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Assessment of errors in water quality data using ion balancing methods - A case study from Cauvery River, South India

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This paper provides an insight into the reliability checking options through error assessment for analytical water quality data with a case study, which will be useful for the researchers working on the analytical chemistry. The reliability of chemical analysis has to be verified in a scientific manner before the data is used for further interpretation. The distributions of data values were presented using box plots. The four ion balancing methods, namely anion-cation balance, measured total dissolved solids (TDS) Vs calculated TDS, measured electrical conductivity (EC) Vs ion sums and calculated TDS to EC ratio were applied on the surface water quality data of Cauvery River in Erode region, Tamil Nadu, India. It was found that the errors of the analysis were within the acceptable limits except 14 samples in percentage difference calculations.

[**Key words**: Box plot; Cauvery River; Ion balancing; Water quality data]

Introduction

Water is one of the fundamental elements of life. It is essentially used by people for domestic, agriculture and industrial purposes. The primary waste disposal option followed throughout the world is dilution by water courses. In this manner, almost all the fresh water sources are constantly being polluted by various anthropogenic activities. The quality of water used for various purposes is a matter of serious concern owing to its detrimental impact. So, the assessment of water quality of any water source is vital for all the purposes[1]. There is always an accepted procedure for water sample collection, preservation, transportation and characterization[2]. In all these stages, one must ensure the correctness of operations carried out. The results of any analysis cannot be reproduced with absolute accuracy and reliability. Statistically, the errors are classified as random errors, systematic errors and gross errors. The errors which are caused by uncontrollable fluctuations in variables that affect experimental results are called as random errors. The errors due to instrumental, methodological, or personal mistakes causing lopsided data, which is consistently deviated in one direction from the true value is known as systematic errors. Gross errors are caused by experimenter carelessness or equipment failure[3]. The reasons for errors in the chemical data were also explained in AMC (2013)[4]. So, it is necessary to evaluate the analytical data for its accuracy and reliability before going for data mining operations. Although a number of approaches available in statistics, ion balancing is the prominent technique which brings out the errors in chemical compound analysis.

Many researchers have used these ion balancing methods for calculating the errors in the chemical analysis[5]. But the exact procedure for calculating those errors was not mentioned in those studies. Das et al.[6] have studied the ion balances of chemical data on rain water. It was stated that out of 341 numbers of samples, 26 were rejected as outliers in the ion balance calculations. The calculation method for electrical conductivity (EC) in natural waters and the calculation of their imbalance were presented by McCleskey et al. [7]. Ion balances provide clear, precise measures of analytical reliability and in many cases related data from site can be used in conjunction with ion balance data to pin point individual sources of errors[8]. The groundwater quality data can also be checked for reliability prior to the assessment of its suitability for various purposes[9]. The limitations of traditional methods followed in the calculation of charge balance of non-potable waters were discussed by Murray and Wade[10]. Diagrammatic representation of different cations and anions gives the clear picture about the abundance of each parameter in a water sample[11]. The water-mineral equilibria was also studied as a function of physico-chemical parameters including major ions[12,13]. Here, an attempt was made to evaluate the reliability of analytical data of the water samples collected from Cauvery River, South India. The mixing of urban sewage, industrial effluents as well as agricultural runoff are being the constant issues in the study area where the data was taken for the present computations.

Methodology

Data

Data pertaining to surface water of Cauvery River stretch from Bhavani (11° 26’07” & 77° 41’1”) to Noyyal (11°03’41” & 77°55’45”) in Tamil Nadu, India was taken for the present study. The data set includes seventeen physico-chemical parameters comprising various cations and anions of fifty surface water samples collected during January 2018 (post monsoon season). Standard methods of analytical procedures were followed in analyzing the samples to determine the physico-chemical parameters[2]. The box plots were drawn to identify the variations in the data. These plots are the graphical representation of data in five point scale (minimum, first quartile, median, third quartile and maximum).

Ion Balancing

The sum in milliequivalents of major cations and anions in any water should be nearly equal. This fact can be verified using some prescribed methods called Ion balancing. The inequality can be directly attributed to errors in the measurement of ions. In other cases, the inequality may be attributed to the dissolution of electrolytes due to anthropogenic inputs. When the pH and conductivity are in normal range, the possibility for the increase of free ions is very low. So, the inequality is because of the incorrectness during the laboratory measurements.

