Technical Assistance
HYDROLOGY PROJECT

World Bank & Government of The Netherlands funded

Training module # WQ - 28

Major Ions in Water

New Delhi, September 1999

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with
HALCROW, TAHAL, CES, ORG & JPS

Table of contents

1. Module context

This module presents the major inorganic ions which are significant to water quality. Modules in which prior training is required to complete this module successfully and other available, related modules in this category are listed in the table below.

While designing a training course, the relationship between this module and the others would be maintained by keeping them close together in the syllabus and placing them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

No.	**Module title**	**Code**	**Objectives**
1.	Basic water quality concepts	**WQ - 01**	• Discuss the common water quality parameters • List important water quality issues
2.	Basic chemistry concepts[a]	**WQ - 02**	• Convert units from one to another • Discuss the basic concepts of quantitative chemistry • Report analytical results with the correct number of significant digits.
3.	Basic Aquatic Chemistry Concepts	**WQ - 24**	• Calculate ion concentrations from ionisation constants

a - prerequisite

2. Module profile

Title : Major Ions in Water

Target group : HIS function(s): Q2, Q3, Q5, Q6, Q7, Q8

Duration : 1 session of 60 min

Objectives : After the training the participants will

- Know the major ions in water and their sources
- Understand the significance of major ion concentrations

Key concepts :

- Sources of major ions in water
- Ion balance
- Hardness, SAR
- Health effects

Training methods : Lecture and discussion

Training tools Required : Board, flipchart, OHS,

Handouts : As provided in this module,

Further reading and references :

- Water Quality Monitoring, ed. J. Bartram and R. Balance
- Water Quality Assessment, ed. D. Chapman, E&FN SPON, London

3. Session plan

No	Activities	Time	Tools
1	***Preparations***		
2	***Introduction***: • Introduce the session • Suggest a number of common aquatic ions and ask the participants whether these would be major or secondary constituents of groundwater • Following discussion use overhead to confirm	10 min	OHS
3	***Introduction to Major Ions*** • Discuss major cations and anions • Talk about how ions become dissolved in water • Discuss the sources of major ions • Show how it is possible to characterise waters graphically	10 min	OHS
4	***Individual Major Ions*** • Discuss calcium and magnesium and what their presence means in water • Discuss the concept of hardness and what that means in terms of water quality • List other major ions and ask the participants what their presence in water indicates • Follow up by showing overhead of various major ions • Discuss sar, %Na, RSC and how it is used to assess potential irrigation waters. Talk about the difference between Indian and International SAR standards. Show USDA classification	15 min	OHS
5	***Ion Balancing*** • Talk about the technique of ion balancing and why it is so useful to the chemical analyst and water quality expert • Show how ion balancing can be done and discuss the acceptability of errors	15 min	OHS
6	***Wrap up and Evaluation***	10 min	Addl. Handout

4. Overhead/flipchart master

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 24-26, maximum two levels
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/ Equations	OHS-Equation	Use of a table will ease horizontal alignment over more lines (columns) Use equation editor for advanced formatting only

Major Ions in Water

- Major and Secondary Constituents of Groundwater
- Sources
- Water Characterisation
- Water Quality Consequences
- Ion Balancing

Major constituents (1.0 to 1000 mg/L)	**Secondary Constituents (0.01 to 10.0 mg/L)**
Sodium	Iron
Calcium	Strontium
Magnesium	Potassium
Bicarbonate	Carbonate
Sulphate	Nitrate
Chloride	Fluoride
Silica	Boron

Major Cations and Anions in Water

CATIONS	**ANIONS**
Calcium (Ca^{2+})	Bicarbonate (HCO_3^-)/ Carbonate (CO_3^{2-})
Magnesium (Mg^{2+})	Sulphate (SO_4^{2-})
Sodium (Na^+)	Chloride (Cl^-)
Potassium (K^+)	

