogenicity.</u> There is no evidence in the review literature indicating that orally ingested lead or its compounds are mutagenic in humans or laboratory animals. However, there is evidence suggesting that certain lead compounds are carcinogenic and teratogenic in certain animal species. For instance, over 90% of a group of male rats fed a diet containing 1% lead acetate for 1 y were found to have either adenomas or adenocarcinomas of the kidney.[71] Teratogenic effects including resorption, fetal deaths, and skeletal abnormalities, are known to follow the intravenous administration of 50 mg/kg of various lead salts (e.g., lead nitrate, lead chloride, lead acetate) to pregnant rats. However, according to the review literature, carcinogenic and teratogenic effects have not been reported in human systems as a result of the ingestion of lead or its compounds.

<u>Recommendation.</u> In summary, the most prevalent forms of lead in natural waters are the divalent cation (Pb^{+2}) and its related salts. These forms exhibit low oral toxicity in adult human systems due to low solubility in water and poor absorption from the gastrointestinal tract. In addition, our calculations indicate that the maximum daily dose of lead for military personnel from the ingestion of field waters ordinarily will not be high enough to produce performance-degrading acute or chronic effects among healthy adults. In fact,

normal concentrations of lead in waters that are not soft waters or associated with lead piping rarely exceed the U.S. drinking-water standard for lead of 0.05 mg/L. Consequently, we conclude that there is no need to establish criteria and recommendations for standards concerning the presence of lead in military field-water supplies.

Lithium

Lithium is not identified in the literature as an element essential for human metabolism. The most prevalent forms of lithium in natural waters are the monovalent cation (Li^+) and its related compounds. Gastrointestinal absorption of lithium compounds in humans is rapid and complete. Ingested lithium compounds exhibit extremely low toxicity, presumably because of very efficient elimination via the kidneys.[46]

Our survey of the toxicity review literature revealed no evidence of any acute or chronic poisonings as a result of elevated lithium levels in drinking waters. In fact, the only reported adverse health effects due to oral exposure to lithium compounds are related to accidental therapeutic overdoses. Such overdoses are common because lithium has widespread use in the treatment and prevention of the manic phase of recurrent manic-depressive psychoses.[46] Exact mechanisms related to the therapeutic actions of lithium are unknown, but rat studies indicate that lithium may aid in the stabilization of alterations in neurotransmission at serotonin synapses, which have been implicated in psychotic disorders.[72,73] Despite its wide use, the dose of lithium necessary to produce adverse health effects has not been firmly established. Nevertheless, our comparisons between the estimated toxic dose and the maximum likely daily dose for military personnel from the ingestion of field waters indicates that it is highly unlikely that military personnel will be exposed to toxic doses of lithium, even if they consume field waters at a 15-L/d maximum rate over a prolonged time.

Acute Toxicity. The lowest adult toxic dose of therapeutically administered lithium chloride (LiCl) is reported to be 243 mg per kg of body weight dispensed over a 13-day period.[28] Acute performance-degrading symptoms include gastrointestinal disturbances, dizziness, tremors, mental confusion, ringing in the ears, and visual disturbances.[46] This toxic dose of lithium chloride corresponds to a total dose of approximately 2.8 g of lithium, based on a 70-kg man. In contrast, the maximum daily dose of lithium military personnel may receive from the ingestion of field waters is 0.75 mg/d. This dose is based on the daily consumption of a maximum of 15 L of field water containing an estimated MLC for lithium of 0.05 mg/L. Thus, the maximum likely daily lithium dose from field waters is approximately two orders of magnitude less than the average daily dose of

lithium (i.e., 214 mg/d) derived from the lowest reported toxic dose of LiCl (i.e., 243 mg/kg) administered orally over 13 d to a 70-kg adult. Thus, it appears highly unlikely that military personnel will receive a toxic dose of lithium from the ingestion of field waters.

Chronic Toxicity. According to our survey of the review literature, debilitating toxic effects due to chronic ingestion of lithium or its compounds have not been shown in humans or laboratory animals. Consequently, chronic lithium toxicity cannot be considered of military concern until additional evidence indicates otherwise.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested lithium compounds are carcinogenic or mutagenic in humans or laboratory animals. However, the teratogenicity of ingested lithium compounds has been reported in laboratory rats and mice. For instance, Venugopal and Luckey[46] cite a 1970 report by Szabo et al. that indicates that daily doses of 300 mg/kg of Li_2CO_3 (56 mg/kg of lithium) administered orally to rats and mice on days 6 to 15 of gestation can induce teratogenic effects in the newborn animals. These teratogenic effects include resorption, a lower fetal-survival rate, and skeletal abnormalities, such as cleft palate and external ear defects. However, lithium has not been reported to induce teratogenic effects in humans at the therapeutic levels used in treating manic psychoses, although some newborn children of mothers that underwent lithium therapy during pregnancy have shown symptoms of acute lithium toxicity.[46]

Recommendation. In summary, the monovalent cation of lithium (Li^+) and its related compounds are the most prevalent forms in natural waters. These forms produce very little toxicity following oral administration in human systems, probably because of rapid and efficient elimination following gastrointestinal absorption. The major health concern about lithium compounds is accidental therapeutic overdoses. Comparison between the lowest reported toxic dose of therapeutically administered lithium and the maximum likely daily lithium dose for military personnel from the ingestion of field waters indicates that lithium concentrations will not be high enough under normal conditions to produce debilitating health effects among military personnel consuming field waters at a 15-L/d maximum rate. Consequently, we conclude that there is no need to establish criteria and make recommendations for standards for lithium in military field-water supplies.

Magnesium

Magnesium is considered to be an element essential for human metabolism, functioning as a cofactor for many enzymes and contained in several metalloenzymes. In addition, magnesium is important in maintaining electrical potential in muscle membranes and nerves.[57] The National Research Committee on Dietary Allowances[57] cites the 1968 report of Wacker and Parisi as showing that magnesium deficiency leads to neuromuscular dysfunctions including muscular excitability and convulsions, along with possible degeneration of neurochemical transmission as manifested by behavioral disturbances. The average daily dietary intake of magnesium for adults in the United States is between 240 and 480 mg.[17] The recommended daily allowance for magnesium is 350 mg for adult males and 300 mg for adult females. An additional allowance of 150 mg/d is recommended for pregnant and lactating women.[57]

The most prevalent form of magnesium in natural waters is the divalent cation (Mg^{+2}) and its related compounds. These forms are reported to be fairly soluble in water, although gastrointestinal absorption in humans is quite limited.[17] Magnesium levels necessary for metabolism are regulated by the kidneys. This mechanism involves filtration of magnesium by the glomeruli, followed by reabsorption through the renal tubules. Any excess magnesium is excreted via the urine.[47]

Magnesium salts are widely used therapeutically as cathartics and laxatives.[40] Therefore it seems reasonable to assume that high levels of magnesium in drinking waters could cause laxative effects among the general population, as well as among a military population deployed in the field. Additionally, there is evidence that magnesium can affect the taste and appearance of water.

Acute Toxicity. The only acute toxic effects due to oral magnesium exposure mentioned in the review literature concern the laxative effects induced by therapeutic administration of magnesium salts. Unfortunately, the dose-response relationship between magnesium ingestion and laxative effects has not been firmly defined. However, various effect levels have been reported by a few investigators.

A report by McKee and Wolf in 1963 is cited in Volume 1 of Drinking Water and Health[17] to indicate that magnesium sulfate $(MgSO_4)$ levels exceeding 700 mg/L have laxative effects on individuals not accustomed to excess magnesium. It is important to mention that humans can develop a tolerance to magnesium's gastrointestinal effects with time.[17] Volume 1 of Drinking Water and Health[17] cites a report published in 1953 by Kehoe stating that sensitive individuals are affected by $MgSO_4$ in drinking water at 400 mg/L, and that the average person suffers laxative effects at around 1000 mg/L of

$MgSO_4$. These levels represent approximately 160 to 400 mg of magnesium after conversion to single oral doses, based on a 2-L/d consumption rate for the general population. In comparison, military personnel in the field can consume up to 750 mg/d of magnesium, based on our estimated MLC for magnesium, of 50 mg/L and a maximum 15-L/d water-consumption rate. This calculated maximum likely daily magnesium dose of 750 mg exceeds the dose range reported to cause laxative effects among unadapted individuals. Therefore, it is conceivable that magnesium could induce acute performance-degrading effects among military personnel consuming field water.

Chronic Toxicity. Our survey of the toxicity data found no evidence of chronic performance-degrading effects of military significance resulting from long-term oral exposure to magnesium compounds. Therefore, definitive data concerning a possible association between chronic oral magnesium exposure and debilitating health effects are required before chronic magnesium toxicity can be considered of military concern.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested magnesium or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Taste and Odor. Magnesium may impart an astringent taste to water that can be detected by individuals at various concentrations. The Safe Drinking Water Committee of the National Research Council[17] reports that Lockhart et al. in 1955 and Kehoe in 1953 found that the taste threshold for magnesium is 100 mg/L in sensitive persons and about 500 mg/L in the average person. However, Bruvold and Pangborn[74] reported that water containing 1000 mg/L of magnesium salts was considered acceptable by a group of taste testers, although they did not consider such water extremely palatable. Palatability is an important consideration to military personnel deployed in the field. Objectionable taste could discourage water consumption and consequently increase susceptibility to dehydration.

Our estimated MLC of magnesium in water is 50 mg/L. This concentration is one-half the minimum concentration at which objectionable taste is detected by sensitive individuals. This indicates that it is highly unlikely that troops will encounter magnesium concentrations equivalent to, or exceeding, the lowest reported taste threshold. However, the possible consequences of objectionable taste cannot be ignored totally, due to the wide range of sensitivities exhibited among individuals. Therefore, we conclude that this organoleptic effect of magnesium is of importance but is probably best addressed by a document addressing criteria for total dissolved solids. We draw this conclusion because

magnesium will be present in natural waters with other dissolved solids that may also impart organoleptic properties to drinking water; the collective effect of all of these substances is more important and is best addressed by criteria for total dissolved solids.

Recommendation. Our survey of the review literature indicates that the maximum daily dose of magnesium received by military personnel, based on an MLC of 50 mg/L in field-water supplies and a 15-L/d maximum water-consumption rate, can potentially produce acute performance-degrading laxative effects among unadapted individuals. In addition, some military field personnel may be sensitive enough to detect an astringent taste imparted to field waters by magnesium at the MLC. Consequently, this objectionable taste may increase the susceptibility of these military personnel to dehydration because they may refuse to drink such poor-tasting water. Therefore, we conclude that the potential acute laxative effects and organoleptic properties that can be associated with elevated magnesium concentrations in military field-water supplies need to be addressed in more detail. We recommend development of criteria and recommendations for standards for magnesium to address potential acute laxative effects. We also recommend development of criteria and recommendations for standards for total dissolved solids to address organoleptic effects.

Manganese

Manganese is considered to be an essential element for human metabolism. It is required for the activity of several enzymatic reactions involving cholesterol, phosphorylation, and fatty-acid synthesis.[47] Manganese deficiency may be associated with lowered serum-cholesterol levels and impaired blood clotting, although these and other possible consequences of low manganese levels have not been firmly established for humans. A review of the literature reported in the ninth edition of Recommended Dietary Allowances[57] indicates that a range of 2.0 to 9.0 mg of manganese per day represents the average human dietary intake. An adequate and safe intake level of 2.5 to 5.0 mg of manganese for adults has been estimated by the Food and Nutrition Board of the National Research Council.[57]

Manganese exhibits valence states ranging from +2 to +6. The most prevalent forms in natural waters are the divalent cation (Mn^{+2}) and the tetravalent cation (Mn^{+4}), along with their related compounds. The divalent species of manganese (Mn^{+2}) is reported as being the more toxic of the two.[17] Gastrointestinal absorption of ingested manganese is poor, owing to the conversion of the divalent cation (Mn^{+2}) to the relatively insoluble trivalent cation (Mn^{+3}) within the alkaline duodenal region of the gut.[46] Manganese

absorption seems to be increased by iron deficiency and decreased with excess levels of dietary calcium or phosphorus, although the functional mechanisms for these processes are not fully understood.[46] Excretion is regulated by an apparent homeostatic mechanism which maintains tissue levels of manganese at a total body burden of about 20 mg.[47] Excretion is almost entirely fecal and involves the liver, pancreas, and possibly the adrenal cortex.[46,47]

Toxicity due to the ingestion of manganese is uncommon. Our survey of the extremely limited oral toxicity data indicates that the presence of manganese in military field-water supplies, even at its MLC, poses no debilitating health threat.

Acute Toxicity. Our survey of the review literature found one reported incident of manganese intoxication occurring in Japan as a result of the consumption of contaminated well water.[40] The presumed cause of contamination was the leaching of manganese from a large quantity of dry-cell batteries buried near a drinking-water well. Six members of one family all suffered from encephalitis-like symptoms as a result of exposure to this water. Manifestations included decreased appetite, constipation, mask-like facial expression, pain and rigidity of leg joints, muscle tremors, and hyperactivity of tendon reflexes. Neurological disturbances, memory loss, melancholia, and temporary double vision also appeared in these victims. As a final consequence of this exposure, one family member died, two were hospitalized, and three remained ambulatory. Ten other individuals utilizing the same water supply were similarly affected.[17,40]

Unfortunately, neither the dose nor the consumption period necessary to produce these symptoms was reported, but analysis of the well water revealed that it contained a concentration of 14 mg/L of manganese tetroxide (Mn_3O_4). This represents a toxic dose of about 20 mg of manganese per day based on a 2-L/d water-consumption rate. In contrast, the maximum likely daily manganese dose for military personnel from the ingestion of field waters is calculated to be 4.5 mg/d. This dose is based on the daily consumption of 15 L of water containing an MLC of manganese of 0.3 mg/L. Comparison of these values reveals that the maximum likely manganese exposure for military personnel from the ingestion of field waters is less than one-fourth of the estimated toxic dose necessary to produce the previously mentioned encephalitis-like symptoms. Consequently, we conclude that this type of health threat, although considered performance-degrading, is not of military concern due to the low probability of ingesting a toxic dose from the consumption of field water, even at a 15-L/d consumption rate.

