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Durov's Classification of Natural Waters and Chemical Composition of Atmospheric Precipitation in USSR: A Review

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Abstract—The present review contains Durov's method of classifying natural waters on the basis of ionic composition. The chemical composition of atmospheric precipitation in USSR is also presented.

Durov's classification of natural waters—*Durov* [1948], who is one of the foremost Soviet hydrologists, divided the natural waters into five classes.

Class I (primary waters)—The simplest or primary waters result from the action of atmospheric precipitation on the Earth's surface which was leached of the readily soluble salts. These waters containing CO_2 easily dissolve limestones and dolomites and, therefore, reach a state of chemical equilibrium with respect to the solution of calcium and magnesium bicarbonates under the prevailing conditions.

The primary waters are only slightly mineralized (100-300 mg/l and less), with Ca/Mg ratio varying from 5 to 10 (apparently in equivalents). The sulfates and chlorides are either absent or present in very small amounts (<0.2 mg-equ/l or ten per cent mg-equ).

Class II (secondary waters)—The secondary waters result from the enrichment of primary waters with sulfates and chlorides of sodium and magnesium which are present in sedimentary rocks. The mineralization increases to 500–1000 mg/l and, occasionally, exceeds 1000 mg/l. Hardness also increases, whereas the Ca/Mg ratio decreases from 3.3 to 1.4 (and less).

The secondary waters acquire $CaSO_4$ as a result of direct solution of gypsum or the following reaction

$$Ca(HCO_3)_2 + MgSO_4 \rightarrow CaSO_4 + Mg(HCO_3)_2$$

Class III (sulfate waters)—The sulfate waters result from secondary waters upon removal of bicarbonates and if the chlorides are of secondary importance. The concentration of secondary waters in closed basins results in the conversion of bicarbonates to slightly soluble carbonates, which precipitate out. Further concentration of these waters eventually gives rise to the sulfate lakes.

The removal of bicarbonates from the secondary waters can also occur as a result of oxidation of pyrite

$$FeS_2 \rightarrow FeSO_4 \rightarrow Fe_2(SO_4)_3 \rightarrow Fe(OH)_3 + H_2SO_4$$

According to *Durov* [1948], the products of this reaction, namely sulfuric acid and ferric sulfate, convert the magnesium and calcium bicarbonates into sulfates. The significance of $Fe_2(SO_4)_3$ in converting the bicarbonates into sulfates, however, is questionable because of its slight solubility in water.

The transitional waters between Classes II and III contain both bicarbonates and sulfates of magnesium. These waters are very corrosive in steam boilers.

Class IV (chloride waters)—As a result of enrichment with chlorides and simultaneous loss of bicarbonates and sulfates, due to precipitation of $CaCO_3$, $CaMg(CO_3)_2$, and $CaSO_4$, the secondary waters change to chloride-predominant waters. These waters appear to be the most stable and result from gradual evaporation in the closed basins. Their formation is also accompanied by cation exchange giving rise to the calcium and magnesium chlorides.

Class V (alkaline bicarbonate waters)—The alkaline waters could have formed from the secondary waters upon colloidal-chemical removal of the $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, and SO_4'' ions by fresh-water clays, etc.

$$Ca(HCO_3)_2 + Na_2SO_4 \rightarrow \mathit{CaSO_4} + 2NaHCO_3$$
$$Mg(HCO_3)_2 + Na_2SO_4 \rightarrow \mathit{MgSO_4} + 2NaHCO_3$$

The alkaline waters are commonly devoid of sulfates, with no notable evidence of biochemical processes. The biochemical processes, however, probably also contributed to the formation of these waters. Low mineralization, low hardness, and low Ca/Mg ratios are also characteristic of alkaline waters. Upon concentration, these alkaline bicarbonate waters give rise to soda lakes.

Durov's diagram (Fig. 1) is a double triangular diagram, where in one triangle the composition of water is expressed in terms of HCO_3', SO_4'', and Cl' anions, whereas the points plotted in the other triangle show the relative proportions of $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, and $Na^{\cdot}$ cations. The amounts of these