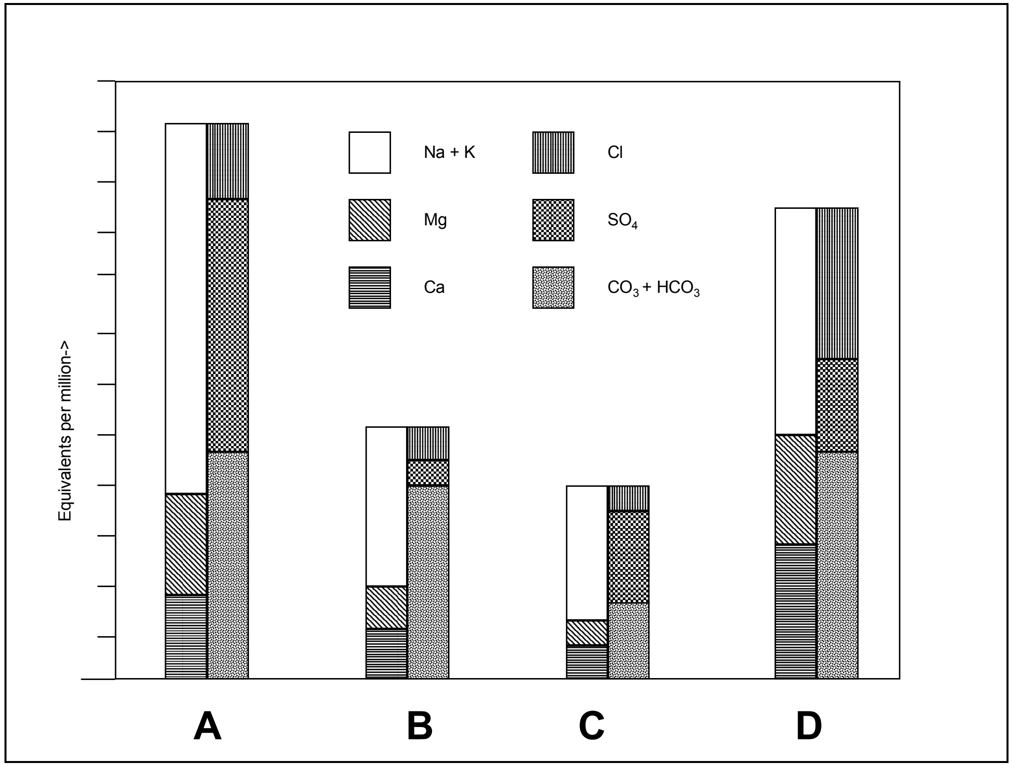
Sources (1)

- Atmospheric Gases Dissolved by Rain and their Reactions
  - *Oxygen*
  - *Nitrogen*
  - *Carbon dioxide*
  - *Nitrogen oxides (NOx)*
  - *Sulphur oxides (SO_x)*

Sources (2)

Calcium	Amphiboles, feldspars, gypsum, aragonite, calcite, pyroxenes, dolomite, clay minerals
Magnesium	Amphiboles, olivine, pyroxenes, dolomite, magnesite, clay minerals
Sodium	Feldspars, clays, halite, mirabilite, industrial wastes
Potassium	Feldspars, feldspathoids, some micas, clays
Bicarbonate/ Carbonate	Limestone, dolomite
Sulphate	Oxidation of sulphide ores, gypsum, anhydrite
Chloride	Sedimentary rock, igneous rock

Water Characterisation (1)



Bar Graphs for 4 different samples

Water Characterisation (2)

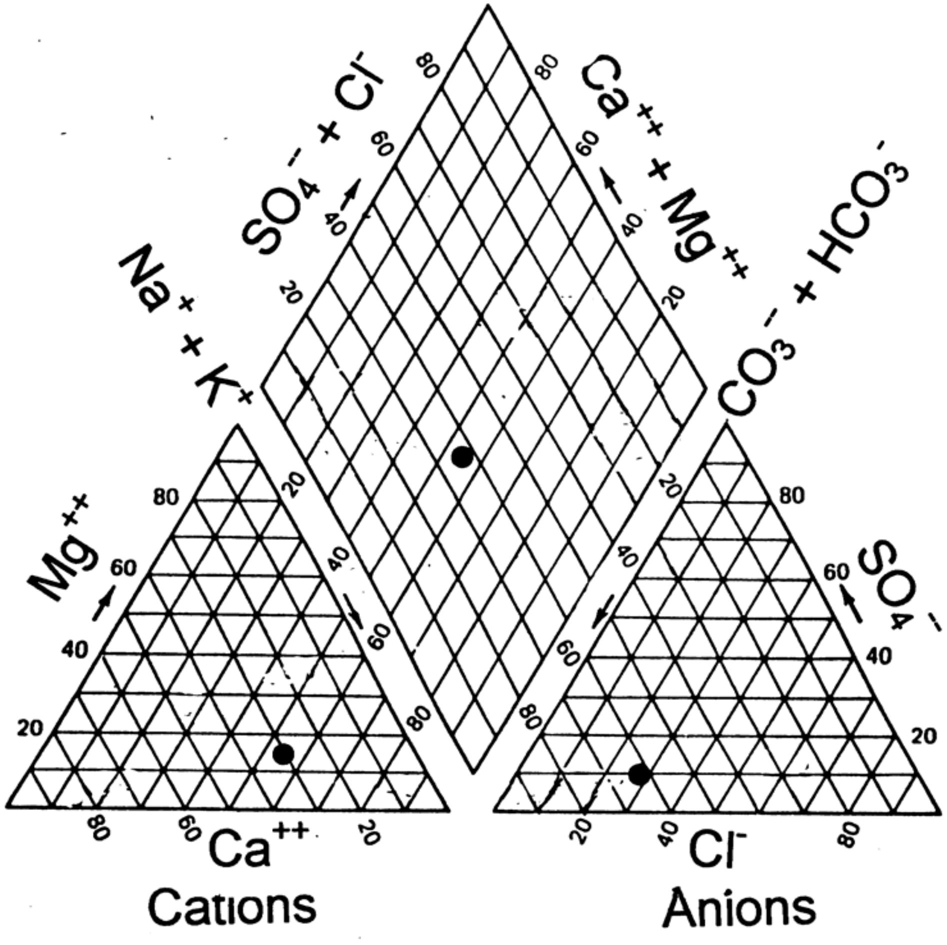


Figure 2 Piper or Hill trilinear diagram for water quality

Water Characterisation (3)

