

1 Basin of Small Rivers as an Indicator of the Environment State

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11 Abstract

12 **Background.** Small rivers are an important component of the natural environment. Water
13 resources of small rivers are part of the shared water resources and are often the main and
14 sometimes the only one source of local water.

15 Small rivers are the regulators of the water regime of the landscapes, the factors for maintaining
16 balance and redistribution of moisture.

17 The aim is analysis of interaction between parameters of the quality of the water environment like
18 conductivity and nitrates on the example of natural waters of small rivers.

19 Objects are small rivers Bist and Rosselle (Saardand lands, Germany) and Mertvovod (Mykolaiv
20 region, Ukraine).

21 **Methods.** We used the method of correlative analysis which is effective and efficient for the
22 determination of connections between the parameters of water quality that helps to identify sources
23 of pollution, as well as interpret phenomena, forecast the situation related to the change in the
24 quality of natural waters.

25 The hydrochemical monitoring data were obtained from autonomous automated stations that are
26 located on the rivers Bist, Rossel and Mertvovod. We investigated the following correlation
27 dependencies between such combinations of natural waters quality parameters: nitrates and
28 conductivity. Monitoring data are processed using software MS Excel; correlation dependence was
29 defined using the CORREL.

30 **Results.** Correlation value is changed in the range from -1 to $+1$ that demonstrates the indirect
31 and direct dependence between the selected parameters. If the value is closer to $+1$, this means the
32 presence of a strong connection, if closer to 0 – weak. The time periods for the calculation of the
33 correlation between the parameters of natural waters quality is selected: 4, 8, 16 and 24 hours
34 respectively. The following time periods allow the best to trace and predict changes in the natural
35 aquatic environment. Correlation analysis of the concentration of nitrates and conductivity showed
36 that for r. Bist and r. Rosselle dominates is the positive value of the correlation between the study
37 parameters, which proves their strong interaction. However, at certain concentrations of nitrate-

38 ions observed custom phenomenon of sharp decrease in correlation to the «-1», which is explained
39 by the Onsager equation, namely an excess concentration of nitrates is associated with erosion of
40 different types of fertilizers from the fields as a result of rainfall.

41 **Discussion.** Trend analysis of the studied indicators of Mertvovod water quality was conducted on
42 an average value of each indicator (pH, phosphates, nitrates, BOD, soluble oxygen). We used trend
43 analysis for Mertvovod because we did not have enough data in time. Found a significant increase
44 in phosphates with time. This can be explained by the arrival of various surface active substances
45 and, to a lesser extent, the lack of quality sewage treatment facilities. Positive changes are founded
46 in water object that is related to a decrease in the value of BOD.

47 **Keywords:** small rivers; correlation method; trend analysis; monitoring of natural waters; quality
48 indicators of the aquatic environment.

49 **Introduction**

50 Basin of a small river is a complex self-regulating system. Basin of small rivers is an indicator of
51 the environment state, due to the level of anthropogenic load which are landscapes, soils, surface
52 and underground water, flora and fauna, the atmosphere. Ecosystem of the small river first reacts
53 to changes in the interaction of the system «human-society-nature». So the actual remains are
54 monitoring of the small river condition (Vasenko, Ribalova, Poddashkin, 2010), (Klymenko,
55 Prishchepa, Voznyuk, 2006), (Mitryasova et al., 2016), (Rybalova, 2011).

56 The main feature of the small rivers is their close ties with the landscape. Small rivers are the
57 regulators of the water regime of the landscapes, the factors for maintaining balance and
58 redistribution of moisture, as well as the factors that determine the hydrological and hydro chemical
59 specific of medium and large rivers.

60 Purpose is an environmental analysis of the state of small rivers, to determine and analyze possible
61 impacts on the state of the water object.

62 Objects are small rivers Bist and Rosselle Saardand lands (Germany)and Mertvovod in Mykolaiv
63 region (Ukraine).

64 The subject is the hydro-chemical indexes such as COD, phosphates and nitrates conductivity,
65 nitrates of small rivers.

