A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data

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Abstract A new hydrochemical diagram is proposed for classification of natural waters and identification of hydrochemical processes. The proposed diagram differs from the Piper and expanded Durov diagrams in that the two equilateral triangles are omitted, and the shape of the main study field is different. In addition, the proposed diagram can be constructed on most spreadsheet software packages. The proposed diagram is constructed by plotting the difference in milliequivalent percentage between alkaline earths and alkali metals, expressed as percentage reacting values, on the X axis; and the difference in milliequivalent percentage between weak acidic anions and strong acidic anions, also expressed as percentage reacting values, on the Y axis. The milliequivalent percentage differences from the X and Y co-ordinates are extended further into the main study sub-fields of the proposed diagram, which defines the overall character of water. Examples of hydrochemical analyses of groundwater are given from Karnataka, India, for each of the three types of diagrams, illustrating the applicability of the proposed diagram in four case histories having different hydrogeochemical aspects. A comparison indicates that the proposed new diagram satisfies the basic requirement for a suitable classification of natural waters, and it also can be effectively used for studies of hydrochemical processes.

Résumé Un nouveau diagramme hydrochimique est proposé dans le but de classer les eaux naturelles et d'identifier les processus hydrochimiques. Ce diagramme est différent des diagrammes de Piper et de Durov étendu par le fait que les deux triangles équilatéraux sont éliminés et que la forme du principal domaine d'étude est différente. En outre, le diagramme proposé peut être construit à l'aide de la plupart des tableurs. Ce diagramme est construit à partir de la différence en pourcentage des milliéquivalents entre les alcalino-terreux et les alcalins, exprimés comme des teneurs en réaction en pourcentage, sur l'axe des X, et de la différence en pourcentage des milliéquivalents entre les anions d'acides faibles et les anions d'acides forts, exprimés aussi comme des teneurs en réaction en pourcentage, sur l'axe des Y. Les différences en pourcentage des milliéquivalents des coordonnées X et Y sont par la suite étendues dans les principaux sous-domaines d'étude du diagramme proposé, qui définit le caractère d'ensemble de l'eau. Des exemples d'analyses hydrochimiques d'eaux souterraines, provenant de Karnataka (Inde) sont données pour chacun des trois types de diagrammes, pour illustrer l'applicabilité du diagramme proposé dans quatre cas présentant des aspects hydrochimiques différents. Une comparaison indique que le nouveau diagramme proposé satisfait aux conditions de base pour une classification des eaux naturelles et qu'il peut aussi être utilisé efficacement pour l'étude des processus hydrochimiques.

Resumen Se propone un nuevo diagrama hidroquímico para la clasificación de las aguas y la identificación de los procesos hidroquímicos. El diagrama propuesto difiere de los de Piper y Durov en que se suprimen los dos triángulos equiláteros y se cambia la forma de la zona restante. Además, el diagrama propuesto puede dibujarse con la mayoría de paquetes de software disponibles. El diagrama se construye de la siguiente manera: en el eje de las X se dibuja la diferencia en miliequivalentes entre las tierras alcalinas y los metales alcalinos, expresados como porcentaje de valores reactivos; en el eje de las Y se dibuja la diferencia (también en miliequivalentes) entre aniones débiles y aniones fuertes, de nuevo expresados como porcentaje de valores reactivos. Las diferencias entre ambas coordenadas se trasladan hacia los sub-campos del diagrama, que definen el carácter global de un agua. Se muestran ejemplos de análisis hidroquímicos de aguas subterráneas en Karnataka, India. Se dibujan los tres tipos de diagramas en cuatro casos que presentan distintas características hidroquímicas. Esto permite comprobar que el nuevo diagrama satisface los requisitos necesarios para caracterizar adecuadamente un agua,

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además de reflejar la utilidad potencial del mismo en los estudios hidroquímicos.

Key words India · groundwater quality · hydrochemical modeling · hydrochemistry · hydrochemical diagrams

