**Posoli za pH**

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**1. Abstract**

In our project, we have tested the GLOBE protocol established method of measuring the pH levels and we have compared the measured electrical conductivity and pH value of the samples of the Kupa River and rainwater without the addition of table salt and with the addition of an appropriate amount of table salt.

We believe in the importance of choosing the best available method for measuring the exact pH values of precipitation since those values directly affect life forms in the earth and water, forests, crops and human health.

Our research question was: Will the addition of table salt to the tested sample significantly affect the measured electrical conductivity and pH value of the Kupa River and rainwater? Electrical conductivity was measured with a conductometer, and pH value with a pH meter and an universal pH indicator paper. We measured the pH value of the Kupa river sample once a week, but we measured rainwater when the amount of precipitation was at least 30 ml. To determine whether there were significant differences in the measured values of electrical conductivity and pH values in the salted and unsalted sample, we used statistical tests that showed that the addition of table salt to river water and rainwater significantly affects the measured electrical conductivity, thus not confirming our hypothesis. Also, tests showed that the addition of table salt to the samples did not significantly affect the measured pH value. We believe that this research should be expanded with a larger number of samples from different parts of the world due to the greater reliability of the obtained measurement results and then it could be said whether it is necessary to salt the sample before measuring the pH value.

Key words: pH value, precipitation, electrical conductivity, table salt

**2. Research question and hypothesis**

Media reports on the high levels of air pollution in the capital city, Zagreb, have prompted us to further test the GLOBE protocol established method of measuring the pH levels of precipitation, that are available on [globe.gov](http://globe.gov). Following the instructions listed in the GLOBE protocol to measure precipitations’ levels of pH it is necessary to first measure the electrical conductivity of the sample, and should that be under 200 μS/cm, table salt must be added to the sample and only then can we measure the pH levels. As we are already on a weekly basis measuring the pH levels of the river Kupa, we have noticed that when adding pH levels to the hydrological data base we also have the possibility of adding the levels of electrical conductivity, that is to say, the pH levels determined post adding the table salt to the samples. That got us curious and we wanted to research whether adding table salt will affect the pH levels.

We have set forth the research question: Will adding table salt to the sample significantly affect the measured electrical conductivity and pH levels of water collected from the river Kupa and rain water?

Our hypothesis is that the measured electrical conductivity and pH levels of both the original sample and the sample with the addition of table salt of river water and rain water will remain within the precise scope of the measuring instruments.

**3. Research methods**

We have measured the pH levels of solutions in two ways: using the pH metre HANNA instruments whose glass electrode contains a doped glass membrane and an inner reference electrode (Ag/AgCl) and inner solution (HCl 0,1 mol/dm3) with measuring precision of pH levels of 0,01, instrumental accuracy ±0,05 and universal pH Macherey-Nagel strips with a measuring scale 6,4 up to 8,6 with a subdivision of 0,2 measuring units. We have calibrated the pH meter prior to every application in calibration solutions pH= 4,01, pH= 6,86 and pH = 9,18. We have prepared calibration solutions by dissolving standard buffers in 250ml of destine water at 25°C.

We have measured pH levels of the river Kupa and rainwater. pH levels of the river Kupa we took once a week and for rainwater when the levels of precipitation were minimal 30ml. We have repeated every measuring three times.

The GLOBE protocol states that the amount of salt to be added before measuring the pH levels is determined by the volume of the sample. In order to determine the amount of salt needed we have have sketched circles 5 mm and 4 mm in diameter using the Geometer's Sketchpad dynamic geometry programme. If the sample size was 50 ml we would use the amount of salt needed to fill the circle 5 mm in diameter, and if the sample size was 30 ml then we would have used the amount of salt needed to fill the circle 4 mm in diameter.

Prior to measuring the pH levels, by using a conductometer (set to factory settings and can automatically adjust temperature) we have determined the quantity of total dissolved solids (TDS) in ppm, for every sample meaning the total quantity of ions in the sample both before adding salt and after the salt was added. The results were recalculated to electrical conductivity using the formula: electrical conductivity (μS/cm) = TDS (ppm) : 0,67.