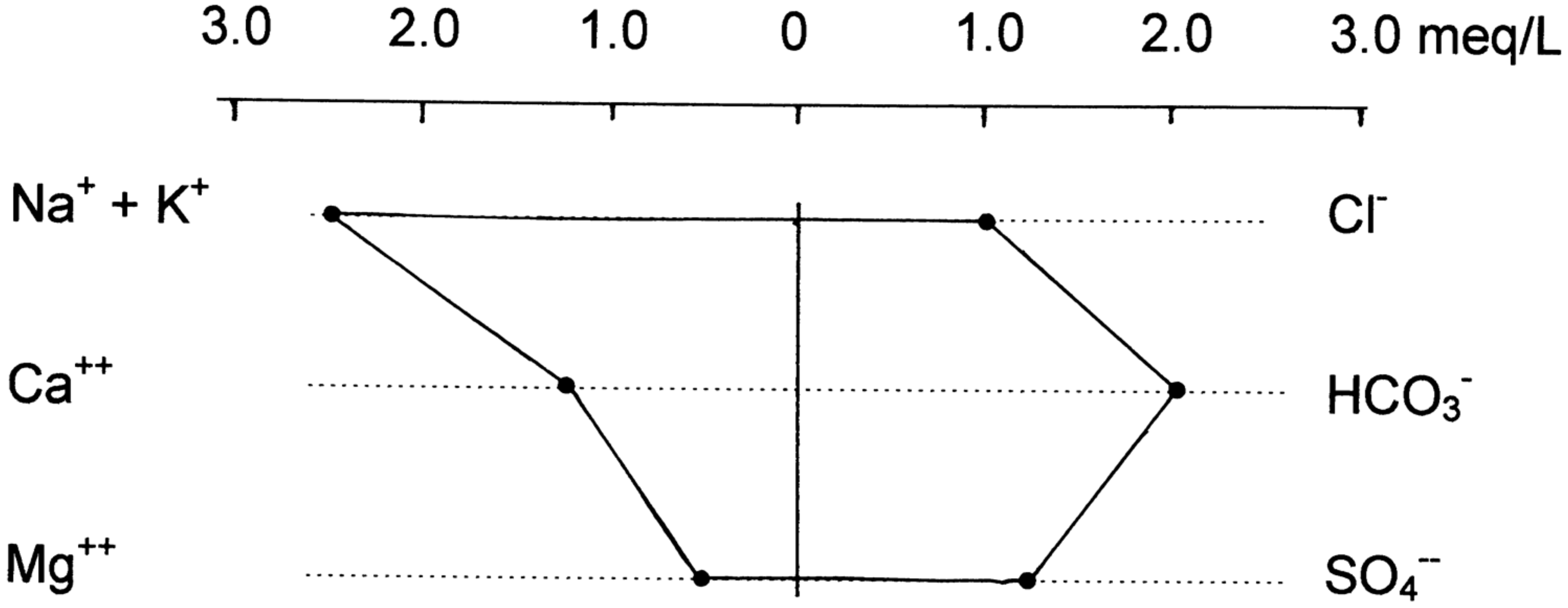


Figure 3 Stiff pattern diagram

Water Quality Consequences

- Calcium and Magnesium

  - *Cause hardness when combined with* HCO^{-3}, CO_2^{-3}, SO_2^{-4} *etc*
  - Ca^{2+} *normally below 15 mg/l*
  - Ca^{2+} *can be above 100 mg/l in carbonate-rich rocks*
  - Mg^{2+} *normally between 1 and 50 mg/l depending upon rock type*

Hardness Classification

Hardness (mg/L as Ca CO_3)	**Classification**
0 - 75	Soft
75 - 150	Moderately hard
150 - 300	Hard
Over 300	Very hard

Other Major Ions Major Ions in Water

- *Sodium – high levels often associated with pollution*
- *Potassium – generally low (<10) in natural fresh waters*
- *Bicarbonate normally ranges from 25 to 400 mg/l*
- *Carbonate in fresh waters is normally dilute (<10 mg/l)*
- *Sulphate is normally between 2 and 80 mg/l*
- *Chloride is normally less than 40 mg/l in unpolluted waters*
- *Nitrate is significant in some areas*

Health Effects

- *Nitrate*
- *Fluoride*
- *Sodium*
- *Potassium*
- *Chloride*

Irrigation Water Quality (1)

- Sodium Adsorption Ratio (SAR) *- in milliequivalents/L*

$$SAR = \frac{Na^{+}}{\sqrt{\left(Ca^{2+} + Mg^{2+}\right)/2}}$$

International SAR Standards	**Indian SAR Standard**
SAR < 3: suitable for irrigation	SAR > 26 unsuitable for irrigation
SAR 3 – 9: use may be restricted	
SAR > 9 unsuitable for irrigation	