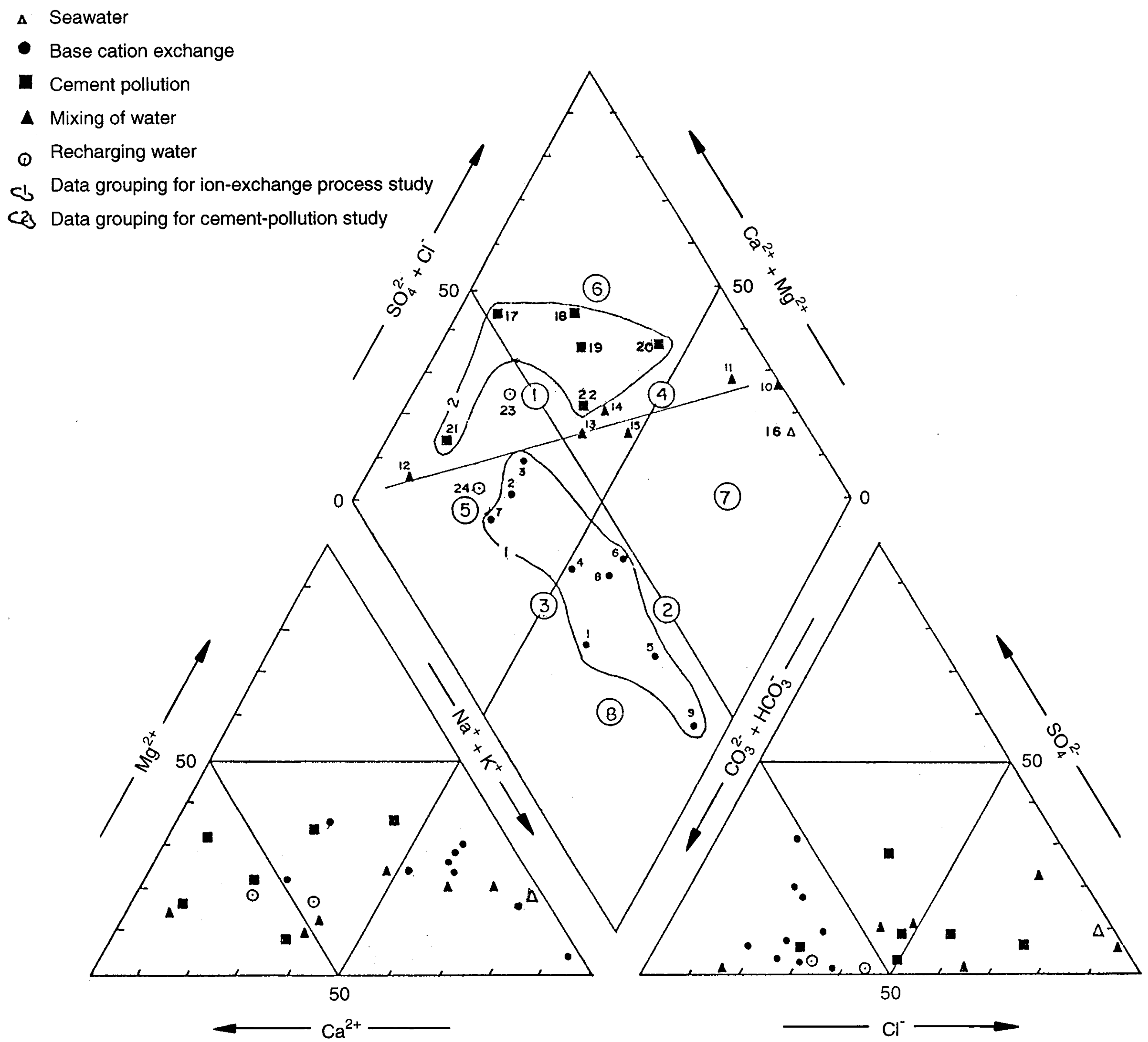
Introduction

Hydrochemical diagrams are aimed at facilitating interpretation of evolutionary trends, particularly in groundwater systems, when they are interpreted in conjunction with distribution maps and hydrochemical sections. A trilinear diagram to describe water chemistry was first attempted by Hill (1940) and refined by Piper (1944). In the Soviet literature, a new diagram was introduced by Durov (1948). An expanded version of the Durov diagram was developed by Burdon and Mazloum (1958) and Lloyd (1965).

An example of the Piper diagram is shown in *Figure 1*. In the Piper diagram, major ions are plotted in the two base triangles as cation and anion milliequivalent percentages. Total cations and total anions are each considered as 100%. The respective cation and anion locations for an analysis are projected into the diamond field, which represents the total ion relationship.

The Piper diagram has been widely used to study the similarities and differences in the composition of waters and to classify them into certain chemical types. The water types demonstrated by the Piper diagram, as

Figure 1 Chemical analyses of water from Karnataka, India, represented as percentage of total milliequivalents per litre on the trilinear diagram originated by Piper (1944)



described by Karanth (1987), show the essential chemical character of different constituents in percentage reacting values, expressed in milligrams equivalent. Piper diagrams allow comparisons to be made among numerous analyses, but this type of diagram has a drawback, as all trilinear diagrams do, in that it does not portray actual ion concentration. The distribution of ions within the main field is unsystematic in hydrochemical-process terms, so the diagram lacks certain logic. Piper suggested the method of encircling the plotted points in the central diamond field with its area proportional to the absolute concentration. This method is not very convenient when plotting a large volume of data. Nevertheless, this shortcoming does not lessen the usefulness of the Piper diagram in the representation of some geochemical processes.