The methods available for calculating the ion balance in water are described below. The methods do not require any experimental or laboratory procedures. It can be performed with the available water quality data set. Concentrations of all the parameters measured in milligram per liter (mg/L) by analytical procedures were converted into milliequivalents per liter (meq/L) by Equation 1[2].

$$\text{meq/L} = (\text{mg/L})*\text{valence} / \text{molecular weight} \quad \text{... (1)}$$

Anion-cation balance

All the water in natural ecosystem are electrically neutral. So, the sum of concentrations of all anions must be equal to the sum of concentrations of all the cations where the concentrations are expressed in meq/L. This test is based on percentage difference (% diff) value as described in Equation 2[2] and the criteria for the acceptance based on this parameter are presented in Table 1[2].

$$\%\text{ diff} = [(\sum \text{cations} - \sum \text{anions}) / (\sum \text{cations} + \sum \text{anions})]*100 \quad \text{... (2)}$$

Measured TDS and calculated TDS

The value of Total Dissolved Solids (TDS) is calculated from other chemical constituents in water using the formula given in Equation 3[2] where all the values are in meq/L. The value of measured TDS value should always be greater than the calculated value because some significant contributor (ion concentrations) may not be incorporated in the computation. The acceptable range is shown in Equation 4[2].

$$\text{Calculated TDS} = (0.6 * \text{Alkalinity}) + Na^{+} + K^{+} + Ca^{2+} + Mg^{2+} + Cl^{-} + SO_4^{2-} + NO_3^{-} + F^{-} \quad \text{... (3)}$$

$$1.0 < (\text{measured TDS} / \text{calculated TDS}) < 1.2 \quad \text{... (4)}$$

Calculated TDS to EC ratio

If the ratio of calculated TDS to conductivity falls below 0.55, the lower ion sum is suspect; reanalyze it. If the ratio is above 0.7, the higher ion sum is suspect. The sample should be reanalyzed. If reanalysis causes no change in the lower ion sum, an unmeasured constituent, such as ammonia or nitrite, may be present at a significant concentration. If poorly dissociated calcium and sulfate ions are present, the TDS may be as high as 0.8 times the EC. The acceptable criterion is as given in Equation 5[2].

$$\text{Calculated TDS/conductivity} = 0.55 – 0.7 \quad \text{... (5)}$$

Measured EC and ion sums

Both the anion and cation sums should be 1/100 of the measured EC value. If either of the two sums does not meet this criterion, that sum is suspect. The sample should be reanalyzed. The acceptable criteria are expressed in Equation 6[2].

Table 1 — Criteria for acceptance of data based on anion-cation balance

Sum of Anions (meq/L)	Acceptable Difference
0 – 3.0	± 0.2 meq/L
3.0 – 10.0	± 2%
10.0 – 800.0	± 5%

meq/L – Milliequivalents per liter

$$100 \times \text{anion (or cation) sum, meq/L} = (0.9–1.1)\ \text{EC} \quad \text{... (6)}$$

Results and discussion

Surface water quality data

The results acquired from the analytical procedure are summarized in Table 2. The variations in chemical composition of the Cauvery River water were very minimum. EC is a measure of the capacity of major ions in a given body to conduct electric current and TDS is the total concentration ions present in the water sample. The EC and TDS have larger variations with mean values of 492.14 mg/L and 342.10 mg/L respectively. Calcium (Ca^{2+}) varies from 50 mg/L to 35 mg/L in the data engaged for analysis. The concentration of magnesium (Mg^{2+}) varies from 9 mg/L to 19 mg/L in the study area. The concentration of sodium (Na^{+}) is often taken as an important parameter in deciding the suitability of water for irrigation. The concentration of Na^{+} and potassium (K^{+}) varied from 21 mg/L to 54 mg/L and 3 mg/L to 10 mg/L, respectively. However, bicarbonate (HCO_3^-) and excess of chloride (Cl^-) in river water are usually taken as an index of pollution. Sewage water, industrial and agricultural effluents increased Cl^-. The Cl^- ion concentration of Cauvery River water was found to be varied between 31 mg/L to 78 mg/L. The sulphate (SO_4^{2-}) concentration in the data varied from 23 mg/L to 51 mg/L. Wastewater from tanneries, paper mills, and textile mills usually contributes to the presence of SO_4^{2-} in natural water, along with some agricultural runoff containing leachate of gypsum, which was evidently the case in Cauvery River. The other important parameters measured in the study area and their statistical characteristics are displayed in Table 2.