Chronic Toxicity. Our survey of the review literature indicates that chronic toxicity from elevated manganese levels in drinking waters is extremely rare. In fact, chronic

manganese intoxication is generally the result of inhaling high concentrations of manganese dust.[17] Chronic manganese inhalation exposure (dose unknown) for at least three months resulted in symptoms similar to those of acute toxicity, including hyperactivity of tendon reflexes, leg cramps, muscular twitching, spastic gait, sleepiness, neurological disturbances, and a fixed facial expression. Permanent crippling may result in extreme cases.[17] Although these symptoms can be performance-degrading, they are not considered to be of military concern as a result of field drinking-water exposure.

The lack of evidence associating manganese ingestion and possible chronic effects indicates that chronic toxicity is poorly defined for manganese. Consequently, chronic toxicity will not be considered of military concern until further data become available.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested manganese or its compounds are carcinogenic, mutagenic or teratogenic in humans or laboratory animals.

Taste and Odor. The main problem associated with manganese in drinking waters is not toxicity, but discoloration and undesirable taste. The current organoleptic threshold for manganese is 0.05 mg/L and is based on domestic complaints of stained laundered goods and impaired taste of beverages, including tea and coffee.[66] However, we conclude that the organoleptic properties of manganese cannot be completely ignored, especially because the MLC is much greater than the aesthetic threshold. Because manganese will be present in natural waters with other dissolved solids and the collective effect of all of these substances is more important, we recommend that it be addressed by criteria for total dissolved solids.

Recommendation. The most toxic forms of manganese in natural waters are the divalent cation (Mn^{+2}), tetravalent cation (Mn^{+4}), and their related compounds. The divalent species (Mn^{+2}) is reported to be the more toxic of the two.[17] This form of manganese is not likely to be present in military field-water supplies at a concentration high enough to cause acute performance-degrading effects, even at a 15-L/d consumption rate. Therefore, acute health effects reported to result from large oral doses of manganese should not occur among personnel consuming field waters. The relationship between manganese ingestion and chronic effects is not well-defined, and without additional data, such effects do not appear to be important from a military perspective. Although manganese can impart an undesirable appearance and taste at its MLC, we conclude that such effects are best addressed collectively by criteria and recommendations for standards

for total dissolved solids. Consequently, data from our survey of the review literature indicate that development of criteria and recommendations for specific standards concerning manganese in military field-water supplies is unnecessary.

Mercury

According to the literature, mercury is not considered to be an element essential for human metabolism. The predominant form of mercury in natural waters is the divalent cation (Hg^{+2}) and its related compounds. These inorganic mercury compounds are considered to be relatively nontoxic to humans.[17] This low order of toxicity prevails primarily because these compounds tend to sorb readily onto a variety of sediment types, thereby lowering their availability in fresh waters. Additionally, gastrointestinal absorption of most ingested inorganic mercury compounds is poor, and excretion via the kidney is rapid and complete.[47]

Our survey of the toxicity review literature leads to the conclusion that inorganic mercury in water poses very little, if any, debilitating health threat to military field personnel. It appears that potential debilitation is related more to the organic mercury compounds, especially methyl mercury compounds that occur in the food chain.

Acute Toxicity. Acute toxicity due to oral ingestion of inorganic mercury compounds is rare. Nevertheless, accidental or intentional overdoses of mercuric chloride have occurred. The immediate effects of acute toxicity include gastrointestinal disturbances from irritation, coagulation, and superficial corrosion of the exposed tissues.[17] Unfortunately, the dose necessary to cause these effects has not been defined.

Although a toxic dose for ingested mercury compounds has not been established, oral doses of 100 to 500 g of metallic mercury (Hg^0) have been administered to humans with no ill effects.[17] Consequently, we consider this to be an adequate estimate of a no-observed-effect level. In contrast, the maximum likely daily dose of mercury for military personnel from the ingestion of field waters is 0.05 mg/d. This dose is based on an estimated MLC of inorganic mercury in natural waters of 3.2×10^{-3} mg/L and a 15-L/d maximum field-water consumption rate. Thus, the minimum no-effect-level dose is over three orders of magnitude greater than the maximum likely dose that could be received by military personnel. This leads to the conclusion that a substantial margin of safety exists between the toxic dose of inorganic mercury and the maximum likely dose of inorganic mercury that military personnel could receive from consuming field water.

<u>Chronic Toxicity</u>. There is no evidence in the review literature associating long-term oral exposure to mercury compounds with the onset of any chronic debilitating health effects. In fact, chronic adverse health effects in man have been reported only as a result of long-term industrial inhalation exposure to mercury compounds. Reported symptoms from such industrial exposure include kidney damage, hemorrhage, and ulceration of the intestinal mucosa.[17] Although these effects can be considered performance-degrading, the route of exposure makes them unimportant to military drinking-water consideration. Consequently, chronic toxicity as a result of the ingestion of mercury or its compounds cannot be considered significant from a military perspective without further evidence.

<u>Methyl-Mercury Toxicity</u>. Based on the previously mentioned information concerning acute and chronic mercury toxicity, it appears that metallic mercury and inorganic mercury compounds occurring in natural waters are not of direct toxicological concern to military populations. Potential debilitation is related more to organic mercury compounds, primarily methyl-mercury compounds, in the food chain. For instance, metallic mercury and inorganic mercury salts introduced into waters are transformed to methyl mercury by microorganisms in sediment and are subsequently bioaccumulated as methyl-mercury compounds in the flesh of fish.

Methyl-mercury compounds exert their main toxicological effects on the nervous system of adults, children, and fetuses.[47] Severe deformities, retardation, seizures, blindness, and death can occur. Two major outbreaks of methyl-mercury poisoning have occurred in human populations in Japan, one in the Minamata Bay region between 1953 and 1961 and the other in Niigata between 1964 and 1965. Both incidents were attributed to the industrial pollution of local waters with mercury and the subsequent accumulation of methyl mercury in fish that were eventually eaten by the local villagers. These fish contained up to 1 mg of mercury per kilogram body weight and were eaten daily or several times a week by the villagers. Mercury in drinking waters was not reported to be a contributor in either outbreak.[17,47] Furthermore, ingestion of seed grain or meat from animals fed on grain treated with organic alkyl-mercury fungicides have also resulted in typical neurological symptoms of organic mercury poisoning in human populations in areas of Pakistan, Guatemala, Iraq, and Ghana.[17]

<u>Carcinogenicity, Mutagenicity, Teratogenicity</u>. There is no evidence in the review literature indicating that ingested inorganic mercury or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. Evidence in the review literature indicates that organic mercury compounds occurring in the food chain represent the major toxicological threat from mercury to human populations. Trace amounts of inorganic mercury present in natural waters exhibit a very low order of toxicity due to low solubility in water and also low gastrointestinal absorption and retention in human systems. Additionally, our comparison between the toxic dose and maximum likely daily mercury dose for military personnel from the ingestion of field water reveals that mercury field-water concentrations are not likely to produce toxic effects, even at a 15-L/d maximum consumption rate. Consequently, we conclude that there is no need to establish criteria or make recommendations for standards for mercury in military field-water supplies.

Molybdenum

Molybdenum has been identified in the literature as an element essential for human metabolism. It is required for the function of important enzymes involved in the production of uric acid and is also involved in the production of the enzymes xanthine oxidase and aldehyde oxidase.[17,57] Adverse health effects due to molybdenum deficiency have not been reported for humans. Consequently, it is reasonable to conclude that normal daily dietary intakes of molybdenum by humans adequately meet physiological requirements. Nevertheless, negative molybdenum balances were observed among a few individuals consuming about 0.1 mg of molybdenum per day.[57] Therefore, an intake of 0.15 to 0.5 mg/d has been recommended as adequate and safe for human metabolism.[57]

Hexavalent molybdenum compounds, Mo(+6), are the most prevalent forms in natural waters. These forms are readily absorbed in the human gastrointestinal tract.[46] However, the available toxicity literature indicates that ingested molybdenum compounds exhibit a very low order of toxicity in human systems. This is attributed to limited retention of ingested molybdenum compounds as a result of rapid elimination via the kidneys.[46] Our comparison of the dose necessary to produce acute or chronic performance-degrading health effects and the maximum molybdenum daily dose likely from the ingestion of field water indicates that naturally occurring molybdenum levels will not reach toxic concentrations, even if military personnel need to consume field waters at a rate of 15 L/d.

Acute Toxicity. Our survey of the toxicity review literature revealed no evidence that ingested molybdenum compounds cause acute performance-degrading effects. Thus, it seems highly unlikely that the trace amounts of molybdenum in natural waters would pose an acute health threat to military personnel deployed in the field. The National Research

Council Committee on Dietary Allowances[57] has established 0.15 to 0.5 mg/d as an estimation of an adequate and safe intake range for molybdenum. Consequently, we consider this to be an acceptable no-observed-effect level. The maximum likely daily dose of molybdenum for military personnel from the consumption of field water is 0.15 mg/d. This dose is based on the daily consumption of 15 L of water containing an MLC of molybdenum of 0.01 mg/L. Since this dose is at the lower end of the range of doses considered adequate and safe for intake (i.e., no-observed-effect range), molybdenum is not likely to be of military concern in field-water supplies from the perspective of acute toxicity.

Chronic Toxicity. Although the review literature indicates that molybdenum poisoning is rarely observed in humans, there is circumstantial evidence associating adverse health effects with long-term exposure to elevated dietary molybdenum levels. For instance, a high dietary intake level of molybdenum in an area of Armenia has been associated with a high incidence of gout.[40] The total daily intake of molybdenum for the average individual in this area of Armenia was calculated to be 10 to 15 mg/d. In contrast, other surrounding areas of Armenia reported daily dietary intakes of 1 to 2 mg of molybdenum.[40] Additionally, a crippling bone disease has been observed among populations in certain areas of India where sorghum (a major dietary food source) apparently contains high levels of molybdenum.[40] Unfortunately, a definite cause-and-effect relationship has not been established for these reported cases of chronic molybdenum poisoning. Consequently, more definitive evidence is required before chronic toxicity due to long-term ingestion of molybdenum compounds can be considered a potential health threat of military significance.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested molybdenum or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendations. In summary, the most prevalent forms of molybdenum in natural waters are compounds of hexavalent molybdenum. Although hexavalent molybdenum compounds are readily absorbed from the human gastrointestinal tract, they exhibit a very low order of toxicity in human systems, probably due to their subsequent rapid elimination. According to the literature, acute debilitating health effects have not been reported in human populations as a result of oral exposure to molybdenum compounds. Consequently, we do not consider acute molybdenum toxicity to be of military significance as far as drinking water is concerned. Chronic effects, including gout and a crippling

disease affecting the bones, have been linked with excess dietary molybdenum intake in areas of Armenia and India. However, these chronic effects are highly speculative and a definite cause-and-effect relationship has not been established. Therefore, we do not consider these chronic effects to be relevant from a military perspective. Additionally, our calculations revealed that the maximum likely daily dose of molybdenum for military personnel from the ingestion of field waters at a 15-L/d consumption rate is well within the established adequate and safe intake range (i.e., no-observed-effect range) for molybdenum. This further supports our conclusion that concentrations of molybdenum in field-water supplies ordinarily will not be high enough to produce debilitating health effects among military personnel consuming the water. Therefore, we conclude that development of criteria and recommendations for standards for molybdenum in military field-water supplies are unnecessary.

Nickel

According to information presented in Drinking Water and Health, Volume 3,[40] it is highly likely that nickel is an essential trace element for human metabolism because of its proven essentiality in animals. However, the widespread occurrence of nickel in various foods has made it virtually impossible to obtain a diet that is naturally deficient in this metal. Such a diet is required to demonstrate that nickel is involved in certain metabolic processes in human systems. Nevertheless, Schnegg and Kirchgessner in 1978, as reported in Drinking Water and Health, Volume 3,[40] estimated from an extrapolation of animal data that a 70-kg human would have a daily requirement of 0.05 mg of nickel. If this were an actual recommended daily allowance, then it would be satisfied by the reported daily dietary intakes of 0.165 to 0.50 mg of nickel consumed by most human populations.[17]

The most prevalent forms of nickel in natural waters are the divalent cation (Ni^{+2}) and its related compounds. The body burden of nickel in humans appears to be regulated by a homeostatic mechanism that limits gastrointestinal absorption and retention except under extremely high exposure conditions; this prevents toxic effects from developing.[40] In fact, our survey of the review literature did not locate any human acute- or chronic-toxicity data concerning ingested nickel or its compounds. This leads us to the conclusion that ingestion of toxic concentrations of nickel is a relatively rare occurrence among human populations. This conclusion is further supported by studies involving oral administration of nickel to rats and data from human industrial exposures to nickel.