66 **Materials & Methods**

67 The following research methods were used: comparisons and analogies; analysis; observation;
68 synthesis; generalization. The following study programs were used for the study: Google Maps,
69 Microsoft Excel, Origin software. Calculations are made using the correlation formulas 1 and 2
70 (River Rossel, 2013), (Rybalova, 2011):

$$71 \quad r = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}. \quad (1)$$

$$72 \quad r = -1; +1,$$

73 where x, y are the numeric values of the variables, which set the correlation connection; where $\bar{x},$
74 \bar{y} – average arithmetic value.

$$75 \quad R = \sqrt{1 - (1 - r_{yx1}^2)(1 - r_{yx2/x1}^2)}, \quad (2)$$

76 $r = 0; +1,$

77 where r_{yx1} – doubles correlation coefficient;

78 $r_{yx2/x1}$ – partial correlation coefficient.

79 To describe the magnitude of the correlation coefficient are the following, which are presented in
80 table (Snedecor, Cochran, 1980):

81 Also in research we used such scientific methods: theoretical methods: analysis, synthesis,
82 monitoring, systematization, generalization (Mazlum, Ozer, Mazlum, 1999), (Mitryasova et al.,
83 2016), (Rybalova, 2011), (Snedecor, Cochran, 1980).

84 Table

85 **The interpretation of the correlation coefficient**

Value	The interpretation of the correlation coefficient
$\leq 0,2$	very weak
$\leq 0,5$	weak
$\leq 0,7$	average
$\leq 0,9$	high
$\geq 0,9$	very high

86
87 The value of the correlation varies between + 1 and -1, respectively, showing the direct and indirect
88 correlation dependency between selected parameters. If the value is closer to 1, then it means the
89 presence of a strong connection, and if the closer to 0, then the weak. If the correlation coefficient
90 is negative, it indicates the opposite: the higher the value of one variable, the lower the value of the
91 other.

92 Water monitoring station (Saardand lands, Germany) allows you to get the results of tests for the
93 determined water quality indicators every 5 minutes (fig. 1).

94 **The Object of the Research**

95 The research was carried out on the rivers Bist and river Rosselle. Bist is river, which flows in the
96 Saarland (Germany) and Lorraine (France). The total length of the River is 26 km, of which 16.2
97 kilometers in Germany. Catchment area is 113 km². The height of the leakage is 300 m. height of
98 the 185 m. River flow is 1,01 m³/s. The river has a low ability to regenerate.

99 The main pollutant of r. Bist in the upper and middle reaches are industrial discharges, the number
100 of which has increased in recent years. Besides anthropogenic load has increased due to the high
101 density of the population living along the river, and also as a result of agricultural use of the river
102 (River Bist, 2013), (River Rossel, 2013), (Water Quality Indicators, 2018).

103 Point sampling on the Bist is about 650 m to the mouth. Meteorological data is obtained from the
104 meteorological station, which is located in 1 kilometer from sampling. R. Rosselle rises about 300
105 meters above sea level. R. Rosselle originates East of Bushpon (France), the length of the river is
106 38 km, 33 km, of which occurs in France. Catchment area covers 203 km², is located at 322 m
107 above sea level. River basin consists of sands and rocks rich in Flint.



108
109 Fig. 1. Water monitoring station (Saardand lands, Germany) (Photo credit: Olena Mitryasova)

110 The river hard hit due to the extraction of coal. Mine and waste water discharged from coal industry
111 enterprises in the area of the upper reaches of the river. River flow is 2,2 m³/s (River Basin
112 Management, 2014), (Water Quality Indicators, 2018).

113 Another object is a small river Mertvovod in Mykolaiv region (Ukraine).

114 The length of the river is near 100 km, the area of the drainage basin is 1820 km². The river valley
115 is predominantly trapezoidal, width up to 3 km, depth up to 40-50 m. The floodplain is 200-300 m
116 wide, up to 1-1,5 km below the ground. The generator is twisted; its average width in the lower
117 reaches is up to 20 m. The slope of the river is 1,8 m/km (South Bug River Basin), (Quality
118 Measurements, 1997).

