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Water quality of the river Váh - Ružomberok (Slovakia), experience after 35-year water treatment

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Abstract: The chemistry of the water in the river Váh in the town of Ružomberok was examined. The waste water treatment plant (WWTP) in Ružomberok was built between 1977 and 1982. It was constructed as a joint WWTP for the town sewage as well as for the treatment of industrial waste water. Industrial waste water in the area is primarily a byproduct of the pulp and paper industry near the town, with Mondi SCP producing approximately 600 000 tons of paper and 100 000 tons of pulp for sale each year. Water testing was performed at six sampling sites; four upriver and two downriver from the treatment station. Samples were collected between September 2011 and January 2017. In total 429 samples were analysed, 70 -72 from each site. A significant increase in water pollution was discovered in Hrboltová, downriver from the WWTP. Significantly higher values of total dissolved solids (TDS), conductivity (COND), chemical oxygen demand (COD), salinity, sulphates and other chemical compounds were found downriver from the WWTP. We hypothesize this is a result of insufficient waste water treatment of water used in the production of pulp and paper. Mondi SCP, currently owns the treatment complex, and is also a large industrial contributer in the area. Our data confirms that following 30 years of operation, the plant may require restoration to effectively treat the water going forward.

Key words: water quality, river Váh, water pollution, paper and pulp production

Introduction

The river Váh in Slovakia is a major affluent of the Danube River. At 402 km long and with a basin of 19 696 km^2, Váh is the longest river in the Slovak republic. The region surrounding the river Váh is characterised by the presence of many industrial sources of pollution, including paper, pharmaceutical, automobile, metalworking, and wood and leather processing complexes. Similarly, the environment near the river is also affected by highly developed regional agriculture, well-developed industrial centres and settlements along its riverbanks (Halmo *et al.* 2009).

The pulp and paper industry is the 5th most energy consumptive industries in the world; accounting for more than 4% of worldwide industrial energy consumption. During the pulp and paper production process, a huge amount of waste is produced. It is estimated that about 500 million tons of paper will be produced per year in 2020. Three main raw materials are used in the pulp industry – non-wood fibres, and both hard and soft wood materials. Waste and wastewaters are a byproduct of both the pulp and bleaching processes. Additionally, 100 million kilograms of toxins are released bythis industry into the environment every year (Ince *et al.* 2011). Solid waste from different parts of the pulp and paper production process are listed in Table 1 below. Table 2 includes types of air pollutants from these production processes.

Mondi SCP, a.s. Ružomberok is a part of the Mondi Group, and produces uncoated fine paper. It is an integrated papermaking factory. Mondi is the biggest employer in this region and one of Slovakia's top 10 exporters of paper. Producing 8 million sheets per hour, each year it yields more than 620 000 tons and exports approximately 32 000 trucks of paper. In 2010, Mondi SCP won the PPI Award for Environmental strategy of year (Mondi SCP 2011). Mondi SCP also produces around 13 500 tons of dangerous waste per year which is stored on the Mondi SCP Ružomberok and WWTP Hrboltová grounds. Waste products are comprised of wood waste, dregs, sulphuric acid, hydrochloric acid, nitric acid and many others (Mondi 2016).

The basic function of wastewater treatment is to speed up the natural processes by which water is purified. There are two basic stages in the treatment of wastes - primary and secondary. During the primary stage, solids settle and can be removed from wastewater. The secondary stage uses biological processes to further purify wastewater. Sometimes these mechanical and biological processes are combined (EPA 1998), as is the case with the treatment plant in Hrboltová. 75% of wastewater treated is a byproduct of the pulp and paper mill, and 25% is municipal wastewater from Ružomberok and the surrounding area. The process of sedimentation of dregs, mechanical cleaning, oxygenating in the biological cisterns, filtrating in the filter bearing and the retaining of

Source	**Waste Type**	**Waste Characteristic**
Wastewater Treatment Plant	Sludge	Organic fraction consists of wood fibres and biosludge. Inorganic fraction consists of clay, calcium carbonate, and other materials 20 - 60 % solid content ph = 7
Caustic Process	Dregs, muds	Green liquid dregs consisting of non – reactive metals and insoluble materials; lime mud
Power Boiler	Ash	Inorganic compounds
Paper Mill	Sludge	Colour waste and fiber clay including slowly biodegradable organics such as cellulose, wood fibers and lignin

Table 1. Solid wastes types and sources from pulp and paper mills (Ince *et al.* 2011).

