Evaluation of monitoring data quality of precipitation chemistry in Russia with help of international QA/QC project

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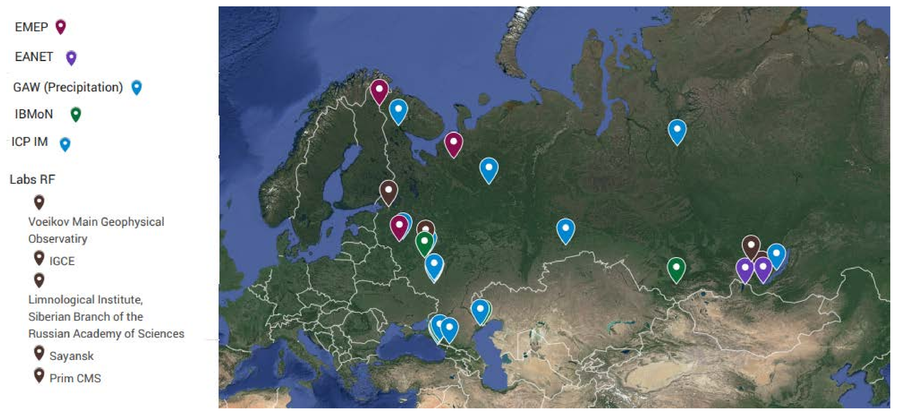
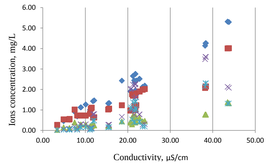
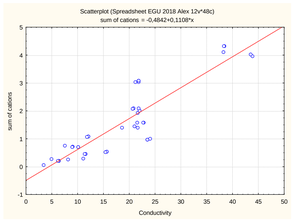
The assurance and precision of analytical data are the key requirements for environmental background pollution information as declared by all international monitoring networks.
As of 2017, there are several precipitation chemistry networks (PCNs) having operated under the umbrellas of national or international monitoring programs in the Russian territory with the provision of similar data which have to be harmonized and verified. To operate the networks and to analyze samples the number of regional laboratories were organized in some regions far from each other along with analytical centers of international programs (see a map). Five of them provide monitoring results for common international databases and, hence, are involved into the laboratory intercomparison studies (LIS) organized by QA/SAC-Americas within the WMO Global Atmosphere Watch (GAW). LIS is conducted twice per year (semi-annual) by exploring artificial “rain water” sample analysis of all recommended substances in each laboratory (WMO, 2017).

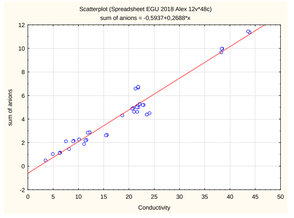


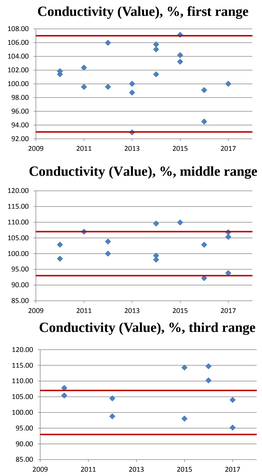
To evaluate operational level and progress of Russian PCN laboratories we analyzed the sets of LIS results conducted during 2010-2017. A number of criteria was used for the assessment of experimental results from each laboratory: accuracy (by difference between Expected and Reported values), precision (range of statistical variability), stability and progress (trend) of above ones for the period of investigation. We present the results of evaluation study summarized in tables and graphs taking into account different level values of prepared concentrations. The correspondent Data Quality Objectives (GAW, 2004) are also used to check appropriateness along the statistical evaluation of LIS performance by laboratories.

At the first stage, an approximate block of errors was identified graphically. True Value was chosen for baseline (100%) , Data Quality Objectives - for limits of acceptable deviations of measured values. Data array was divided into 3 parts based on the ranges of sample conductivity (EC). EC was selected as the general index of substance quantities in sample. The ranges are: lower (first one) - < 10 µS/cm, middle – from 10 to 20 µS/cm, higher (the third) - more than 20 µS/cm. According to the reported data, the most satisfactory results were obtained from LIN SB RAS.









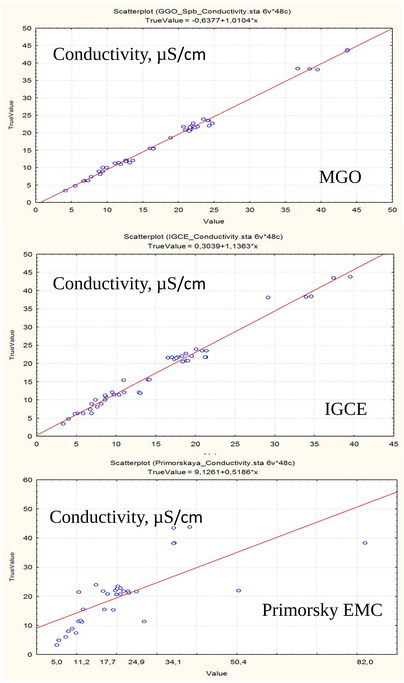
Precipitation Chemistry - Data Quality Objectives	
Measurement	DQO (before January 2018)
pH < 4.00	± 0.07 units
pH: 4.00 - 4.99	± 0.07 units
pH ≥ 5.00	± 0.07 units
conductivity	± 7%
acidity	± 25%
sulfate	± 7%
nitrate	± 7%
ammonium	± 7%
chloride	± 10%
sodium	± 10%
potassium	± 20%