119 **The Research Results and Discussions**

120 The analysis of samples carried out for the following parameters: electrical conductivity of water
121 is an indicator of geological conditions in the water region, and also reflects the industrial load on
122 the water (Mazlum, Ozer, Mazlum, 1999), (Pohrebennyk, Romaniuk, 2013).

123 Conductivity (or specific conductance) of an electrolyte solution is a measure of its ability to
124 conduct electricity. Conductivity measurements are used routinely in many environmental
125 applications as a fast, inexpensive and reliable way of measuring the ionic content in a solution. In
126 many cases, conductivity is linked directly to the total dissolved solids. Specific electric
127 conductivity of thawing snow (60 mkSm/cm) approaches the conductivity of distilled water (15-
128 30 mkSm/cm). Mineral water have values of specific electrical conductivity from 160 mkSm/cm
129 to 750 mkSm/cm (Pohrebennyk, Romaniuk, 2013).

130 Electrical conductivity is a numerical expression of the capacity of a water solution to conduct
131 electrical current. Electric conductivity of natural water depends largely from the concentration of
132 dissolved mineral salts and temperature. Natural water is the solution mixtures of strong
133 electrolytes. The mineral portion of water make up ions: Na^+ , K^+ , Ca^{2+} , Cl^- , SO_4^{2-} , HCO_3^- . These
134 ions showed electrical conductivity of natural waters. The presence of other ions, such as Fe^{3+} ,
135 Fe^{2+} , Mn^{2+} , Al^{3+} , NO_3^- , HPO_4^- , H_2PO_4^- especially not affect into conductivity (Water Quality
136 Indicators, 2018).

137 The value of the conductivity shows the degree of mineralization of natural waters. Complications
138 arise when evaluating the total content of mineral substances (salinity) from specific electrical
139 conductivity is associated with different specific electrical conductivity of solutions of various salts
140 with increased electrical conductivity with increasing temperature. Conductivity value is roughly
141 measure the total concentration of electrolytes, mainly inorganic, and used in programs of
142 observations as the water environment for assessing salinity waters. Specific electrical conductivity
143 is a convenient total indicator of anthropogenic influence, is an indicator of geological conditions
144 and also reflects the industrial load onto water basin (South Bug River Basin).

145 Electric conductivity of natural waters depends on the concentration of dissolved mineral salts and
146 temperature. Pure water is characterized by a very low electrical conductivity, water saturated
147 chemical compounds characterized by high electrical conductivity.

148 Nitrates are an indicator that explains of eutrophication's reason; is used as an important indicator
149 of diffuse pollution by fertilizers (leaching from the soil), as well as the characteristics of the
150 sewage works. In fig. 2 shows the graph of correlation relationship between electrical conductivity
151 and NO_3^- .