Some of the shortcomings of the trilinear diagrams of the type developed by Hill and Piper are removed in the diagram developed by Durov (1948), but, like the Piper diagram shown in *Figure 1,* suitable software is not available for plotting data on the Durov diagram or on an expanded version of the Durov diagram, shown in *Figure 2*. In this diagram, the cations and anions are plotted in separate triangles, which, in this respect, is similar to the Piper diagram. Whereas the Piper diagram is normally based upon milliequivalent percentage of major-ion values, where total cations and total anions are each considered as 100%, the Durov diagram considers total cations and total anions together as 100%. The intersection of lines extended from the two sample points on the triangle to the central rectangle gives a point that represents the major-ion compositions on a percentage basis. From this point, lines extending to the adjacent scaled rectangles provide for representations of the analyses in terms of two parameters selected from various possibilities, such as total major-ion concentrations, total dissolved solids, ionic strength, specific conductance, hardness, total dissolved inorganic carbon, or pH.

In *Figure 2,* the cation and anion triangles are recognised and separated along the 25% axes so that the main field is conveniently divided. The expanded Durov diagram has the distinct advantage over the Piper diagram in that it provides a better display of hydrochemical types and some processes, and in practical terms it has less line work in the main field (Lloyd and Heathcote 1985).

Proposed Diagram

The proposed diagram, shown in *Figure 3*, is a somewhat modified version of the Piper diagram shown in *Figure 1* and the expanded Durov diagram shown in *Figure 2.* The difference is that the two equilateral triangles are omitted, and the shape of the main study field is different. In the Piper diagram, the milliequivalent percentages of the major cations and anions (percentage reacting values) are plotted in each triangle and the type of water is determined on the

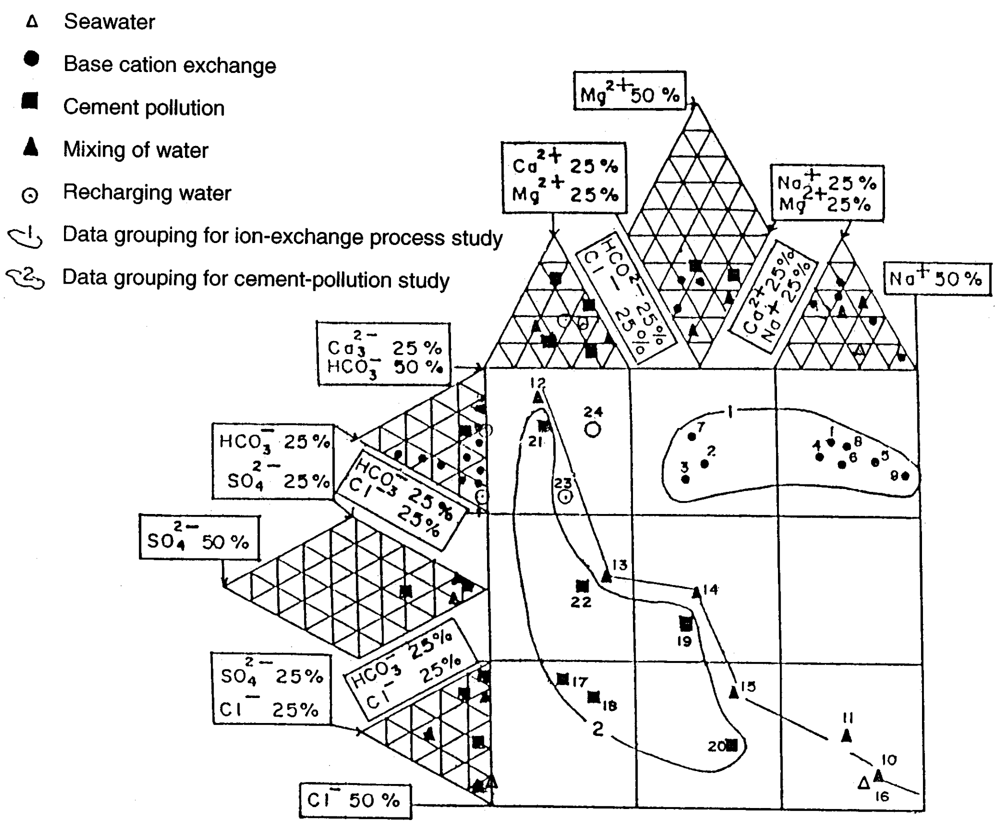


Figure 2 Expanded Durov diagram introduced by Burdon and Mazloum (1958) and Lloyd (1965), demonstrating major-ion chemistry of groundwater from Karnataka, India