Acute Toxicity. Hammond and Beliles[47] report that doses of nickel sulfate ($NiSO_4$) in humans of 0.1 to 0.5 mg/kg for 161 days can produce myocardial and liver damage. This

corresponds to 2.7 to 13 mg/d of nickel for a 70-kg adult over 161 days. In contrast, an average field soldier would consume up to 0.15 mg of nickel per day from the ingestion of field water. This dose is based on the daily consumption of 15 L of water containing an MLC of nickel of 0.01 mg/L. This maximum likely daily nickel dose for military personnel is 18 times smaller than the lowest estimated toxic dose associated with acute performance-degrading effects in humans. Thus, we conclude that it is highly unlikely that military personnel will be exposed to a toxic dose of nickel from the ingestion of field waters.

Chronic Toxicity. Most cases of reported chronic toxicity are the results of dermal and inhalation exposure in the industrial environment. Dermatitis, known as "nickel itch," is the most frequent complaint from repeated exposure to nickel and occurs from skin contact with nickel-containing alloys used in commercial manufacturing plants.[17] Contact with jewelry, coins, and stainless steel appliances may also produce dermatitis-like effects. Dermatitis, which can be severe enough to be potentially performance-degrading to military personnel, is not of immediate concern with regard to nickel in field waters because nickel concentrations in natural waters should not reach levels high enough to induce severe dermatitis in exposed troops. Chronic industrial inhalation exposure to nickel carbonyl [$Ni(CO)_4$], the most toxic of nickel compounds, induces performance-degrading, noncarcinogenic effects of vomiting and severe headache.[40] However, these performance-degrading effects are not likely to occur in military personnel because ordinarily water is not a principal route of exposure for this substance.

Carcinogenicity, Mutagenicity, Teratogenicity. Although epidemiological studies have revealed a significantly higher incidence of cancers of the lungs and nasal cavities in workers after repeated inhalation exposure to nickel carbonyl when compared with control workers,[17] there is no evidence in the review literature indicating that ingested inorganic nickel compounds are carcinogenic in humans or laboratory animals. Additionally, there is no evidence in the review literature indicating that ingested nickel or its compounds are mutagenic or teratogenic in humans or laboratory animals.

Reproductive Toxicity. Venugopal and Luckey[46] cite a 1972 article by Waltshcewa et al. that found a daily oral intake of 23 mg of nickel sulfate ($NiSO_4$) per kilogram of body weight for a period of 3 months can decrease the reproductive capacity of male rats by causing a reduction of spermatogenesis and sperm motility. Additionally, disintegration of spermatozoa, shrinkage of the central tubules, and congestion of intertubular capillaries

were observed in male rats approximately 18 hours following a single oral dose of 2.3 mg $NiSO_4$. However, these effects are reported to be reversible. There is no evidence in the review literature indicating that such reproductive effects occur in humans following oral exposure to nickel or its compounds.

Recommendation. In summary, the divalent cation (Ni^{+2}) of nickel and its related compounds are the most prevalent forms in natural waters. Our survey of the review literature revealed a lack of human data concerning acute or chronic toxic effects in relation to ingested nickel compounds. Assessment of data from the oral administration of nickel compounds to rats and human inhalation data led us to the conclusion that nickel exhibits a low order of toxicity in human systems and that concentrations of nickel in military field-water supplies are not ordinarily high enough to induce performance-degrading effects among military personnel, even at a maximum consumption rate of 15 L/d. Consequently, further investigation and development of criteria and recommendations for standards concerning nickel in military field waters is unnecessary.

Nitrate

Nitrate is not identified in the literature as essential for human metabolism. The most prevalent form of nitrate in natural waters is the nitrate anion (NO_3^-) and its related compounds. Typical concentrations of these forms in water are considered to be nontoxic to adults when ingested.[17] This low order of toxicity in adults can be attributed to poor absorption from the gastrointestinal tract, along with rapid excretion of any excess nitrate via the kidney. Our assessment of the toxicity literature indicates that the presence of nitrate in military field-water supplies poses no acute or chronic performance-degrading health threats to military populations in the field.

Acute Toxicity. According to evidence presented in the review literature, healthy adult human populations can consume large quantities of nitrate in drinking waters with little or no adverse health effects. For instance, epidemiological studies have shown that nitrate in drinking waters at a concentration less than or equal to 1000 mg/L is of no concern to adults as an acute toxicant.[17] Thus, we consider 1000 mg/L of nitrate to be an adequate estimation of a no-observed-effect level. This corresponds to a daily no-observed-effect dose of 2000 mg/d, based on a 2-L/d water consumption rate for the general adult population. In contrast, military field personnel could conceivably receive a maximum of 345 mg/d of nitrate from the ingestion of field water. This dose is based on an MLC of nitrate in natural waters of 23 mg/L and a 15-L/d maximum water-consumption rate. The

maximum likely daily dose of nitrate for military personnel is less than one-fifth of the estimated no-observed-effect level. Therefore, the concentrations of nitrate in military field waters ordinarily will not reach levels high enough to produce acute performance-degrading effects among troops consuming the water.

The major health concern related to high levels of nitrate in drinking waters is the induction of infant methemoglobinemia. This syndrome involves the reduction of nitrate to nitrite by nitrate-reducing bacteria characteristically found only in the upper gastrointestinal tract of infants. The presence of nitrite in the blood oxidizes infant hemoglobin to methemoglobin, which will not carry oxygen to the tissues. This may result in severe oxygen depletion and infant death.[17,47] Although this syndrome is an important public health problem that warrants further investigation in terms of removal of excess nitrates from drinking-water supplies, it is of no military significance because military personnel are not physiologically at risk to this condition.

Chronic Toxicity. Our survey of the toxicity review literature revealed no evidence that elevated levels of ingested nitrates cause noncarcinogenic, chronic, debilitating health effects among healthy adult human populations. Consequently, we cannot consider chronic nitrate toxicity as a significant performance-degrading health threat to military field personnel without the establishment of a definitive cause-and-effect relationship.

Carcinogenicity, Mutagenicity, Teratogenicity. Nitrate has been implicated in the review literature as being carcinogenic in humans. For instance, a 1973 article by Hill et al. (cited in Volume 1 of Drinking Water and Health[17]), showed that a 25% higher incidence of gastric cancer occurred in the general population of Worksop, England, when compared with similar populations in other towns used as controls. The daily contribution of nitrate from water consumed by inhabitants of Worksop was approximately 86 mg/d in contrast to a nitrate intake of about 15 mg/d by individuals living in the control towns. Similarly, Hawksworth et al. reported in 1975, according to Volume 1 of Drinking Water and Health,[17] an unusually high incidence of stomach cancer occurring among populations living in certain mountainous areas of Colombia, where 110 mg/L of nitrate was present in their drinking-water supplies. The study indicated that populations in regions of Colombia where nitrate concentrations in drinking water were much lower did not show this increased incidence. Although these findings suggest that correlations exist between increased cancer incidence and elevated levels of nitrate in drinking waters, they do not provide firm evidence of a causal relationship. Nevertheless, these findings do indicate a need for further research concerning nitrate as a human carcinogen.

Another, highly speculative health hazard proposed for nitrate in drinking waters, is its activity as a procarcinogen.[17] Nitrates presumably have the ability to form N-nitroso compounds, many of which are potent carcinogens, through a series of reactions with secondary amines and similar nitrogenous compounds found in waters, as well as in some foods.[17]

There is no evidence in the review literature indicating that ingested nitrates are mutagenic or teratogenic in humans or laboratory animals.

Recommendation. Evidence in the review literature indicates that infant methemoglobinemia represents the major toxicological threat to human populations from ingestion of nitrate in drinking-water supplies. Typical amounts of the nitrate ion (NO_3^-) and its related compounds exhibit a very low order of toxicity in adult human systems due to poor gastrointestinal absorption and retention. Furthermore, our comparison between the maximum likely daily dose of nitrate for military personnel from the ingestion of field waters and the dose necessary to induce performance-degrading health effects indicates that nitrate concentrations typically will not reach toxic levels, even if individuals consume water at 15 L/d over a prolonged period. Consequently, we conclude that development of a criteria and recommendations for standards concerning the presence of nitrate in military field-water supplies is unnecessary.

Phosphate

According to the National Research Council Committee on Dietary Allowances,[50] phosphorus, in the form of phosphate, is essential for human metabolism. Phosphates are present in blood and cells, as well as in lipids, proteins, carbohydrates, and energy-transfer enzymes. Phosphates serve as catalysts for many of the B group of vitamins (i.e., these vitamins are effective only when combined with phosphate in the human body). They also aid in the maintenance of the skeletal structure of the body. Phosphate deficiency results in weakness, malaise, pain in the bones, and anorexia. However, these symptoms do not normally occur due to dietary phosphate deficiency directly, but as a result of excessive and prolonged intake of nonabsorbable antacids. The recommended daily allowance of phosphorus for normal human metabolism has been established as 800 mg for adults 19 years of age and older.

The trivalent anion of phosphate (PO_4^{-3}) and its related compounds are the most prevalent forms in natural waters. According to the review literature, these forms are poorly absorbed from the gastrointestinal tract of humans and thereby exhibit a very low order of toxicity in human systems. A 1974 report by Mazess and Mather (cited in

Drinking Water and Health, Volume 3[40], notes that a high phosphate content characteristic of the Eskimo diet may be associated with the onset and development of osteoporosis, a degenerative bone disease. However, this remains to be substantiated, and there have been no further reported cases of any type of acute or chronic effects associated with the ingestion of phosphate compounds. Such paucity of human toxicity data indicates that the presence of phosphates in drinking waters is not likely to be a public health problem of major concern.

Our best estimation of the MLC for phosphate in natural waters of 1.50 mg/L, based on available water-quality data, reveals that phosphate levels should not reach toxic concentrations under normal conditions. For instance, the maximum likely daily dose of phosphates military personnel may receive from consuming field water is 22.5 mg/d. This dose is based on the daily consumption of 15 L of water containing an MLC for phosphate of 1.50 mg/L. Thus, the maximum possible daily phosphate dose for military personnel is nearly 40 times smaller than the recommended daily allowance of 800 mg phosphorus. Consequently, the daily phosphorus contribution from the ingestion of field waters is negligible, which further supports our conclusion that the ingestion of phosphates from field water poses no acute or chronic health threat to field troops.

Acute Toxicity. Our survey of the review literature revealed no evidence that ingested phosphates produce acute adverse health effects in humans.

Chronic Toxicity. Our survey of the review literature revealed no definitive evidence that ingested phosphates produce chronic adverse health effects in humans.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested phosphate or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. Due to a lack of evidence associating the ingestion of phosphates with the induction of acute or chronic adverse health effects in humans, we conclude that there is no need to develop criteria and recommendations for standards concerning the presence of phosphates in military field-water supplies.

Potassium

Potassium is identified in the literature as an element essential for human metabolism. It is the predominant intracellular cation and assumes a vital role in the

maintenance of electrical excitability of nerve and muscle fiber. Potassium also plays an important role in the maintenance of acid-base balance and electrolyte balance and acts as an insulin antagonist in carbohydrate metabolism.[40] Potassium deficiency is characterized by cardiac arrhythmia, muscle weakness, paralysis, adrenal hypertrophy, loss of weight, and in extreme cases, death.[46] The estimated adequate and safe intake range for potassium has been set at 1875 to 5600 mg/d.[40]

The most prevalent form of potassium in natural waters is the monovalent cation (K^+) and its related compounds. Although these forms are rapidly and completely absorbed from the gastrointestinal tract of humans, they exhibit an extremely low order of toxicity following oral administration. This can probably be attributed to an efficient homeostatic mechanism that maintains potassium at physiological-requirement levels by rapidly eliminating excess intakes of potassium via the urine and feces.[46] Because of this efficient regulatory mechanism, only large oral overdoses of therapeutic potassium compounds have resulted in acute performance-degrading effects that are considered to be of military concern. However, comparison between the maximum likely daily dose of potassium for military personnel from the ingestion of field waters and the dose necessary to produce toxic effects reveals that it is highly unlikely that field personnel will receive an acute toxic dose of potassium, even at a 15-L/d maximum consumption rate. Chronic toxicity has not been reported in humans as a result of ingested potassium compounds, and therefore chronic toxicity is not considered to be significant.

Acute Toxicity. According to the review literature, acute poisoning due to the ingestion of potassium is rare. In fact, much of the existing data pertaining to acute oral potassium toxicity is based on accidental therapeutic overdoses. For instance, cited in Drinking Water and Health, Volume 3[40] is the 1942 report of Keith et al. that ingestion of eight 4-g potassium chloride tablets caused acute symptoms of gastric irritation, cyanosis (i.e., slight discoloration of the skin), shallow respiration, and cardiac arrhythmia. The total dose of potassium chloride ingested (i.e., 32 g) corresponds to a single oral toxic potassium dose of 16.8 g. Also cited in Drinking Water and Health, Volume 3[40], the 1920 report of Blum indicates that 25 g of potassium chloride per day, which corresponds to 13.1 g of potassium per day, can induce symptoms of acute toxicity. However, the minimum acute toxic dose is lower because the induction of diarrhea and other gastrointestinal disturbances has occurred following the ingestion of 7 to 10 g of potassium per day.[34] In contrast to these figures, the maximum likely daily dose military personnel would ingest from field water is 240 mg. This dose is based on the daily consumption of 15 L of water containing an MLC for potassium of 16 mg/L. Thus, the maximum likely dose of potassium for military personnel from the ingestion of field waters is almost 30 times less than the

lowest reported toxic dose (i.e., 7 g) necessary to cause performance-degrading effects of military concern. These calculations indicate that it is highly unlikely that potassium concentrations in military field waters will ever reach levels high enough to induce acute performance-degrading effects among personnel consuming the water.

