

# International Journal of Sciences: Basic and Applied Research (IJSBAR)



ISSN 2307-4531  
(Print & Online)

<http://gssrr.org/index.php?journal=JournalOfBasicAndApplied>



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## Study on Some Pollutants in the Leather Industry: A Case Study in Albania

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### Abstract

In Albania, major environmental problems are linked with the wastewaters and solid wastes disposal in tanneries. River systems are the primary means for disposal of waste, especially the tannery effluents. The current study was carried out to assess some physical, chemical and microbiological parameters in tannery wastewaters, and consequently their risk into Osumi River water body. Determination of such parameters indicates in a way the pollution status of Osumi River by leather effluents and other anthropogenic activities that are discharged into river water. Furthermore the objective of this study was extended in determination on some parameters of air emissions in workplace within tanneries, such as ammonia, hydrogen sulfide, CO<sub>2</sub>, ethyl alcohol. Each effluent sample was analyzed for physical, chemical, and bacteriological parameters. All water quality parameters were estimated by standard methods. The range values mean, standard deviation, coefficient of variation, and threshold were calculated for each parameter. The results of this study showed that physico-chemical and microbiological parameters of tannery wastewater, such as pH, COD, ammonia ions, nitrate, phosphate, chloride, sulfate, TSS, TDS, H<sub>2</sub>S, chromium (VI), Escherichia Coli, and Streptococcus Faecalis exceeded the prescribed limits. Gaseous emissions posed no serious environmental impact and health hazards for the workers. However, problems were found to remain in the tannery wastewater. Therefore, the author recommends that be reduced to a permissible limit before they discharged into river water.

**Keywords:** Air emissions; Environmental impact; Leather effluents; Pollutants; Osumi River; Workplace.

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## **1. Introduction**

Industrial wastewaters vary widely in composition, strength, flow and volume. A typical industry that produces a significant volume of wastewater is the leather industry [12]. In tanneries, high quantities of water and chemicals are required, including sodium sulfite, basic chromium sulfate, ammonium sulfide, ammonium chloride, bactericides, sodium chloride, wetting agents, enzymes, etc [11]. It has been reported that only 20% of the chemicals used in the tanning process are absorbed by leather - the rest is released as waste [11]. Three categories of waste are emitted within the leather industry: wastewater (liquid), solid wastes (solids), and air emissions (gaseous). Data show that 50-150 liters of water is used for the conversion of 1 kg of raw skin into leather. After completion of the process, the same quantity is also drained out [7]. In most developing countries, tannery effluents are discharged into inland surface waters, causing them to become highly polluted in terms of chemical oxygen demand (COD), suspended solids, total dissolved solids, ammonium, sulfate, chloride, sulfide, chromium, and bacteria. Thus tannery wastewater is a serious threat to the environment [7]. Solid wastes include the remains of flesh, hair, fats, and proteins. Due to the bad smell they produce during their putrefaction and their harmful chemical content, untanned hide wastes have been found to have negative effects on the soil and water of the environment, into which they are discharged [6]. There are two types of gaseous emissions within tanneries: inside of them and outside of them. The first type of gaseous emission is produced from stacks of boilers and generators during the processing of leather. The second type of gaseous emission is related to hydrogen sulfide, ammonia and volatile organic compounds (VOC), odors, which are emitted during the process and into the surrounding area. These emissions may pose a health hazard for tannery workers when their values exceed the required limits. High levels of pollutants in air emissions have a direct negative impact on human health, such as asthma, chronic bronchitis, allergy, skin irritation, decreasing lung function, etc [22]. In developing countries, such as Albania, all types of emissions from tanneries, are generally not treated or only partially treated [21]. In Albania, major environmental problems are linked with the tannery waste. In total, there are 17 tanneries [21] and many of them carry out tanning operations locally (i.e. "wet-blue" leather chrome tanned) [15]. River systems are the primary means for disposal of waste, especially, tannery effluents. These effluents greatly pollute the receiving body of water, because they can alter the physical, chemical and biological nature of it [4]. Water pollution can have a deleterious effect on the plant and animal species that are native to the given area. Each of the three types of pollution, are not mutually exclusive, entire ecosystems are often impacted and possibly destroyed [22]. The current study was conducted to analyze physical, chemical and microbiological parameters of tannery wastewaters, and their effect on the Osumi River in Berati, Albania. Determination of such parameters, directly illustrates the negative effect tannery effluents have on the river. Osumi River passes through the city of Berati and plays an important role in the aesthetics of the city. Furthermore the objective of this study was extended to determine various parameters of air emissions within the workplace of tanneries, such as ammonia, hydrogen sulfide, CO<sub>2</sub>, and ethyl alcohol.