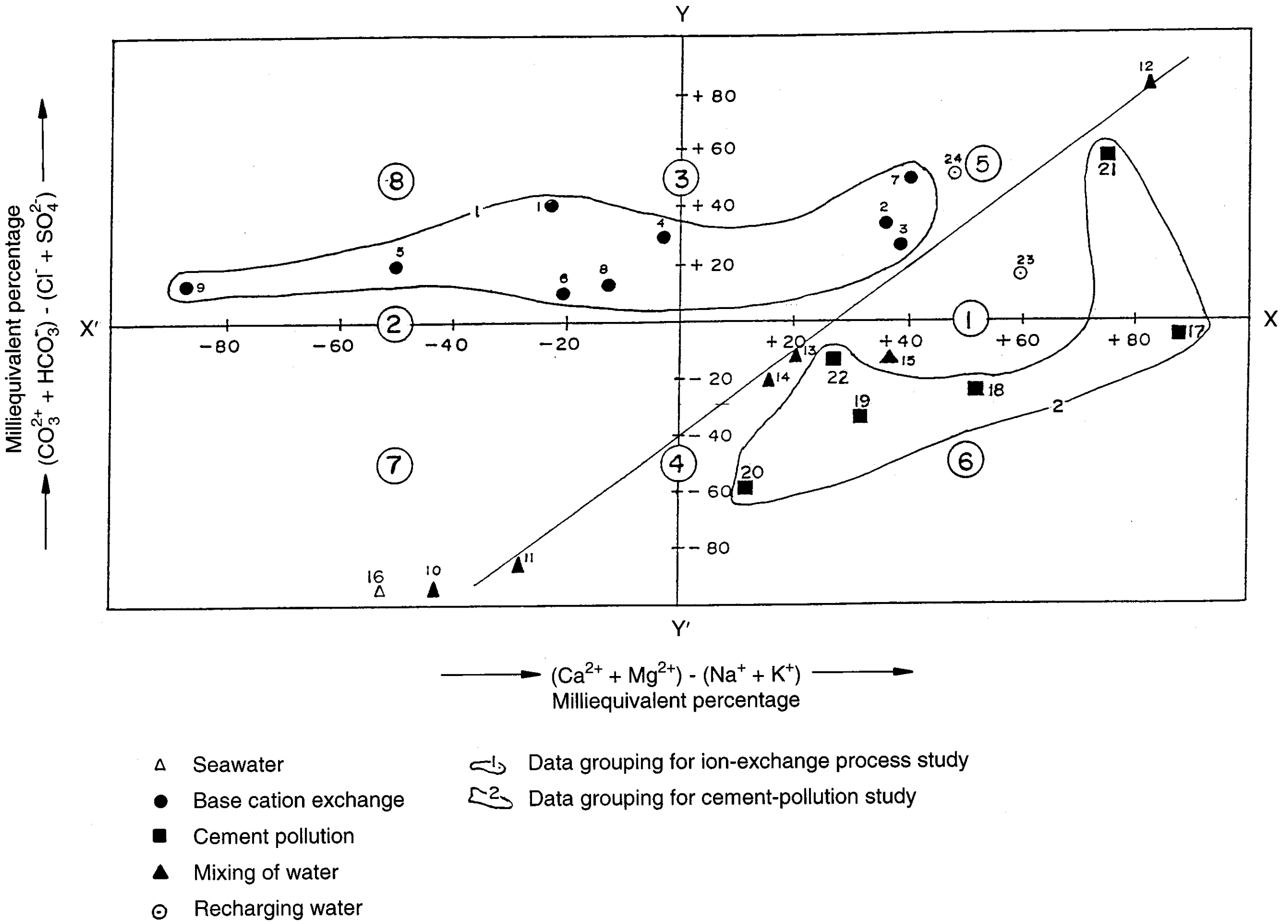


Figure 3 Proposed new diagram demonstrating geochemical classification and hydrochemical processes of groundwater from Karnataka, India

basis of position of the data plot in the respective cationic and anionic triangular fields. The plotting from triangular fields is extended further into the central diamond field, which provides the overall character of the water.

In contrast, in the proposed diagram, the difference in milliequivalent percentage between alkaline earths (calcium plus magnesium) and alkali metals (sodium plus potassium), expressed as percentage reacting values, is plotted on the X axis, and the difference in milliequivalent percentage between weak acidic anions (carbonate plus bicarbonate) and strong acidic anions (chloride plus sulphate) is plotted on the Y axis. The resulting field of study is a square or rectangle, depending upon the size of the scales chosen for X and Y co-ordinates. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions, would plot in one of the four possible sub-fields of the proposed diagram. The main advantage of the proposed diagram is that it can be made simply on most spreadsheet software packages.

