

WATER QUALITY ASSESSMENT OF HASBANI RIVER IN SOUTH LEBANON: MICROBIOLOGICAL AND CHEMICAL CHARACTERISTICS AND THEIR IMPACT ON THE ECOSYSTEM

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Abstract

The present work was managed to study the water quality of Hasbani river in South Lebanon, in order to assess the chemical and microbiological characteristics and their impact on the ecosystem. Physico-chemical parameters, heavy metal, inorganic ions and pesticides were determined using standard methods. It was noticed that during January, August and November respectively; pH (7.4;7.9), (6.81;7.5) & (4.01;7.72); BOD (4.07-4.98 mg/L), (5.07-6.41 mg/L) & (4.05-10.89 mg/L); EC (461-474 μ S/cm), (4980-529 μ S/cm) & (481-654 μ S/cm); TDS (299.65-308.1 ppm), (323.7-343.85 ppm) & (312.65-425.1 ppm). Inorganic ion concentrations and heavy metals recorded high levels that exceeded WHO guideline especially in November during the olive period. Heterotrophic bacteria, total and fecal coliform, *Salmonella* sp. and *Shigella* sp. indicated significant levels of pollution from untreated sewage and olive mill effluent (OME). High levels of pesticides from agricultural activities are of a serious concern due to their carcinogenic effect. In conclusion, results of this study reflect a continuous exposure of Hasbani river to various types of contaminants resulting from, mostly, domestic and agricultural activities.

Key words: Water quality, Hasbani River, Trace metals, Ionic compositions, pesticides, Bacterial pollution, Gas Chromatography-Mass spectrometry.

1. INTRODUCTION

Lebanon, like other countries in the Middle East, is facing a major problem of water scarcity due to global warming phenomenon that the world endures (Giannakopoulos et al., 2009), and increasing in water pollution (Fan et al., 2010). Actually, the exponential demographic growth in the last two decades and the excess in water demand led to a major problem concerning water quality and thus, water availability. This problem is increasing by the lack of waste treatment facilities, forcing the local authorities to discharge wastewater directly into rivers without any prior treatment (SOER, 2001). Thus, the quality of surface water is relatively hassled by sewage from urban waste, agricultural and industrial wastes (Fadel et al., 2000; Jurdi et al., 2001 and SOER, 2001). For its domestic supply, Lebanon depends mainly on ground water that is deteriorating rapidly due to salinisation by seawater intrusions and contamination by wastewater (Khair et al., 1994).

Hasbani River is one of the rivers found in south Lebanon. It's originating from north-western slopes of Mount Hermon in Hasbaya. It runs for 25 miles in Lebanon before coming out to Palestine where it is called the Jordan River. Hasbani river is the main source of water to Hasbaya and near villages. It is used as a source of drinking water, for house holding, for irrigating agricultural fields, providing water to livestock, for fishing activities or even as a source of enjoyment through water-swimming.

The increase in the waste disposal throughout the river especially in November during the olive season needs a serious plan to control water pollution and to find solution for this problem. The aim of the present study is to evaluate water quality in the South Lebanese Hasbani River. Study the organic/inorganic chemical parameters and bacteriological parameters of water and its effect on the biota that can be transferred from the sediment into benthic organisms and fish and further up into the food chain.

2. MATERIALS AND METHODS

Water samples were collected from 20 locations along the Hasbani River. Totally 60 water samples were collected throughout the year. Water samples were collected in triplicates on a monthly basis in January, 2013 (during winter), in August, 2013 (during summer) and in November, 2013 (during olive period) using autoclaved bottles, which were previously washed by an acid solution (1:1 HCl / water) then by distilled water. After collecting, samples were stored at -5°C and analyzed.

The following physical and chemical parameters were analyzed including pH, electrical conductivity (EC), total dissolved solids (TDSs), biochemical oxygen demand (BOD), ammonium, nitrate, nitrite, phosphate, sulfate, chloride, sodium, potassium, calcium and magnesium. pH, BOD, TDS and EC were analyzed using standard procedures in accordance to "The Standard Methods for the Examination of Water and Wastewater" (APHA & AWWA, 1999). Potassium and sodium concentration were measured using Flame photometry provided by STS Model 360. The remaining parameters were analyzed spectrophotometrically with pertinent and certified reagents.

Bacterial analysis was done using the membrane filtration technique to detect the presence of total and fecal coliform followed by confirmatory test to detect the presence of *E.coli*. SS agar plate was used to detect the presence of *Salmonella* sp. and *Shigella* sp. Furthermore; the trace amounts of heavy metals in water samples (Cu, Cd, Co, Pb, and Zn) were estimated using Graphite furnace atomic absorption spectrometry (GFAAS). For pesticides analysis, 10 water samples were taken from the Hasbani river between July and November 2013 using autoclaved bottles and stored in dark at -4°C. Pesticide analysis was done using SPE work station followed by GC-MS.

