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Project Summary

Identification of Sources of Ground-Water Salinization Using Geochemical Techniques

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This report deals with salt-water sources that commonly mix with and deteriorate fresh ground water. It reviews characteristics of salt-water sources and geochemical techniques that can be used to identify these sources after mixing has occurred.

The report is designed to assist investigators of salt-water problems in a step-by-step fashion. Seven major sources of salt water are distinguished: (1) natural saline ground water, (2) halite solution, (3) sea-water intrusion, (4) oil- and gas-field brines, (5) agricultural effluents, (6) saline seep, and (7) road salting. The geographic distribution of these sources was mapped individually and together, illustrating potential sources at any given area in the United States. In separate chapters, each potential source is then discussed in detail regarding physical and chemical characteristics, examples of known techniques for identification of mixtures between fresh water and that source, and known state-by-state occurrences. Individual geochemical parameters that are used within these techniques are presented in a separate chapter, followed by a discussion concerning where and how to obtain them. Also provided is a description of basic graphical and statistical methods that are used frequently in salt-water studies. An extensive list of references for further study concludes this report.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The purpose of this report is to summarize geochemical techniques that can be used in studies of salinization of fresh water. The report is designed to assist investigators through detailed discussion of potentially useful chemical parameters and techniques, as well as of physical and geographical characteristics of potential salinization sources. The topic of salt-water contamination has been extensively researched, evidenced by the list of hundreds of references compiled for this report. No compendium of the overall topic, however, has previously been compiled. The purpose of this document is not to develop new geochemical techniques for identifying sources of ground-water salinity, but to summarize known approaches for all different sources into a single document to allow a researcher to have a reference manual reviewing available work.

Salinization of fresh water is perhaps the most widespread threat to ground-water resources, as saline ground water (total dissolved solids [TDS]>1,000 ppm) of variable origin underlies approximately two-thirds of the United States. This document deals with geochemical characteristics of major known sources of salinity, and as such will be helpful to investigators of salt-water problems. The extent to which this document will be of help will depend to a large degree on the investigator's background knowledge of the problem. To an experienced researcher in the field of ground-water quality, this document may

serve as a summary of and reference to some of the known techniques that are being used. To investigators new in this field, we suggest the following possible methodology of investigation in combination with this report.

Step 1: The general geographic distribution of major potential salinization sources, that is (1) natural saline ground water, (2) halite solution, (3) sea-water intrusion, (4) oil- and gas-field brines, (5) agricultural effluents, (6) saline seep, and (7) road salt, is addressed through a series of maps that show the distribution of each source as well as the overlap between these sources. These maps provide the investigator with a general idea about the potential salinization source or sources that exist at her/his local area of interest at any given area of the country.

Step 2: After potential sources of salt water have been identified, the discussion of individual sources should be consulted. This will provide the researcher with the necessary background information about the source(s) of interest. Each of the seven sources is discussed in detail, including mechanisms of mixing with fresh ground water, chemical characteristics, geochemical case studies, recommended chemical techniques for identification of salinization caused by these sources, and a state-by-state summary of occurrences.

Step 3: After having selected techniques that are useful for the particular problem case, the geochemical parameters of interest can be reviewed. This will give the investigator a general overview of parameter characteristics as well as sampling techniques and likely costs of laboratory analyses.

Step 4: Depending on the area of interest, chemical data may or may not be available to the investigator from published sources, agency files, or computerized data banks. Some of the selected techniques may be applicable using existing data from state and federal data bases, but others may necessitate collection of water samples for parameters that are not determined on a regular basis (for example, isotopes). Data should be selected carefully, because existing data can be helpful but also misleading. Chemical analyses that may be representative of potential salinization sources can be found in the referenced literature.

Step 5: Once data have been selected from existing sources or collected in the field, evaluation can be accomplished using a variety of graphical and statistical techniques. Hopefully, the source of salinity can then be determined.

Background

All natural waters contain some dissolved minerals through the interaction with atmospheric and soil gases, mixing with other solutions, and/or interaction with the biosphere and lithosphere. In many cases, these processes result in natural waters that contain TDS concentrations above those recommended for drinking water. Salinization, that is the increase in TDS, is the most widespread form of water contamination. The effect of salinization is an increase in concentrations of specific chemical constituents as well as in overall chemical content.