In addition, the maximum likely daily dose of potassium for military personnel from the ingestion of field waters is nearly eight times smaller than the lowest reported safe and adequate potassium intake level of 1875 mg/d,[40] our estimation of the no-observed-effect level. Thus, a substantial margin of safety appears to exist between the maximum potential daily dose of potassium for military personnel from the ingestion of field waters and the dose that could cause acute debilitating health effects.

Chronic Toxicity. Our survey of the review literature found no evidence that long-term exposure to ingested potassium and its compounds induces chronic performance- degrading effects of military concern. Consequently, chronic potassium toxicity is not considered of immediate military significance.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence presented in the review literature indicating that ingested potassium or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendations. In summary, the most prevalent forms of potassium in natural waters are the monovalent cation (K^+) and its related compounds. Although gastrointestinal absorption of potassium compounds is rapid and complete in humans, toxicity due to the ingestion of potassium compounds is rare because of an efficient homeostatic mechanism that maintains levels within physiological requirements. Nevertheless, accidental therapeutic overdoses have been reported to cause acute performance-degrading effects of military significance. However, our calculations reveal that potassium concentrations occurring in military field-water supplies probably will not reach levels high enough to produce acute debilitating effects among field troops. Chronic effects due to ingestion of elevated potassium levels have never been reported in humans, and therefore chronic effects are not considered to be of military concern. Consequently, the development of criteria and recommendations for standards concerning potassium in military field-water supplies is unnecessary.

Selenium

Selenium has been defined as an element essential for the metabolism of many animal species and therefore has been considered to be essential for man as well.[57] The National Research Council Committee on Dietary Allowances[57] cites a 1974 publication by Hoekstra that indicates that the primary metabolic function of selenium is to serve as a component of the enzyme glutathione peroxidase, which protects vital cell components against extensive damage. Toxic symptoms attributed to selenium deficiency or excess in man have not been established, and for this reason a recommended daily allowance has not been quantitatively defined. However, it is possible to extrapolate from numerous animal experiments and human metabolism studies to make an estimate of an adequate and safe intake range for selenium. This was done by the National Research Council Committee on Dietary Allowances in the ninth edition of Recommended Dietary Allowances,[57] and as a result, they recommend 0.05 to 0.2 mg/d as the adequate and safe intake range.

The hexavalent oxidation state of selenium, Se(+6), and related compounds are the most soluble forms in natural waters.[17] The less-soluble tetravalent oxidation state, Se(+4), and its compounds also occur quite frequently, along with the hexavalent forms. Although organic selenium compounds are generally considered to be quite toxic, our survey of the toxicity review literature indicates that most inorganic selenium salts in natural waters are relatively nontoxic to humans. Poor gastrointestinal absorption and rapid elimination are probably the major reasons for this low order of selenium toxicity. Additionally, oral toxicity due to excess dietary or accidental therapeutic consumption of selenium compounds is quite rare. Occupational inhalation exposure to selenium dusts and fumes appears to be the primary cause of selenium toxicity in humans.

Acute Toxicity. Little information exists concerning acute human toxicity attributable to the ingestion of selenium compounds. However, acute symptoms of inhalation exposure to selenium dusts or fumes have resulted in irritation of eyes and mucous membranes, vomiting, nausea, headaches, dizziness, pulmonary edema, and characteristically an accompanying "garlic" breath odor in the exposed individual.[17] Although these acute toxic symptoms can be considered to be performance-degrading from a military perspective, they have not been associated with the ingestion of selenium compounds. Therefore, it appears highly unlikely that the trace amounts of selenium typically occurring in military field-water supplies will reach the toxic concentrations necessary to produce acute debilitating effects in field personnel.

Chronic To~~city. The dose necessary to produce chronic oral selenium toxicity in humans is poorly dei_.ed. A daily selenium intake of 18.0 mg/d was reported to cause listlessness, hair loss, and weakened nails in a family of Indians residing in Colorado.[40] This intake was estimated from an analysis of the well water used by the family, which showed a selenium content of 9.0 mg/L, and by assuming a 2-L/d water-consumption rate for each individual. However, this evidence is considered to be highly circumstantial and has not been supported by other cases of toxicity resulting from consumption of excess selenium in drinking waters.

In contrast, Smith and Westfall reported in 1937, according to Urinking Water and Health, Volume 3,[40] that a dietary ingestion of 0.70 to 14.0 mg selenium per day caused no acute or chronic ill effects in subjects living in a highly seleniferous area of the United States. Although duration of exposure was not defined by the investigators, 14.0 mg selenium per day can be considered an estimation of a maximum no-observed-effect level for our screening purposes.

The maximum likely daily dose military personnel could ingest from field-water supplies is 0.11 mg/d. This dose is based on a maximum daily consumption rate of 15 L of water containing a selenium MLC of 0.007 mg/L. In comparison with the estimated no-observed-effect level of 14.0 mg/d, the maximum likely daily dose from field water is two orders of magnitude lower, and it seems evident that selenium concentrations in field-water supplies should not cause performance-degrading chronic health effects among personnel consuming the water. In addition, the maximum likely daily dose of selenium from water for military personnel is in the range of the recommended adequate and safe intake level. This further confirms the existence of a margin of safety between the maximum likely selenium dose that could be consumed by military populations from the ingestion of field waters and the dose necessary to cause toxic effects.

Carcinogenicity, Mutagenicity, Teratogenicity. The review literature suggests that elevated selenium levels might cause fetal toxicity and teratogenic effects in humans. Robertson[75] found that occupational inhalation exposure to selenite-containing powder for a period of five years by 10 women of childbearing age may have induced teratogenic effects among the group of 10 women. For instance, four certain pregnancies and a possible one occurred among eight of the women, and all of these pregnancies ended in miscarriages, except for one that went to term. The infant from that pregnancy was born with a bilateral clubfoot. However, it is possible that other clinical factors may have interfered with the pregnancies. Additionally, the urinary selenium levels of this group of women were checked periodically during the five years, along with a control group living in the same area. Comparison of the selenium levels revealed no differences between the

two groups. This study remains highly controversial; teratogenic effects have not occurred among women performing comparable work in other industries utilizing selenium compounds. Teratogenicity has not been experimentally produced in laboratory animals. Carcinogenicity and mutagenicity have not been associated with the ingestion of selenium or its compounds by humans or laboratory animals. In fact, recent epidemiological investigations identified by Hammond and Beliles[47] have reported a correlation between decreased human cancer death rates and increasing selenium content of certain crops.

Recommendation. The most prevalent forms of selenium in natural waters are the tetravalent and hexavalent oxidation states and their related compounds. These forms of selenium are not readily absorbed from the gastrointestinal tract and thus exhibit a low order of toxicity following ingestion by humans. In fact, the relationship between selenium ingestion and any possible performance-degrading acute effects is not firmly established and without further evidence cannot be considered to be of concern from a military perspective. Although consumption of elevated selenium levels in drinking waters has been reported to cause chronic effects in humans, it is not likely that selenium concentrations will reach levels high enough to cause these effects in military populations, even at a 15-L/d maximum consumption rate. Consequently, we conclude that development of criteria and recommendations for standards concerning selenium in military field-water supplies is unnecessary.

Silver

The monovalent cation of silver (Ag^+), which is the most prevalent form of silver in natural waters, is not identified in the literature as an element essential for human metabolism. Gastrointestinal absorption of monovalent silver and its salts is quite poor. Excretion is efficient and occurs primarily via the feces with much lesser amounts lost through the urine.[47] Retention of any excess absorbed silver in human tissues is extremely low, but when it occurs, the greatest concentrations are found in the reticuloendothelial organs, such as the liver and the spleen.[17] Although the accumulation of silver in the reticuloendothelial organs may be significant clinically, it is not considered to be toxicologically significant from a military perspective because this condition is not associated with the onset of any performance-degrading health effects.

Our survey of the review literature revealed no evidence that silver toxicity is associated with high levels of silver in drinking waters. In fact, silver toxicity is quite rare overall and results primarily from therapeutic and occupational exposures. Unfortunately, the dose necessary to cause toxic effects has not been clearly defined.

Nevertheless, it is our conclusion that the trace amounts of silver typically found in natural waters will not produce toxic symptoms in military personnel after ingestion.

Acute Toxicity. Although acute human toxicity data concerning silver are limited, it has been reported that accidental therapeutic overdoses of caustic silver salts can induce health effects that would be considered performance-degrading from a military perspective. For instance, accidental therapeutic overdoses of silver nitrate ($AgNO_3$) can cause acute debilitating symptoms including severe gastroenteritis, diarrhea, decreased respiration, fall in blood pressure, and central nervous system afflictions followed by death in extreme cases.[46] However, these silver salts are not likely to be ingested from field-water supplies in doses like those administered therapeutically because these salts are generally insoluble in natural waters. In addition, the soluble monovalent silver salts (sulfates and nitrates) are converted into insoluble chlorides within the gastrointestinal tract, thus decreasing their toxic potential.[17]

Chronic Toxicity. Evidence in the review literature indicates that prolonged therapeutic intake of silver salts can result in chronic toxicity. Symptoms include kidney and liver dysfunction, morphological changes in blood cells, and argyria. Argyria involves the permanent discoloration of the skin, eyes, and mucous membranes as a result of deposition of a silver-protein complex or its metabolized products within the elastic fibers of these tissues.[17] Although this syndrome does not produce any significant physiological effects, there has been speculation that a degeneration of night vision and arteriosclerotic changes are associated with deposition in the eyes and kidneys, respectively.[17] Argyria is also a relatively common occupational disease following exposure of skin and eyes to silver particles or salts. Occupational argyria, according to a 1939 publication by Hill and Pillsbury cited in Volume 1 of Drinking Water and Health,[17] develops after 2 to 25 years of silver exposure and results from the gradual accumulation of 1 to 5 g of silver within the body.

Although liver and kidney dysfunction can be considered to be performance-degrading to military personnel, these effects are not considered to be of military significance because such symptoms have only been reported after long-term therapeutic oral exposures to silver compounds. In addition, manifestation of these effects occurs only after a latent period of 6 months to one year after exposure.[17] Argyria is not considered to be performance-degrading by military standards, nor is the military a susceptible population based on the fact that argyria occurs primarily in those individuals occupationally exposed to silver compounds.

<u>Carcinogenicity, Mutagenicity, Teratogenicity</u>. There is no evidence in the review literature indicating that ingested silver or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

<u>Recommendation</u>. In summary, the most prevalent forms of silver in natural waters are the monovalent cation and its related compounds. These forms exhibit very poor absorption from the gastrointestinal tract, thus reducing its toxic potential in human systems. In fact, our survey of review literature found no evidence indicating that silver toxicity is associated with high levels of silver in drinking waters. The only reported incidents of acute or chronic silver poisoning were caused by excess therapeutic or occupational exposures to silver compounds. Consequently, we conclude that silver concentrations in field waters are not likely to induce performance-degrading acute or chronic toxic effects among military personnel, even at a 15-L/d water-consumption rate. Therefore, development of criteria and recommendations for standards concerning silver in field-water supplies is unnecessary.

Sodium

Sodium is identified in the literature as an essential element for human metabolism. Sodium is a very important contributor to osmotic-pressure regulation and maintenance of extracellular fluid volume.[57] It is required for the propagation of impulses in excitable tissues and is involved in the electrophysiology of cells. Sodium is also essential for the active transport of nutrients across the intestinal mucosa.[17]

Gastrointestinal absorption of virtually all sodium compounds is rapid and complete. Excretion is regulated by the kidney, which maintains sodium homeostasis through the regulatory control of the hormone aldosterone. For instance, when the daily intake of sodium decreases, the aldosterone level increases, which, in turn, rapidly lowers the rate of urinary sodium excretion. Conversely, when sodium intake increases, the aldosterone level decreases, thus increasing the rate of urinary sodium excretion.[57]

Daily intake levels of sodium vary greatly among individuals. Dahl in 1972, as cited in the ninth edition of <u>Recommended Dietary Allowances</u>,[57] reported that the average daily intake of sodium ranges between 2300 and 6900 mg. The estimated range for an adequate and safe intake of sodium is between 1100 and 3300 mg/day for healthy adults.[57]

The monovalent cation of sodium (Na^+) and its related compounds are the most prevalent forms in natural waters and in most foods.[40] A survey of the review literature indicates that the amount of sodium consumed from drinking water is not considered to be

a toxicological threat to the majority of the population. Most excess sodium that is ingested and associated with adverse health effects is consumed in foods which are either naturally high in sodium or are high in sodium due to the addition of table salt (NaCl).