Irrigation Water Quality (2)

- Percent Sodium = $Na^+ / (Ca^{++} + Mg^{++} + Na^+ + K^+) \times 100$
  - *should be less than 60*
- Residual Sodium Carbonate

$$RSC = (CO_3^{--} + HCO_3^{-}) - (Ca^{++} + Mg^{++})$$

> 2.5 not suitable

1.25 - 2.5 marginal

< *1.25 safe*

Irrigation Water Quality (3)

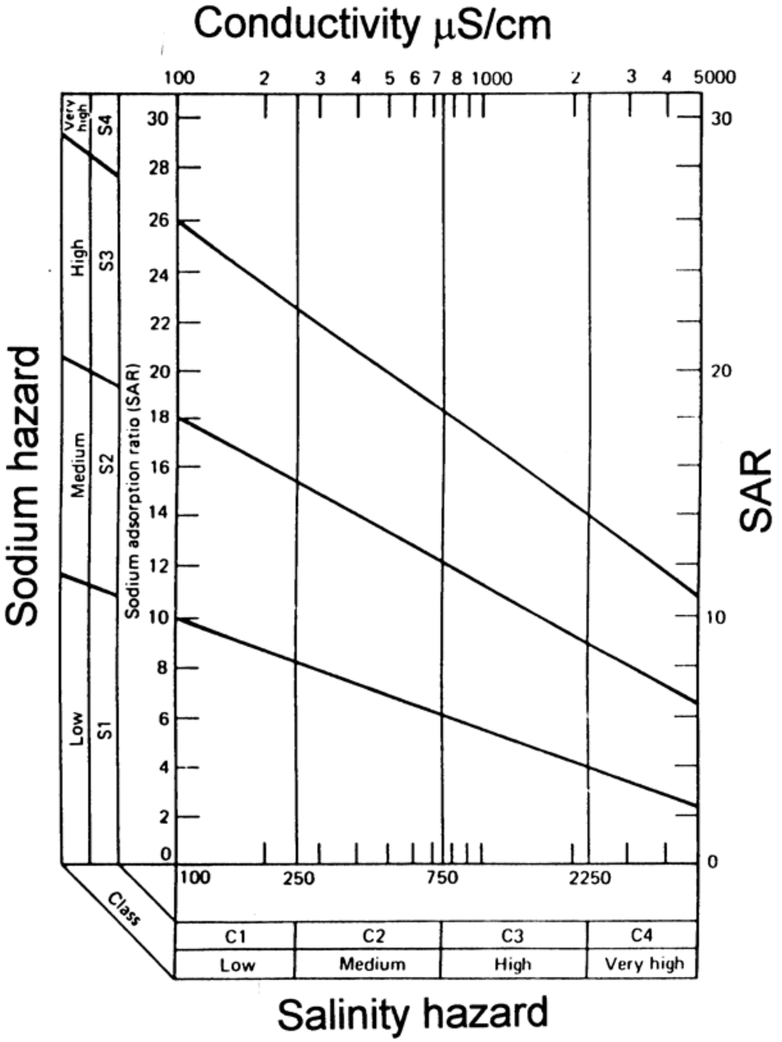


Figure 4 USDA classification for agricultural waters

Major Ions in Water

- Ion Balancing

$$\% \; balance \; error = \frac{\sum cations - \sum anions}{\sum cations + \sum anions}$$

  - *concentrations in milliequivalents.*

- Error should be < 10% for surface and ground waters

5. Evaluation sheets

6. Handout

Major Ions in Water

- Major and Secondary Constituents of Groundwater
- Sources
- Water Characterisation
- Water Quality Consequences
- Ion Balancing

Major constituents (1.0 to 1000 mg/L)	**Secondary Constituents (0.01 to 10.0 mg/L)**
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    - *Nitrogen oxides (NOx)*
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Sources (2)

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Potassium	Feldspars, feldspathoids, some micas, clays
Bicarbonate/Carbonate	Limestone, dolomite
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Chloride	Sedimentary rock, igneous rock

Water Quality Consequences

- Calcium and Magnesium

    - *Cause hardness when combined with HCO-3, CO2-3, SO2-4 etc*
    - *Ca2+ normally below 15 mg/l*
    - *Ca2+ can be above 100 mg/l in carbonate-rich rocks*
    - *Mg2$^+$ normally between 1 and 50 mg/l depending upon rock type*

Hardness Classification

Hardness (mg/L as Ca CO_3)	**Classification**
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- *Chloride is normally less than 40 mg/l in unpolluted waters*
- *Nitrate is significant in some areas*

Health Effects

- *Nitrate*
- *Fluoride*
- *Sodium*
- *Potassium*
- *Chloride*

Irrigation Water Quality (1)

- Sodium Adsorption Ratio (SAR) *- in milliequivalents/L*

$$SAR = \frac{Na^+}{\sqrt{\left(Ca^{2+} + Mg^{2+}\right)/2}}$$

International SAR Standards	**Indian SAR Standard**
SAR < 3: suitable for irrigation	SAR > 26 unsuitable for irrigation
SAR 3 – 9: use may be restricted	
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Irrigation Water Quality (2)