Statistical analysis

Descriptive analysis was performed. Quantitative variables were described in terms of frequencies, mean, standard deviation, min and max. Paired correlations were performed between the studied parameters using Pearson's correlation coefficient. For testing the difference between the physical parameters and ion concentrations in January, August and November, paired sample t-test was used. The Type-1 error α was set at 5%. The analyses were performed using SPSS 17 for windows.

3. RESULTS AND DISCUSSION

3.1. Physico-chemical parameters

3.1.1. pH

The mean pH value recorded 7.83, 6.98 and 5.32 in January, August and November respectively (Table 1). Compared to the WHO guideline for drinking water (2004), the pH value in November is below the normal limits. Low pH level in November is due to the direct discharge of olive mill effluent (OME) into the river. OME is highly acidic thus it decreases the pH level of water (Mekki et al., 2013). Low pH can allow toxic elements to be more available for uptake by aquatic plants and animals. This can produce conditions that are toxic to aquatic life (Faragallah et al., 2009).

3.1.2. Biochemical Oxygen Demand (BOD)

BOD concentration recorded a mean value of 4.357, 5.898 and 7.945 mg/L in January, August and November respectively (Table 1). Most rivers have BOD₅ below 1 mg/L. Moderate polluted rivers may have a BOD₅ value in the range of 2 to 8 mg/L. However; high BOD₅ levels (>8mg/L) can be a result of high levels of organic pollution, caused usually by poorly treated wastewater or from high nitrate levels (EEA, 2001). High level of BOD₅ in November is due to the direct discharge of OME into the river. OME contains an enormous supply of organic matter which will raise the BOD₅ level (Mekki et al., 2013).

3.1.3. Electrical Conductivity (EC) and Total dissolved solids (TDS)

EC recorded an average mean of 464.25, 516.25 and 585.45 μ S/cm in January, August and November respectively (Table 1). Moreover; total dissolved solids (TDS) recorded a mean value of 301.76, 335.56 and 380.54 ppm in January, August and November respectively (Table 1). TDS directly influence water conductivity, the higher the TDS the higher the EC (Lawson, 2011). In fact, coefficient correlation was strongly positive between EC and TDS during the three months of this study. High levels of TDS are caused by the presence of potassium, chlorides and sodium and by toxic ions (lead arsenic, cadmium, nitrate and others). Moreover; high TDS level indicates hard water and

results in undesirable taste which could be salty, bitter, or metallic due to the presence of toxic minerals (Lawson, 2011). In this study, high levels of TDS and EC observed in November during olive oil production is due to the discharge of OME which is highly rich in nutrients (potassium, nitrate, phosphate and others).

3.2. Trace metals detection

Results reported that trace metals' mean concentration for Zn, Pb and Co in August and November was higher than the value expected for rivers except for Cd whereas Cu recorded a mean value higher than WHO guideline (2004) in all the three months (Table 2). High values for trace metals were recorded in August due to domestic sewage and in November during the olive period due to the direct discharge of olive mill effluent into the river (Fig.1). Moreover; some of the metals like Cu and Zn are essential as micronutrients for the life processes in animals and plants (Kar et al., 2008; Suthar & Singh, 2008 and Aktar et al., 2010). However; high concentrations of Cu and Zn are of toxic effect. The prolonged consumption of large doses of Zn can result in some health complications such as fatigue, dizziness and neutropenia (Hess & Schmid, 2002). However; Cd is toxic even at low concentrations. Cd is one of the most toxic elements with widespread carcinogenic effects in humans (Goering et al., 1995). Moreover; according to USEPA (1986), Pb has classified as being potentially hazardous and toxic to most forms of life. It has been found to be responsible for chronic neurological disorders in fetuses and children especially when it is greater than 0.1 mg/l (Lawson, 2011).

3.3. Inorganic Ion

Phosphate (PO_4^{3-}) concentrations recorded a mean value of 1.67, 7.54 and 49.125 ppm in January, August and November respectively (Table 3). Comparing these results with LIBNOR, these results exceed the average level of PO_4^{3-} (1.35 mg/L) in rivers. In fact, phosphate and sulfate come from anthropogenic sources, mainly, agricultural runoff, animal waste, raw sewage and household detergents (Amacha et al., 2012). Excess phosphate in surface runoff leads to what known as "cultural eutrophication". During eutrophication, PO_4^{3-} in freshwater leads to a favorable condition for algae and weed growth, which ultimately brings a rapid reduce in the ecosystem through oxygen depletion. Moreover; the high level of PO_4^{3-} recorded in November might be due to the direct discharge of OME into the river. According to Mekki et al. (2013), OME is highly rich in PO_4^{3-} . Sulfate (SO_4^{2-}) recorded a mean value of 9.34, 15.437 and 35.76 ppm in January, August and November respectively (Table 3). Comparing with LIBNOR guideline, sulfate concentration in November is above the range (2-30 mg/L). High level of sulfate in November is due to waste disposal and OME discharged into the river. Chloride (Cl^-) concentration recorded a mean value of 174.49, 230.238 and 237.295 ppm in January, August and November respectively (Table 3). Comparing with LIBNOR guideline, the level of chloride in August and November exceeds the range (200 mg/L) for drinking water. Chloride in drinking-water originates from natural sources, sewage and industrial effluents, urban runoff. Excessive chloride concentrations increase the concentrations of metals in water (WHO, 2004). Moreover; Amacha et al. (2012) recorded that chloride range <180 mg/L, water is deemed suitable for most applications including drinking, domestic use, irrigation, and livestock.