Of the variety of potential sources of salinity, some are natural and others are anthropogenic. Precipitation interacts with atmospheric gases and particles even before it reaches the earth's surface, as reflected in often low pH values in areas of high sulfur dioxide content in the atmosphere (formation of sulfuric acid "acid rain"). Strong winds carry mineral matter and solution droplets (for example, ocean spray) that can be dissolved and incorporated into precipitation. Surface runoff dissolves mineral matter on its way toward a surface-water body, where it mixes with water of different chemical composition. Water that enters the soil is subject to additional chemical, physical, and biological changes, such as evapotranspiration, mineral solution and precipitation, solution of gases, and mixing with other solutions. Changes in chemical composition continue in ground water along flow paths from recharge areas to discharge areas. Water-rock interaction and mixing are the dominant processes. Mixing of different waters is often enhanced by human activities. For example, improper drilling, completion and final construction of wells may create artificial connections between fresh-water aquifers and saline-water aquifers. Pumping of fresh water may change directions of ground-water flow and may cause encroachment of saline water toward the pumped well. Improper waste-disposal activities or techniques may introduce artificial solutions that contaminate natural ground water. Some areas of the country experience very few problems regarding salinization of fresh-water resources, whereas in other areas most of the available ground water is saline, reflecting natural and human-induced degradation.

Potential Salinization Sources

Many sedimentary basins are known to contain saline ground water and large deposits of rock salt in the form of salt beds or salt domes. Some of these deposits occur at great depths, such as those in southern Florida at greater than 10,000 ft below land surface. Others occur close to land surface, such as in parts of Utah. Shallow occurrences of salt in Texas, Louisiana, Alabama, and Mississippi along the Gulf of Mexico are due to salt diapirism; the solution of salt and salinization of local ground waters will occur where ground water comes into contact with salt domes, often enhanced by heavy drilling and mining activities.

Where coastal aquifers are interconnected with the open ocean, sea-water intrusion can occur. The potential of well-water salinization exists when formation water has not been flushed out, sea water has intruded or is intruding coastal aquifers as a result of high sea-water levels, or pumping induces landward flow of sea water.

Associated with the exploration of oil and gas is the creation of avenues for water migration from great depths into the shallow subsurface. Subsequent production brings huge amounts of brine to land surface. These drilling activities and the disposal of these brines are some of the biggest salinization hazards in the country. Parts of 25 producing states are potentially affected by this hazard.

Salinization as a result of agricultural activities is found nationwide. Irrigation-return waters pose a potential threat in the western half of the United States, where precipitation rates are low and where evapotranspiration rates and salt contents in soil are high. Another salinization source enhanced by agriculture is dryland saline seep. Terracing of land and destruction of natural vegetation added to this phenomenon in several states results in salinization of soil and ground water.

Due to weather conditions, road salting is concentrated in the northeastern part of the country. There, millions of tons of salt are applied to roads each winter, imposing a salinization threat to soil, plants, and surface and ground water in the vicinity of highways.

Mapping of potential salinization sources is helpful in determining sources of salinity at any particular area in the country. By overlaying maps of potential sources, a variety of combinations between these sources becomes evident. This large variety complicates generic approaches to salt-water studies, because salt-water characteristics change considerably from area

to area depending on the kind of combination of sources involved. But not only do the potential salinization sources change from area to area, the chemical characteristics of individual sources may also change, greatly increasing the number of potential combinations of possible mixing between fresh-water and salt-water sources. As the composite map (Figure 1) of the above-mentioned potential sources indicates, approximately three-quarters of the country could possibly be affected by two or less of the selected sources. In these areas, identification of an actual salinization source should be easier than in other areas, where three or more potential sources exist.

Geochemical Parameters

It is important in a salinization study to know which methods and parameters are the best to use for the particular problem. Through the years, a variety of chemical constituents and constituent ratios have been used as possible tracers of salinity sources (Table 1). Parameters used most often include the major cations, Ca, Mg, Na, the major anions, HCO_3, SO_4, Cl, some minor elements, K, Br, I, Li, and some isotopes, ^{18}O, ^{2}H, ^{3}H, ^{14}C.

Natural Saline Ground Water

Most of the salinity sources described in this report occur naturally at some place or another where they mix with fresh ground water. In other cases, mixing of naturally saline water with fresh water is initiated or facilitated by anthropogenic activities, such as heavy pumpage of fresh water, drilling through fresh-water- and salt-water-bearing zones, or disposal of produced water. In most instances, chemical characteristics will not differ significantly between natural mixing of fresh water and salt water and artificial mixing of the same salt water with fresh water. Therefore, significant parameters for identification of natural salinization are the same as those for any individual source discussed in this report.