## **2. Materials and Methods**

### *2.1 Study area*

The study area was comprised of two tanneries in the region of Berati, Albania. One was located in a suburb of the city, and the other was located in the village of Vodica, approximately 5 km away from the city. The suburban tannery regularly carries out activities in a building that has great capacity. It is situated at a distance of 300-350 m from the river bank. The rural tannery is older and less active; it is positioned about 200-250 m from the Vodica Brook, a branch of the Osumi River. In both tanneries, the different hides of animals are worked out at the stage of "wet-blue leather chrome tanned."

## 2.2 Sample collection

The study was conducted during 2012- 2013. Three sampling stations were established: Station 1 (St.1) was the main drain of tanneries wastewaters. The samples were collected three-four times a month, in one liter polyethylene bottles, rinsed with water sample before the sampling. Different wastewaters were generated at different times. Thus, effluent characteristics vary significantly. Most of the samples were collected from the tannery within the city, because of the infrequent rate of production of the other tannery in Vodica. Station 2 (St.2) was located where tannery effluents were discharged into the Osumi River waters. Station 3(St.3) was, where tannery effluents were discharged into the Vodica brook. After collection, samples were transported into cooler boxes within a laboratory.

## 2.3 Analysis methods

Each effluent sample was analyzed for physical, chemical, and bacteriological parameters. All water quality parameters were estimated by standard methods. pH was determined by a "Selecta" pH-meter. Total alkalinity was determined with the standard method [24]. COD was analyzed with the permanganate index [25]; (note that dilution is applied in many cases). Ammonia ions were determined by the Nesslerization method [24]. Chlorides were analyzed with the standard method of titration (Argentometria) [24]. Nitrate ions and phosphates were determined with Photometric Test Kits /2, 6 dimethylphenol and ammonium molybdate. TSS and TDS were determined with filtration and the gravimetric method [24]. Sulfate analysis was performed by precipitation with barium chloride to filtered effluent [24]. H<sub>2</sub>S was determined by titration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> [26]. Chromium (VI) was determined with Photometric Test Kits/reaction with diphenylcarbazide. E. Coli and St. Faecalis were determined with the dilution method with multiple tubes [20]. Indoor air emissions were analyzed by short-term detector tubes (MSA/ Auer; SIGMA- ALDRICH).The obtained data were subjected to descriptive statistical analysis (95% confidence limit). The range values mean, standard deviation, coefficient of variation, and threshold were calculated for each parameter.

## 3. Results and Discussions

Table 1. Characterisation of tanneries wastewaters at Station 1.

| Parameters                                       | Minimum | Maximum | Mean    | Median  | Standard Deviation | Coefficient of Variation | Threshold X+ 2S |
|--|---------|---------|---------|---------|--------------------|--------------------------|-----------------|
| pH   | 9.8     | 11      | 9.5     | 9.3     | 0.59               | 0.06                     | 10.68           |
| Total Alkalinity (mg/L CaCO <sub>2</sub> )       | 123     | 600     | 236.16  | 210     | 104.19             | 0.44                     | 444.54          |
| Ammonia ions NH <sub>4</sub> <sup>+</sup> (mg/L) | 1.5     | 30      | 8.79    | 7.5     | 6.24               | 0.7                      | 21.27           |
| Nitrate ions NO <sub>3</sub> <sup>-</sup> (mg/L) | 5       | 70      | 32.7    | 25      | 21.21              | 0.65                     | 75.12           |
| Phosphates (mg/L)                                | 0.1     | 20      | 7.44    | 5       | 6.29               | 0.84                     | 20.02           |
| Chloride (mg/L)                                  | 97.72   | 30205   | 3859.63 | 1932.25 | 6352.72            | 1.64                     | 16565.07        |
| COD (mg/L O <sub>2</sub> )                       | 88      | 2560    | 510.14  | 312     | 572.29             | 1.12                     | 1654.72         |
| Sulfate (mg/L)                                   | 53.49   | 2492.04 | 675.23  | 365     | 681.12             | 1.008                    | 2037.47         |
| TSS (mg/L)                                       | 41      | 9955    | 1912.18 | 796     | 2728.75            | 1.43                     | 7369.7          |
| TDS (mg/L)                                       | 918     | 31295   | 5877.36 | 3687    | 6844.66            | 1.16                     | 19566.7         |
| Chromium (VI) (mg/L)                             | 0.1     | 0.5     | 0.2     | 0.2     | 0.095              | 0.47                     | 0.39            |
| H <sub>2</sub> S gas (mg/L)                      | 115.6   | 935     | 297     | 178.5   | 214                | 0.72                     | 725             |
| Iron ions (mg/L)                                 | 0.01    | 0.8     | 0.27    | 0.06    | 0.34               | 1.25                     | 0.95            |
| Fe <sup>2+</sup> /Fe <sup>3+</sup>               |         |         |         |         |                    |                          |                 |
| Faecal coliform                                  | 1609    | > 1609  | > 1609  | 1609    | 0                  | 0                        | >1609           |
| E. Coli (MPN <sup>+</sup> )                      |         |         |         |         |                    |                          |                 |
| St. Faecalis(MPN)                                | 918     | 1609    | > 975   | 918     | 195.1              | 0.2                      | >1365           |