We have calculated the mean value, the arithmetic value, of the results of measuring the electrical conductivity and pH values, by adding all the amounts and then dividing this sum by the number of measuring taken. In order to determine whether the mean value corresponds to the values determined by measuring the electrical conductivity and pH levels, we have also calculated the levels of deviations of the mean value and standard levels of deviation that occur when measuring each parameter. We have taken the calculated absolute value that deviates the most from the mean value to be the maximum absolute mistake.

In order to determine whether there are significant differences in the measured levels of electrical conductivity and pH levels in both salted and unsalted samples we have used statistical tests. Using the statistical tests we have tested the null hypothesis- there is no difference in the measured electrical conductivity and pH levels between the salted and unsalted samples. In order to test the null hypothesis, we have first done the F- test where we compared the deviations between the measured electrical conductivity and middle pH value levels. Following that we have conducted a t- test where we compared the measured mean levels of electrical conductivity and pH of both the salted and unsalted sample.

**4. Data representation and analysis**

The electrical conductivity is and indirect measure for the sum of total dissolved solids in the water. By determining the electrical conductivity in the water sample we are determining the ability of conducting electricity of our sample (glove.gov).

pH solution is experimentally determined using a universal indicator paper that shows a different colour for different pH levels. On a much more precise level the pH solution is determined by a pH meter which is actually a precise voltmeter that measures the difference in potential between the glass electrode submerged in a solution of unidentified pH levels and a standard electrode. The difference in these electrodes’ potentials depends on the concentration of oxonium ion H3O+ (aq) and is proportional to the pH.

Seeing as how only ions can conduct electricity in a solution, it can be concluded that pure water is dissociated. In pure water the H3O+(aq) and OH- (aq) ions are present only from water dissociation. By adding acid the level of oxonium ions H3O+ (aq) increases while the concentration of hydroxide ions OH- (aq) decreases. For practical reason chemists have introduced a separate scale to express the concentration of H3O+(aq) ions as determined by (pH = -log c(H3O+). The solutions where the concentration of H3O+ (aq) is equal to the concentration of (OH) aq are called neutral. From that we determine that neutral solutions’ pH is 7. For acidic solutions the pH is under 7 while in alkaline pH is over 7 (Sikirica, Korpar-Čolig 1991).

Saline solutions that are a result of neutralising strong acids and strong alkalines are always pH neutral. Natrium chloride is also a result of a reaction of strong hydrochloric acid and a strong natrium alkaline (Sikirica, Korpar-Čolig 1991).

**Table 1.**  Presentation of mean values and medial absolute mistake values of electrical conductivity and pH sample of the river Kupa

**Table 1.** Representation of the mean value of the measurement results and the mean absolute error of electrical conductivity and pH of the Kupa river sample