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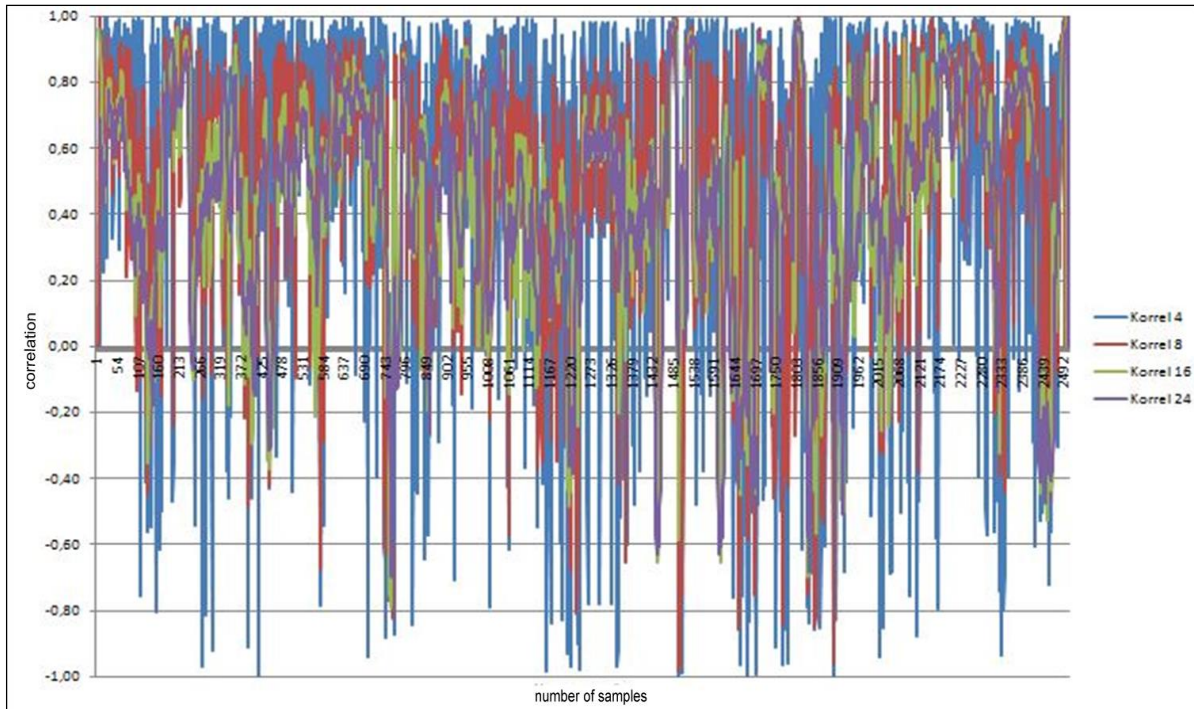


Fig. 2. Diagram of correlation between electrical conductivity and NO_3^-

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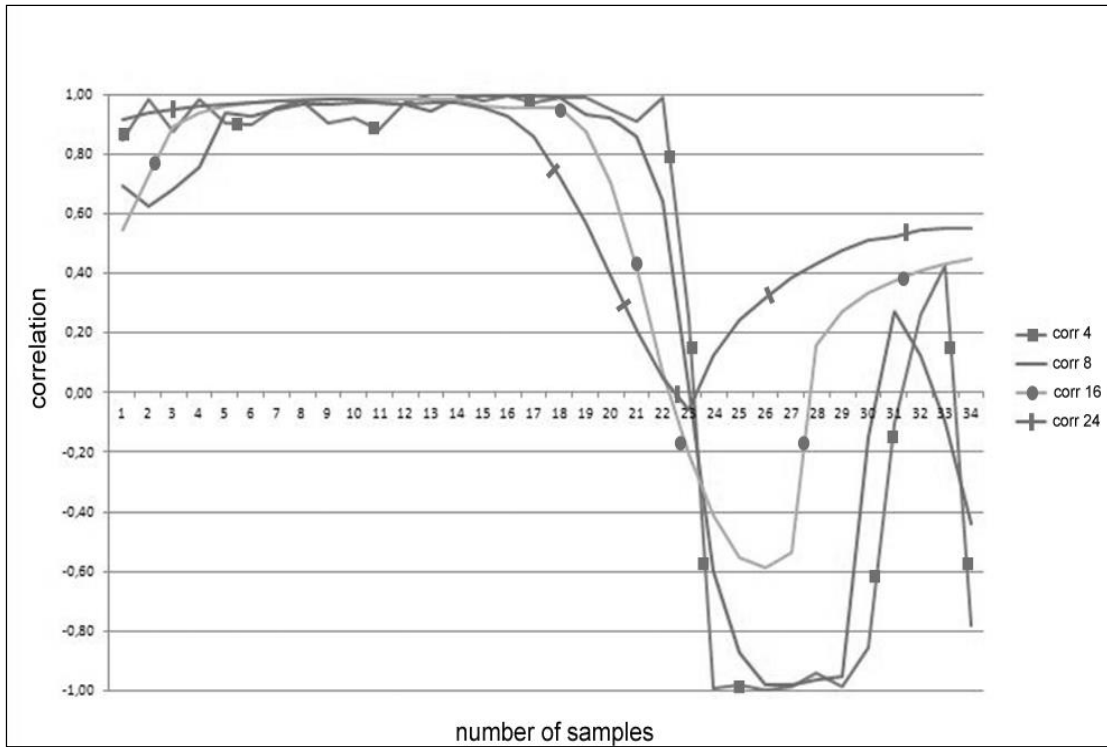
156 The fig. 3, which was investigated, is the electrical conductivity of natural water, which depends
157 on the concentration of dissolved mineral salts and temperature.