Table 2. Characterisation of tannery wastewaters at Station 2.

| Parameters  | Minimum | Maximum | Mean    | Median | Standard Deviation | Coefficient of Variation | Threshold X + 2S |
|---|---------|---------|---------|--------|--------------------|--------------------------|------------------|
| PH  | 7.8     | 10.5    | 8.63    | 8.6    | 0.756              | 0.09                     | 10.14            |
| Total Alkalinity (mg/L CaCO <sub>3</sub> )          | 65      | 460     | 141.87  | 79     | 130.47             | 0.91                     | 402.81           |
| Ammonia ions NH <sub>4</sub> <sup>+</sup> (mg/L)    | 0.16    | 15      | 3.69    | 2      | 4.62               | 1.25                     | 12.92            |
| Nitrate ions NO <sub>3</sub> <sup>-</sup> (mg/L)    | 1       | 50      | 17.68   | 15     | 15.25              | 0.86                     | 48.18            |
| Phosphates (mg/L)                                   | 0.05    | 7       | 2.17    | 2      | 1.83               | 0.84                     | 5.83             |
| Chloride (mg/L)                                     | 17.72   | 1949.7  | 392.95  | 170.16 | 524.77             | 1.33                     | 1442.49          |
| COD (mg/L O <sub>2</sub> )                          | 3.2     | 286     | 99.35   | 64.4   | 96.63              | 0.97                     | 292.61           |
| Sulfate (mg/L)                                      | 12.34   | 288.87  | 114.33  | 72.27  | 94.91              | 0.83                     | 304.15           |
| TSS (mg/L)  | 17      | 18926   | 1963.73 | 242.5  | 4949.96            | 2.52                     | 11863.65         |
| TDS (mg/L)  | 87.8    | 4471    | 1035.67 | 607    | 1158.95            | 1.1                      | 3353.57          |
| Chromium (VI) (mg/L)                                | 0.05    | 0.2     | 0.12    | 0.1    | 0.051              | 0.42                     | 0.22             |
| H <sub>2</sub> S gas (mg/L)                         | 68      | 374     | 173.21  | 131    | 94.25              | 0.54                     | 361.71           |
| Iron ions (mg/L) Fe <sup>2+</sup> /Fe <sup>3+</sup> | 0.01    | 0.7     | 0.12    | 0.02   | 0.2                | 1.66                     | 0.52             |
| Fecal coliform E.Coli (MPN <sup>4</sup> )           | 918     | > 1609  | 1436.25 | 1609   | 309.02             | 0.21                     | 2054.29          |
| St. Faecalis(MPN)                                   | 542     | > 918   | 777     | 918    | 188                | 0.24                     | 1153             |

Table 3. Characterisation of tannery wastewaters at Station 3.