Source	**Major Pollutants**
Pulping Process	VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, methyl ethyl ketone. (MEK)) Reduced sulphur compounds (TRS) Organo-chlorine compounds
Bleaching	VOCs (acetone, methylene chloride, chloroform, MEK, chloromethane, trichloroethane)
Wastewater Treatment Plant	VOCs (terpenes, alcohols, phenols, methanol, acetone, chloroform, MEK)
Power Boiler	SO2, Nox, fly ash, coarse particulates
Evaporator	Evaporator nonconcondensibles (TRS, volatile organic compounds: alcohols, terpenes, phenols)
Recovery Furnance	Fine particulates, TRS, SO2, Nox
Calcining (Lime Clin)	Fine and Coarse particulates

Table 2. Air pollutant sources and types from pulp and paper mills (Ince *et al.* 2011).

dregs, (which are then energetically evaluated) all takes place at this location (Sika 2013).

Primary treatment, which includes screening and grit removal, is carried out at the start of the treatment process. Primary treatment includes removing solid objects as well as oil and grease, which impede efficient wastewater treatment and are unwanted in the final biosolid product. Primary treatment also reduces the biochemical oxygen demand of the wastewater. Biochemical oxygen demand is a measure of the strength or pollution potential of the wastewater (Watercare 2016).

Secondary treatment is used to convert dissolved and suspended pollutants into a form that can be removed, producing a relatively highly treated effluent. Secondary treatment normally utilizes biological treatment processes followed by settling tanks and removes nearly 85% of the biochemical oxygen demand and TSS in wastewater (www.cctexas.com 2016). Biological wastewater treatmeant began in the early twentieth century and is now foundational to wastewater treatment worldwide. It involves confining naturally occurring bacteria at much higher concentrations in tanks. These bacteria, together with protozoa and other microbes, are collectively referred to as activated sludge. The bacteria remove small organic carbon molecules by consuming them. Then, the bacteria grow, and the wastewater is cleansed. The treated wastewater or effluent can then be discharged to receiving waters (Davies 2005).

While the concept is simple, control of the treatment process can be very complex, because of the large number of variables that can affect it. As a result of variation in the composition of bacterial flora in the treatment tanks, as well as in the sewage passing into the plant, the influent can show variations in chemical composition, flow rate, pH, and temperature. Many municipal plants also have to contend with surge flows of rainwater following storms. Plants treating industrial wastewater must cope with both chemicals that are slowly degradable, as well as more toxic chemicals that inhibit the function of the activated sludge bacteria. High concentrations of toxins can produce a toxic shock that kills the bacteria. When this happens the plant may pass untreated effluent directly into the environment, until the dead bacteria have been removed from the tanks and new bacterial ‘seed’ is introduced (Davies 2005).

New pollutants have placed additional stress on wastewater treatment systems. Today’s pollutants, including heavy metals, chemical compounds, and toxic substances, are more difficult to remove from water. The increasing need to reuse water calls for better wastewater treatment. These challenges are being met through better methods of removing pollutants at treatment plants, or through prevention of pollution at the source. To return more usable water to receiving lakes and streams, new methods for removing pollutants are being developed. Advanced waste treatment techniques in use or

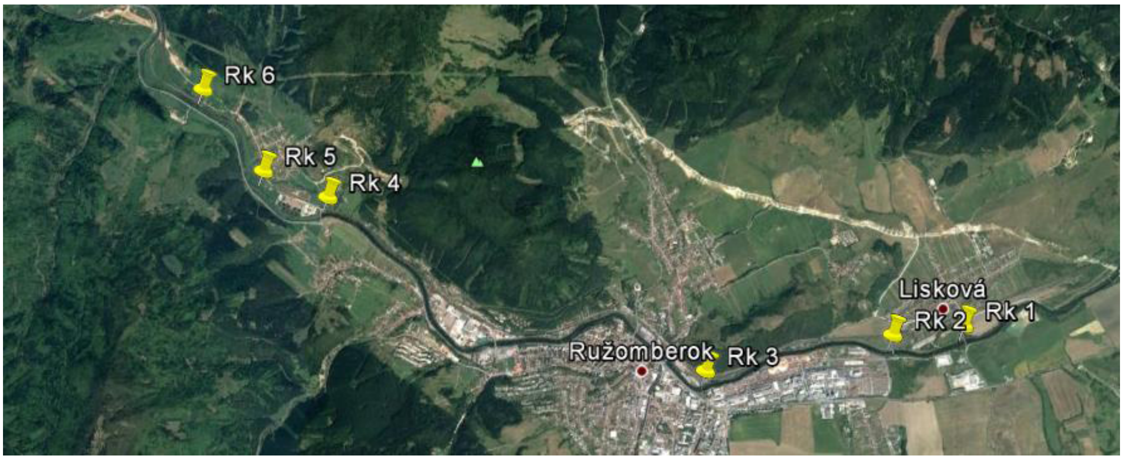

Fig. 1. Sampling sites of the water quality in area of Ružomberok (source: Google Earth 2016).