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| DATE | ELECTRICAL CONDUTIVITY WITHOUT SALT/ µS/cm | ELECTRICAL CONDUTIVITY WITH SALT/ µS/cm | Ph METER WITHOUT SALT | Ph METER WITH SALT | UNIVERSAL INDICATOR PAPER  SAMPLE WITHOUT SALT | UNIVERSAL INDICATOR PAPER  SAMPLE WITH SALT |
| 23.10.2019. | 183,3 ± 0,6 | 352,3 ± 0,6 | 8,17± 0,01 | 8,08±0,01 | 7,4± 0,0 | 7,2± 0,0 |
| 30.10.2019. | 175,7 ±0,6 | 349,3 ±0,6 | 8,21±0,01 | 8,22±0,00 | 7,2± 0,0 | 7,0± 0,0 |
| 6.11.2019. | 135,3±0,6 | 410,6±0,6 | 8,19±0,00 | 8,14±0,00 | 7,2± 0,0 | 7,0± 0,0 |
| 15.11.2019. | 191,6±0,6 | 384,0±0,0 | 8,17±0,01 | 8,13±0,01 | 7,4± 0,0 | 7,2± 0,0 |
| 20.11.2019. | 185,3±0,6 | 362±1,0 | 8,17±0,00 | 8,09±0,01 | 7,0± 0,0 | 7,0± 0,0 |
| 27.11.2019. | 145,3±0,6 | 345,3±1,2 | 8,21±0,00 | 8,26±0,00 | 7,2± 0,0 | 7,2± 0,0 |
| 4.12.2019. | 143,0±0,0 | 293,0±1,0 | 8,16±0,01 | 8,03±0,01 | 7,2± 0,0 | 7,2± 0,0 |
| 13.12.2019. | 140,6±1,2 | 403,0±1,0 | 8,22±0,00 | 8,20±0,00 | 7,4± 0,0 | 7,2± 0,0 |
| 18.12.2019. | 175,0±0,0 | 492,6±0,6 | 8,18±0,00 | 8,26±0,00 | 7,0± 0,0 | 7,2± 0,0 |
| 27.12.2019. | 136,0±1,0 | 400,3±0,6 | 8,36±0,00 | 8,29±0,01 | 7,0± 0,0 | 7,2± 0,0 |

We have measured the electrical conductivity of the river Kupa for ten time. The lowest measured value of electrical conductivity in a sample taken from the river Kupa was 135,3 µS/cm and the highest 191,6 µS/cm. By adding salt to the sample the level of electrical conductivity increases in all samples and at every measuring for more then 150 µS/cm.

Using the statistical F-test we have determined F= 5.39 > Fcritical one-tail = 3.1 which leads us to conclude that the deviation from the mean value of electrical conductivity is high for both the salted and the unsalted sample of the river Kupa. The T-test showed tstat=11,93 > tcritical two-tail= 2,18 which again leads us to conclude that there are significant differences between the mean values of electrical conductivity in both the salted and the unsalted sample.

**Figure 1.** Mean pH value of Kupa river samples before and after addition of salt

The lowest measured pH value of the unsalted sample was 8,16, and the highest 8,36. Adding the salt to the sample the lowest measured pH value was 8,03 and the highest 8,29. The biggest difference between the measured pH values of salted and unsalted sample was -0,09. Of our ten measuring, by adding salt, in the eight of them the pH value decreased and twice it increased. The measured pH values of all the samples taken from the river Kupa have been alkaline.

The lowest measured pH value of the unsalted sample tested with the universal indicator paper was 7,0 and the highest 7,4. By adding salt to the sample the lowest measured pH value was 7,0 and the highest 7,2. The biggest difference between the measured pH values of salted and unsalted sample was ± 0,2. Of our ten measuring, by adding salt, in five of them the pH value decreased, twice it increased and for three time it remained unchanged. The measured pH values of all the samples taken from the river Kupa have been alkaline.

The F-test of the measured pH value of the river Kupa using the pH metre showed F=2,29 < Fcritical one-tail =3,18 which indicates that the deviations from mean value between the salted and unsalted samples do not differentiate. The t test indicated tstat= -1,01 < tcritical two-tail= 2,18 which shows that there is no significant difference in the pH levels of both salted and the unsalted samples of the river Kupa when compared to its mean pH value.

The F-test of the measured pH value of the river Kupa using the universal indicator paper F=2,29 < Fcritical one-tail =3,188 which indicates that the deviations from mean value between the salted and unsalted samples do not differentiate. The t test indicated t stat= 1 < tcritical two-tail= 2,13 which shows that there is no significant difference in the pH levels of both salted and the unsalted samples of the river Kupa when compared to its mean pH value.