| Parameters  | Minimum | Maximum | Mean    | Median | Standard Deviation | Coefficient of Variation | Threshold X + 2S |
|---|---------|---------|---------|--------|--------------------|--------------------------|------------------|
| PH  | 7.8     | 9       | 8.3     | 8.2    | 0.35               | 0.04                     | 9.01             |
| Total Alkalinity (mg/L CaCO <sub>3</sub> )          | 61      | 145     | 83.56   | 80     | 16.17              | 0.2                      | 115.9            |
| Ammonia ions NH <sub>4</sub> <sup>+</sup> (mg/L)    | 0.1     | 3       | 0.53    | 0.25   | 0.68               | 1.28                     | 1.89             |
| Nitrate ions NO <sub>3</sub> <sup>-</sup> (mg/L)    | 0.5     | 10      | 3.88    | 3      | 3.14               | 0.8                      | 10.16            |
| Phosphates (mg/L)                                   | 0.05    | 3       | 0.93    | 0.5    | 0.89               | 0.95                     | 2.71             |
| Chloride (mg/L)                                     | 21.27   | 1169.85 | 204.79  | 49.68  | 300.66             | 1.47                     | 806.11           |
| COD (mg/L O <sub>2</sub> )                          | 4.8     | 74.4    | 37.9    | 48.2   | 29.85              | 0.78                     | 97.6             |
| Sulfate (mg/L)                                      | 2.86    | 182     | 57.96   | 42.38  | 51.68              | 0.89                     | 161.32           |
| TSS (mg/L)  | 9       | 37522   | 1761.24 | 88     | 7488.83            | 4.25                     | 16738.9          |
| TDS (mg/L)  | 74      | 1955    | 613.11  | 455    | 547.29             | 0.89                     | 1707.69          |
| Chromium (VI) (mg/L)                                | 0       | 0.15    | 0.037   | 0.01   | 0.043              | 1.15                     | 0.12             |
| H <sub>2</sub> S gas (mg/L)                         | 0       | 170     | 51.82   | 34     | 55.23              | 1.06                     | 162.28           |
| Iron ions (mg/L) Fe <sup>2+</sup> /Fe <sup>3+</sup> | 0       | 0.2     | 0.021   | 0.01   | 0.042              | 2                        | 0.1              |
| Fecal coliform E.Coli (MPN <sup>4</sup> )           | 542     | > 1609  | 1317.56 | 1609   | 371.5              | 0.28                     | 2060.56          |
| St. Faecalis(MPN)                                   | 240     | 918     | 732.7   | 918    | 223.49             | 0.3                      | 1179.68          |

Table 4. Some parameters of indoor air emissions in tannery.

| Parameters  | Minimum | Maximum | Mean    | Median | Standard Deviation | Coefficient of Variation | Threshold X+ 2S |
|---|---------|---------|---------|--------|--------------------|--------------------------|-----------------|
| Temp. °C  | 19.7    | 29.5    | 23.53   | 23.25  | 2.8                | 0.118                    | 29.13           |
| Rel. Humidity (%)                                     | 65      | 78      | 73.69   | 74     | 3.61               | 0.048                    | 80.9            |
| CO <sub>2</sub> (mg/m <sup>3</sup> )                  | 1830    | 5490    | 3648.56 | 3477   | 1044.79            | 0.28                     | 5738.14         |
| NH <sub>3</sub> (mg/m <sup>3</sup> )                  | 0.35    | 8.4     | 2.19    | 1.4    | 2.047              | 0.93                     | 6.28            |
| H <sub>2</sub> S (mg/m <sup>3</sup> )                 | 0.14    | 14.1    | 2.91    | 1.41   | 4.46               | 1.53                     | 11.83           |
| C <sub>2</sub> H <sub>5</sub> OH (mg/m <sup>3</sup> ) | 361     | 855     | 616.47  | 532    | 179.62             | 0.29                     | 975.71          |

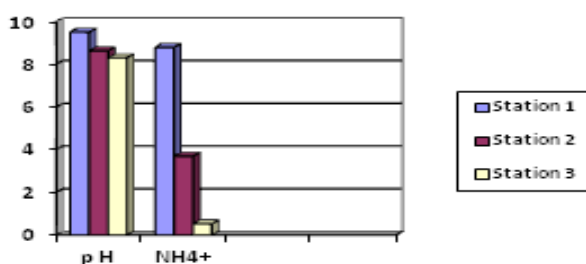


Fig 1. Variation of average pH and NH<sub>4</sub><sup>+</sup> values at three sampling stations.