- Percent Sodium = $Na^+ / (Ca^{++} + Mg^{++} + Na^+ + K^+) \times 100$
    - *should be less than 60*
- Residual Sodium Carbonate

$$RSC = (CO_3^{--} + HCO_3^-) - (Ca^{++} + Mg^{++})$$

> 2.5 not suitable
1.25 - 2.5 marginal
< 1.25 safe

Major Ions in Water

- Ion Balancing

$$\%\, balance\, error = \frac{\sum cations - \sum anions}{\sum cations + \sum anions}$$

- *concentrations in milliequivalents.*

- Error should be < 10% for surface and ground waters

Add copy of Main text in chapter 8, for all participants.

7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

Questions

A water sample is known to contain calcium, sodium chloride and bicarbonate. The result of an analysis were as follows:
Calcium 60 mg/L, Sodium 46 mg/L, Chloride 71 mg/L
(Mol. wt. Ca^{++} 40, Na^{+} 23, Cl^{-} 35.5, HCO_3^{-} 61.)

(1) Estimate the concentration of bicarbonates.

---

(2) Calculate percent sodium and residual sodium carbonate.

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(3) Comment on the suitability of water for irrigation.

Questions and Answers

A water sample is known to contain calcium, sodium chloride and bicarbonate. The result of an analysis were as follows:
Calcium 60 mg/L, Sodium 46 mg/L, Chloride 71 mg/L
(Mol. wt. Ca^{++} 40, Na^+ 23, Cl^- 35.5, HCO_3^- 61.)

(1) Estimate the concentration of bicarbonates.

Calculate concentrations in meq/L

Ca^{++} = 60/20 = 3, Na^+ = 46/23 = 2, Cl^- = 71/35.5 = 2

Sum of cations = 5 meq/L
Therefore, for ion balance sum of anions is also = 5 meq/L
Hence HCO_3^- = 5 - 2 = 3 meq/L, or 3 x 61 = 183 mg/L

(2) Calculate percent sodium and residual sodium carbonate.

Percent sodium = [2/(3 + 2)] x 100 = 40
RSC = 3 - 3 = 0

(3) Comment on the suitability of water for irrigation.

The water is safe for irrigation, since both the parameters % Na and RSC do not exceed the limits.

8. Main text

Contents

Major Ions in Water

1. Introduction

All waters in the environment contain dissolved salts. However, some species occur more frequently and at greater concentrations than others. This is illustrated in Table 1.

Major constituents (1.0 to 1000 mg/L)	Secondary Constituents (0.01 to 10.0 mg/L)
Sodium	Iron
Calcium	Strontium
Magnesium	Potassium
Bicarbonate	Carbonate
Sulphate	Nitrate
Chloride	Fluoride
Silica	Boron

Table 1: Major and Secondary Constituents of Groundwater

With regard to ions, Table 2 shows the cations and anions which normally constitute the major ions in water and it is these ions which are discussed in this module.

CATIONS	ANIONS
Calcium (Ca^{2+})	Bicarbonate (HCO_3^-) / Carbonate (CO_3^{2-})
Magnesium (Mg^{2+})	Sulphate (SO_4^{2-})
Sodium (Na^+)	Chloride (Cl^-)
Potassium (K^+)	

Table 2: Major Cations and Anions in Water

2. Sources of the Major Ions

Rain water, as it passes through the air and through and over the land, dissolves many chemical species. Passing through the atmosphere, for example, it dissolves the gases which constitute air including nitrogen, oxygen and carbon dioxide. The fact that it dissolves carbon dioxide from the air is important because when carbon dioxide in present in water it forms carbonic acid and this acid enhances water's ability to dissolve chemical species (salts) contained in rocks and soil. In passing through polluted atmosphere it is also possible for the water to dissolve gases associated with pollution such as sulphur and nitrogen oxides. Some of these gases can also make the water acidic, further adding to the water's ability to dissolve salts.

By the time that rain water has passed over and through land to become groundwater or surface water it has normally acquired many dissolved chemical species. Clearly, the precise chemical composition of the water will depend upon the types of rock and soils with which the water has been in contact and this can be used to characterise a particular water by determining its chemical make-up. As a guide to this characterisation process Table 3 gives some of the primary sources of the major ions.

Major Ions	Some Primary Sources
Calcium	Amphiboles, feldspars, gypsum, pyroxenes, aragonite, calcite, dolomite, clay minerals
Magnesium	Amphiboles, olivine, pyroxenes, dolomite, magnesite, clay minerals
Sodium	Feldspars, clay minerals, halite, mirabilite, industrial wastes
Potassium	Feldspars, feldspathoids, some micas, clay minerals
Bicarbonate/Carbonate	Limestone, dolomite
Sulphate	Oxidation of sulphide ores, gypsum, anhydrite
Chloride	Sedimentary rock, igneous rock

Table 3: Primary Sources of the Major Ions

3. Water Characterisation

It is possible to characterise waters by performing a chemical analysis of their major ions. Once this is done the results can be plotted in a variety of formats to allow comparison between different waters. Figure 1 shows how this can be done by means of a bar chart for 4 different samples. The cations are plotted as the left half of the bar and the anions as the right half. The height of the chart represents the total concentration of major ions in the water in milliequivalents per litre.