The square or rectangular field describes the overall character of the water. The proposed diagram has all the advantages of the diamond-shaped field of the Piper diagram and can be used to study various hydrochemical processes, such as base cation exchange, cement pollution, mixing of natural waters, sulphate reduction, saline water (end-product water), and other related hydrochemical problems. In order to define the primary character of water, the rectangular field is divided into eight sub-fields, each of which represents a water type, as follows:

1. Alkaline earths exceed alkali metals.
2. Alkali metals exceed alkaline earths.
3. Weak acidic anions exceed strong acidic anions.
4. Strong acidic anions exceed weak acidic anions.
5. Alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions, respectively. Such water has temporary hardness. The positions of data points in the proposed diagram represent Ca^{2+}–Mg^{2+}–HCO_3-type, Ca^{2+}–Mg^{2+}-dominant HCO_3^--type, or HCO_3^--dominant Ca^{2+}–Mg^{2+}-type waters.
6. Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions. Such water has permanent hardness and does not deposit residual sodium carbonate in irrigation use. The positions of data points in the proposed diagram

represent Ca^{2+}–Mg^{2+}–Cl^- type, Ca^{2+}–Mg^{2+}-dominant Cl^--type, or Cl^--dominant Ca^{2+}–Mg^{2+}-type waters.

7. Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions. Such water generally creates salinity problems both in irrigation and drinking uses. The positions of data points in the proposed diagram represent Na^+–Cl^--type, Na_2SO_4-type, Na^+-dominant Cl^--type, or Cl^--dominant Na^+-type waters.
8. Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions. Such waters deposit residual sodium carbonate in irrigation use and cause foaming problems. The positions of data points in the proposed diagram represent Na^+–HCO_3^--type, Na^+-dominant HCO_3^--type, or HCO_3^--dominant Na^+-type waters.

Various hydrochemical processes as represented by the Piper diagram and the proposed diagram are listed in *Table 1.*

Case Histories Illustrating Applicability of the Proposed Diagram

The chemical quality of groundwater in the deccan plateau, Karnataka State, India, is highly variable (Jaganathan et al. 1991). The nature of this variation can be understood by plotting the difference in milliequivalent percentages of the alkaline earths and alkali metals on the X axis, and weak acidic anions and strong acidic anions on the Y axis in the proposed diagram.

In order to illustrate the usefulness of the proposed diagram, groundwater samples were collected from various locations in Karnataka State, as shown in *Figure 4.* The region is underlain mainly by peninsular gneisses, granites, and Dharawarian schists in association with other metamorphic rocks of Archaean age. The basaltic rocks of Cretaceous–Palaeocene age are confined to the northern part of the State, and these rocks are also laterised. Sedimentary rocks of Precambrian age, viz. quartzite, sandstone, limestone, and shale, occur in limited areas in the northern part of the State. Recent unconsolidated alluvium is restricted to the coastal plain in the west, to narrow valley fills, and along the major stream courses.

Groundwater samples were collected from different geological formations, as summarised in *Table 2.* Results of analyses were plotted on the proposed diagram to test its applicability, for geochemical classification of groundwater, and to study hydrochemical processes. The data are plotted on an anion–cation balance control chart for assessing the data quality, as shown in *Figure 5.*

The control chart of anion–cation balance (*Figure 5*) is a graphic representation of data quality. The anionic sum in milliequivalents per liter should equal the cationic sum in milliequivalents per liter, although they are seldom equal in practice. This inequality increases as the ion concentration increases. The difference between anion and cation sum in milliequivalents is acceptable within ±1 SD, as expressed by the equation:

$$\sum \text{anions} - \sum \text{cations} = \pm(0.0155 \sum \text{anions} + 0.1065).$$

Case History 1: Base Cation Exchange

The Krishna River and its tributaries (Bhima, Tungbhadra, Malaprabha, Ghataprabha, upper Krishna, and Vedavati) drain an area of 114,321 km^2 in Karnataka. The basin area is underlain by unconsolidated to

Table 1 Comparison of the Piper diagram and the proposed diagram in representing water types and hydrochemical processes

Percentage reacting values		X-axis	Percentage reacting values		Y axis	Combination of X,Y co-ordinates	Fields of study		Hydrochemical processes
Ca^{2+} + Mg^{2+}	Na^+ + K^+		CO_3^{2-} + HCO_3^-	Cl^- + SO_4^{2-}			Proposed diagram	Piper diagram	
100	00	+100	100	00	+100				
90	10	+ 80	90	10	+ 80				
80	20	+ 60	80	20	+ 60	+X+Y	5	5	Recharging water: $Ca(HCO_3)_2$-type
70	30	+ 40	70	30	+ 40				
60	40	+ 20	60	40	+ 20	−X−Y	6	6	Cement pollution or reverse ion-exchange water: $CaCl_2$-type
50	50	00	50	50	00	X=0, Y=0			
40	60	− 20	40	60	− 20				
30	70	− 40	30	70	− 40				
20	80	− 60	20	80	− 60	−X−Y	7	7	End-product water: NaCl-type
10	90	− 80	10	90	− 80				
00	100	−100	00	100	−100	−X+Y	8	8	Base-exchanged water: $NaHCO_3$-type

$X = (Ca^{2+} + Mg^{2+}) - (Na^+ + K^+)$
$Y = (CO_3^{2-} + HCO_3^-) - (Cl^- + SO_4^{2-})$