This study showed that pH ranged from 9.8- 11mg/L at St.1, 7.8- 10.5mg/L at St. 2 , and 7.8-9 mg/L at St.3. High pH values of tannery wastewaters at St.1 and St.2, were probably found as a result of the amount of chemicals used during leather processing, which are very high compared to standards [16, 17]. Mean values of ammonia ions in tannery effluents vary from 1.5-30 mg/L at St.1, 0.16-15 mg/L at St.2 and 0.1-3 mg/L at St.3. Mean values were 8.79mg/L, 3.69 mg/L, 0.53 mg/L, at the three stations, respectively These results exceeded many times the permissible limits of tannery wastewaters [16, 17, 18] . This fact presents a crucial issue related to the condition of surface waters at pH 8.5 and temperature 25°C, 40% of NH<sub>4</sub><sup>+</sup> returns in NH<sub>3</sub>, which is 300-400 times more toxic than NH<sub>4</sub><sup>+</sup>, to fish and other aquatic life [12, 14]. High concentration of microbial nutrients promotes an after-growth of significantly high coli form types and other microbial forms, such as Escherichia Coli and Streptococcus Faecalis [4]. E.Coli MPN varies from 1609- > 1609 at St.1, 918- >1609 at St.2, and 542- > 1609 at St.3. St. Faecalis MPN varies from 918- 1609 at St.1, 542- > 918 at St.2, 240- 918 at St.3.The presence of E.Coli and St. Faecalis indicates faecal contamination of surface waters, high alkalinity and ammonia are favourable conditions for their growth [4]. The mean values of E.Coli MPN (> 1609, 1436.25, 1317.56) and St. Faecalis MPN (> 975, 777,732.7) at the three stations, exceed the standard prescribed limits [17]. Temperature values ranged from 13.5°C- 33°C at St.1, the mean value was 23.39°C; at St.2 the temperature varied from 16°C-29°C and had a mean value of 21.6°C; at St.3, the temperature ranged from 13.5°C-30°C with a mean value of 23.6°C. Temperature values at St.1 were higher compared to the temperature values at St.2 and St.3, but all mean temperature values at the three stations were near the permissible limits for surface waters [18]. Total alkalinity values ranged 123-600 mg/L CaCO<sub>3</sub> at St.1, 65-460 mg/L CaCO<sub>3</sub> at St.2, and 61-145 mg/L CaCO<sub>3</sub> at St.3. Mean values were 236.16 mg/L CaCO<sub>3</sub>, 141.87 mg/L CaCO<sub>3</sub>, and 83.56 mg/L CaCO<sub>3</sub>, at St.1, St.2 and St.3, respectively. Total alkalinity values at St.1 were higher compared to

St.1 and St.2. This is due to the alkaline nature of tannery wastewaters. Low p H values at St.2 and St.3 can be attributed to the dilution of the wastewater by the river.

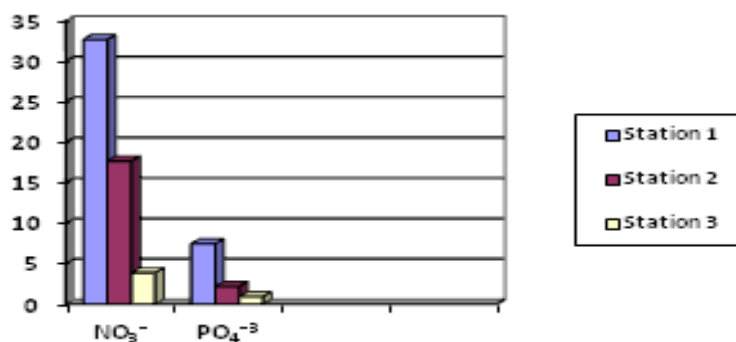


Fig. 2. Variation of mean NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>-3</sup> values at three sampling stations.