under development range from biological treatment capable of removing nitrogen and phosphorus to physical-chemical separation techniques such as carbon adsorption, distillation, filtration and reverse osmosis. These wastewater treatment processes, separately or in combination, can achieve almost any degree of pollution control needed. Waste effluents purified by such treatment, can be used for agricultural, industrial, or recreational purposes, or even drinking water (EPA 1998).

The main aim of this study was to describe and evaluate the impact of the paper industry and human activities on the water quality of the river Váh in Ružomberok and well as to evaluate the effectiveness of the WWTP built approximately 30 years ago.

Material and Methods

For a detailed description of location and methods see Gondová *et al.* (2017). Water samples were collected from 6 sampling sites (Fig. 1). The sampling sites were selected in suitable places where we expected different water quality in the Váh river. The first sampling site was at the upstream of Lisková village (RK1). The second sampling site downstream of Lisková village (RK2), where we expected to see the effect of the village on water quality. The third sampling site was in Ružomberok (RK3) near the pulp and paper factory (Mondi SCP), where we expected to see the effect of pulp production on water quality. The fourth sampling site was upstream of the WWTP Hrboltová (RK4). The fifth sampling site was situated downstream from the WWTP Hrboltová but before Hrboltová village (RK5), where we would expected to measure the effect of treatment on water quality. The sixth sampling site downstream of Hrboltová village (RK6). The following number of samples were collected at each site: RK1 – 72, RK2 – 72, RK 3 – 72, RK4 – 72, RK5 – 71 and RK6 – 70. Seasonal variations in water chemistry are presented in Gondová *et al.* (2017). This paper examines and discusses the special diffences between sampling sites.

At each sampling sites physical parameters were measured (in situ), including salinity, temperature of water, pH, conductivity (COND), total dissolved solids (TDS), and oxygen (O_2), using the Multi 3430 device (WTW GmbH, Weilheim, Germany). Water samples were collected for chemical analysis into sterilized 700 ml polyethylene bottles, conserved hermetically and transported to the laboratory. Colorimetry (YSI inc., Ohio, USA, YSI 9500) was used to detect the concentration of chlorides, sulphates, nitrates, phosphates, ammonia iones and $CaCO_3$. Chemical consumption of oxygen was measured by oxidative titration analysis using potassium permanganate. All analysis was completed 24 hours after sampling.

Data was analysed using Statistica 12 software (StatSoft, USA). Principal component analysis was performed to identify the potential relations betwen variables. This analysis uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. The differences between categories of row data or among component scores were compared by variance analysis. Levels of TDS, Cl, S amount and conductivity and their difference among sampling sites are presented in Gondová *et al.* (2017).

Results

The results from each sampling site - RK1, RK2, RK3, RK4, RK5, RK6 are presented in Fig. 2 through 6. The quality of water was significantly lower below WWTP Hrboltová (sites RK5 and RK6).

At sites RK5 and RK6, the indicators were significantly different from sites R1 to RK4 (upstream from treatment). These sampling sites are located downstream from the WWTP and the treatment plant likely had a significant impact on water quality. The quality of the hydrological environment deteriorated as evidenced through increasing concentration of TDS, COND, COD, salinity, Cl, NaCl, S, SO_4^{2-} and PO_4^{2-}. This pollution is likely a result of insufficient purification of wastewater by the WWTP. At the RK5 sampling site, the TDS concentration increased from 281.3729 mg/l (RK4) to 364.3263 mg/l and at the RK6, the TDS concentration slightly decreased to 355.9359 mg/l. Conduc-

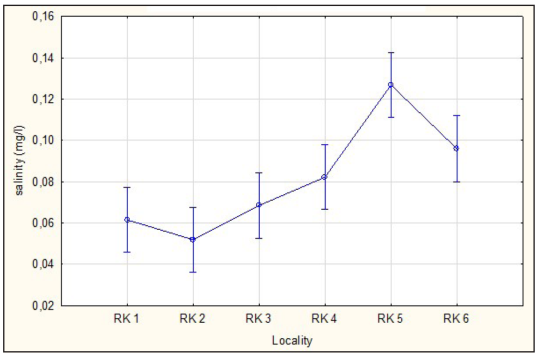

Fig. 2. Differences of measured values of salinity in the Váh river [One – way ANOVA F(5,423)=11.414, p=0.00000]. Salinity raised below WWTP hrboltová (RK5 and RK6).