158 Fig. 3 exhibits a clear shift from the correlation value «+» to «-». Nitrate concentration gradually
159 increases and reaches a value of 6,5 mg/l (MPC \leq 5 mg/l), which leads to an increase in the
160 electrical conductivity of the water, which reaches 350 mkSm/cm (MPC 300mkSm/cm).

161 After samples №22 (fig. 3 and 4) observed custom phenomenon between the parameters. The
162 concentration of nitrates continues to increase with decreasing values of electrical conductivity of
163 the water environment.

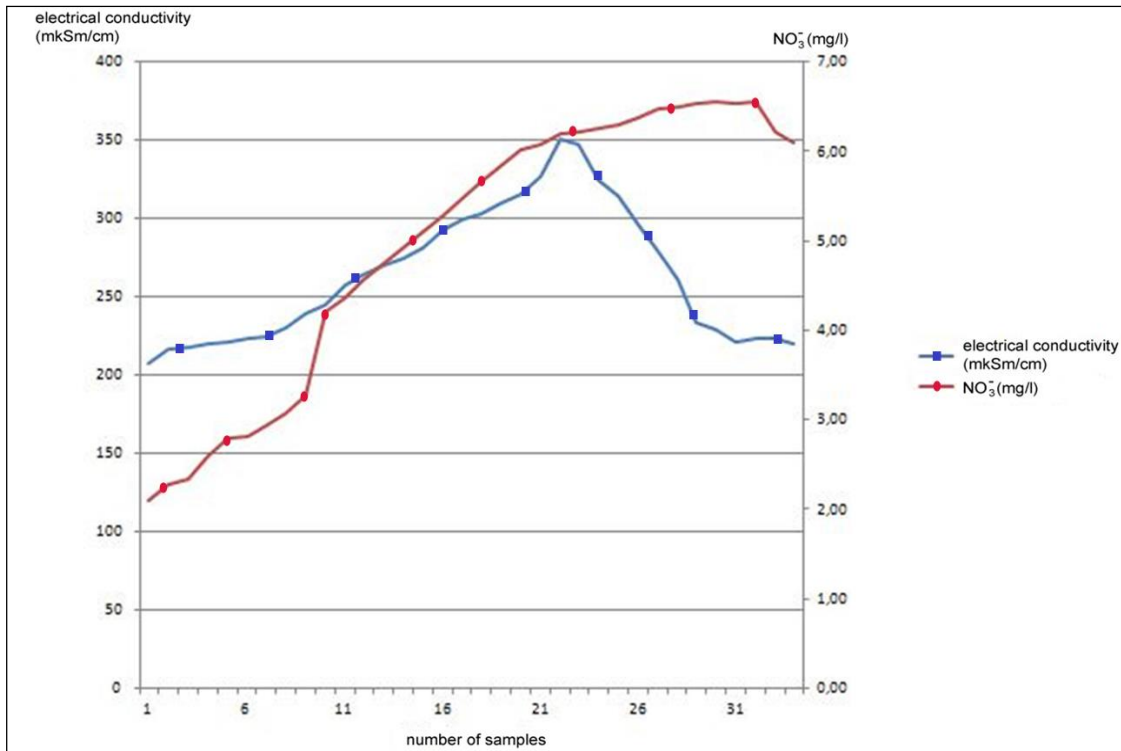
164 Dominant is the positive value of the correlation between the study parameters. Exception of this
165 dependence can be traced, starting with 22 tests and then, when the correlation between electrical
166 conductivity and concentration of nitrates is «-1». This pattern is a confirmation of the Onsager
167 equation, which proves that when increasing the concentration of relatively large size of nitrate-
168 ions decreases their mobility in water, which is the reason for the decreasing conductivity. It is an
169 excess concentration of nitrates is associated with erosion of different types of fertilizers from the
170 fields as a result of rainfall.