Acute Toxicity. Healthy adults rarely, if ever, suffer symptoms of acute sodium toxicity from the ingestion of sodium compounds. This low order of oral toxicity is attributed to efficient homeostatic sodium regulation via the kidneys.[40] Nevertheless, Meneely and Battarbee[76] report that acute visible edema may occur in healthy adults after consumption of 35 to 40 g/d of sodium chloride. This corresponds to a single oral dose of 13.8 to 15.7 g of sodium per day. In contrast, the maximum likely daily dose of sodium for military personnel from the ingestion of field waters is 7.5 g/d. This dose is based on an MLC of 500 mg/L of sodium and a 15-L/d maximum water-consumption rate for military personnel. Thus, an adequate margin of safety appears to exist between the possible daily dose of sodium for military troops and the dose necessary to cause toxic effects. In addition, edema is not considered to be a performance-degrading effect by military standards and is therefore not of concern for field personnel.

Chronic Toxicity. Available evidence suggests that excessive, chronic sodium intake may be associated with hypertension, a condition characterized by an age-related increase in blood pressure following a long latency period. Although a definite quantification of a dose-response relationship has not yet been established, salt (NaCl) intakes exceeding 30 g/d, which corresponds to 11.8 g/d of sodium, have been associated with the onset of hypertension among adults. However, lower doses have been reported to induce chronic sodium toxicity among persons susceptible to hypertension and those already suffering from hypertension, renal disease, cirrhosis of the liver, and congestive heart failure.[40]

Hypertension, however, is not considered to be a performance-degrading health threat to military populations due to the fact that it is a latent symptom normally occurring in adults 40 y of age or older. This exceeds the average age of typical field personnel. Additionally, there is evidence in the literature indicating that some individuals are susceptible to hypertension while others are not. For instance, susceptibility may depend on risk factors such as psychosocial stress and obesity, and these conditions may not be readily identified.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested sodium or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. In summary, the most prevalent forms of sodium in natural waters are monovalent cationic sodium (Na^+) and its related compounds. Acute toxicity resulting from oral ingestion of these forms rarely occurs in adults due to an efficient homeostatic regulation of sodium by the kidneys. Although the sodium ion is implicated as the etiologic agent for hypertension, development of this manifestation involves several other causative agents including psychosocial stress factors and obesity.[17] Additionally, comparison between the maximum likely daily dose of sodium for military personnel from the ingestion of field waters and the dose necessary to produce acute or chronic adverse health effects indicates that it is highly unlikely that military personnel will be exposed to a toxic dose in field waters, even if they consume water at a rate of 15 L/d over a prolonged period. Consequently, we conclude that there is no need to develop specific criteria and recommendations for standards concerning sodium in military field-water supplies.

Strontium

The divalent cation of strontium (Sr^{+2}), which is the most prevalent form in natural waters, is not identified in the literature as an element essential for human metabolism. Gastrointestinal absorption of divalent strontium and its compounds is limited. Elimination is rapid and occurs primarily via the urine with lesser amounts lost through the feces.[45]

Our survey of the review literature revealed that strontium toxicity is quite rare and results primarily from therapeutic overdoses. In fact, there were no available reports concerning strontium toxicity in relation to elevated strontium levels in drinking waters. Consequently, we concluded that the trace amounts of strontium present in military field-water supplies pose no health threat to field personnel.

Acute Toxicity. Although acute oral strontium poisoning is extremely rare in humans, performance-degrading effects, including vomiting, colic, and diarrhea, have been associated with accidental therapeutic overdoses.[46] Unfortunately, the dose necessary to cause these effects has never been quantified. It is assumed, however, that doses similar to those administered therapeutically are not likely to be encountered by military personnel from the consumption of field water.

Volume 4 of Drinking Water and Health[45] cites the 1974 work of Dawson, which extrapolates from experimental minimum lethal-dose data for animals to determine that a maximum ambient environmental level for strontium in potable water is 10 mg/L. This is not an extremely reliable extrapolation, but it does allow estimation of what can be

considered to be a no-observed-effect level. Assuming that 10 mg/L is an adequate no-observed-effect level and that the average person consumes 2 L/d of water, the no-observed-effect dose for strontium is 20 mg/d. In contrast, the maximum likely daily dose of strontium for military personnel from the consumption of field-water supplies is 7.5 mg/d. This calculation is based on an estimated MLC for strontium of 0.50 mg/L and a 15-L/d maximum water-consumption rate. The extrapolated no-observed-effect level is over two times greater than our calculated daily dose for military personnel. Based on this information, it is unlikely that strontium concentrations in military field-water supplies will reach levels high enough to induce performance-degrading acute effects among field personnel.

Chronic Toxicity. Our survey of the review literature revealed no cases of toxicity resulting from chronic oral exposure to strontium compounds. Therefore, chronic effects due to long-term ingestion of strontium cannot be considered consequential from a military perspective until further data become available.

Carcinogenicity, Mutagenicity, Teratogenicity. Teratogenicity has been induced among laboratory animals as a result of exposure to elevated strontium levels.[47] Human teratogenicity from exposure to strontium was not reported in the review literature. Additionally, there is no evidence in the review literature indicating that ingested strontium or its compounds are carcinogenic or mutagenic in humans or laboratory animals.

Recommendation. In summary, the most prevalent forms of strontium in natural waters are the divalent form (Sr^{+2}) and its related compounds. Gastrointestinal absorption of these forms is poor, thereby reducing the toxic potential of strontium compounds in human systems. Comparison between the maximum likely daily dose of strontium from the consumption of 15 L/d of military field-water supplies and the dose considered to be necessary to produce toxic effects reveals that even the MLC of strontium occurring in field waters will not induce acute debilitating effects among military personnel. There is no available evidence associating long-term oral exposure to strontium compounds with performance-degrading chronic effects. Consequently, we conclude that development of criteria and recommendations for standards concerning strontium in military field-water supplies is unnecessary.

Sulfate

The divalent anion of sulfate (SO_4^{-2}) is the major form of sulfate in natural waters. Most inorganic sulfates, with the exception of lead and barium sulfate, are quite soluble in water.[17] Gastrointestinal absorption of this form, however, is reported to be poor in human systems.[77] Sulfate is not considered to be an essential element, although it does play an important role in human metabolism, attaching to several natural metabolites and foreign substances, thereby enhancing their elimination due to increased water solubility.[78]

Sulfate salts are widely known to cause laxative effects, as is indicated by their therapeutic use as laxatives and cathartics.[17] The mechanism of their laxative effects involves the retention of fluid in the intestinal lumen due to an exertion of osmotic pressure caused by the incomplete absorption of these salts from the gastrointestinal tract.[77] This increase in bulk indirectly increases intestinal transit.

Although toxicity data concerning sulfate are quite limited, our survey of the review literature indicates that high levels of sulfate in drinking waters can potentially induce laxative effects, especially in those individuals not acclimated to consuming waters high in sulfate. In addition, high concentrations of sulfate can affect the appearance and taste of water.

Acute Toxicity. The Safe Drinking Water Committee of the National Research Council[17] conducted an extensive survey of information concerning laxative effects induced by high sulfate concentrations in drinking waters and found that ingestion of waters containing less than 500 mg/L of sulfate will not produce adverse health effects among healthy human populations. However, acute physiological effects including diarrhea and gastrointestinal irritation have been induced by the consumption of waters containing greater than 500 mg/L sulfate. For instance, according to data from a North Dakota State Department of Health survey on the reactions of water consumers, waters containing at least 750 mg/L of sulfate were reported to cause laxative effects.[17,65] Persons living in the Shimilova Settlement in the USSR were reported to experience diarrhea and adverse organoleptic effects (taste) when the sulfate level in drinking-water supplies increased from 571 to 1235 mg/L.[17] Finally, according to information presented in Volume 1 of Drinking Water and Health,[17] an analysis of water-quality data was performed by Moore in 1952 which indicates that sulfate plus magnesium in excess of 1000 mg/L can induce laxative effects among consumers. The same survey led to the conclusion that sulfate alone at a concentration of 1000 to 1500 mg/L produces these effects; this suggests that the presence of magnesium in the water increases the toxic potential of sulfate.

In summary, available evidence indicates that 500 mg/L of sulfate in drinking waters is an adequate estimation of a no-observed-effect level. Acute debilitating toxic effects have been reported to occur after consumption of waters containing approximately 570 to 1500 mg/L of sulfate. In comparison, military personnel deployed in the field can conceivably be exposed to field waters containing 700 mg/L of sulfate (according to our estimate of the MLC of sulfate in natural waters). This concentration falls within the estimated toxic concentration range for sulfate of 570 to 1500 mg/L. Therefore, it seems highly probable that such a concentration could induce potential performance-degrading effects among military personnel, especially at a 15-L/d drinking-water consumption rate.

It must be recognized, however, that people can acclimate to the gastrointestinal effects of sulfates,[65] although it has not been determined how quickly resistance is acquired or lost. Evidence of acclimation is based on the absence of reported gastrointestinal problems for the many public water supplies containing high levels of sulfates. However, even people acclimated to high-sulfate waters can suffer a laxative effect if the sulfate concentration increases suddenly.

Chronic Toxicity. Our survey of the review literature revealed no case reports of debilitating health effects resulting from chronic exposure to high levels of sulfates in drinking waters. In fact, the studies previously mentioned reported finding no evidence of obvious chronic effects. The association between sulfate ingestion and chronic effects is not clearly defined and is therefore not considered to be of military significance.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested sulfate or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Taste and Odor. Sulfate is known to impart an astringent taste to waters at concentrations of 200 to 400 mg/L, which is the basis for most of the recommended standards for sulfates in drinking water.[66] High levels of sulfates in waters may also be biochemically converted to sulfide and then to hydrogen sulfide under anaerobic conditions, which can lead to serious odor problems.[49]

The estimated MLC of sulfate in natural waters of 700 mg/L is over three times higher than the lowest reported taste threshold of 200 mg/L of sulfate. This evidence indicates that the presence of sulfate in waters could potentially discourage water consumption among military personnel deployed in the field and result in cases of dehydration. However, sulfate will not be the only dissolved material present in natural waters, even though it can be a predominant one; therefore, such potential taste problems

that result from elevated sulfate levels are best addressed by developing criteria and recommendations for standards for total dissolved solids in field-water supplies.

Recommendation. Sulfate, particularly at its MLC in field-water supplies (i.e., 700 mg/L), may induce a performance-degrading laxative effect among military personnel consuming the water. Additionally, the MLC of sulfate may cause the taste and appearance of field waters to be undesirable for consumption which could, in effect, increase susceptibility of field personnel to dehydration. Therefore, we conclude that the potential acute toxic effects and organoleptic properties that can be associated with elevated sulfate concentrations in military field-water supplies need to be addressed in more detail. We recommend development of criteria and recommended standards for sulfate to address potential acute laxative effects, and development of criteria and standards for total dissolved solids to address organoleptic effects.

Thallium

Thallium is not identified in the literature as an element essential for human metabolism. The most prevalent forms of thallium in natural waters are the monovalent cation (Tl^+) and its related compounds. Although gastrointestinal absorption of these salts is rapid and complete in humans,[46] it is highly unlikely that toxic doses necessary to produce acute or chronic performance-degrading effects of military significance will be encountered from the ingestion of field waters.

Acute Toxicity. According to our survey of the review literature, only very large oral accidental therapeutic overdoses of thallium have resulted in symptoms of acute poisoning that can be considered performance-degrading from a military perspective. These symptoms include gastrointestinal irritation, vomiting, diarrhea, acute ascending paralysis, pain in the extremities, and neurological symptoms such as delirium, hallucinations, and convulsions. In extreme cases of thallium poisoning, coma followed by death due to respiratory failure may occur.[46]

Although quantification of a dose necessary to cause these acute effects has not been firmly established, it is highly unlikely that military personnel will encounter concentrations of thallium in field-water supplies that would equate to very large oral doses, even at a water-consumption rate of 15 L/d. For instance, the standard therapeutic dose of thallium acetate (the most commonly used therapeutic form of thallium) is 8.0 mg/kg body weight per day.[53] This dose corresponds to a no-observed-effect level for thallium of about 435 mg, based on a 70-kg man. The maximum likely dose of thallium

from field-water supplies, based on a daily consumption of 15 L of water containing an MLC of thallium of 2.0×10^{-5} mg/L, is calculated to be 3.0×10^{-4} mg/d. Thus, the maximum likely dose of thallium from military field waters is over six orders of magnitude smaller than the estimated no-observed-effect level.

Chronic Toxicity. Long-term therapeutic thallium intake has resulted in cases of chronic poisoning with symptoms including cardiac and renal disorders, gastroenteritis, pulmonary edema, and some paralysis of the extremities.[47] Unfortunately, just as in the case of acute thallium toxicity, quantification of a dose-response relationship has never been established. However, it can be assumed that this chronic dose must be quite high, based on the previously mentioned therapeutic dose of 435 mg/d for thallium. Consequently, it is concluded that a wide margin of safety exists between the daily dose of thallium necessary to produce chronic debilitating effects and the maximum likely daily dose that could be encountered by military personnel from the ingestion of field water.

Carcinogenicity, Mutagenicity, Teratogenicity. Our survey of the review literature found evidence that thallium might exhibit teratogenic effects in humans. According to Venugopal and Luckey,[46] Moeschlin, in a 1965 publication, indicated that chronic exposure to excess thallium levels during the first trimester of pregnancy can result in deformities in newborns. If chronic exposure leading to intoxication occurs during the second to third trimesters, the newborns may suffer central nervous system damage. This finding has been further substantiated by subsequent laboratory experiments that indicate that intraperitoneal injections in a rat of thallium sulfate (Tl_2SO_4) of 20 µg/g of body weight, followed three days later by a second injection of 40 µg/g, may induce dwarfism in the rat.[79] There is no evidence in the review literature indicating that ingested thallium or its compounds are carcinogenic or mutagenic to humans or laboratory animals.