Ammonium (NH_4^+) and nitrite (NO_2^-) were not detected during the 3 months (Table 3). Natural levels of ammonia and nitrite in groundwater and surface water are usually below 0.2 mg/L (WHO, 2004). Ammonia contamination is usually an indicator of sewage pollution which most certainly applies to Lebanon for its lack of a national wastewater treatment system (Amacha et al., 2012). Ammonia in the environment originates from metabolic, agricultural and industrial processes and from disinfection with chloramine (WHO, 2004). Moreover; nitrate (NO_3^-) concentration recorded a mean value of 65.92, 164.107 and 262.48 ppm in January, August and November respectively (Table 3). Comparing with LIBNOR guideline, nitrate levels are above the range (45 mg/L). According to WHO guideline (2004), the nitrate concentration in surface water is normally low but it can reach high levels as a result of leaching, runoff from agricultural land or contamination from human and animal wastes. Excessive amounts of nitrate obtained in January and August are usually attributed to intensive agricultural practices and contamination from domestic sewages. In other hand, comparing with Mekki et al. (2013), the high levels of nitrate in November attributed to the high level of nitrate in OME directly discharged into the river.

Sodium (Na^+) concentration recorded a mean value of 6.45, 8.102 and 16.47 ppm in January, August and November respectively (Table 3). Whereas potassium (K^+) concentration recorded a mean value of 1.028, 2.132 and 5.52 ppm in January, August and November respectively (Table 3). According to

WHO guideline (2004), concentration of sodium in potable water are typically less than 20 mg/L, however; no health based guideline for the level of potassium in drinking water. Whereas according to LIBNOR guideline, potassium level was above the range for rivers (1.5 mg/L). High levels of potassium and sodium in November may attribute to OME where according to Al-Malah et al. (2000), OME contain sodium and enormous level of potassium.

On the other hand, calcium mean value was 94.1685, 118.196 and 142.79 ppm in January, August and November respectively (Table 3). Calcium is an important micronutrient in the aquatic environment. Calcium and magnesium enter water mainly through the weathering of rocks. Concentration of calcium in rivers may reach 100 mg/L. Results obtained in August and November are above the range (100 mg/L). However; the mean concentration of magnesium was 56.504, 70.916 and 81.98 ppm in January, August and November respectively (Table 3). Magnesium is essential for chlorophyll and acts as a limiting factor for the growth of phytoplankton (Garg et al., 2010). Concentration of magnesium up to 30 ppm is recommended for drinking waters (Ravindra et al., 2003). In rivers, concentration of magnesium may reach 50 ppm. Results obtained revealed high levels of magnesium in August and November. This increase in the levels of calcium and magnesium is due to the domestic sewages and olive mill effluent. High levels of calcium and magnesium increase the total hardness of water (WHO, 2004).

3.4. Pesticides

3.4.1. Propoxur-1

The mean value of propoxur-1 recorded 2.833ng/L ranging from 1.003ng/L at site 1 and 9.36ng/L at site 17 (Table 4). Propoxur-1 is an insecticide used to control cockroaches, flies, mosquitoes, lawn and turf insects. EPA (2000) has not classified propoxur-1 for carcinogenicity. Propoxur-1 is highly toxic to freshwater invertebrates and slightly or moderately toxic to fish (WHO, 2004). Federal Environmental Protection Agency (FEPA) recommended the level of propoxur-1 in rivers must not exceed 0.01µg /L (WHO, 2004). Results in this study falls within the range.