Salinization is generally indicated by an increase in chloride concentration. If this increase is substantial, occurs sud-

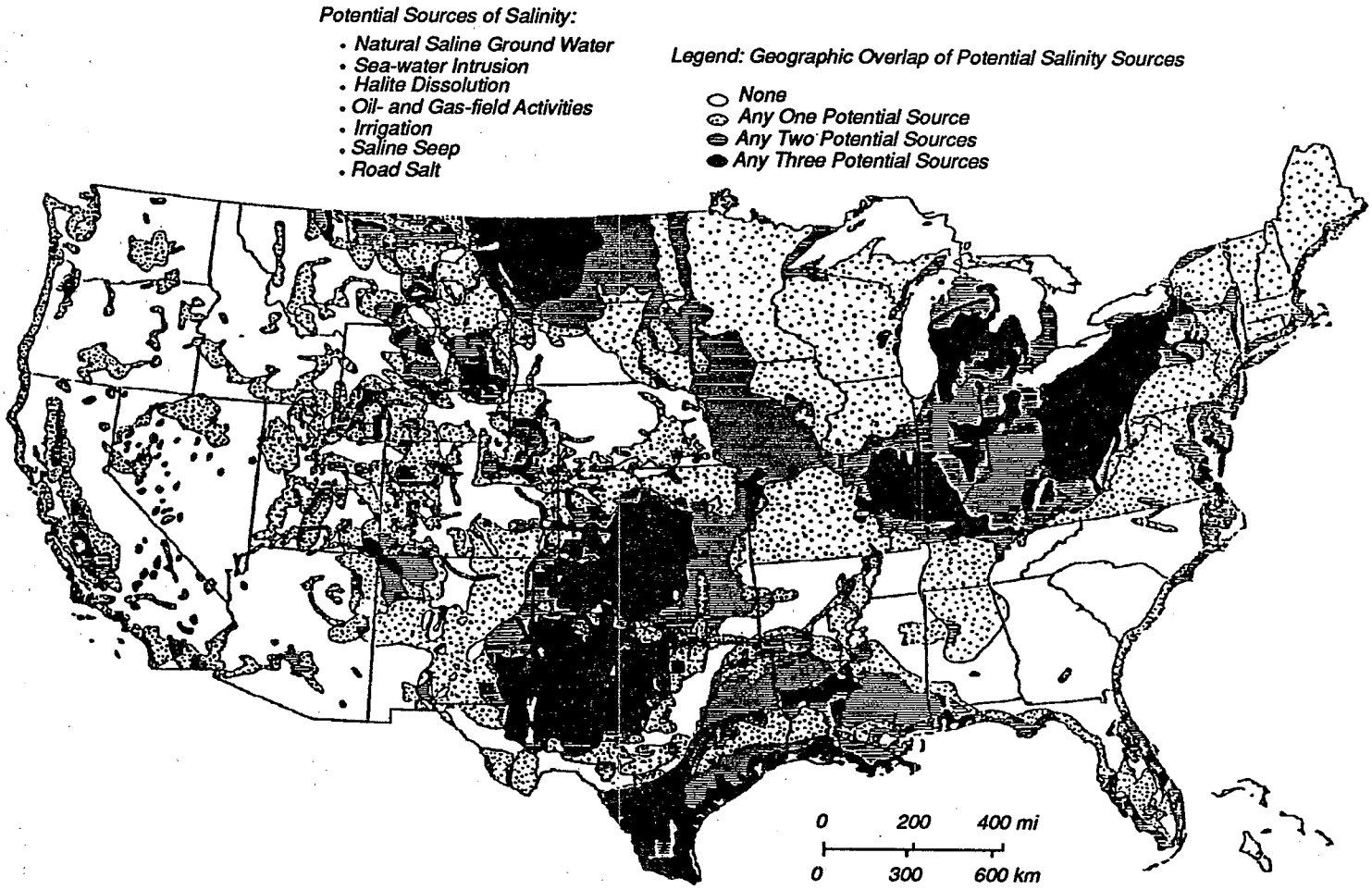

Figure 1. Composite map of major potential sources of salinity in the United States.