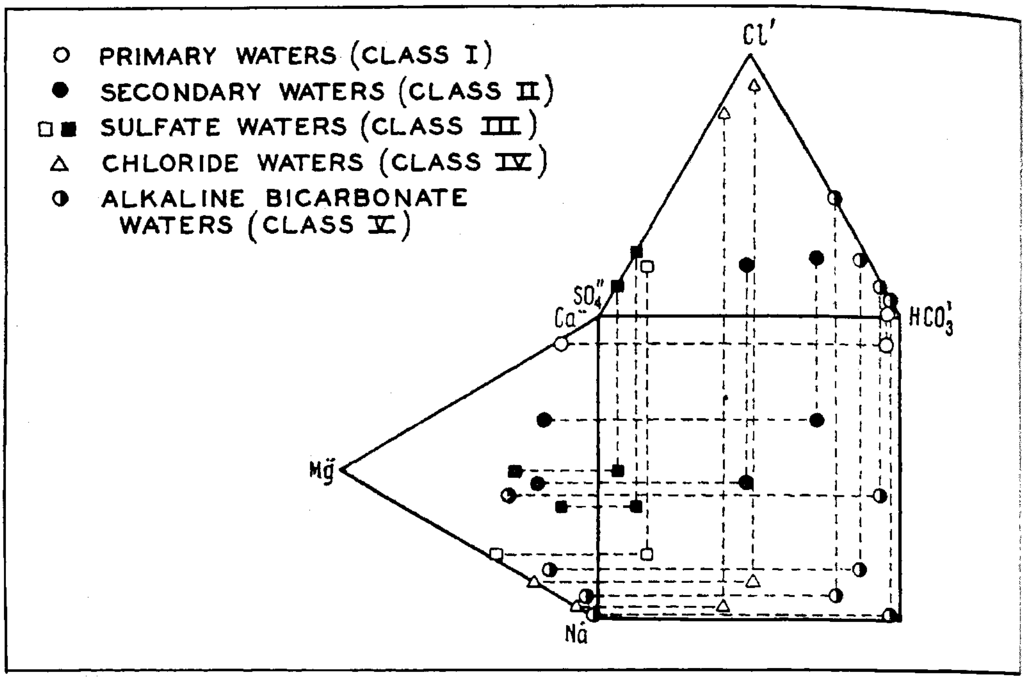

FIG. 1 – Durov's diagram [*Durov*, 1948, p. 90]

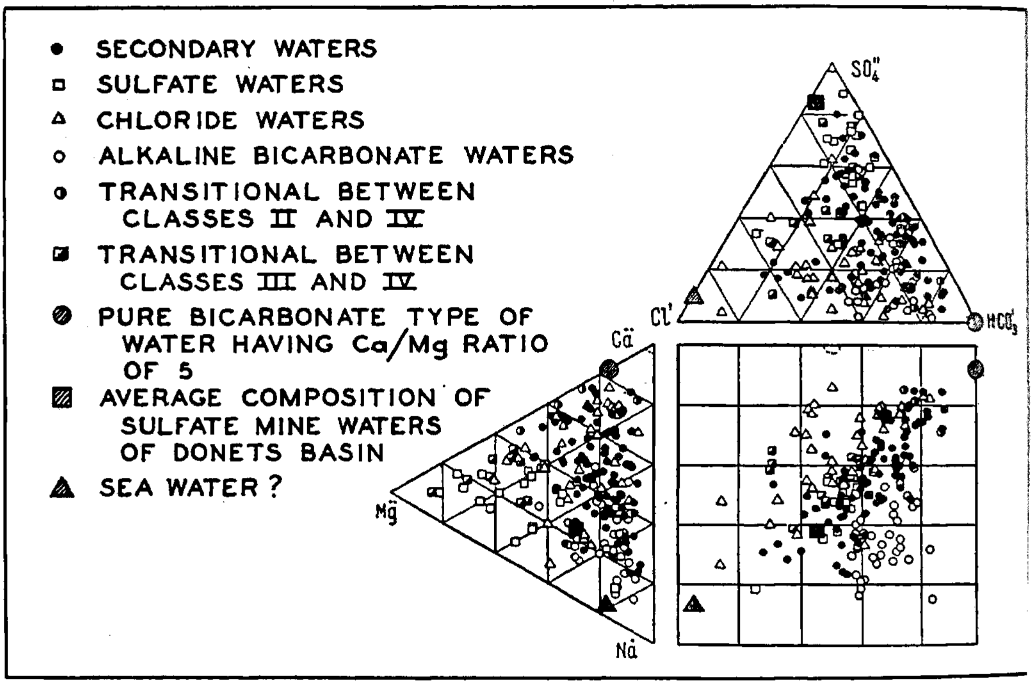

FIG. 2 – Ionic composition of atmospheric precipitation in USSR plotted on Durov's diagram [*Durov* and *Fedorova*, 1955, p. 664]

ions are expressed in per cent mg-equivalents, taking the sum of anions and cations as 100 pct each. In plotting these points, the CO_3'' anion is combined with HCO_3', and $K^{\cdot}$ cation with $Na^{\cdot}$.

In order to obtain a point inside the square, perpendiculars are drawn from the two points plotted in the triangles, and extended until they intersect. In Durov's square, the points occupying the upper right corner represent the primary waters, whereas the points representing mine waters (black squares), waters of sulfate lakes (open squares), chloride waters (open triangles), and soda waters (semi-open circles) are located along the periphery in the opposite part of the square. The points located along the HCO_3'—$Na^{\cdot}$ diagonal represent the secondary waters (black circles), and show change from the $Ca(HCO_3)_2$ to Na_2SO_4. The transition from the secondary to alkaline waters occurs along the direction perpendicular to the above mentioned diagonal, as a result of loss of $CaSO_4$ and $MgSO_4$.