Recommendation. In summary, the most prevalent forms of thallium in natural waters are the monovalent cation and its related compounds. Although these forms are readily absorbed from the gastrointestinal tract of humans, they are not likely to occur naturally in field waters at a concentration high enough to induce acute or chronic performance-degrading effects of military concern, even at the consumption rate of 15 L/d. Consequently, we conclude that there is no need to develop criteria and recommendations for standards concerning thallium in military field-water supplies.

Tin

Tin is not identified in the literature to be an element essential for human metabolism. The divalent cation of tin (Sn^{+2}) and its related compounds are the most prevalent forms of tin in natural waters. Average water concentrations of these forms of tin are considered to be nontoxic to human systems after ingestion.[15] This low order of toxicity is probably due to extremely poor absorption of tin from the gastrointestinal tract. Nevertheless, large oral doses of tin compounds have been reported to produce adverse human health effects that are of military significance. However, it is highly unlikely that military personnel will be exposed to concentrations of tin high enough to produce such toxic effects, even at a 15-L/d maximum consumption rate.

Acute Toxicity. Cases of acute toxicity resulting from oral exposure to tin and its compounds are limited, and most available data are based on symptoms following consumption of canned juices and foods.[17] The World Health Organization in 1973, as cited in Volume 1 of Drinking Water and Health,[17] stated that single oral doses of 5 to 7 mg of tin per kilogram of body weight are necessary to produce acute symptoms of nausea, vomiting, and diarrhea in humans. These doses correspond to single oral doses of 350 to 490 mg of tin, based on a 70-kg man.

This evidence indicates that 350 to 490 mg of tin can be considered an adequate estimation of a toxic dose. In contrast, the maximum likely daily dose of tin that military personnel may receive from the consumption of field water is 0.03 mg. This dose is based on the daily consumption of 15 L of water containing an MLC for tin of 2.0×10^{-3} mg/L. Thus, the lowest toxic dose of 350 mg of tin is over four orders of magnitude greater than the maximum likely dose of tin that may be consumed by military personnel from field waters. Therefore, a substantial margin of safety exists between the maximum likely daily dose from field water and the dose necessary to produce acute performance-degrading effects.

Chronic Toxicity. Our survey of the review literature revealed no cases of toxicity due to chronic oral exposure to tin compounds. However, long-term industrial inhalation exposure to tin dusts and fumes have resulted in benign pneumoconiosis (i.e., fibrosis of the lungs) among workers.[47] Although this is a significant health effect, it would not necessarily result from consumption of tin contained in military field-water supplies. As indicated by lack of data in the review literature, chronic effects due to long-term oral tin exposure are not well-defined, and without further data these effects cannot be considered of military significance.

<u>Carcinogenicity, Mutagenicity, Teratogenicity</u>. There is no evidence in the review literature indicating that ingested tin or its compounds are carcinogenic, mutagenic or teratogenic in humans or laboratory animals.

<u>Recommendation</u>. The most prevalent forms of tin in natural waters are the divalent cation (Sn^{+2}) and its related compounds. These forms of tin are not readily absorbed from the gastrointestinal tract of humans and thus exhibit a low order of oral toxicity. Comparison between the maximum likely daily dose of tin from the ingestion of field-water supplies (i.e., 0.03 mg/L) and the minimum dose necessary to cause acute effects (i.e., 350 mg/L) reveals that the trace amounts of tin typically present in field waters will not induce acute performance-degrading effects among military personnel. Chronic effects due to long-term oral exposure of tin have not been demonstrated in human systems. Consequently, we conclude that there is no need to prepare criteria and recommendations for standards concerning the presence of tin in military field-water supplies.

<u>Uranium</u>

The review literature does not indicate that uranium is an element essential for human metabolism. The most prevalent form of uranium in natural waters is hexavalent uranium, U(+6), as the uranyl ion (UO_2^{+2}) and its related compounds.[40] These forms of uranium exhibit a very low order of toxicity in human systems. This can probably be attributed to poor gastrointestinal absorption, along with rapid and complete excretion via the kidneys.[47]

Our survey of the review literature did not reveal any cases of adverse health effects due to oral exposure to uranium or its compounds. In fact, Russian investigators found that a relatively high uranium concentration of 0.04 to 0.05 mg/L in drinking water did not produce any acute or chronic adverse effects among the exposed population of one town, compared to a similar population of a nearby town that was exposed to 0.002 to 0.004 mg/L of uranium in their drinking water.[40] Such evidence indicates that the ingestion of uranium compounds from drinking water poses little, if any, performance-degrading health threat to an exposed population. Additionally, our best estimation of the uranium MLC in natural waters of 0.002 mg/L falls within the concentration range of uranium found in the control town, which is approximately one-tenth of the concentration found in drinking waters of the town with exceedingly high

concentrations. This indicates that there is a substantial margin of safety between the MLC of uranium in military field-water supplies and concentrations necessary to produce debilitating toxic effects of military significance.

Acute Toxicity. There is no evidence in the review literature indicating that uranium or its compounds ingested with drinking water produce acute performance-degrading effects of military significance.

Chronic Toxicity. There is no evidence in the review literature indicating that ingested uranium or its compounds produce chronic performance-degrading effects of military significance.

Carcinogenicity, Mutagenicity, Teratogenicity. Evidence does suggest that exposure to radioactive uranium may be associated with the formation of cancers in humans. For instance, Archer et al. in 1973, according to Drinking Water and Health, Volume 3,[40] reported that excess deaths due to malignancies of lymphatic and hematopoietic tissues occurred within a group of uranium mine workers during a 17-year study period. However, there is no evidence in the review literature indicating that ingested nonradioactive uranium or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that orally ingested nonradioactive uranium compounds pose a significant acute or chronic performance-degrading health threat to human populations. Consequently, we conclude that development of criteria and recommendations for standards concerning the presence of uranium in military field-water supplies is unnecessary.

Vanadium

The review literature does not indicate that vanadium is an element essential for human metabolism. The most prevalent and soluble forms of vanadium in natural waters are the pentavalent forms, which are anionic (VO_3^-). These forms of vanadium exhibit extremely poor absorption from the gastrointestinal tract of humans, which may be the reason for their low order of toxicity in human systems.[17] Nevertheless, extremely high oral doses of therapeutically administered vanadium compounds have resulted in

debilitating health effects. However, it is highly inconceivable that vanadium concentrations in military field-water supplies will reach levels equivalent to a therapeutic dose necessary to cause toxic effects.

Acute Toxicity. Acute human oral toxicity data concerning vanadium is extremely limited. In Volume 1 of Drinking Water and Health,[17] an extrapolation from oral animal studies has been made that suggests that "a daily dose of 10 mg of vanadium may be slightly toxic in humans under certain conditions." This extrapolation seems to be supported by the work of Dimond et al. in 1963, as cited in Drinking Water and Health, Volume 3,[40] who reported that oral doses of 4.5 to 18 mg vanadium per day administered to human volunteers for 6 to 16 weeks produced cramps and diarrhea only at the larger dose.

Schroeder et al. in 1963, as cited in Drinking Water and Health, Volume 3,[40] administered oral doses of up to 9 mg/d of vanadium for 6 to 16 months to individuals confined to a mental institution. There was no evidence of any ill effects resulting from this type of exposure. Therefore, this dose can be considered an adequate estimation of a no-observed-effect level for vanadium. In contrast, the maximum likely daily dose of vanadium that military personnel may receive from the consumption of field water is 0.23 mg. This dose is based on the daily consumption of 15 L of water containing an MLC for vanadium of 1.5×10^{-2} mg/L. Therefore, the maximum probable vanadium dose from field-water supplies is approximately 39 times smaller than the no-observed-effect level. This indicates that it is highly unlikely that vanadium concentrations occurring in field-water supplies will be high enough to induce acute performance-degrading effects in military personnel.

Chronic Toxicity. Our survey of the toxicity data found no evidence of chronic performance-degrading effects of military significance resulting from long-term oral exposure to vanadium compounds. In fact, the previously mentioned study involving long-term therapeutic administration of relatively large doses (9 mg/d for 6 to 16 months) of vanadium to individuals confined to a mental institution reported no occurrence of obvious chronic or acute effects. Therefore, more definitive data concerning a possible association between chronic, oral vanadium exposure and debilitating health effects are required before chronic vanadium toxicity can be considered of military concern.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that ingested vanadium or its compounds are carcinogenic, mutagenic, or teratogenic in humans or laboratory animals.

Recommendation. In summary, the most prevalent, soluble forms of vanadium in natural waters are the pentavalent forms, which are anionic (e.g., VO_3^-). These forms are very poorly absorbed from the gastrointestinal tract of humans, which probably accounts for their low order of toxicity. Additionally, the evidence reviewed in our survey indicates that vanadium will not be encountered in field waters at concentrations high enough to cause acute or chronic performance-degrading effects among military personnel even at a 15-L/d consumption rate. Consequently, we conclude that development of criteria and recommendations for standards concerning vanadium in military field-water supplies is unnecessary.

Zinc

The divalent cation of zinc (Zn^{+2}) is the most stable form of zinc in natural waters. It is this form that is considered to be an essential trace element for human metabolism and is involved in several physiological reactions.[57] Zinc contributes to enzymatic functions, DNA and protein synthesis, insulin storage, and carbohydrate metabolism.[46] It is also necessary for normal growth and development. For example, human dwarfism and lack of sexual development in populations of individuals in Iran and Egypt are attributed to diets grossly deficient in zinc.[17]

Metabolic studies have shown that healthy adults require dietary intakes of at least 12.5 mg of zinc per day to maintain the equilibrium or positive zinc balance necessary for normal metabolism.[80] Additionally, radioisotope studies show that the turnover of zinc in a healthy individual is 6 mg/d.[57] Based on these data and allowing for gastrointestinal absorption of about 40 to 50% dietary zinc, the recommended daily allowance for zinc has been set at 15 mg/d for adults, with an additional 5 mg recommended during pregnancy and 10 mg recommended during lactation.[57]

Evidence indicates that the normal body burden of zinc is regulated by a homeostatic mechanism.[46] Absorption, however, is primarily dependent upon the adequacy of zinc stored in the body and can therefore vary among zinc-deficient individuals.[47] Elimination of any excess zinc above physiological requirements occurs largely via the feces, with lesser amounts lost through the urine. Extreme excesses of zinc may result in accumulation within several organs including the kidney, liver, pancreas, and eyes, along with small amounts occurring in the muscles and the blood.[47] However, this accumulation is not considered to be toxicologically significant from a military perspective because it is not associated with any performance-degrading effects.

In general, ingested zinc compounds exhibit a very low order of toxicity in humans and are not likely to be performance-degrading to field troops in the concentrations normally found to occur in military field-water supplies. Zinc, at certain concentrations, may also affect the appearance and taste of water.

Acute Toxicity. Our survey of the review literature revealed no evidence that the ingestion of zinc at concentrations that occur naturally in food or water can produce acute toxic effects in adults. In fact, the majority of the existing data concerning zinc toxicity pertains to accidental therapeutic overdoses. For example, Venugopal and Luckey[46] cite a 1970 report by Murphy documenting acute debilitating effects, including nausea, vomiting, diarrhea, lightheadedness, and staggering gait in a sixteen-year-old boy after he consumed 12 g of metallic zinc that was given therapeutically in an attempt to hasten healing of a minor laceration. Full recovery was reported in this teenager after chelation therapy. In another case, a lethal dose of 6 g of zinc in the form of zinc sulfate ($ZnSO_4$) was consumed by an adult woman and caused vomiting, cramps, and renal and pancreatic dysfunction prior to death.[46] There is no evidence that any type of treatment was administered in an attempt to reverse the toxic symptoms in the woman.

These data indicate that 6 to 12 g of zinc will induce acute debilitating symptoms (and possibly death, depending on whether or not treatment is promptly administered) after ingestion of zinc compounds. These doses, however, are quite high compared to the doses that could be encountered by military personnel from the consumption of zinc in field-water supplies. For instance, the maximum likely dose military personnel could ingest daily from field water is 3 mg. This calculation is based on our estimation of an MLC for zinc in natural waters of 2.0×10^{-1} mg/L and a 15-L/d maximum daily water-consumption rate. Thus, the maximum likely daily dose of zinc for military personnel from the ingestion of field water is more than three orders of magnitude less than the lowest reported lethal dose. These calculations indicate that it is highly improbable for military personnel to consume enough zinc from drinking water to accumulate a toxic dose that will cause performance-degrading acute effects.

It is important to mention that there have been reports of acute zinc poisoning associated with the consumption of water from galvanized pipes. Consumption of water containing 40 mg/L of zinc has been reported to cause nausea, muscular stiffness and pain, irritability, and loss of appetite in two adults.[17] However, this concentration is well above our estimate of the zinc MLC in natural waters (i.e., 2.0×10^{-1} mg/L). Therefore, military populations consuming natural waters are not likely to suffer these effects.

Chronic Toxicity. There is no evidence in the review literature indicating that long-term exposure to zinc at concentrations typically occurring in field waters will produce chronic debilitating toxic effects in military personnel. However, chronic debilitating effects including hematologic, hepatic, and renal toxicities have been known to result after chronic exposure to therapeutic zinc compounds.[81] Unfortunately, a dose-response relationship for such toxic therapeutic overdoses has yet to be firmly established.