Table 1. ***Geochemical Parameters Used for Identification of Salinity Sources***

Salinization Sources	*Chemical Parameter*
Natural saline water versus others	*Cl, Br, I, S-34, ^{18}O, D, Br/Cl, Na/Cl, I/Cl, I Mg/Cl, K/Cl, Ca/Cl, (Ca+Mg)/SO_4, Sr*
Halite-solution brine versus others	*K/Na, Br/TDS, (Ca+Mg)/(Na+K), Na/Cl, Ca/Cl, Mg/Cl, SO_4/Cl, Br/Cl, K/Cl, (Ca+Mg)/SO_4, I/Cl, ^{18}O/D, I/Cl, SO_4/(Na+K), SO_4/TDS, SO_4/Cl*
Sea-water intrusion versus others	*Cl, Major ions (Piper), ^{14}C, ^{3}H, I/Cl, B, Ba, I ^{18}O, ^{2}H, ^{13}C, Ca/Mg, Cl/SO_4, B/Cl, Ba/Cl Br/Cl*
Oil-field brines versus others	*Cl, Major ions, Na/Cl, Ca/Cl, Mg/Cl, SO_4/Cl, Br/Cl, I/Cl, Major ion ratios, Cl, Br, (Na+Cl)/TDS, Li/Br, Na/Br, Na/Cl, Br/Cl*
Agricultural effluents versus others	*Cl, NO_3, Cl/NO_3, K, TDS*
Saline seep versus others	*SO_4, Ca/Cl, Mg/Cl, SO_4/Cl, NO_3*
Road salt versus others	*Cl, Major ion ratios, Br/Cl, Dye*

denly, and is localized, a nonnatural mechanism and source should be suspected. If, however, the change is subtle and of regional scale, a natural mechanism or source may exist. Mixing of fresh water with naturally saline ground water or the evolution of ground water toward higher salinities (as opposed to mixing with road-salt solutions, mixing with brine along boreholes, or disposal of produced oil-field brine) can be expected to be a relatively slow process during which the water has time to react extensively with the aquifer matrix. Therefore, saline ground water in its natural environment will reflect conditions of chemical equilibrium more closely than artificially induced mixtures of fresh water and saline water. This may be used to distinguish natural mixing or evolution from induced mixing.

The stable isotopes Oxygen-18 and deuterium are generally useful in distinguishing between local precipitation water and water that is derived from a nonlocal source and in identifying evaporation of local recharge water. Molar ratios of major chemical constituents, such as Na/Cl, Ca/Cl, and Mg/Cl, can be used to differentiate an evaporation trend (1:1 slope) from a mixing trend (typically not a 1:1 slope). Mixing trends can best be evaluated using the most conservative constituents dissolved in ground water, that is, chloride and bromide. These constituents are often useful not only to identify the mixing source of salinity, but also to estimate the mixing ratio.

Halite Solution, Oil- and Gas-Field Brines

Halite solution produces some of the lowest Br/Cl ratios found in natural salt waters. Ratios are typically less than approximately 10 x 10^{-4} in halite-solution brines and greater than 10 x 10^{-4} in oil-field and formation brines. Ratio differences between these two potential end-members of mixing with fresh water are generally big enough to allow differentiation of the respective source in brackish water down to chloride concentrations of a few hundreds of milligrams per liter, although identification is best at high concentrations. Sea water also has a much higher Br/Cl ratio than halite-solution brine, which could allow differentiation between halite solution and sea-water intrusion in coastal salt-dome areas.

The ratio of Na/Cl works well to distinguish halite-solution brine from oil-field brine at high chloride concentrations. Sodium and chloride occur in halite at equal molar concentrations (Na/Cl molar = 1, Na/Cl weight = 0.648). Brines that originate from solution of halite within a shallow ground-water flow system will exhibit a similar ratio as long as concentrations are high enough to keep the Na/Cl ratio from being appreciably affected by ion exchange reactions. In most oil-field brines molar Na/Cl ratios are much less than one. Exchange of calcium and magnesium for sodium on clay mineral surfaces and alteration of feldspar may account for the low ratios in formation and oil-field brines. The Na/Cl ratio is also much smaller in sea water (mNa/mCl = 0.85) than in halite-solution brine.

Ratios of I/Cl in halite-solution brines are typically small and less than oil-field/deep-basin brines, which allows separation between these two major sources of salt water.