Nitrate and phosphate values were significantly higher in tannery effluents. They ranged from 5-70mg/L and the mean value was 32.7 mg/L for nitrate, and phosphate ranged from 0.1-20 mg/L, mean value was 7.44 mg/L at St.1. These high levels of nitrate and phosphate might have occurred as a result of tannery effluents containing nitrogen and phosphorus as a part of the structure of different chemicals used during leather processing [1]. These values did not meet the standard values for the discharged tannery effluents into rivers [16, 17]. Nitrate and phosphate levels dropped at St.2, nitrate ranged 1-50 mg/L, mean value was 17.68mg/L, phosphate ranged 0.05- 7mg/L, mean value was 2.17mg/L. Their levels were low relative to St.1, because they were diluted by river waters. However, they were still higher compared to standards [16, 17, and 18]. Nitrate values ranged from 0.5-10mg/L with a mean value of 3.88mg/L. Phosphates ranged from 0.05-3mg/L and had a mean value of 0.93mg/L at St.3. These values are lower compared to St.1 and St.2 and fell within the range set up limits [16, 17], but still higher than the permissible limits for surface waters [18]. The low levels of nitrate and phosphate at St.3 were due to the dilution and lower amount of tannery effluents that discharged irregularly into the Vodica stream. Fig.3 illustrates how chloride ranged from 97.72-30205mg/L and had a mean value of 3859.63mg/L at St.1, 17.72 – 1949.7 mg/L, mean value was 392.95 mg/L at St.2, recorded values of chloride at St.3 ranged 21.27-1169.85 mg/L, mean value was 204.79 mg/L. High levels of chloride at St.1 were due to large amounts of common salts used in hide and skin preservation or possibly the pickling process in tanneries [9]. Lower values of chloride at St.2 and St.3 were due to the dilution of tannery effluents by river waters and the lower amount of tannery effluents discharged into the brook. High chloride content in the effluents can affect aquatic plants and certain species of animals [5]. Chloride levels at St.1 exceeded the limit set by [17]. Chloride values at St.2 were lower compared with [17], but higher compared with the limit set by USEPA [10]. Conversely, chloride values at St.3 fell within all the permissible limits [16, 17, and 10]. TSS varied from 41-9955mg/L and had a mean value of 1912.18 mg/L at St.1. The TSS level ranged from 17-18926mg/L with a mean value of 1963.73 at St.2. Recorded values of TSS varied from 9-37522mg/L and had a mean value of 1761.24mg/L at St.3. Suspended matter ( i.e. lime, hair, flesh, etc) of tannery effluents can make surface waters turbid as they slowly settle to the bottom. Both processes create unfavorable conditions for aquatic life [12]. At St.2, TSS values were higher compared to TSS values at St.1. This may have occurred as a result of soil erosion and different anthropogenic activities. Suspended matter is a crucial problem for all surface waters in Albania. TSS mean values were lower than TSS values at St.1 and St.2, but the maximum value at St.3 exceeded the maximum TSS values in two stations. This fact can be explained by higher soil erosion, since the samples were collected during rainy conditions. TSS values in three stations exceeded many times all permissible limits [10, 16, 17, and 18].

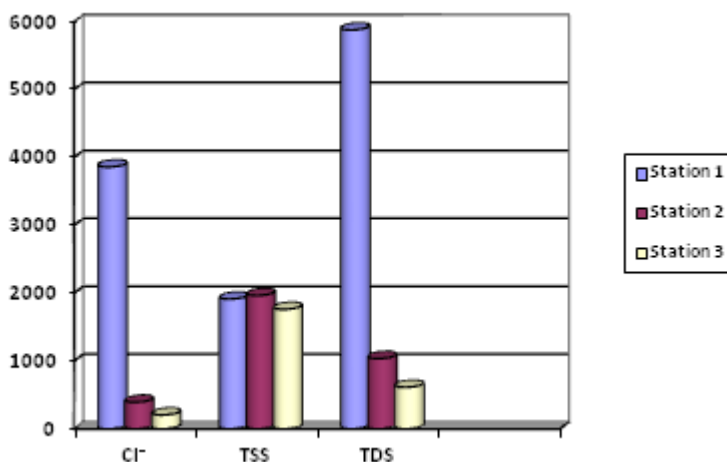


Fig. 3. Variation in average chloride, TSS, TDS values between three sampling stations