Our survey of the review literature did produce one estimation of a no-observed-effect level for long-term therapeutic exposure to zinc. According to a study published in 1970 by Greaves and Skillen that is cited by the National Research Council Zinc Subcommittee,[81] 18 patients (presumably adults) given a daily dose of 165 mg of zinc for 16 to 26 weeks during treatment of venous leg ulcerations displayed no evidence of any chronic or acute effects. Consequently, we consider ingestion of up to 165 mg zinc per day to be a "safe" intake level for military personnel deployed in the field. In comparison, the maximum likely daily dose military personnel could ingest from field water is 3 mg, based on our estimate of the MLC and a 15-L/d water-consumption rate. This maximum likely daily dose for military troops is less than one-fiftieth of the estimated no-observed-effect level. These calculations indicate that it is highly unlikely that zinc concentrations in field drinking-water supplies will cause chronic performance-degrading effects among military personnel.

Carcinogenicity, Mutagenicity, Teratogenicity. There is no evidence in the review literature indicating that zinc or its compounds are carcinogenic, mutagenic, or teratogenic when ingested by humans or laboratory animals.

Taste and Odor. The present secondary U.S. drinking-water standard for zinc is 5 mg/L.[17] This is not established on the basis of toxicity, but rather on the basis of taste and appearance. Zinc concentrations above this level are reported to give an unpleasant, astringent taste and a milky appearance to drinking waters. Although this could enhance susceptibility to dehydration due to decreased water consumption by military personnel, such concentrations have a very small probability of occurrence according to our estimate of the MLC for zinc in natural waters. Consequently, these organoleptic properties are not considered to be significant from a military perspective.

Recommendation. The most prevalent forms of zinc in natural waters are the divalent cation and its related compounds. Our survey of the review literature revealed that toxicity due to the ingestion of these compounds is quite rare. In fact, only very large therapeutic overdoses and consumption of waters unusually high in zinc due to galvanized

piping have been reported to induce performance-degrading effects in humans. Our calculations indicate that it is highly unlikely that zinc concentrations in field waters will reach levels required to produce these debilitating effects, even if military personnel consume water at a 15-L/d maximum rate. In addition, normal concentrations of zinc in field waters should not produce undesirable organoleptic effects of taste and color that could lead to decreased consumption and subsequent susceptibility to dehydration. Consequently, there is no need to develop specific criteria and recommendations for standards concerning zinc in military field-water supplies.

Total Dissolved Solids

Mineral salts and small amounts of other inorganic and organic substances constitute the filterable residue content of water (i.e., the material that will pass through a standard glass-fiber-filter disk). The concentration of filterable residue is commonly referred to as salinity but expressed as milligrams per liter (mg/L) of total dissolved solids (TDS). The principal cations constituting TDS are calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^+), sodium (Na^+), aluminum (Al^{+3}), iron (Fe^{+3}), and manganese (Mn^{+3}). The principal anions include bicarbonate (HCO_3^-), carbonate (CO_3^{-2}), chloride (Cl^-), sulfate (SO_4^{-2}), and in ground waters, nitrate (NO_3^-).[20]

According to our survey of the review literature, TDS concentrations in drinking water commonly range from levels below 500 mg/L to levels exceeding 2000 mg/L, and ingestion of water containing TDS concentrations exceeding 1000 mg/L have been reported to induce laxative effects.[65,66,82] Although populations have been reported to adapt to such high TDS levels,[77] the possibility of debilitating laxative effects occurring during the period of initial exposure to such high-TDS waters is considered to be of military significance. Additionally, and probably most importantly, high TDS concentrations can impart an undesirable taste to drinking waters; the major consequence of poor-tasting water is decreased consumption.[83] This relationship between TDS concentration, undesirable taste, and decreased consumption is important from a military perspective because decreased consumption could make personnel susceptible to the performance-degrading effects of dehydration, especially in situations where large volumes of water must be consumed to replace sweat losses.

Recommendation. We recommend that criteria and recommendations for standards be prepared concerning TDS in field drinking-water sources. This recommendation is based

on the evidence that indicates TDS concentrations can be encountered in field drinking-water sources that could directly and indirectly produce human health consequences that are of military significance.

Dissolved Gases

The dissolved gases that occur most commonly in natural waters, depending on the pH and oxidized or reduced state of water, are oxygen, nitrogen, hydrogen sulfide, methane, and carbon dioxide.[18] There is no evidence in the review literature to suggest that any of these dissolved gases could be present at concentrations in water that could directly produce degraded performance in exposed military personnel. However, dissolved hydrogen sulfide (H_2S), which originates primarily in bottom sediments of wells and other ground waters as a result of bacterial reduction of sulfate and anaerobic decomposition of sulfur-containing organic matter[84,85] can produce an undesirable "rotten egg" odor that can be detected at very low concentrations. For example, the olfactory threshold for hydrogen sulfide in air generally ranges from 0.02 to 0.13 ppmv, although exposure to such concentrations have no known human health consequences. Interestingly, at a concentration of 100 ppmv of H_2S in air, olfactory fatigue may result, and under such conditions the ability to detect the H_2S odor can be temporarily lost.[86] Furthermore, according to the 1958 work of Campbell et al. cited by McKee and Wolf,[87] the minimum taste threshold for H_2S is 0.05 mg/L. Nevertheless, these organoleptic properties of H_2S are considered to have little significance from a military perspective because the aqueous solubility of H_2S is reduced substantially as water becomes aerated.[20] Such aeration will probably be accomplished during the normal practices of acquisition, storage, and distribution of field waters employed by the military. Additionally, field-water supplies containing H_2S are easily recognized and can be avoided in favor of alternative supplies.

Recommendation. Generally, dissolved gases do not represent constituents of field waters that are likely to degrade performance in exposed field troops. Although dissolved hydrogen sulfide can produce an undesirable taste and odor in water that is easily detected and could discourage water consumption, aerating such waters significantly reduces the aqueous solubility of the dissolved gas and thereby effectively removes the objectionable taste and odor from the water. Such aeration will probably be accomplished during collection, storage, and distribution of field waters by the military. For these reasons, we do not believe that criteria and recommendations for standards need to be prepared for dissolved gases.

Turbidity and Color

Turbidity in water is attributed to suspended materials such as clay, silt, soluble colored organic compounds, finely divided organic and inorganic matter, and microscopic organisms, such as plankton.[52] Turbidity may be the result of natural processes such as erosion, or the result of industrial and domestic waste discharges to surface waters. The degree of turbidity is measured either by reduction in the amount of light transmitted through a column of water (spectrophotometry) or by the amount of light reflected by the suspended particles (nephelometry).

Color in water may result from the presence of natural metallic ions such as iron and manganese, or from the presence of other materials including humus and peat, plankton, weeds, and industrial wastes.[52] In the water-treatment industry, there are two generally accepted types of color for water: "true" and "apparent" color. True color refers to the color of water after the turbidity has been removed, and water with low turbidity is considered to be clear in the water-treatment industry.[87] Apparent color refers to the color of water that is produced by substances in solution and suspended materials. There are various methods used to measure color. These include the visual comparison method, spectrophotometric method, and the tristimulus filter method (i.e., three special light filters are combined with a specific light source and photoelectric cell in a filter photometer in order to obtain color measurements).[52]

Our survey of the review literature indicates that turbidity and color are generally aesthetic water-quality parameters. High levels of turbidity and color can make the water appear objectionable to many individuals. An undesirable appearance of a source of drinking water can lead to decreased consumption by exposed individuals. Consequently, turbidity and color water-quality parameters are of concern from a military perspective because decreased water consumption can make military personnel susceptible to the performance-degrading effects of dehydration, especially in situations where large volumes of water must be consumed to replace sweat loss. Our survey of review literature revealed that there is no evidence indicating that adverse acute or chronic human health effects are related directly to the presence of turbidity and color in water.

Recommendation. We recommend the preparation of criteria and recommendation for standards for turbidity and color in military field-water supplies. This recommendation is based on the evidence that increasing turbidity and color could make field water undesirable for consumption, and decreased consumption could make exposed military personnel susceptible to the adverse health effects associated with dehydration.

APPENDIX C

REVIEW OF HUMAN HEALTH IMPLICATIONS ASSOCIATED
WITH EXTERNAL EXPOSURE TO POSSIBLE INORGANIC
CONSTITUENTS OF MILITARY FIELD-WATER SUPPLIES

We surveyed the review literature for information concerning the human health implications from external exposure (e.g., bathing, showering, or swimming) of troops to the possible inorganic constituents of field-water supplies. Only those inorganic constituents of field water that can produce adverse human health effects following external exposure are identified in this appendix along with the related health effects. Additionally, the significance of each health effect is evaluated in terms of performance degradation for exposed military personnel.

The human health consequences that may result from external exposure to the inorganic constituents of field-water supplies include dermal, ocular, and systemic effects. The most likely dermal effects range from a mild localized contact dermatitis (i.e., mild rash), urticaria (i.e., hives), and itching, to a more serious destruction of cutaneous tissue caused by the generalized formation of vesicular and pustular sores and caustic burns.[88,89] Ocular effects typically include irritation to the conjunctiva (i.e., the mucous membrane that lines the eyelid), but may also include corneal ulceration and blindness in extreme cases.[88,89] Systemic effects, unlike dermal or ocular effects, require that the toxicant be absorbed from the site of exposure (e.g., the skin) and then distributed via the blood system to a distant site (e.g., central nervous system, liver, kidney) at which toxic effects are produced.[88] In general, chemicals (especially inorganic substances) are absorbed more slowly and less completely from the skin than from any other route of exposure, and thus toxic effects are less likely to occur when the skin is exposed to a toxicant than when it is ingested or inhaled.[89]

Our survey of the review literature revealed that the existing information concerning the possible toxic effects from external exposure to those inorganic substances identified as possible constituents of field water is qualitative in nature and deals primarily with exposure to highly concentrated solutions present in the industrial environment. From our list of possible inorganic constituents of field-water supplies, only ammonia, antimony, arsenic, chromium, cyanide, iodine, mercury, nickel, potassium, selenium, silver, vanadium, and zinc are reported in the review literature to exhibit irritant or caustic dermal and/or ocular effects following single or repeated external exposure, and these reports are for industrial settings. Although the reported dermal and ocular effects for these substances could be performance-degrading in extreme cases, we

do not consider these effects to be of significance to troops in the field. Our reasoning is based on the assumption that typically occurring concentrations of these metals or their compounds in field-water supplies are not high enough to correspond to the highly concentrated solutions frequently handled in the industrial workplace. Furthermore, any concentrated solution of these metals of concern that might find its way into field waters (e.g., industrial dumping or sabotage attempts) should become sufficiently dilute, or volatilize into the atmosphere, after mixing with the water. Moreover, avoiding waters where industrial contamination or sabotage is likely represents a key precaution in reducing health risks from water.

With the exception of cyanide, none of the inorganic constituents of military field-water supplies is reported in the review literature to exhibit skin absorption to a significant degree. Therefore, the occurrence of performance-degrading systemic effects following external exposure to these substances is a very remote possibility. Cyanide, however, is readily absorbed from the skin and is indicated in the review literature to be a severe toxicant, regardless of route of exposure.[89,90] Because of the severe toxicity that can be induced by exposure to cyanide or its compounds, we recommend that cyanide be further investigated to determine if data exist for computing the concentrations in water necessary to cause systemic effects following external exposure.

In summary, there is no evidence in the review literature indicating that external exposure to typical concentrations of the possible inorganic constituents of field water can induce performance-degrading dermal, ocular, or systemic effects among military personnel utilizing the water. In fact, there are no reports of such effects occurring as a result of external exposure to high levels of any inorganic substance occurring in natural waters. The only data available at present concern the external exposure of industrial workers to highly concentrated solutions of these substances. This lack of pertinent data indicates that such toxic effects are a result of atypical exposures that should not be encountered from water by military populations in the field. Therefore, we conclude, with the possible exception of cyanide, that external exposure to typical levels of the possible inorganic constituents of field-water supplies does not present a dermal, ocular, or systemic health threat to field personnel.

Ammonia

Our survey of the review literature reveals that cases of performance-degrading dermal or ocular effects due to external exposure (e.g., showering, bathing, or swimming) to natural waters containing elevated levels of ammonia are unknown. However, the

review literature does indicate that, in the industrial environment, accidental external exposures to the ammonium ion (NH_4^+) and aqueous ammonia solutions, such as ammonium hydroxide (NH_4OH), have resulted in irritation to the skin, eyes, and mucous membranes.[88,91] Eye symptoms are reported to include lacrimation (i.e., secretion and discharge of tears), blepharospasm (i.e., twitching of the eyelids), palpebral edema (i.e., swelling of the eyelids), and a rise of intraocular pressure leading to corneal ulceration and blindness in extreme cases.[91] Adverse dermal effects following direct contact with these substances include corrosive burns and blister formation.[91] There is no evidence in the review literature indicating that external exposure to ammonia or its compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of the ammonium ion (NH_4^+) or its compounds in military field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in field personnel experiencing repeated or prolonged external exposure to such waters. Consequently, there is no need for the development of criteria and recommendations for standards for external exposure to ammonia in field-water supplies.