Halite deposits are often associated with abundant beds of gypsum and anhydrite. Dissolution of these beds is reflected in molar (Ca+Mg)/SO_4 ratios close to one, which is much smaller than the respective ratio in oil-field brines (>>1) or in sea water (2.3).

Sea-Water Intrusion

The chemical composition of sea water changes as it intrudes a fresh-water aquifer. Changes occur in response to mixing and chemical reactions, and are most pronounced within the initial sea-water front that mixes with fresh water. Subsequent intrusion deviates little from sea-water composition.

Mixing of fresh water and sea water occurs within a transition zone and is characterized by chloride concentrations somewhat between high background concentration values to somewhat below sea-water concentration. The front part of this transition zone is characterized by ion exchange as discussed below. Behind the ion-exchange front, simple dilution characterizes the deviation of brackish water from sea-water composition. This can easily be identified on trilinear plots in the straight-line relationship between data points. On bivariate plots of major cations and anions versus chloride, data points plot close to the theoretical mixing line between local fresh water and sea water.

Clay minerals, especially montmorillonite, have free negative surface charges that are occupied by cations in proportion to the abundance of cations in the water and to the sorption characteristics of the cations and the minerals. In a typical fresh-water aquifer, these sites are saturated mainly with calcium ions, whereas in a typical salt-water aquifer, the sites are occupied mainly by sodium ions. Whenever the relation of calcium to sodium in the water changes (for example, in response to sea-water intrusion into a fresh-water aquifer), ion exchange will occur, sodium will be taken out of solution, and calcium will be released from mineral exchange sites. Magnesium and potassium may also be exchanged for calcium, but the Na-Ca exchange is the most significant one. For example, more than 96 percent of the base exchange in the Chalk aquifer of east-central England has been attributed to Na-

Ca exchange. This exchange is assumed to be instantaneous. On a Piper diagram, ion exchange between calcium and sodium produces a cluster in the cation triangle, whereas mixing produces a straight line in the anion triangle as chloride content increases. The diamond-shaped field will reflect the slight increase in Ca+Mg, the matching decrease in Na+K, and the high increase in $Cl+SO_4$ percentages. Intrusion of fresh water into a salt-water aquifer will cause the opposite ion exchange.

The chloride concentration is not affected by ion exchange, which makes the Na/Cl ratio a potential tracer of intrusion. If sea water intrudes a fresh-water aquifer, Na/Cl ratios will decrease from those often >1 to those often less than the value in sea water. In contrast, if fresh water replaces marine water or washes out marine sediments, very high Na/Cl ratios can result. No changes in the Na/Cl ratio will occur in water that intrudes behind the front of ion exchange because all the exchange sites are already occupied. Therefore, the Na/Cl ratio should approach the ratio of sea water (0.85 molar ratio), which differs from the typical ratio of halite-dissolution brines (0.64 molar ratio) and from the small ratio characteristic for many oil-field/deep-basin brines (<0.50 molar ratio). The degree of change that occurred because of ion exchange may not only indicate the position within the intruding front, but also the timing of the intrusion. Recent sea-water intrusion would be expected to be associated with data points predominantly showing ion exchange, whereas old sea-water intrusion would be expected to include many data points with little or no evidence of ion exchange.

Mixing of fresh water and sea water, both saturated with calcium carbonate, can result in a mixing water that is undersaturated with calcium carbonate. This mixing water can dissolve carbonates; thus, calcium and bicarbonate concentrations will increase. Additional calcium carbonate dissolution may occur in the presence of sulfate reduction of organic-rich sediments because of the associated change in pH and CO_2 content of the water. Sea water is relatively high in dissolved sulfate content. Under reducing conditions in ground-water systems, and with the presence of compounds that can be oxidized as well as of reaction catalysts, sulfate will be reduced. This results in a decrease in sulfate concentration relative to the sea-water composition.

Agricultural Effluents

Degradation of ground-water quality by agricultural activities can be caused by solution and transport of chemicals, such as herbicides, pesticides, and fertilizers, disposal of animal wastes and waste water from animal farms, and irrigation-return flow. With respect to ground-water salinity, irrigation-return flow is the most important source of degradation. Evapotranspiration and leaching of soil minerals accounts for increases in most chemical components in drainage waters from irrigated areas. Typically, chloride and sodium concentrations show the highest increases, although other constituents may be high in some areas, reflecting local conditions. Significant parameters in irrigation-return flow may change over time, as original soil minerals are dissolved in the initial irrigation stage of an area and minerals brought in by irrigation water are dissolved in subsequent irrigation phases.