The box plots of various parameters in the data were plotted and given in Fig. 1. It was identified that the distribution of concentrations of many parameters were uniform. The box plots of total alkalinity, total hardness, Ca^{2+}, NO_2^-, NO_3^- and pH were comparatively short which meant that the values have high level of agreement with each other. Even though the median of Cl^- and PO_4^{2-} plots were lies close to the average, the top whisker shows high deviation from the normal distribution. Also, it indicates outliers in the data set which needs to be verified with further examination of samples to get trustable results. The plots for turbidity and K^+ shows the median merges with first quartile of the data, whereas in Fe plot, the minimum value merges with first quartile data. For the parameters Na^+, SO_4^{2-} and NO_3^-, the median was very close to the third quartile of the plot. These skewed plots are the indicative of the abnormal distribution of the parameter concentrations.

Ion Balancing

The concentrations of parameters considered for ion balancing calculations were converted from

Table — 2 Statistical properties of Cauvery River water quality data

Sl. No.	Parameters	Unit	Minimum	Maximum	Mean	Median	Mode	Variance	Standard Deviation
1	EC	µS/cm	392.00	642.00	492.14	484.00	480.00	2345.14	48.43
2	TDS	mg/L	274.00	448.00	342.10	339.50	336.00	1037.23	32.21
3	pH	-	7.36	8.89	7.90	7.73	7.63	0.16	0.40
4	TH	mg/L	144.00	190.00	156.14	152.00	152.00	99.43	9.97
5	Ca^{2+}	mg/L	35.00	50.00	42.26	42.00	42.00	14.03	3.75
6	Mg^{2+}	mg/L	9.00	19.00	12.10	12.00	12.00	2.66	1.63
7	Na^{+}	mg/L	21.00	54.00	37.32	40.00	41.00	54.14	7.36
8	K^{+}	mg/L	3.00	10.00	4.66	4.00	4.00	2.80	1.67
9	Fe	mg/L	0.00	0.21	0.05	0.03	0.00	0.00	0.06
10	NO_2^-	mg/L	0.00	0.06	0.02	0.01	0.01	0.00	0.02
11	NO_3^-	mg/L	0.00	3.00	1.58	2.00	2.00	0.49	0.70
12	HCO_3^-	mg/L	124.00	178.00	144.54	144.00	140.00	90.66	9.52
13	Cl^-	mg/L	31.00	78.00	47.28	45.00	40.00	127.86	11.26
14	F^-	mg/L	0.04	0.60	0.33	0.30	0.30	0.01	0.10
15	SO_4^{2-}	mg/L	23.00	51.00	32.26	35.00	35.00	41.58	6.45
16	PO_4^{2-}	mg/L	0.02	0.75	0.17	0.18	0.05	0.02	0.13
17	NH_3	mg/L	0.00	1.59	0.14	0.00	0.00	0.09	0.30

µS/cm – Microsiemens per centimeter
mg/L – Milligrams per liter

mg/L to meq/L using the relationship described in Equation 1. The sum of cations comprising of the concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and Fe expressed in meq/L. The sum of anions comprising of the concentrations of parameters such as NO_3^-, HCO_3^-, Cl^-, F^-, SO_4^{2-}, PO_4^{2-} and NH_3 expressed in meq/L. The % diff in Table 3 was calculated using the Equation 2. The average % diff between the major ions in the studied samples was -1.602 meq/L. The maximum and minimum % diff values were found to be -4.531 meq/L and 0.120 meq/L respectively. As per Table 3, the samples having % diff more than ±2 meq/L are suspected to have improper measurements. The studied data have 14 samples exceeding the limiting difference value of ± 2 meq/L (Table 3). So, it was suggested that these samples needs to be reanalyzed for better results.

The calculated TDS values in Table 3 were computed using the Equation 3. The ratio between the calculated TDS and Measured TDS was computed for all the 50 samples and the ratio should fall between 1.0 and 1.2. It was found that this ratio satisfies the condition given in Equation 4 in all the sampled studied. The ratio between calculated TDS and EC was computed and presented in Table 3. This ratio satisfies the condition given in Equation 5 (between