Antimony

Accidental external exposure to elevated levels of antimony trioxide can occur occupationally and result in a dermatitis commonly referred to as "antimony spots," which are associated with an intense itching followed by skin eruptions.[91] Antimony halides, including antimony trichloride and pentachloride, are reported to be highly corrosive upon direct contact with the skin and mucous membranes. Effects following contact include the formation of papular eruptions that can develop into vesicular and pustular sores.[91] Although these symptoms have the potential to be performance-degrading from a military perspective, they have been reported only as a result of direct contact with very high concentrations of these antimony compounds in the industrial environment.[91] Because there are no documented adverse health effects in the general population as a result of external exposure to typical, natural water concentrations antimony or its compounds, we feel that antimony in field-water supplies will not reach concentrations high enough to adversely affect field troops after single or repeated total body exposures.

Little information exists about the absorption of antimony through the skin. Gross, in a 1955 experiment reported by the EPA,[50] applied a paste of antimony trioxide (25 mg) to the skin of rabbits and could see no signs of systemic effects. However, this study did

not involve the determination of concentrations of antimony in blood or tissue. Nevertheless, there is no definitive evidence in the review literature indicating that external exposure to antimony or its compounds results in systemic toxicity in humans.

Recommendation. According to our survey of the review literature, there is no evidence indicating that the presence of antimony or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel experiencing repeated or prolonged external exposure to such waters. Consequently, there is no need for the development of criteria and recommendations for standards for external exposure to antimony in field-water supplies.

Arsenic

There is limited evidence in the review literature indicating that external exposure in the industrial environment to elevated levels of trivalent arsenic compounds can be corrosive to the, eyes, and intact skin. According to Sitting,[91] brief contact with such compounds produces no noticeable effects; however, prolonged contact may result in a local hyperemia (i.e., redness of the skin due to an increase in blood flow to the area), followed by vesicular or pustular eruptions. Additionally, repeated exposure to elevated levels of arsenic trioxide and pentoxide are capable of producing skin sensitization and contact dermatitis.[91] Although extreme manifestations of these effects can be considered to be potentially performance-degrading from a military perspective, they have not been reported as a result of direct contact by individuals with natural waters containing elevated levels of arsenic. This lack of association between adverse dermal and eye effects and typical arsenic concentrations in natural waters suggests that it is not an immediate problem for the general population. Therefore, we feel that it is safe to assume that the presence of arsenic or its compounds in field-water supplies should not pose a debilitating health threat to those troops experiencing repeated or prolonged total body exposure to such waters. Furthermore, there is no evidence in the review literature indicating that external exposure to arsenic or its compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of arsenic or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel

experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to arsenic in field-water supplies.

Chromium

Accidental external exposure to certain chromium compounds in the industrial environment is known to cause potentially debilitating dermal effects among workers.[91] For instance, hexavalent chromium compounds produce deep and penetrating ulcers on the hands and forearms. Trivalent-chromium compounds exhibit a necrotizing effect on the skin that results in a contact dermatitis with symptoms ranging from a dry erythematous condition to extensive eczema of the exposed areas. There are no reports in the review literature of any adverse dermal or ocular effects resulting from external exposure to natural waters containing average or elevated levels of chromium or its compounds. Additionally, there is no evidence in the review literature indicating that external exposure to trivalent and hexavalent chromium or their respective compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of chromium or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to chromium in field-water supplies.

Cyanide

Our survey of the review literature reveals that cases of performance-degrading dermal or ocular effects due to external exposure (e.g., showering, bathing, or swimming) to elevated levels of cyanide in natural waters are unknown. However, cyanides are reported to be "acute local irritants".[89] For instance, workers experiencing daily external exposure to cyanide solutions have been reported to develop a rash that is characterized by itching, by macular, papular, and vesicular eruptions, and by secondary infections.[89]

According to Sax,[89] cyanide is reported to be absorbed by all routes of exposure, including the skin. Additionally, the cyanide ion is known to exhibit the same systemic toxicity, regardless of the route by which it is absorbed.[89] This fact implies that skin

absorption due to external exposure could result in serious performance–degrading effects in humans. For instance, as reported in Appendix B of this document, the acute human toxic effects of ingested cyanide include headache, nausea, breathlessness, weakness, cardiac palpitations, giddiness, and tremors. Convulsions, paralysis, coma, and death as a result of cardiac dysfunction can occur in extreme cases. Furthermore, all of these symptoms are reported to manifest themselves almost immediately after exposure. Because these acute toxic effects due to oral exposure are considered to be performance–degrading from a military perspective, it seems reasonable to assume that skin absorption from external exposure to high levels of cyanides can result in very similar effects, although the dose from cutaneous absorption that can produce such effects was not identified in the review literature.

Recommendations. In summary, cyanide is a potent, fast–acting human poison that is rapidly absorbed through all routes of exposure, including the skin. Although our survey of the review literature did not reveal any cases of adverse dermal, ocular, or systemic effects due to external exposure to elevated levels of cyanide in natural waters, we feel that cyanide toxicity in association with external exposure must be further evaluated in criteria and recommendations for standards. Further evaluation is particularly appropriate because cyanide represents a potential chemical threat agent.

Iodine

Information in Drinking Water and Health, Volume 3[40] indicates that occupational exposure to saturated iodine vapor can cause general skin irritation to exposed areas, and possible loss of the corneal epithelium upon exposure to the human eye. However, eye symptoms are reported to be fairly mild, with complete healing usually occurring within two to three days following initial exposure.

Although data concerning the dose–response relationship between the presence of iodine in public water supplies and the possible induction of adverse dermal, ocular, or systemic effects in humans are quite limited, our survey of the review literature revealed one such investigation. According to Drinking Water and Health, Volume 3,[40] Byrd et al., in 1963, evaluated eye and skin irritation in members of a college swim team after a single exposures and after one week and one month of daily repeated exposures to an iodine concentration of approximately 0.4 mg/L of pool water. Eye and skin irritation were reported to be notably absent. Additionally, absorption of iodine through the intact skin was considered to be negligible. This consideration was based upon the lack of significant change in protein–bound iodine or urinary iodine.

We consider this type of exposure (i.e., swimming) to be representative of the total body exposure that military field personnel might receive from bathing or swimming in field water. Therefore, it seems reasonable to assume that 0.4 mg/L of iodine is an adequate estimation of a no-observed-effect concentration for potential debilitating dermal and eye effects. In comparison, our best estimation of the MLC of iodine in natural waters (i.e., 0.04 mg/L) is one-tenth of this no-observed-effect concentration. Such evidence indicates that typical iodine levels in field-water supplies should not be high enough to induce potential performance-degrading dermal or ocular effects in troops experiencing repeated total body exposure to such waters over a prolonged period of time. Furthermore, there is no evidence in the review literature indicating that external exposure to iodine or its compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of iodine or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to iodine in field-water supplies.

Mercury

Venugopal and Luckey[46] report that human skin readily absorbs mercury salts and even elemental mercury if it is dispersed in a suitable medium. Additionally, Block et al.[9] indicate that accidental external occupational exposures to mercuric chloride ($HgCl_2$) solutions can result in irritation to the mucous membranes and intact skin. However, there is no evidence in the review literature indicating that debilitating dermal or ocular effects can result from external exposure to elevated levels of mercury or its compounds in natural waters. Furthermore, there is no evidence in the review literature indicating that external exposure to inorganic mercury or its compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of mercury or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel

experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to mercury in field-water supplies.

Nickel

External exposure to nickel or its compounds is known to produce a dermatitis that is characterized by chronic eczema with lichenification (i.e., cutaneous thickening and hardening from continuous irritation) that resembles atopic- or neurodermatitis. This manifestation is frequently referred to as "nickel itch".[47] External exposure to nickel may also irritate the conjunctiva of the eye.[91] Although the dose necessary to produce these effects has not been quantified to date, Spruit et al.[92] report that Wahlberg conducted a 1976 investigation in which 20% of a population hypersensitive to contact with nickel reacted to a 0.04% nickel sulfate solution. We consider this concentration to be the lowest reported toxic dose available in the review literature. In contrast, our best estimation of the MLC of nickel in natural waters (i.e., 0.01 mg/L) is several orders of magnitude less than the concentration considered to be a toxic dose. This evidence indicates that typical nickel levels occurring in field-water supplies should not be high enough to induce potential debilitating dermal or ocular effects in exposed military personnel. Finally, there is no evidence in the review literature indicating that external exposure to nickel or its compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of nickel or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to nickel in field-water supplies.

Potassium

The most prevalent forms of potassium in natural waters (i.e., the monovalent cation (K^+) and its related compounds) are not reported in the review literature to be skin irritants. However, Sitting[91] reports that repeated or prolonged skin contact with

potassium hydroxide (KOH) may cause erythema and vesication of the skin. Direct eye contact with potassium hydroxide may result in permanent corneal opacification. This irritant action is attributed to the caustic nature of the hydroxide ion (OH⁻).

The RTECS data-base[28] reports that 50 mg of potassium hydroxide applied to intact human skin over a 24-hour period produces severe skin effects including erythema (i.e., diffused redness over the skin), eschar (i.e., scab) formation, and extensive edema of the exposed area. However, there are no reports in the review literature indicating that external exposure to elevated levels of potassium hydroxide occurring in public water supplies have resulted in adverse dermal or ocular effects among users. Furthermore, there is no evidence in the review literature indicating that external exposure to potassium or its compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of potassium or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to potassium in field-water supplies.

Selenium

Sitting[91] reports that accidental occupational exposure to selenium compounds can result in irritation and destruction of intact skin. For instance, exposure to selenium dioxide and oxychloride can cause contact dermatitis, allergy in the form of hives, and slight irritation to the eyes. Selenium dioxide can also cause intense pain in the nailbeds and paronychia (i.e., acute or chronic infection of marginal structures about the nail) after exposure to the hands. However, these symptoms are typically characteristic of external exposure occurring in the industrial environment. There is no evidence in the review literature indicating that external exposure (e.g., bathing, showering, or swimming) to typical or elevated levels of selenium or its compounds in natural waters results in adverse dermal or ocular effects. Furthermore, there are no reports in the review literature of any cases of systemic toxicity due to the dermal absorption of selenium or its compounds in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of selenium or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel experiencing

repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to selenium in field-water supplies.

Silver

The review literature indicates that concentrated silver nitrate ($AgNO_3$) solutions are caustic and irritating to the skin and mucous membranes.[91,93] However, dilute solutions are used therapeutically as topical anti-infection agents with no reported adverse effects.[91] For instance, silver ointments that are widely used therapeutically have not been shown to pass the dermal barrier, and absorption of silver compounds from even abraded, nonintact skin averages less than one percent.[94] Furthermore, information presented in Volume 1 of Drinking Water and Health[17] indicates that the 1954 work of Norgard, which examined the use of silver preparations to treat bath waters, did not reveal any noticeable adverse skin or eye effects among users of the water. From this evidence, we conclude that external exposure of military personnel to field water containing silver compounds is not likely to result in the manifestation of performance-degrading dermal or ocular effects, even if the water contained silver at the estimated MLC of 0.002 mg/L. Furthermore, there is no evidence in the review literature indicating that external exposure to silver or its compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of silver or its compounds in field-water supplies will produce dermal, ocular, or systemic health effects in military personnel experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to silver in field-water supplies.

Vanadium

Our survey of the review literature reveals that cases of performance-degrading dermal or eye effects due to external exposure (e.g., bathing or swimming) to elevated levels of vanadium or its compounds in natural waters are unknown. However, Sitting[91] reports that accidental external exposure to vanadium pentoxide (V_2O_5) in the industrial environment has produced irritation to the eyes and intact skin of workers. The skin lesions are reported to be of the eczematous type and produce intense itching.[91] Eye

symptoms are reported to include profuse lacrimation (i.e., tearing) and a burning sensation of the conjunctiva. Corrosive effects such as tissue destruction are not reported to occur.[91] Additionally, there is no evidence in the review literature indicating that external exposure to vanadium or its compounds results in systemic toxicity in humans or laboratory animals.

Recommendation. There is no evidence in the review literature indicating that the presence of vanadium or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to vanadium in field-water supplies.

Zinc

Our survey, of the review literature reveals that cases of performance-degrading dermal or eye effects due to external exposure (e.g., showering, bathing, or swimming) to elevated levels of zinc or its compounds in natural waters are unknown. However, zinc chloride ($ZnCl_2$), which is widely used in the industrial environment, is reported to be highly caustic to the intact skin of humans. Deep and painful ulcers may result following direct contact. Repeated exposures to zinc chloride may also produce a sensitization reaction in the form of eczematoid dermatitis.[91] Eye effects may also occur following external exposure to $ZnCl_2$. These ocular effects include pain and inflammation of the conjunctiva and may be followed by corneal ulceration.[89,91] The RTECS data base[28] reports that a total of 0.3 mg of zinc powder applied periodically over a period of 3 days to the intact skin produces a mild dermal effect. Symptoms constituting a mild effect include a well-defined erythema and slight edema (edges of area well-defined by definite raising).

The EPA[95] reports that work of Keen and Hurley in 1977 shows certain zinc salts can be absorbed through the intact skin of laboratory rats. However, there are no reports of zinc absorption through the intact skin of humans. Furthermore, there is no evidence in the review literature indicating that external exposure to zinc or its compounds results in systemic toxicity in humans or laboratory animals.

<u>Recommendation</u>. There is no evidence in the review literature indicating that the presence of zinc or its compounds in field-water supplies will produce performance-degrading dermal, ocular, or systemic health effects in military personnel experiencing repeated or prolonged external exposure to such waters. Consequently, we feel that there is no need for the development of criteria and recommendations for standards for external exposure to zinc in field-water supplies.

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