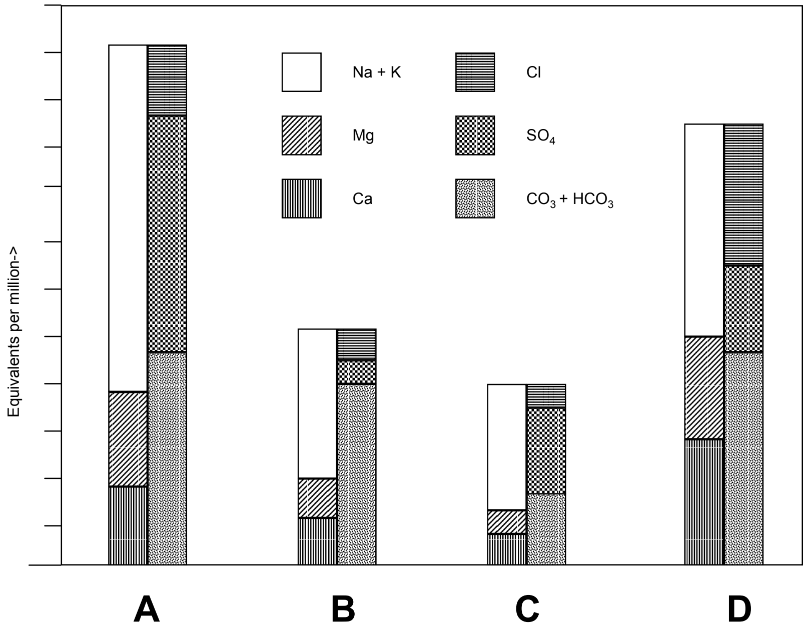

Figure 1: Vertical Bar Graphs for Characterising Waters

A number of different types of plot can be constructed to show the same information but the type shown in Figure 1 is probably the easiest to use and understand and most common.

Figure 2 shows a trilinear diagram known as Piper or Hill diagram. Here cations, expressed as percentages of total cations in meq/L, plot as a single point on the left triangle; while anions similarly plot on the right triangle. These two points are then projected in the central diamond-shaped area. This single point is thus uniquely related to the total ionic distribution. In order to use this method, Na^+ and K^+ and CO_2 and HCO_3^- are combined. The points shown on the diagram correspond to the following analysis:

Ca^{++} = 30 %, Mg^{++} = 15% $Na^+ + K^+$ = 55%
SO_4^{--} = 10% Cl^- = 28% HCO_3^- = 62%

Such plots conveniently reveal similarities and differences among different samples because those with similar qualities will tend to plot together as groups.

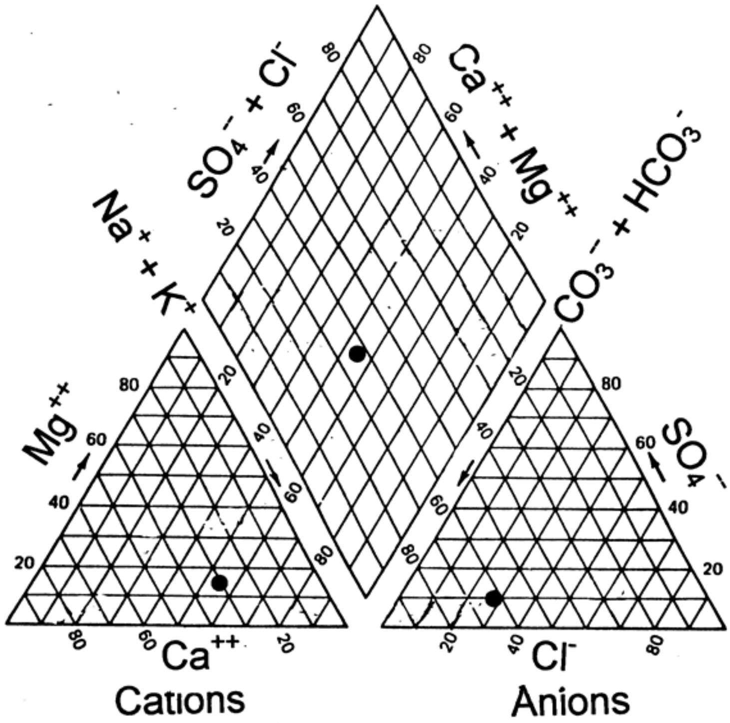

Figure 2 Piper or Hill trilinear diagram for water quality

Another method of plotting chemical characteristcs, devised by Stiff, is shown in Figure 3. The scale is used to plot the ion concentrations for a specific water sample. When the points are connected, the resulting pattern provides a pictorial representation of the water sample. Such plots are used to trace similar formation groundwaters over large areas.