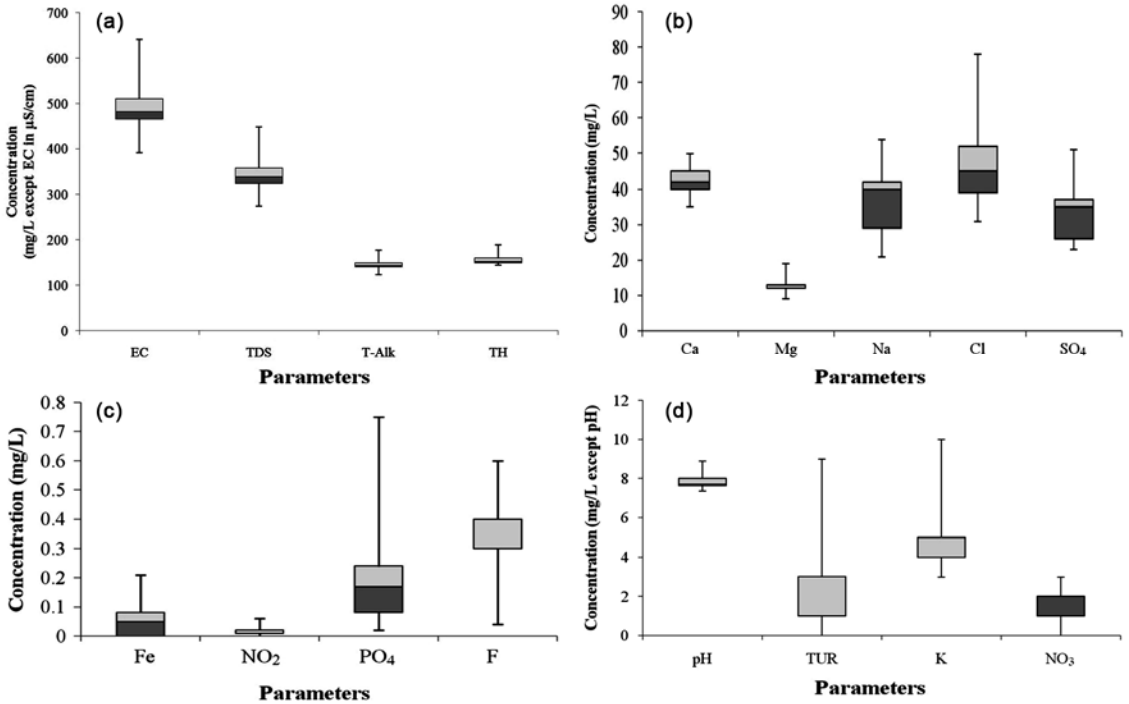

Fig. 1(a-d)— Box plots of various water quality parameters (a) EC, TDS, T-Alk and TH; (b) Ca^{2+}, Mg^{2+}, Na^{+}, Cl^- and SO_4^{2-}; (c)Fe, NO_2^-, PO_4^{2-} and F^- & (d) pH, Turbidity, K^+ and NO_3^-

Table 3 — Calculated parameters for checking the correctness of the analysis

S.No.	Sum of Cations (meq/L)	Sum of Anions (meq/L)	% diff (meq/L)	Calc. TDS (mg/L)	Calc. TDS/ meas.TDS	Calc. TDS/ EC	100*cation sum	0.9* EC	1.1*EC
1	4.276	4.984	-2.392	286.300	1.044	0.669	427.648	385.200	470.800
2	6.316	7.364	-2.407	419.300	1.068	0.653	631.638	577.800	706.200
3	5.039	5.813	-1.876	335.300	1.050	0.667	503.905	452.700	553.300
4	4.266	5.009	-2.759	285.300	1.055	0.663	426.639	387.000	473.000
5	4.463	5.126	-1.657	295.300	1.036	0.676	446.343	393.300	480.700
6	4.857	5.588	-1.742	322.300	1.043	0.671	485.719	432.000	528.000
7	4.731	5.380	-1.160	311.300	1.044	0.669	473.082	418.500	511.500
8	3.890	4.538	-2.435	259.300	1.057	0.661	388.997	352.800	431.200

(*Contd.*)

Table 3 — Calculated parameters for checking the correctness of the analysis (*Contd.*)