**Table 2**. Representation of the mean value of the results and the mean absolute error for the measurement of the electrical conductivity and pH of the rainwater sample

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| DATUM | ELECTRICAL CONDUCTIVITY WITHOUT SALT  µS/cm | ELECTRICAL CONDUCTIVITY WITH SALT  µS/cm | pH METER WITHOUT SALT | pH METER WITH SALT | UNIVERSAL INDICATOR PAPER SAMPLE WITHOUT SALT | UNIVERSAL INDICATOR PAPER SAMPLE WITH SALT |
| 30.10.2019. | 21,0±1,0 | 264,7±0,6 | 7,18±0,01 | 6,81±0,00 | 6,6±0,0 | 6,4±0,0 |
| 4.11.2019. | 15,0±1,0 | 277,6±0,6 | 6,98±0,00 | 6,68±0,00 | 6,4±0,0 | 6,4±0,0 |
| 6.11.2019. | 10,0±1,0 | 280,3±0,6 | 6,98±0,01 | 6,70±0,01 | 6,4±0,0 | 6,4±0,0 |
| 12.11.2019. | 35,3±0,6 | 310,0±1,0 | 6,93±0,01 | 6,74±0,00 | 6,4±0,0 | 6,6±0,0 |
| 13.11.2019. | 15,0±1,0 | 276,0±1,0 | 6,79±0,01 | 6,65±0,00 | 6,6±0,0 | 6,6±0,0 |
| 16.11.2019. | 28,3±0,6 | 251,3±0,6 | 6,91±0,00 | 6,78±0,00 | 6,6±0,0 | 6,6±0,0 |
| 17.11.2019 | 23,0±1,0 | 253,0±1,0 | 6,91±0,01 | 6,87±0,01 | 6,6±0,0 | 6,6±0,0 |
| 20.11.2019. | 21,0±1,0 | 254,6±0,6 | 6,58±0,00 | 6,75±0,01 | 6,4±0,0 | 6,4±0,0 |
| 21.11.2019. | 22,0±0,0 | 270,0±0,0 | 7,12±0,00 | 7,05±0,01 | 6,4±0,0 | 6,4±0,0 |
| 2.12.2019. | 43,0±0,6 | 337,0±0,0 | 7,21±0,01 | 7,12±0,01 | 6,4±0,0 | 6,4±0,0 |
| 3.12.2019. | 9,0±1,0 | 273,0±0,0 | 6,81±0,01 | 6,64±0,00 | 6,4±0,0 | 6,4±0,0 |
| 10.12.2019. | 10,6±0,6 | 278,6±0,6 | 7,28±0,01 | 7,00±0,00 | 6,4±0,0 | 6,4±0,0 |
| 14.12.2019. | 6,3±0,6 | 346,3±0,6 | 7,07±0,01 | 6,91±0,00 | 6,4± 0,0 | 6,4±0,0 |
| 21.12.2019. | 22,0±0,0 | 261,0±0,0 | 7,19±0,01 | 7,20±0,00 | 6,4±0,0 | 6,4±0,0 |
| 22.12.2019. | 9,3±0,6 | 342,0±0,0 | 7,23±0,00 | 7,24±0,00 | 6,4±0,0 | 6,4±0,0 |
| 23.12.2019. | 6,0±1,0 | 472,0±0,0 | 7,07±0,01 | 6,87±0,00 | 6,4±0,0 | 6,4±0,0 |

We have measured the electrical conductivity of rain water sixteen times. The lowest measured electrical conductivity of the unsalted sample was 6,0 µS/cm and the highest 43,0 µS/cm. Adding the salt to the sample increased the electrical conductivity in all of the samples and with every measuring the increase was more than 230 µS/cm.

Using the statistical F-test we have calculated F= 28,51 > Fcritical one-tail = 24,03 which indicates that the deviations from mean value between of the electrical conductivity in the salted and unsalted samples of rainwater differentiate significantly. T Test showed t stat=19,38 > t critical two-tail= 2,12 which indicates that the mean values of electrical conductivity in both salted and the unsalted samples differentiate significantly.