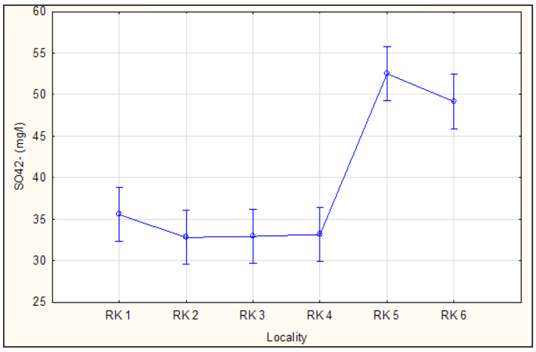

Fig. 3. Differences of measured values of sulphates (SO_4^{2-}) in Váh river [One – way ANOVA F(5,404)=29.467, p=0.0000]. The highest value of sulphate was measured in RK5 – 52.529 mg/l.

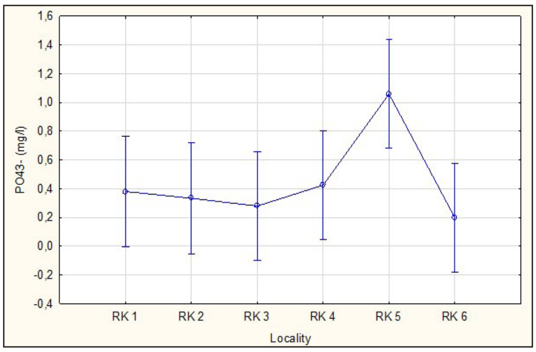

Fig. 4. Differences of measured values of phosphates (PO_4^{3-}) in the Váh river [One – way ANOVA F(5,332)=2.6130, p=0.02461]. Phosphate increased in RK5 – 1.059 mg/l and consequently the value dropped.

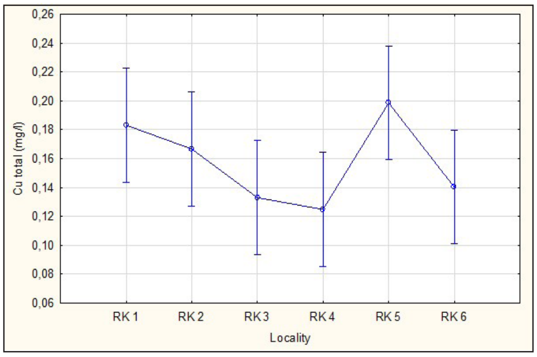

Fig. 5. Differences of measured values of copper (Cu) in Váh river [One – way ANOVA F(5,282)= 2.1898, p=0.05552]. Copper decreased from RK1 to RK4 and than rose in RK5 – 0.199 mg/l.

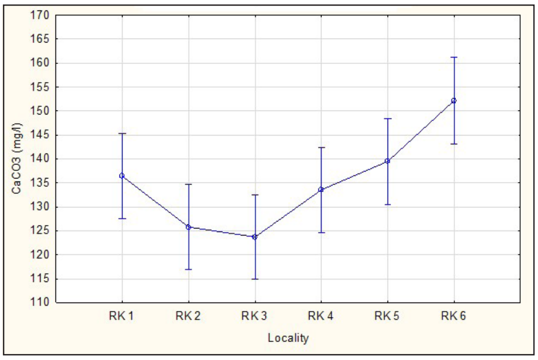

Fig. 6. Differences of measured values of calcium carbonates ($CaCO_3$)in Váh river [One – way ANOVA F(5,405)= 5.1378, p=0.00014]. The highest measured value was in RK6 – 152.164 mg/l.

tivity also increased from 274.4856 μs/cm (RK4) to 362.3083 μs/cm (RK5), COD from 3.977344 (RK4) to 5.778436 (RK5), salinity from 0.082250 mg/l (RK4) to 0.126887 mg/l (RK5), Cl from 6.632356 mg/l (RK4) to 8.364179 mg/l (RK5), NaCl from 11.23220 mg/l (RK4) to 13.97069 mg/l (RK5), S from 11.38333 mg/l (RK4) to 19.52542 mg/l (RK5), SO_4^{2-} from 33.17391 mg/l to 52.52941 mg/l (RK5) and PO_4^{2-} from 0.424386 mg/l (RK4) to 1.058596 mg/l (RK5). We found that highest concentration of pollution at the RK5 sampling place, downstream from the WWTP.