S.No.	Sum of Cations (meq/L)	Sum of Anions (meq/L)	% diff (meq/L)	Calc. TDS (mg/L)	Calc. TDS/ meas.TDS	Calc. TDS/ EC	100*cation sum	0.9* EC	1.1*EC
9	4.554	5.156	-0.940	300.300	1.039	0.673	455.401	401.400	490.600
10	4.391	5.176	-2.955	296.300	1.043	0.670	439.056	397.800	486.200
11	4.420	5.050	-1.394	291.300	1.047	0.668	441.996	392.400	479.600
12	4.438	5.088	-1.566	292.300	1.054	0.663	443.779	396.900	485.100
13	4.174	5.078	-4.531	287.300	1.048	0.667	417.402	387.900	474.100
14	4.396	5.061	-1.775	291.300	1.050	0.665	439.560	394.200	481.800
15	4.432	5.325	-3.908	303.300	1.058	0.661	443.189	413.100	504.900
16	4.872	5.738	-2.911	325.300	1.076	0.651	487.211	450.000	550.000
17	4.596	5.407	-2.857	309.300	1.054	0.664	459.560	419.400	512.600
18	4.789	5.438	-1.086	315.300	1.031	0.678	478.863	418.500	511.500
19	4.782	5.407	-0.874	314.300	1.034	0.676	478.216	418.500	511.500
20	4.743	5.407	-1.283	313.300	1.034	0.677	474.270	416.700	509.300
21	4.389	5.249	-3.677	299.300	1.046	0.640	438.907	421.200	514.800
22	4.865	5.538	-1.210	321.400	1.061	0.661	486.521	437.400	534.600
23	4.871	5.619	-1.874	324.400	1.054	0.665	487.066	439.200	536.800
24	5.342	5.976	-0.340	353.200	1.090	0.642	534.208	495.000	605.000
25	4.721	5.444	-1.856	314.400	1.072	0.654	472.137	432.900	529.100
26	5.890	6.555	-0.081	385.200	1.064	0.658	589.047	526.500	643.500
27	4.725	5.547	-2.751	318.400	1.071	0.654	472.503	438.300	535.700
28	5.173	5.762	-0.124	337.200	1.121	0.633	517.341	479.700	586.300
29	4.870	5.597	-1.689	323.400	1.061	0.660	487.030	441.000	539.000
30	5.186	5.806	-0.378	339.200	1.114	0.628	518.601	486.000	594.000
31	4.867	5.526	-1.081	320.400	1.077	0.540	486.736	533.700	652.300
32	5.200	5.737	0.354	334.400	1.068	0.657	520.039	458.100	559.900
33	4.794	5.518	-1.764	319.400	1.058	0.663	479.385	433.800	530.200
34	5.612	6.273	-0.299	363.500	1.065	0.657	561.204	497.700	608.300
35	5.130	5.846	-1.265	337.500	1.064	0.659	513.014	460.800	563.200
36	5.053	5.852	-2.072	336.500	1.061	0.660	505.261	459.000	561.000
37	5.536	6.487	-2.658	371.600	1.082	0.647	553.591	516.600	631.400
38	5.078	5.682	-0.351	331.400	1.062	0.659	507.786	452.700	553.300
39	4.935	5.506	-0.206	321.400	1.080	0.649	493.510	445.500	544.500
40	5.227	5.957	-1.268	345.500	1.071	0.654	522.715	475.200	580.800
41	4.887	5.417	0.120	317.400	1.052	0.665	488.696	429.300	524.700
42	4.915	5.638	-1.594	325.200	1.070	0.656	491.499	446.400	545.600
43	4.651	5.331	-1.555	309.400	1.070	0.653	465.144	426.600	521.400
44	4.809	5.512	-1.554	320.200	1.049	0.667	480.903	432.000	528.000
45	4.802	5.474	-1.281	317.040	1.060	0.661	480.154	432.000	528.000
46	5.167	5.767	-0.225	337.200	1.118	0.626	516.689	485.100	592.900
47	4.903	5.617	-1.529	325.400	1.054	0.664	490.301	441.000	539.000
48	5.288	6.129	-2.111	355.200	1.081	0.647	528.846	494.100	603.900
49	4.744	5.471	-1.861	316.400	1.062	0.659	474.420	432.000	528.000
50	5.203	5.832	-0.438	341.300	1.011	0.625	520.268	491.400	600.600

meq/L – Milliequivalents per liter
mg/L – Milligrams per liter

0.55 and 0.7) and therefore all the studied samples were good to be used for further analyses. The comparison between measured EC and ion sums were performed using Equation 6. The cation sums were taken for the calculation in this comparison and it was clear that all samples were found to be good in terms of its ion balance as per Equation 6.

Conclusion

This study elaborates the use of ion balancing methods for water quality data with a case study from Cauvery River water quality data. The distribution of data for each parameter was studied using box plots. The ion balancing study reveals that 14 samples were not fit during the calculation of % diff and it may be because of the ignorance of some other contributing ions in the calculations. All the fifty samples were satisfied the conditions of remaining ion balancing calculations. These calculations may be used as base work for further research on any water quality data interpretation studies.

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