**Figure 2**. Mean value from pH of rainwater samples before and after addition of salt

The lowest measured pH value, using the pH metre, of the unsalted sample was 6,58 and the highest 7,28. Adding the salt to the sample the lowest measured pH value was 6,64 and the highest 7,24. The biggest difference between the measured pH values of salted and unsalted sample was -0,37. Of our sixteen measurings, by adding salt, in thirteen t of them the pH value decreased and thrice it increased. The measured pH values of all the samples of rainwater are slightly acidic.

The lowest measured pH value of the unsalted and salted sample tested with the universal indicator paper was 6,4 and the highest 6,6. The biggest difference between the measured pH values of salted and unsalted sample was ± 0,2. Of our sixteen measuring, by adding salt, once the pH value decreased, once it increased and for fourteen time it remained unchanged. The measured pH values of all the samples of rainwater are slightly acidic.

The F-test of the measured pH value of rainwater using the pH metre showed F=1,05 < Fcritical one-tail =2,40 which indicates that the deviations from mean value between the salted and unsalted samples do not differentiate. The t test indicated t stat= -2,05 < tcritical two-tail= 2,04 which shows that there is no significant difference in the pH levels of both salted and the unsalted samples of rainwater when compared to its mean pH value.

The F-test of the measured pH value of rainwater using the universal indicator paper showed that variations between the salted and the unsalted sample the same 0,008 so F=1 < Fcritical one-tail =2,04 which indicates that the deviations from mean value between the salted and unsalted samples do not differentiate.

1. **Discussion and conclusions**

By analysing our results of measuring the electrical conductivity of the river Kupa and rainwater we conclude that every time the electrical conductivity was less than 200 μS/cm so, according to GLOBE protocol, it was necessary to add table salt to the samples. After adding table salt the electrical conductivity increased in all of the samples.

Statistical tests showed that adding table salt to river water and rainwater affects the measured levels of electrical conductivity significantly, which states that we have not confirmed our hypothesis.

We conclude that adding table salt to the sample causes the salt to chemically breakdown to free ions and it increases their concentration which leads to significant increase of the electrical conductivity in the samples of both river water and rain water.

Statistical tests showed that adding table salt to the samples did not significantly affect the measured pH levels in both river water and rainwater which states that we have confirmed our hypothesis.

The accuracy of the results when pH is measured using pH metre or pH indicators, depends on the electrical conductivity. If the levels of electrical conductivity are below 200 μS/cm then there is a risk of the gathered data not being correct ([globe.gov](http://globe.gov)).

In order to determine the pH of the solution as precise as possible, other ions have to be present as well, in order to create a sufficient current conduction in order to be able to measure. When the ion concentration in the solution is too low the pH metre is slow to read and if the read is too slow then the values remain at the incorrect levels ([globe.gov](http://globe.gov)).

While conducting the measuring of pH levels, we have, subjectively, noticed that if the sample was unsalted the pH metre took a lot of time to determine the measured value.

We feel that the cause of the change in pH values was not the addition of salt to the sample since its water solution is pH neutral. By dissolving it in water hydrathized natrium and chloride ions occur. The ions do not react with water, so the concentration of oxonium H3O+ (aq) and hydroxide OH-(aq) ions does not change. (Sikirica, Korpar-Čolig 1991).

We have also noticed that when measuring pH levels of rainwater sample and the river Kupa sample using the universal pH indicator, the difference was always ±0,2 pH units both with unsalted and salted samples. Such a difference occurs because of the scale division since when measuring (subjectively speaking) one must assess the colour of the pH indicator with the colour it matches the best on the universal indicator paper. We think that using the pH metre is a more precise way to measure pH values.

Although the statistical tests showed that adding table salt to the samples did not significantly affect the measured pH levels of river water and rainwater we believe that this research should be expanded by using more samples from all over the world in order to a chief a higher level of reliability of the results and then we would be able to determine whether the sample should be salted before measuring the pH levels. We feel that the method with which the pH levels are measured is of great importance since pH levels of precipitation affect life in the ground and water, forests, crops and consequently human health.

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