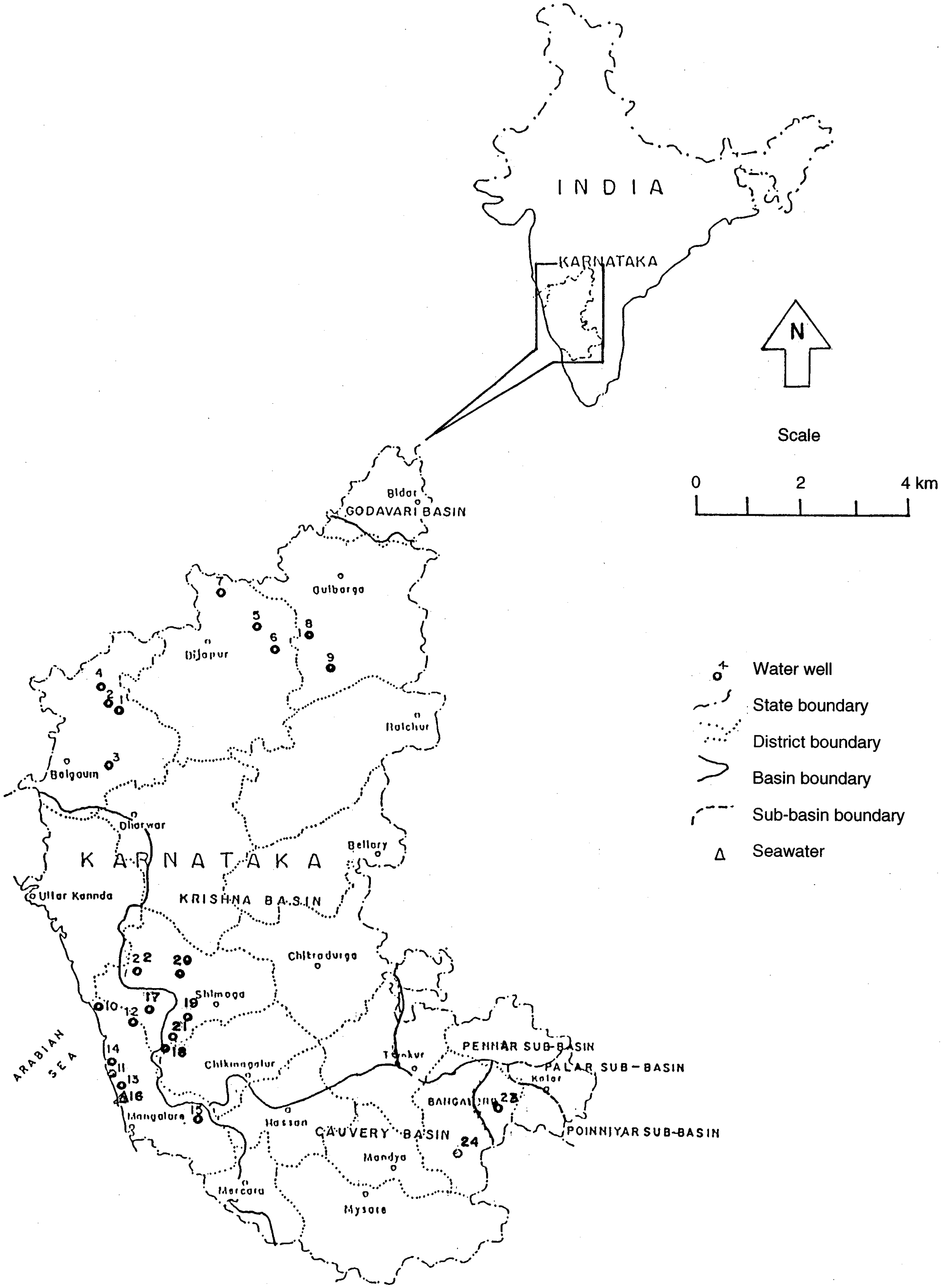


Figure 4 Location of four case-history areas, showing sampling points

Table 2 Chemistry of selected groundwater samples from Krishna basin and Ponnaiyar basin, Karnataka, India