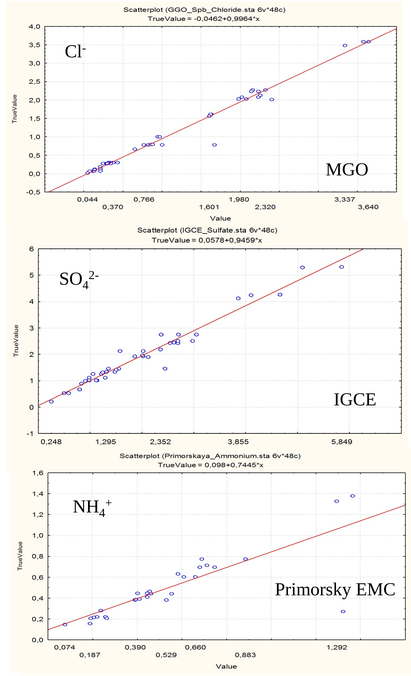
Measurement are marked as "dissatisfied" if deviation of its value from True Value is off acceptable range limits specified in Data Quality Objectives. The examples of EC results are presented on the picture above:
- *Red line* is DQO limits,
- *dots* are measurement values from Labs

Dots above upper DQO line or under lower one are classified and tagged as "dissatisfied".

Check of stability of measure was provided without separation into ranges. Main target of that part of investigation was to detect any significant changes in results and presence of a systematic error

Lab	Significance	Compounds	Brief description
MGO	95%	Nitrate	The most likely change from a small overstatement to understatement
	99%	Ammonium	The most likely change from a small understatement to overstatement
	95%	Sodium	The most likely change from a small overstatement to more considerable understatement
	95%	Calcium	The deterioration in the direction of a significant underestimation
IGCE	90%	Conductivity	A small change. Most likely there is no real change, and the reason is a variability in the results
LIN SB RAS	99%	Sulfate	A small change. Most likely there is no real change, and the reason is a variability in the results
	90%	Nitrate	A small change. Most likely there is no real change, and the reason is a variability in the results
	95%	Calcium	A small change. Most likely there is no real change, and the reason is a variability in the results
Primorsky EMC	95%	Nitrate	Change from a strong understatement to a significant overstatement
	90%	Sodium	Change from a small overestimation to understatement
	90%	Calcium	Improvement. Change from a strong overstatement to small overstatement
Sayansk PCLab	95%	Conductivity	A small change. Most likely there is no real change, and the reason is a variability in the results
	90%	Nitrate	A small change. Most likely there is no real change, and the reason is a variability in the results
	95%	Sodium	Improvement. Change from understatement
	95%	Potassium	Change from a small understatement to overstatement





Number of dissatisfied results, MGO (Main Geophysical Laboratory, S.Peterburg)									
	Conductivity	Sulfate	Nitrate	Ammonium	Chloride	Sodium	Potassium	Calcium	Magnesium
First range	7	7	4	8	8	10	7	7	7
Middle range	2	5	5	5	7	7	10	10	4
Third range(upper)	2	11	9	3	3	7	8	18	10
Number of samples	48	45	45	44	43	37	37	40	44

Number of dissatisfied results, LIN SB RAS (Limnological Institute, Irkutsk)									
	Conductivity	Sulfate	Nitrate	Ammonium	Chloride	Sodium	Potassium	Calcium	Magnesium
First range	4	3	0	8	1	0	1	5	3
Middle range	3	2	1	6	1	1	5	2	3
Third range(upper)	2	0	1	2	1	0	2	1	0
Number of samples	42	42	42	42	42	42	42	42	42

Number of dissatisfied results, IGCE (Institute of Global Climate and Ecology, Moscow)									
	Conductivity	Sulfate	Nitrate	Ammonium	Chloride	Sodium	Potassium	Calcium	Magnesium
First range	8	9	6	9	8	9	8	9	9
Middle range	14	8	5	13	6	12	10	14	9
Third range(upper)	18	10	10	14	10	12	11	16	9
Number of samples	45	42	42	39	42	39	39	39	39

Number of dissatisfied results, Primorsky EMC (Primorskiy Environmental Monitoring Centre, Vladivostok)									
	Conductivity	Sulfate	Nitrate	Ammonium	Chloride	Sodium	Potassium	Calcium	Magnesium
First range	4	5	5	6	7	7	6	6	7
Middle range	17	19	13	11	19	11	17	16	20
Third range(upper)	6	6	6	3	3	3	2	1	5
Number of samples	33	30	33	31	29	23	15	31	32

Number of dissatisfied results, Sayansk PCLab (Precipitation Chemistry Laboratory in Sayansk, Irkutsk region)								
	Conductivity	Sulfate	Nitrate	Ammonium	Chloride	Sodium	Potassium	Fluoride (optional)
First range	6	9	5	6	9	8	7	9
Middle range	5	8	5	5	6	11	10	11
Third range(upper)	6	9	3	4	2	13	11	5
Number of samples	42	40	42	41	39	36	30	39

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