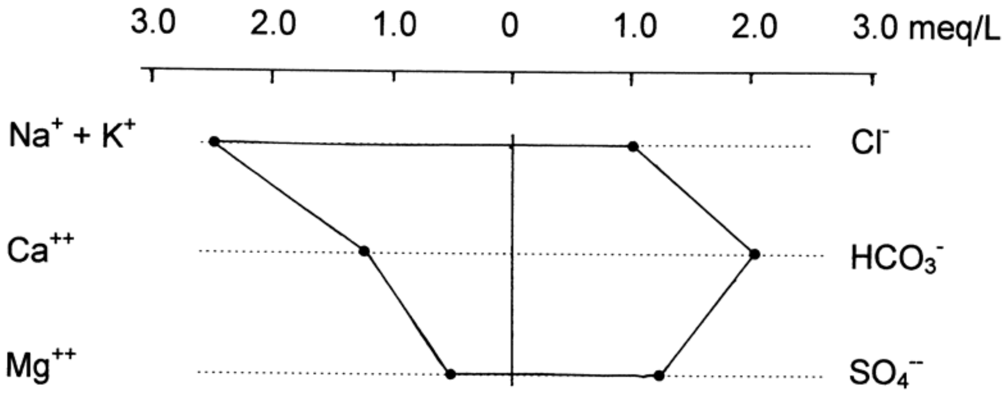

Figure 3 Stiff pattern diagram

4. Water Quality Consequences of the Major Ions

Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) ions are both common in natural waters and both are essential elements for all organisms. Calcium and magnesium, when combined with bicarbonate, carbonate, sulphate and other species, contribute to the hardness of natural waters. The effect of this hardness can be seen as deposited scale when such waters are heated. Normally hardness due to calcium predominates although in certain regions magnesium hardness can be high. In some river catchments, hardness can vary seasonally reaching peak values during low flow conditions. It is possible to analyse waters to determine hardness and then classify them as shown in Table 4 below.

Hardness (mg/L as $Ca\ CO_3$)	Classification
0 – 75	Soft
75 – 150	Moderately hard
150 – 300	Hard
Over 300	Very hard

Table 4: Hardness Classification of Water

In natural waters, calcium concentrations are normally below 15 mg/L although this can rise to 100 mg/L where waters are associated with carbonate-rich rocks. Magnesium concentrations also vary widely and can be from 1 to over 50 mg/L depending upon the rock types within the catchment.

All natural waters contain sodium ions (Na^+) as the element is one of the most abundant on the planet. High concentrations in inland waters, however, are normally associated with pollution from industrial discharges or sewage effluent or, in coastal areas, sea water intrusion. Normally, however, sodium concentrations are below 200 mg/L (this is also the World Health Organisation guideline limit for sodium in drinking water).

When water is to be used for irrigation purposes it is important to know the sodium concentration as sodium can have a negative effect on soil structure by defloculating it, which can affect plant growth. To evaluate the suitability of water for irrigation the Sodium Adsorption Ration (SAR) is used as follows:

$$SAR = \frac{Na^+}{\sqrt{\left(Ca^{2+} + Mg^{2+}\right)/2}}$$

where the concentrations of the ions in milliequivalents per litre are used.

From an international perspective, if the value of the SAR is less than 3 the water is suitable for irrigation use. Values from 3 to 9 represent some use restriction whilst SAR values in excess of 9 normally mean that water cannot be used for irrigation. In India, however, the SAR standard for irrigation water is set to 26 which reflects the fact that sodium does not build up in the soil and cause damage because every monsoon season the soil is thoroughly flushed and renewed.

A related parameter to asses the suitability of water for irrigation is sodium percentage [Nax100/(Na + K + Ca + Mg)], where all values are expressed in meq/L. It is recommended that sodium percentage should not exceed 60.

In waters where the bicarbonate content is high, there is a tendency for calcium and magnesium if present, to precipitate out as carbonates, thus increasing SAR. The residual sodium carbonate (RSC) is defined as:

$$RSC = (CO_3^{--} + HCO_3^{-}) - (Ca^{++} + Mg^{++})$$

If its value exceeds 2.5 meq/L the water is not suitable, 2.5 to 1.25 is marginal and less than 1.25 is safe.

Figure 4 shows a diagram for classification of irrigation waters proposed by US Department of Agriculture, which is widely used in India.

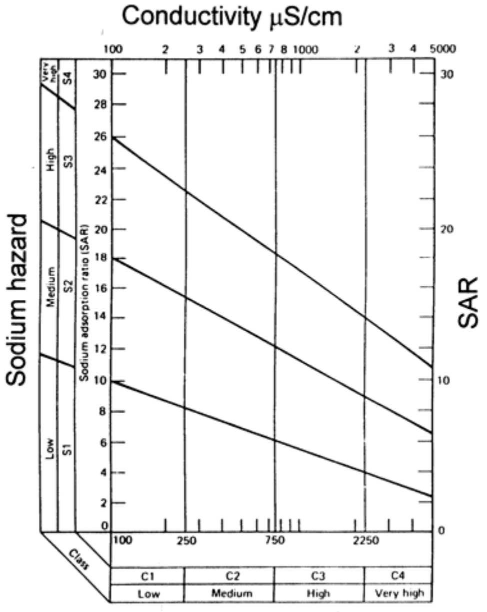

Figure 4 USDA classification for agricultural waters

The concentration of potassium ions (K^+) in natural fresh waters is generally low (normally less than 10 mg/L). Sea water and brines contain much higher concentrations, however. Potassium ions are highly soluble and are essential for most forms of life. Potassium in the water environment is readily taken up by aquatic life, therefore.