Location and well designation	pH	Specific cond. (μmhos/cm 25 °C)	Concentration (mg/L)										
			Total hardness as $CaCO_3$	Ca	Mg	Na	K	CO_3	HCO_3	Cl	SO_4	NO_3	F
Krishna Basin													
Belgaon													
1. Belkud 47L3D1	7.93	880	180	26	28	126	1.2	NIL	397	80	17	1.6	0.71
2. Hubruvadi 47L3D5	7.98	610	220	42	28	43	2.5	NIL	256	67	9.0	Tr	0.42
3. Khanapur 48I2Cl	8.01	420	145	40	11	25	4.9	NIL	153	50	2.4	10	0.20
4. Yedra 47L2C4	8.21	640	155	30	19	75	Tr	Tr	26	53	25	6.2	0.6
Bijapur													
5. Nadkurd 56C4A2	8.4	1650	195	20	35	290	1.60	24	543	137	144	1.6	1.04
6. Shivangi 56D1A1	8.0	860	180	26	28	122	Tr	NIL	287	43	137	5.0	0.42
7. Zalki 47O3D2	8.5	600	205	46	22	37	1.8	30	201	37	20	1.6	0.48
Gulberga													
8. Jeratgi 56C4B3	8.52	840	185	22	32	120	2.10	24	268	59	89	3.0	0.80
9. Malgatti 56D2C3	8.14	3600	130	18	21	600	340	NIL	134	410	180	1.6	2.5
South Kanara coast													
South Kanara													
10. Baidnur 48K1C1	7.8	10200	1500	154	271	1680	45	NIL	67	3379	300	3.0	0.32
11. Malpe 48K3C1	7.98	800	245	82	9.70	56	26	NIL	226	124	44	7.0	0.10
12. Kollur 48K1D1	7.72	195	90	30	3.6	3.8	Tr	NIL	104	11	Tr	Tr	Tr
13. Hebri 48K3D2	7.24	205	55	12	6.1	18	9	NIL	49	39	Tr	16	Tr
14. Kundapur 48K2C1	8.15	310	95	30	4.8	24	9	NIL	79	57	17	1.9	Tr
15. H'kata 48K3C3	7.25	2800	535	92	74	400	27	NIL	165	689	318	1	0.45
16. Seawater	NA	NA	NA	400	1350	10500	380	NA	142	19000	2700	2.2	1.3
Shimoga													
17. Hosanagara 48O1A1	8.10	340	155	40	13	5	1	NIL	98	60	3	Tr	Tr
18. Ambigolla 48N4B1	8.1	340	115	16	18	26	24	NIL	49	85	13	2.5	0.05
19. Megaravalli 48O2A3	8.5	180	85	28	3.6	4	1	12	92	14	6	Tr	Tr
20. Theerthahalli 48O2A2	8.0	340	125	26	15	21	5	NIL	73	43	48	Tr	Tr
21. Thalaguppa 48J4D1	8.1	125	40	14	1.2	10	1.2	NIL	31	21	6	Tr	Tr
22. Agumbe 48O2A1	8.3	90	35	10	2.4	3.5	2.5	Tr	18	18	4.2	Tr	Tr
Ponnaiyar basin													
Bangalore													
23. Chokkamahalli 57G4C5	8.4	430	190	60	9.7	16	7.2	24	110	71	3	3.8	0.21
24. Kottohalli 57H2B4	8.6	400	160	48	9.7	20	5.4	48	98	36	6.6	Tr	0.30

NA, not analysed; Specifid cond., specific conductivity

consolidated effusive sedimentary, metasedimentary, and metavolcanic rocks; basalt, crystalline, and unclassified crystalline rock types. The aquifer comprises kaolinitic clay, basalt, sandstone, shale, limestone, dolomite, phyllite, schist, granite, gneiss, and intrusives. Silt, sand, and clay occur only along the stream courses to a limited extent (Jaganathan et al. 1991).

The range of groundwater chemistry present in the upper Krishna River basin, consisting of the districts of Belgaon Bijapur, and Gulberga, is illustrated in the Piper diagram (*Figure 1*), expanded Durov diagram (*Figure 2*), and the proposed diagram (*Figure 3, envelope 1*). This study area is generally underlain by basalt with interbedded clay. Limestone, sandstone, dolomite, and other aquifers occur only in patches at isolated places. The data points in fields 5 and 8 of the Piper diagram (*Figure 1*), the proposed diagram (*Figure 3*), and in fields 3 and 4 of the Durov diagram (*Figure 2*) indicate possible groundwater evolutionary paths and suggest the presence of zeolite in basalt. Sodium clays at places encounter recharging water from limestone, sandstone, and other aquifers, and these clays play a key role in the evolution of sodium-bicarbonate-type water. HCO_3^-- and Na^+-dominant water normally indicates ion-exchanged waters, although the generation of CO_2 at depth can produce HCO_3^- where Na^+ is dominant under certain circumstances (Winograd and Farlekas 1974).