171 The correlation between electrical conductivity and nitrates in the river Rosselle, has mostly
172 positive nature, i.e. traced dependency, when the increase of nitrates in water leads to an increase
173 in electrical conductivity. However, the correlation between the tests is definitely a negative
174 character values of the correlation at this period reaches the "-1".



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Fig. 3. Graph the correlation dependence between electrical conductivity and NO_3^- (r. Bist)



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Fig. 4. Graph the relationship between electrical conductivity (mkSm/cm) and NO_3^- (mg/l) r. Bist

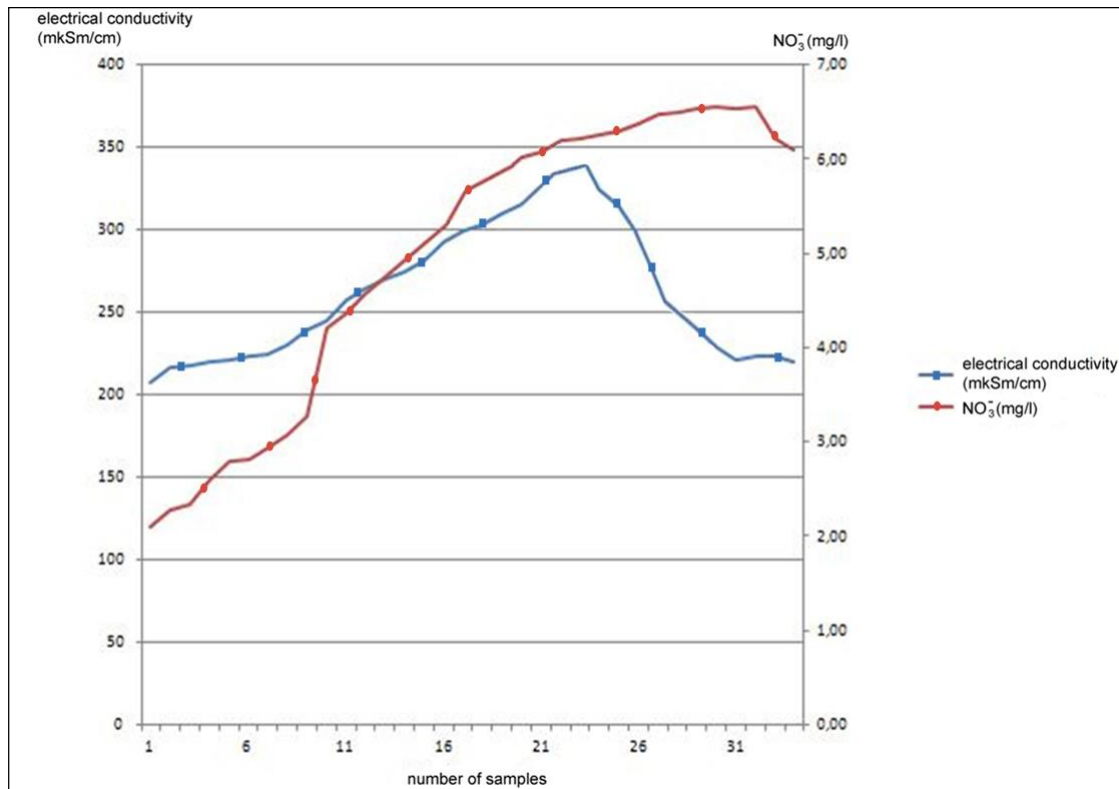
181 The increase in the concentration of nitrate increases the conductivity of the water to a certain
182 boundaries. Nitrate concentration reaches a level of 6 mg/l (MPC \leq 5 mg/l), which leads to an
183 increase in the electrical conductivity of the water, which reaches 350 mkSm/cm (MPC
184 300mkSm/cm).