Ionic composition of atmospheric precipitation in USSR—Fedorova [in *Durov* and *Fedorova*, 1955] analyzed 190 samples of atmospheric precipitation (rain, snow, and hail, together with salts of various origin brought down by them) from 41 hydrometeorological stations in USSR. About half of these stations were located along the shores of Black Sea, Azov Sea, Arctic Ocean, and Sea of Okhotsk. The results of her analyses were subsequently plotted on Durov's diagram (Fig. 2).

The examination of Figure 2 reveals the absence of primary waters. Eighty three samples belong to Class II (black circles); 19, to Class III (open squares); 36, to Class IV (open triangles); and 36, to Class V (open circles). Five samples are transitional between Classes II and IV (semi-open circles), and 11 samples are intermediate between Classes III and IV (semi-open squares). The examination of Figure 2 also reveals that the major portion of points is located between the following two points: (1) big dashed circle representing a pure bicarbonate type of water, having a Ca/Mg ratio (in equivalents) of 5; and (2) big black square showing the average composition of sulfate mine waters of Donets Basin, over the period of 40 years—1911–1951. The absence of points near the gypsum point (dotted) probably indicates that the direct solution of gypsum made very small contribution to the chemical composition of atmospheric precipitation.

Most of the samples (72.6 pct) belong to the continental type of waters (Classes II, III, and V). These waters are obviously not of marine origin. The composition of chloride waters, however, also differs markedly from the sea water. These results are in close accord with those of *Maksimovich* [1953], who calculated that the salts of continental origin constitute 67 pct of all salts present in the atmospheric precipitation of USSR.

The average ionic composition of 190 samples of atmospheric precipitation analyzed by Fedorova is presented in Figure 3 and Table 1.

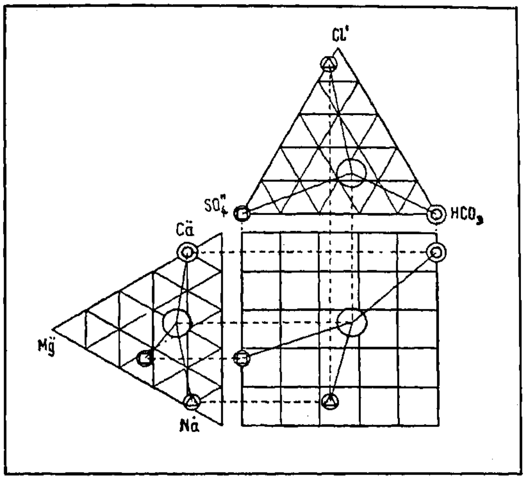

FIG. 3 – Average chemical composition of atmospheric precipitation in USSR [*Durov* and *Fedorova*, 1955, p. 665]

TABLE 1 – *Average chemical composition of atmospheric precipitation in USSR*

Ion	Composition	Aver. pct equ	Pct equ of different salts			Sulfates (pct of total sulfates)
			Marine salts	Bicarbonates	Sulfates	
	mg/l					
$Mg^{\cdot\cdot}$	1.74	26.53	4.77	8.90	12.86	44.8
$Ca^{\cdot\cdot}$	4.82	40.00	0.95	35.48	3.57	12.5
$Na^{\cdot}$	5.12	33.47	21.23	...	12.24	42.7
		100.00	26.95	44.38	28.67	100.0
HCO_3'	18.20	44.45	0.07	44.38	...	...
SO_4''	9.17	31.18	2.51	...	28.67	100.0
Cl'	5.46	24.37	24.37	...	...	...
	44.51	100.00	26.95	44.38	28.67	100.0

Apparently, in calculating the per cent equivalents (pct equ) of various salts, it was assumed that all Cl' (24.37 pct equ) is of marine origin; and the pct equ of other ions in the 'marine salts' column were made to correspond to the percentage composition of dissolved solids in sea water (same proportions). The pct equ of other salts were calculated by the process of elimination—remainder of HCO_3' (44.45 − 0.07 = 44.38 pct equ) belonging to bicarbonates, remainder of SO_4'' (31.18 − 2.51 = 28.67 pct equ) belonging to sulfates, etc.

Conclusions—According to *Durov* and *Fedorova* [1955], the marine salts constitute only about 27 pct of all salts present in the atmospheric precipitation. The remainder of salts can form in the continental environment (bicarbonates and sulfates of oxidation zone). The bicarbonate and sulfate waters, however, also contain some admixture of chlorides from the relic seas of the geologic past. The effect of oceans on the chemistry of atmospheric precipitation is, therefore, less than 25 pct and, possibly, as low as 20 pct.

The results obtained by Durov and Fedorova indicate that the major portion of salts in the atmospheric precipitation of USSR owes its origin to dust and aerosols, which are brought mainly from the arid portions of the continent. The man-made sources, which are not mentioned by Durov and Fedorova, probably also contributed to the chemical composition of atmospheric precipitation. At the present time, Soviet investigators are studying the places of origin of dust masses and directions of their migration.

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[a] The Russian references listed in the bibliography can be obtained through interlibrary loan from Miss Mildred Oelke, Head of Technical Library, Wright-Patterson Air Force Base, Dayton, Ohio.