Case History 2: Cement Pollution

The Karnataka government drilled tubewells in different parts of the State, particularly in the Krishna River basin, to supplement drinking-water supplies during the severe drought of 1985–86. Because of normal rainfall in subsequent years, most of these

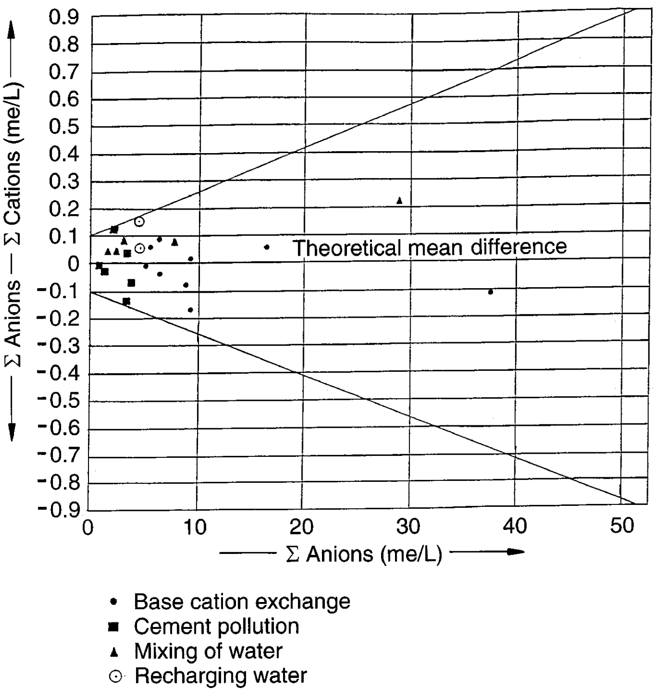


Figure 5 Control chart for anion–cation balances, demonstrating data quality for groundwater analysis from Karnataka, India

water-abstraction structures were abandoned, resulting in the plugging of wells due to the deposition of cementing encrustation by groundwater (Tamta 1993).

The groundwater chemistry represented by groundwater samples from the abandoned wells is illustrated in the three diagrams (*Figures 1, 2, 3, envelope 2*). The chemistry indicates evolution of calcium-chloride-type water from calcium-bicarbonate-type water, as a result of cement pollution, with no evidence of reverse ion exchange.

Case History 3: Seawater Intrusion

Groundwater along the south Kanara coast, Karnataka, varies in quality evidently due to seawater intrusion. In this region the west-flowing rivers include Kalindi, Sharavathi, Sitasverna, and Netravathi, and these basins drain an area of 12188 km^2. The area is underlain by consolidated metasedimentary and metavolcanic rocks, basalt, and unconsolidated crystalline rocks. The aquifer comprises granite, gneiss, and intrusive rocks. Sand, silt, and clay with calcareous concretions occur along the west coast.

The nature of the variation in groundwater quality was assessed (1) by comparing the ionic ratio of groundwater composition with that of seawater and rainwater; results are shown in *Table 3*; and (2) by plotting the difference $(Ca^{2+}+Mg^{2+})-(Na^{+}+K^{+})$ and $(CO_3^{2-}+HCO_3^{-})-(Cl^{-}+SO_4^{2-})$ in terms of percentage reacting values in the proposed diagram (*Figure 3*). The data points lie in study fields 5, 6, and 7, almost in a straight line, indicating mixing of seawater with groundwater. In *Table 3,* the ionic ratios of groundwater from Baidnur are comparable to those of seawater, with the exception of Ca^{2+}/Cl^{-} which is derived from another source in the groundwater. The Piper diagram (*Figure 1*) and expanded Durov diagram (*Figure 2*) also indicate the mixing of groundwater and seawater.

Table 3 Ratio of cations to chloride ions in seawater, rainwater, and groundwater from South Kanara district (Well Baidnur 48K1C1, Karnataka, India)

Source	$Na^{+}Cl^{-}$	K^{+}/Cl^{-}	Ca^{2+}/Cl^{-}	Mg^{2+}/Cl^{-}
Seawater	0.552	0.020	0.021	0.071
Rainwater	0.548	0.032	0.075	0.071
Groundwater	0.500	0.019	0.045	0.079

Case History 4: Recharging Waters

Groundwater in limestone, sandstone, and many other aquifers in recharge areas is dominated by HCO_3^{-} and Ca^{2+}, whereas groundwater in lavas and gypsiferous deposits in recharge areas may have a $CaSO_4$-type chemical composition. Recharging waters from the Bangalore District in the Ponnaiyar basin, Karnataka, were selected for testing the applicability of the proposed diagram for geochemical classification of groundwater. The Ponnaiyar basin is underlain by unconsolidated deposits, basalt, and unclassified crystalline rocks; the aquifer comprises granite, gneiss, and intrusive rocks. Sand, silt, and sandy clay occur only along the streambeds. The milliequivalent percentage differences between alkaline and alkali metals and between weak acridic anions and strong acidic anions were plotted on the proposed diagram. The data points lie in study field 5 of the diagram, suggesting dominance of Ca^{2+} and HCO_3^{-} ions in the recharging waters.

Conclusions

The proposed diagram helps in developing an understanding of water-quality data, because it satisfies the basic requirement for a suitable classification of natural waters, and it also can be effectively used in the study of hydrochemical processes. The chemical-analysis data plot in the same study fields on the Piper diagram and on the proposed diagram, but the advantage in the latter diagram is the ease of construction of the diagram. Unlike for the Piper and Durov diagrams, suitable software is available for plotting data on the proposed diagram.

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