In Table 3 the principal component weights of the original measured variables are presented. The components (factors in the table) indicate mutual interactions among physico–chemical properties of water samples. Highlighted numbers in bold represent the link between the most significant variables for each factor. Seasonal effects on the first three component scores are presented in Figs. 7-9.

The most serious effect of waste in the waters of the Váh is synergy of increased sulphates, carbonates and conductivity. The increased pollution is most significantly evident during summer and autumn (Fig.7).

Increased ammonia content and water temperature in summer is a natural phenomenon and did not differ between localities. The lowest levels of ammonia in water were found during the cold weather in winter, and the highest levels were measured during warmer weather in the spring and summer (May to September) (Fig. 8).

The third factor describes the synergy among sulphates, salinity, TDS and conductivity. The effects were more visible at localities below the treatment plant and increased during summer and autumn (Fig. 9).

Discussion

Our results show a deterioration in water quality of the Váh river, downstream from the WWTP Hrboltová, (sampling sites RK5 and RK6). Indicators such as COD, TDS, COND, S, SO_4^{2-}, Cl, NaCl and PO_4^{3-} significantly increased at these sampling sites. This deterioration is largely a result of high quantities of wastewater from that paper industry, which the WWTP is responsible for treating, but urban ag-

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Temperature (˚ C)	0.200	**0.426**	0.285	0.122	0.225	0.023
pH	-0.129	-0.118	-0.107	-0.081	0.203	-0.147
COND (S/cm)	**0.513**	-0.001	**0.610**	-0.300	-0.160	-0.045
TDS (mg/l)	0.391	0.015	**0.582**	-0.393	-0.192	-0.132
salinity (mg/l)	0.181	0.121	0.425	0.001	-0.255	0.176
O_2 (%)	0.187	0.184	0.211	0.214	0.079	0.382
$CaCO_3$ (mg/l)	**0.910**	-0.106	-0.368	0.027	0.019	-0,117
$CaCO_3$ (mmol/l)	**0.910**	-0.106	-0.368	0.027	0.019	-0.117
$CaCO_3$ (mg Ca^{2+}/l	**0.910**	-0.106	-0.368	0.027	0.019	-0.117
$CaCO_3$ (˚ dH)	**0.910**	-0.106	-0.368	0.027	0.019	-0.117
N (mg/l)	-0.115	0.097	-0.109	0.003	**0.554**	0.140
NO_3 (mg/l)	-0.029	0.357	-0.027	0.095	**0.676**	0.262
N-ammonia (mg/l)	-0.055	**0.895**	-0.234	-0.033	-0.187	-0.123
NH_3 (mg/l)	-0.015	**0.912**	-0.216	-0.016	-0.178	-0.100
NH_4 (mg/l)	0.020	**0.833**	-0.256	0.017	-0.188	-0.040
Cl (mg/l)	0.170	0.064	0.393	**0.820**	-0.018	-0.284
NaCl (mg/l)	0.156	0.001	0.392	**0.833**	0.013	-0.259
SO_4^{2-} (mg/l)	**0.563**	0.285	**0.478**	-0.281	0.316	0.032
S (mg/l)	**0.686**	0.203	**0.418**	-0.201	0.190	0.131
Cu total (mg/l)	-0.133	0.044	0.129	-0.161	-0.316	-0.234
PO_4^{3-} (mg/l)	0.189	-0.077	0.003	0.196	-0.424	**0.627**
P (mg/l)	0.401	0.002	-0.204	0.259	-0.239	**0.554**

Table 3. Principal component (Factors) vectors (loadings), which indicate mutual interaction of physico-chemical properties of water samples. (Factor coordinates of the variables, based on correlations).