The concentration of total dissolved solid ( TDS) varied from 918-31295mg/L and had a mean value of 5877.36mg/L at St.1, 87.8-4471mg/L, and a mean value of 1035.67 mg/L at St.2, and 74-1955mg/L with a mean value of 613.11mg/L at St.3. A high value of TDS at St.1 was the result of many dissolved chemicals used in the tannery. Mineral tannery wastewater that is discharged on land, will affect the soil productivity and quality of surface waters, consequently affecting the aquatic ecosystem [12]. Concentration of TDS dropped at St.2 due to the dilution with river water. The lower value of TDS at St.3 was due to the dilution with the stream and lower amount of tannery wastewaters that discharged irregularly into the brook. TDS values in three stations were significantly above the prescribed limit for surface waters [10]. Fig.4 represents the range of COD values 88-2560 mg/L O<sub>2</sub>, mean value was 510.14mg/L O<sub>2</sub> at St.1, 3.2-286mg/L O<sub>2</sub>, mean value 99.35mg/LO<sub>2</sub> at St.2, 4.8-74.4mg/L O<sub>2</sub>, mean value 37.9mg/LO<sub>2</sub> at St.3. A high level of COD was found at St.1 due the complexity of tannery effluents, which depends on the chemicals used in different leather making processes and their rate of biodegradability [9]. There were many fluctuations in St.2 and St.3, which probably depended on the amount of tannery effluents that were discharged into the river. COD levels at St.1 were above the limits [16, 17], whereas COD values at St.2 and St.3 were within the permissible limit [16, 17]. However, they were still above the limit set by [10], for supporting fish and aquatic life in river waters. High values of sulfate at St.1 ranged from 53.49-2492.04mg/L and had a mean value of 675.23mg/L. This was not surprising, because they are compounds of tannery effluents, emanating from the use of sulfuric acid or products with high sodium sulfate content [1]. The sulfate levels dropped at St.2 12.34-288.87mg/L, mean value was 114.33mg/L, due to dilution by river waters. At St.3 sulfate levels ranged from 2.86-182mg/L with a mean value of 57.96mg/L, due to dilution with stream and lower amount of effluents discharged into stream. Sulfate levels at St.1 exceeded all the limits and were within norms at St.2 and St.3 [10, 17]. Sulfide in tannery effluents releases hydrogen sulfide gas, which has an objectionable smell even in trace amounts. It is highly toxic for many forms of life. Higher concentrations may also be lethal to fish [7]. H<sub>2</sub>S gasses ranged from 115.6-935mg/L and had a mean value of 297 mg/L at St.1, 68-373mg/L with mean value of 173.21mg/L at St.2, and 0-170mg/L with mean value of 51.82mg/L at St.3. H<sub>2</sub>S gas values at the three stations greatly exceeded the limit [16, 17]. Fluctuations at St.3 were due to irregular activity of the tannery in Vodica village.

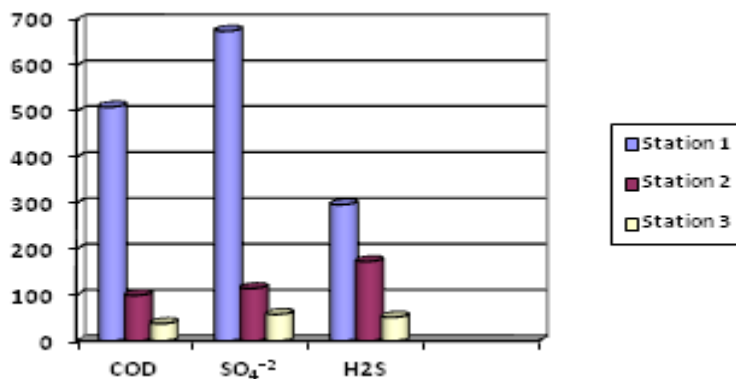


Fig. 4. Variation of average COD, SO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>S between three sampling stations.

Fig. 5 shows the values of chromium hexavalent in three stations, at St.1 they ranged from 0.1-0.5 mg/L with a mean value of 0.2mg/L, at St.2 0.05-0.2mg/L, mean value was 0.12mg/L, at St.3 0-0.15mg/L with a mean value of 0.037mg/L. Higher values of chromium (VI) at St.1 may be attributed to the use of chromium sulfate, which is the basic tanning chemical [7]. The chromium (VI) level was lower at St.2 due to the dilution of river water. And it was lower at St.3 due to dilution with stream and irregular discharged effluents. At St.1 and St.2 chromium levels were above the limit; at St.3, the chromium level was below the limit [16, 17]. The sensitivity to chromium of different species of aquatic organisms varies greatly. Chromium (VI) is a strong oxidizing agent meaning, it is very toxic; it deactivates cellular proteins [6] and the effect is accumulative [9]. Values of iron ions ranged from 0.01 to 0.8 mg/L at St.1, 0.01-0.7mg/L at St.2, and 0-0.2mg/L at St.3. Mean values were found as follows; 0.27mg/L at St.1, 0.12mg/L at St.2, 0.021mg/L at St.3, as shown in Fig.5. The relatively high concentrations of iron, especially at St.1, might be attributed to the fact that some of the chemicals used in the tanning process contain high levels of iron [1]. Lower values of iron at St.2 and St.3 may be due to the dilution into river water. In three stations, concentrations of iron were above the limit [18] for surface waters.

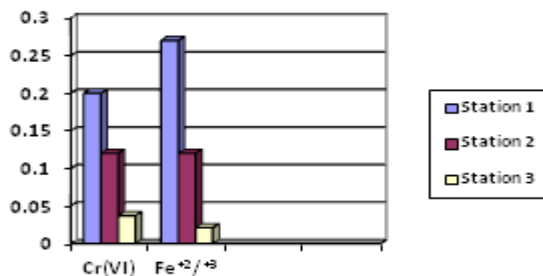


Fig. 5. Variation of mean Cr (VI), iron ions values between three sampling stations.