185 Dependence of electrical conductivity of concentration has a maximum, and then the increasing of
186 the concentration of electrolyte aqueous solution leads to a decrease of the conductivity. In this
187 case, this amount to a maximum is 6mg/l, which is exceeding the maximum admissible values.

188 Electrical conductivity is determined by the amount of electricity that is transferred through the
189 cross-section of conductors. Conductivity depends on the nature of the electrolyte and the solvent,
190 temperature, concentration of the electrolyte. Electrical conductivity of solutions depends on the
191 number of ions in a unit volume of solution from u of mobility of these ions, i.e. from the ease with
192 which they move in an electric field.

193 Electrical conductance is caused by a number of carriers, i.e., ions, as well as the speed of their
194 movements. In the area of dilute electrolytes speed little depends from the concentration and
195 electrical conductance rises almost directly proportional to the concentration.

196 As the increasing of concentration interaction between the ions will be intensified, ion density of
197 the atmosphere will be increased, which leads to a decrease in velocity of the ions. This effect
198 begins to prevail over the increase in the number of ions, so at high concentrations the electrical
199 conductivity is reduced. After sample № 24 (fig. 4, 5) the concentration of nitrates continues is
200 increased, and the conductivity of the water environment is reduced.



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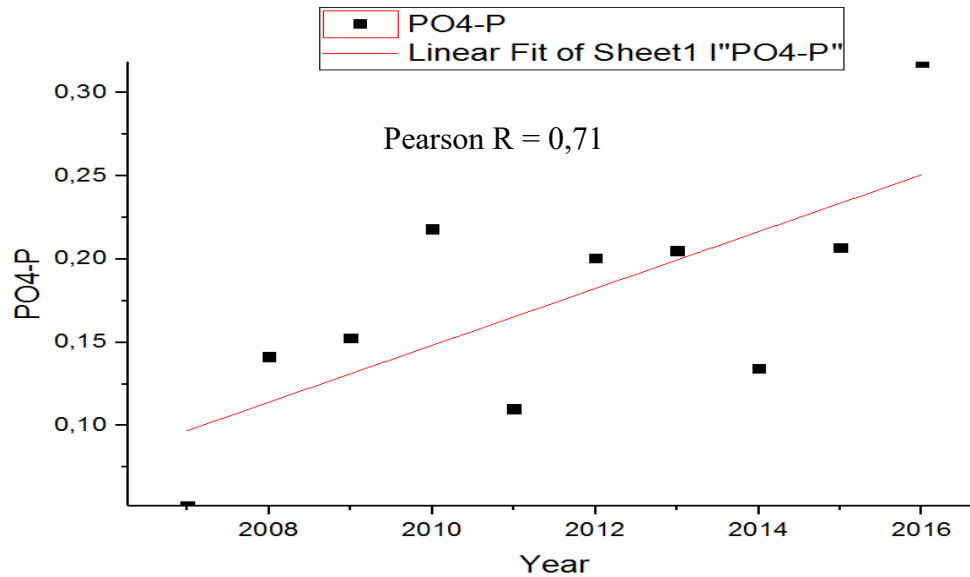
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Fig. 5. Graph the relationship between electrical conductivity (mkSm/cm)
and NO₃⁻ (mg/l) r. Rosselle