A significant parameter that differentiates agricultural-induced contamination from other salinization sources discussed in this report is nitrate. In agricultural areas, nitrate concentrations are often above background values. Salinization associated with other sources, such as sea-water intrusion or oil-field pollution, in contrast, is typically associated with increases in chloride, sodium, calcium, and magnesium concentrations and with small NO_3/Cl ratios.

Saline Seep

Saline-seep water chemistry is governed by evaporation, resulting in an increase of all constituents in the water. The increase is reflected on constituent plots as evaporation trends, in contrast to mixing trends toward a saline-water source observed for the other salinization sources discussed in this report, with exception of irrigation-return waters. At low salinities, this increase is characterized by more or less constant constituent ratios of major ions, such as Ca/Cl, Mg/Cl, or SO_4/Cl. With increasing salinity, mineral precipitation will change these ratios as carbonates and sulfates begin to form. Precipitation products will vary from area to area depending on the chemical composition of soil and water. Where sources of sulfate are abundant, dissolved sulfate concentrations may by far exceed the concentration of dissolved chloride, which distinguishes seep water from most other saline ground water. Miscellaneous trace constituents may serve as good tracers on a local basis, as these are more concentrated in evaporated ground waters than in most mixing waters between fresh ground water and brine at similar salinities.

Road Salt

By far the most widely used parameter in identification of street-salt contamination is the chloride ion. Chloride is a good tracer because it is the most conservative ion dissolved in ground water, it is the most abundant ion in street-salt solutions, and it is analyzed on a routine basis. Background chloride concentrations are known for a vast number of water wells all over the country. Because contamination from street salt is a seasonal phenomenon with high chloride concentrations in spring runoff and decreasing (dilution) concentration throughout the remainder of the year, deviation of chloride concentrations from background levels are in most instances a good measure of the degree of salt contamination. Accumulation of salt may occur in the soil and in ground water, which means that background levels may increase over the years. When salt-brine runoff infiltrates the vadose zone and the saturated zone, sodium is often absorbed into soil and aquifer material. Therefore, the Na/Cl ratio may be smaller in salt-affected ground water than in salt-affected surface water.

Because of its conservative nature once dissolved in ground water, bromide can be a good tracer of salinity. Expressed as Br/Cl weight ratios, it can be used to differentiate salinity derived from road salt (halite) as opposed to oil- and gas-field brines, deep-formation waters, and sea water, as halite solution produces some of the lowest Br/Cl ratios measured in naturally saline waters.

On a local basis, high concentrations of calcium and chloride may be indicative of road-salt contamination where large amounts of $CaCl_2$ are added to the salt mixture. Because road-salt contamination involves the current production of salt water, dye tracers (for example, rhodamine) may be useful for identifying point sources of alleged street-salt contaminations.

Graphical and Statistical Techniques

Evaluation of chemical analyses is often accomplished with graphical display and statistical manipulation of physical and chemical data. Which technique is used depends largely on the amount of data and on the type of information that is needed. In salt-water studies, techniques are used that maximize the separation of chemical characteristics between potential salt-water sources, and illustrate to which salt-water source a contaminated water sample belongs. Graphical techniques are used to (1) illustrate the chemical character of a single analysis, (2) compare the characteristics of several analyses, (3) assist in

identifying the relationship that exists between water samples, and (4) calculate mixing ratios between fresh water and the contaminating source. Various approaches include analysis of a single parameter, for example on contour maps, or of multiple parameters, as on Stiff diagrams, Schoeller diagrams, Piper diagrams, or bivariate plots.

The application of statistics depends to a high degree on the number of observations in the data base and the nature of the required information. Statistical techniques are most useful and appropriate when a large data base of observations is available. The literature abounds with questionable applications of statistical procedures. Statistics should be used as a means to test and verify theories instead of creating theories from statistical data. Statistical approaches vary from simple techniques, such as maxima, minima, or means, to complex multivariate analyses, such as Stepwise Discriminant Analysis.

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The complete report, entitled "Identification of Sources of Ground-Water Salinization Using Geochemical Techniques," (Order No. PB92-119650/AS; Cost: $35.00, subject to change) will be available only from:
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