Furthermore, this study aimed to investigate some parameters related to the microclimate, such as temperature, CO<sub>2</sub>, humidity, and emissions of some gases, such as H<sub>2</sub>S and NH<sub>3</sub>, which are released during leather processing in working environment within tannery. Range and mean values of all parameters of the microclimate are represented in Table 4. Temperature ranged from 19.7-29.5°C and had a mean value of 23.5°C. Relative Humidity ranged from 65-78% with a mean value of 73.7%. CO<sub>2</sub> emissions ranged from 1830-5490mg/m<sup>3</sup> with a mean value of 3648.56 mg/m<sup>3</sup>. Temperature values were within the prescribed limit [19], Humidity values, however, were above the limit [19]. This may be due to the water vapors that were released during leather processing as well as weather conditions. Values of CO<sub>2</sub> emissions were within the limit [19]; this may have been due to efficient ventilation of the tannery building. C<sub>2</sub>H<sub>5</sub>OH emissions ranged from 361-855mg/m<sup>3</sup> with a mean value of 616.47mg/m<sup>3</sup>. Its values were within



the limit [19], although Ethyl Alcohol is not classifiable to cause cancer following occupational exposure. Chronic health effects occur at some time after exposure to Ethyl Alcohol [23].

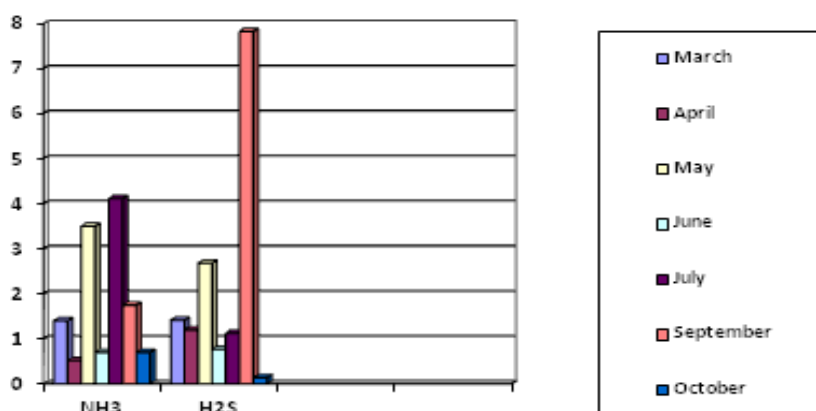


Fig. 6. Monthly fluctuation of NH<sub>3</sub>, H<sub>2</sub>S emissions in workplace within tannery.

As shown in Fig.6, H<sub>2</sub>S and NH<sub>3</sub> emissions values were within the limit [19]. They ranged from 0.14-14.1mg/m<sup>3</sup> with a mean value of 2.91mg/m<sup>3</sup> for H<sub>2</sub>S, and 0.35-8.4mg/m<sup>3</sup> with a mean value of 2.19mg/m<sup>3</sup> for ammonia, which are emitted during delimiting and unhairing, hydrogen sulfide is released during unhairing as a derivate of sodium sulfide. Also, H<sub>2</sub>S is released due to the conversion of alkaline sulfate to hydrogen sulfide at low pH levels (less than 8) [8]. Gastrointestinal, skin diseases, respiratory illnesses, anemia, and headaches were ranked as the health problems most frequently occurring among the workers in this industry [23]. In the concrete case there was no such evidence of these health problems.

#### 4. Conclusion

This study showed that physic-chemical and microbiological parameters of tannery wastewaters at St.1, such as pH, COD, ammonia ions, nitrate, phosphate, chloride, sulfate, TSS, TDS, H<sub>2</sub>S, chromium (VI), Escherichia Coli and Streptococcus Faecalis exceeded the prescribed limits [16, 17]. Lower values of these parameters at St.2 and St.3 were due to dilution of tannery effluents in river water and irregular discharge of effluents into the Vodica stream. Gaseous emissions were well within the limit [19] and posed no serious environmental impact or health hazard for the workers. Significant problems remain within tannery wastewaters, due to their chemical composition and properties. Therefore, these wastes must be reduced to a permissible limit before they are discharged. Control and reduction of organic waste during the treatment of effluents, as well as substitution of hazardous chemicals, are points that should be considered when trying to improve the environmental performance of leather processing in tanneries.

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