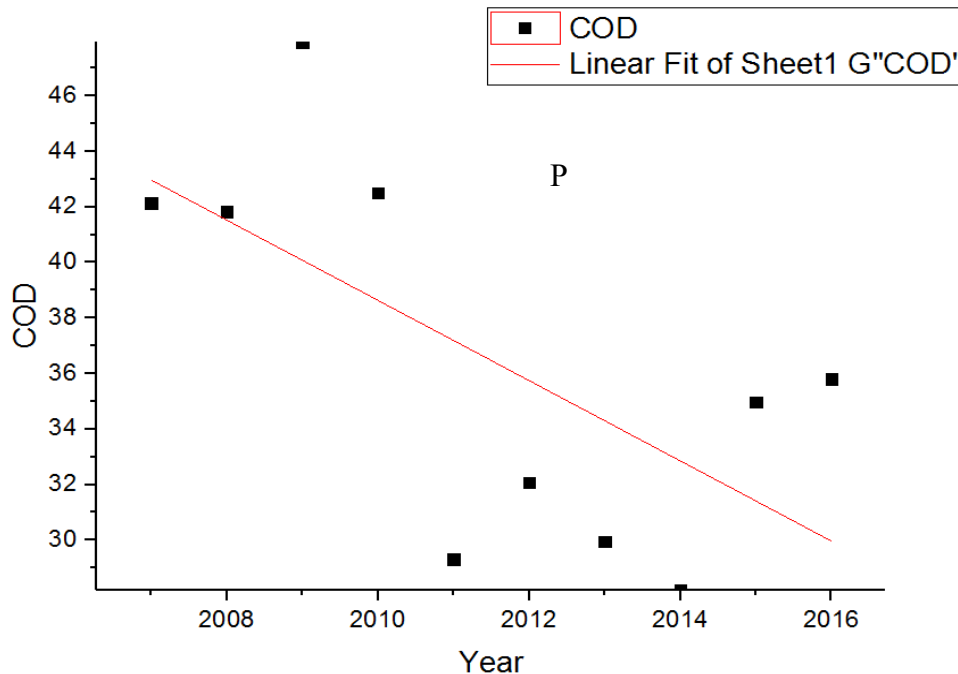
204 Trending analysis of the studied indicators of Mertvovod water quality was conducted on an
 205 average value of each index. We used trend analysis for Mertvovod because we did not have
 206 enough data in time. Found a significant increase in phosphates with age, with a coefficient of
 207 correlation $R=0,71$ (fig. 6), indicating that contamination of the water facility. This phenomenon
 208 can to explain by using of various detergents with waste dumping and to a greater extent with the
 209 lack of quality sewer facilities.

210 Positive changes are founded that is conect with decrease in the content of COD (fig. 7), which
 211 indicates about reduction in the use of oxygen on oxidation of inorganic and organic substances.



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Fig. 6. Dependence of concentration of phosphates with years



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Fig. 7. The dependence of the COD with years

217 **Conclusions**

218 The status of the small river is an indicator of the water security of natural surface water.

219 Large drainage basins carry the influence of many factors that gives the opportunity to identify and
220 predict events, therefore, for the prevention and suppression of sources of pollution of the water
221 environment of large rivers it is necessary to analyze in detail the state of water quality of small
222 rivers.

223 The method of correlative analysis is useful for the detection of custom periods between the
224 parameters of water quality, which further helps to identify sources of pollution, interpret
225 phenomena and predict the situation related to the change in the quality of the water environment.

226 Correlation analysis of the concentration of nitrates and conductivity showed that for r. Bist and r.
227 Rosselle dominates is the positive value of the correlation between the study parameters, which
228 proves their strong interaction. However, at certain concentrations of nitrate-ions observed custom
229 phenomenon of sharp decrease in correlation to the «-1», which is explained by the Onsager
230 equation, namely an excess concentration of nitrates is associated with erosion of different types
231 of fertilizers from the fields as a result of rainfall.

232 Using the data of correlative analysis, you can manage processes that occur in water basins.
233 Established and documented dependencies can be used not only for the study of rivers Bist and
234 Rosselle, as well as for any natural pools for the analysis and explanation of the processes that
235 occur in the aquatic environment.

236 Using of trend analysis for r. Mertvovod gave a clear idea about the change of each indicator over the
237 years. A significant increase by phosphates is detected, which is associated with the collection of
238 cleansers with domestic waters and more with the lack of quality sewer facilities. A significant
239 reduction of COD over the years is detected.

240 Further perspective is the study of the ways of reducing intake of phosphates to water facility by
241 the reconstruction and improvement of sewage. It is also relevant to further study the dependencies
242 between water quality indicators, as well as their interpretation.

243 **Acknowledgements**

244 We would kindly thank the department of inorganic and analytic chemistry of the Saarland
245 University (Germany) for the opportunity to conduct the experimental work in the framework of
246 the project DAAD.

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