The concentration of carbonates and bicarbonates in water has a major effect on both the hardness (see also calcium and magnesium above) and the alkalinity (capacity to neutralise acid) of water. The relative amounts of carbonate, bicarbonate and carbonic acid (dissolved carbon dioxide gas) in water is related to the pH. Under normal surface water pH conditions (i.e., less than pH = 9), bicarbonate predominates. Bicarbonate concentrations in natural waters range from less than 25 mg/L in areas of non-carbonate rocks to over 400 mg/L where carbonate rocks are present. Carbonate concentrations in surface and ground waters by contrast are usually low and nearly always less than 10 mg/L.

Sulphate is present in all surface waters as it arises from rocks and from sea water which contains a high sulphate concentration. In addition to its role as a plant nutrient, high concentrations of sulphate can be problematic as they make the water corrosive to building materials (e.g., concrete) and are capable of being reduced to hydrogen sulphide (a toxic, foul-smelling gas) when zero dissolved oxygen conditions prevail in the water body. Normally, sulphate concentrations in surface waters are between 2 and 80 mg/L although they may exceed 1000 mg/L if industrial discharges or sulphate-rich minerals are present. The WHO guideline value for sulphate in drinking water is 400 mg/L.

Chlorides in fresh waters generally come from rocks, the sea or sewage, agricultural and industrial effluents. Fresh water concentrations of chloride are normally less than 40 mg/L and can be as low as 2 mg/L in waters, which have not been subject to pollution. Chloride concentrations over 100 mg/L give the water a salty taste and thereby make it unsuitable for drinking by humans or animals.

Though nitrate is not listed as a major ion, high concentrations of nitrate upto 200 mg NO_3-N/L have been reported from many sites in the country where municipal wastewater or leachate from garbage dumps has contaminated the groundwater. Excessive amount of nitrate in drinking water causes methaemoglobinaemia in bottle fed infants. WHO has recommended a guideline value of 10 mg NO_3-N/L.

5. Ion Balancing

When a water quality sample has been analysed for the major ionic species, one of the most important validation tests can be conducted: the cation-anion balance.

The principle of electroneutrality requires that the sum of the positive ions (cations) must equal the sum of the negative ions (anions). Thus the error in a cation-anion balance can be written as:

$$\%\ balance\ error = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} \text{ x } 100$$

where the ions are expressed in meq/L.

For groundwater and surface water, the % error should be less than 10. If it is greater, the analysis does not pass the validation check.

Example

A laboratory measures the following concentrations of ions in a sample of water. Perform the validation check.

Cation	Conc (mg/l)	Anion	Conc (mg/l)
Ca^{2+}	93.8	HCO_3^-	164.7
Mg^{2+}	28.0	SO_4^{-2}	134.0
Na^+	13.7	Cl^-	92.5
K^+	30.2		

1. First the concentrations of cations and anions must be converted from mg/l to meq/l.

(a) This conversion is made using the mg/meq value for each major ion species. This value is equal to the atomic weight of the species divided by the ion charge.

For Calcium (Ca^{2+}):

- atomic weight = 40
- ion charge = 2
- mg/meq = 40/2 = 20

(b) Dividing the concentration (mg/l) by the mg/meq value for each species results in meq/l.

For Calcium (Ca^{+2}):

- Concentration (mg/l) = 93.8
- mg/meq = 20
- 93.8/20 = 4.69 meq/l

(c) A table should be completed with all the values per species, and the sum of cations and anions.

Cation	Concentration		
	(mg/l)	(mg/meq)	(meq/l)
Ca^{+2}	93.8	20.0	4.69
Mg^{+2}	28.0	12.2	2.3
Na^{+}	13.7	13.7	0.60
K^{+}	30.2	39.1	0.77
Total Cations			**8.36 meq/l**

Anion	Concentration		
	(mg/l)	(mg/meq)	(meq/l)
HCO_3^{-}	164.7	61.0	2.74
SO_4^{-2}	134.0	48.0	2.79
Cl^{-}	92.5	35.5	2.61
Total Anions			**8.14 meq/l**

2. Check accuracy (% balance error)

$$\%\ balance\ error = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} \text{ x } 100$$

$$= \frac{8.36 - 8.14}{8.36 + 8.14} \times 100 = 1.3\%$$

This is less than the allowed error, so the sample results can be accepted.
If error > 10% then check results, and possibly re-analyse samples.

Note: An accurate ion balance does not necessarily mean that the analysis is correct. There may be more than one error and these may cancel each other out.