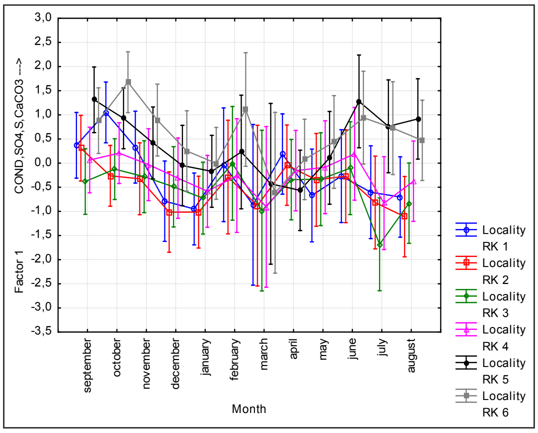

Fig. 7. Comparison of mean monthly COND, SO_4, S, $CaCO_3$ among localities by ANOVA [Locality (F=11.5, p=0.000) * Month (F=5.9, p=0.000) Interactivity: F (55, 210) =0.743, p=0.903].

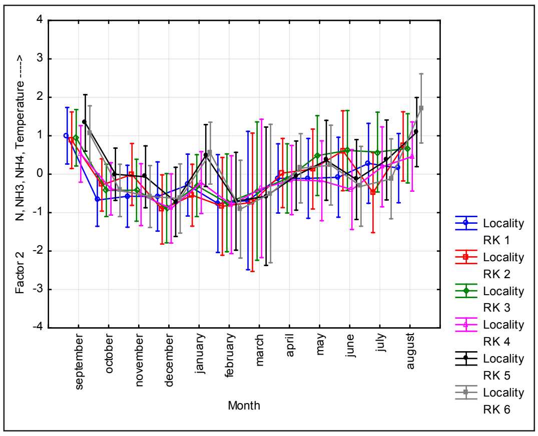

Fig. 8. Comparison of mean monthly N, NH_3, NH_4 among localities by ANOVA [Locality (F=0.801, p=0.550) * Month (F=8.997, p=0.000) Interactions: F (55,210) = 0.383, p=0.999].

glomeration is a secondary factor. To improve water quality, wastewater treatment must be improved.

Primary treatments such as more effective floatation are generally employed prior to biological purificationt. Some smaller enterprises use filtration as the only treatment of waste water, and according to Garcilaso (2001), the removal rate for dissolved solids (TDS) may be between 60-90%. Secondary treatment uses aerobic and anaerobic methods. Aerobic methods are used for sewage water, which contains a large amount of degradable organic substances.The process of separating activated sludge is the most widespread process in secondary treatment. Using activated sludge separation, BOD is reduced by 85-96% and COD by 75-90%. Tertiary treatment processes wastewater that still contains fine particles and nutrients, particularly phosphorus and nitrogen.

Numerous studies exist that discuss the potential improvement of wastewater treatment. Many

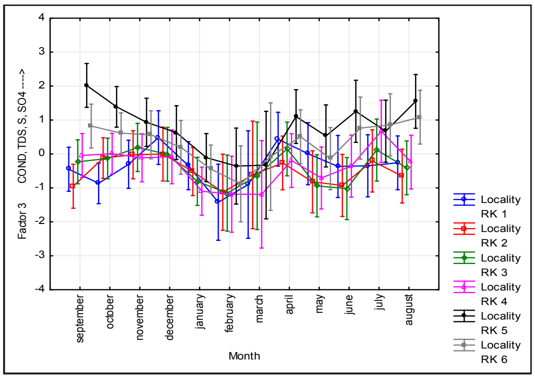

Fig. 9. Comparison of mean monthly COND, TDS, S, SO_4 among localities by ANOVA [Locality (F=15.31, p=0.000) * Month (F=4.97, p=0.000) Interactions: F (55, 210) =0.983, p= 0,515].

researchers are analysing increasing the effect of biological cleaning throught he use of active bilge. Wastewater from the paper industry contains a high volume of solid particles like bark chips, sawdust and other wood byproducts. Haarhoff and Bezuidenhout (1999) suggest the implementation of floatation propr to biological cleaning, which has had a significant impact on the effectiveness of biological cleaning in Great Britain and Sweden. Through this method, the reduction of insoluble substances in wastewater reached 90% (Wenta and Hartmen 2002).

In addition to active bilge, other cleaning methods are emerging, such as utilizing an aeration lagoon and a dosing sequential reactor. Anaerobic biological cleaning produces less biopass, a lower energy output, and requires a smaller physical footprint for the reactor building when compared to aerobic biological cleaning. The combination of both aerobic and anaerobic biological cleaning of wastewaters for the paper industry significantly reduces industrial sulphates (Chen *et al.* 2003). Other common wastewater treatment techniques include ultrafiltration, ozonation, adsorption and membrane technologies. The combination of coagulation, floatation and multimedial filtration could be the most effective tertiary cleaning method for wastewater produced by the pulp and paper industry.

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