3.4.2. Hexachlorobenzene (HCB)

The mean value of hexachlorobenzene recorded 1.02 ng/L, ranging from 0.17ng/L at site 18 and 2.7ng/L at site 3 (Table 4). HCB was widely used as a pesticide. Chronic oral exposure to HCB in humans results in a liver disease with associated skin lesions. Epidemiologic studies of persons orally exposed to HCB have not shown an increased cancer incidence. However, based on animal studies, EPA has classified HCB as a probable human carcinogen. According to EPA (2000), HCB has been listed as a pollutant due to its persistence in the environment, potential to bioaccumulate, and toxicity to humans and the environment. The typical predicted environmental concentration for HCB in both estuarine and marine waters is less than 0.001 µg/l (<1 ng/l). Results obtained from the present study recorded a concentration of HCB approximately 1ng/L in 90% of the samples. Moreover; some people who drink water containing HCB in excess of 0.001 mg/L (1µg/L) over many years could experience liver or kidney problems, reproductive difficulties and increased risk of cancer (EPA, 2000).

3.4.3. Diazinon

The mean value of diazinon recorded 57.472 ng/L, ranging from 1.41ng/L at site 18 and 210.58ng/L at site 17 (Table 4). Almost all concentrations of diazinon measured in the rivers throughout this study were above the guideline (9ng/L) recommended by the National Academy of Sciences (1973) for the protection of aquatic life. Higher level of diazinon detected at site 17 (210.58 ng/L) may attribute to the larger proportion of urban/residential land in the watershed (Wall & Phillips, 1997). In fact, diazinon is an organophosphate pesticide. Pesticides in this chemical family work by blocking an enzyme in the nervous system that acts as a stop switch for a nerve signal. If the enzyme is blocked, the nervous system can not work properly and eventually it fails (EPA, 2000).

3.4.4. Polychlorinated biphenyls (PCB 52)

PCBs represent the most noted classes of persistent organic pollutants (POPs) possess a potential to bioaccumulate throughout the food web (Poustka et al., 2008). These compounds can not only occur in water; they deposit in sediments or accumulate in the tissues of aquatic animals and can also be metabolized to compounds that are even more toxic and/or carcinogenic (Polkowska et al., 2011). EPA categorized PCB as carcinogenic. According to EPA, PCB level must not exceed 0.0017 µg/L (1.7 ng/L). The present study revealed high level of PCB 52 at all sites ranging from 35.43 ng/L to

121.61 ng/L (Table 4). These alarming results have a severe toxic effect in humans since the Hasbani river is used for drinking, recreational activities and agricultural purposes.

4.4.5. Dichlorodiphenyldichloroethylene (DDE)

The mean value of DDE recorded 2.03 ng/L, ranging from 1.12ng/L at site 9 and 4.99ng/L at site 6 (Table 4). DDE is a pesticide that is widely used to control insects on agricultural crops and insects that carried diseases such as malaria and typhus. DDE has been listed as a pollutant of concern due to its persistence in the environment, potential to bioaccumulate, and toxicity to humans and the environment (EPA, 2000). Oral exposure to high doses of DDT in humans results in central nervous system (CNS) effects, such as headaches, nausea, and convulsions. EPA has classified DDE as probable human carcinogen. According to EPA, DDE levels in water must not exceed 8.3ng/L. Results obtained in this study fell within the range for DDE (<8.3 ng/L).

4.4.6. Endosulfanbeta

The mean value of endosulfanbeta recorded 24.46 ng/L, ranging from 3.26 ng/L at site 3 and 107.39 ng/L at site 20 (Table 4). Endosulfanbeta is an insecticide used to control pests on fruit, vegetables and tea and on non-food crops such as tobacco and cotton. The central nervous system is the primary target affected by exposure to endosulfanbeta. High doses of endosulfanbeta can cause tremors, hyperactivity, breathing disorder, convulsions and death. The effects of being exposed to low doses of endosulfanbeta over a long period of time are not known. EPA, the Department of Health and Human Services and the International Agency for Research on Cancer have not classified endosulfanbeta as a cancer-causing substance. EPA prohibits no more than 0.1mg/L (100 µg/L) of endosulfanbeta to be presented in water. Results of the present study recorded a mean value of 24.46 ng/L, which is very low comparing with EPA guideline (2000).

3.5. Bacteriological assessment

The results of the present study revealed a 100% occurrence rate for heterotrophic bacteria in January, August and November. Genus *Salmonella* showed a great variation between the studied period with an occurrence rate of 15, 55 and 65% in January, August and November respectively. Similarly genus *Shigella* showed a great variation with an occurrence rate of 10, 35 and 50% in January, August and November 2013.

High microbiological contamination for both fecal and total coliforms was revealed in all water samples which are above the internationally accepted limits. Total coliform counts recorded the highest value during August and November (Table 5). It was also revealed that 45% of the studied water samples were not suitable for swimming during January, 95% during August and 75% during November. Moreover; fecal coliforms (FC) counts recorded the highest value of 900 CFU/100ml during August and November and 100% of the sites unsuitable for swimming during January, August and November (WHO guideline). *E.coli* was detected in all sites indicating 100% occurrence. These levels represent an alarming situation for the bacterial quality of the water at the sampled sites. The bacterial quality indicates sewage waste disposal in the Hasbani river, implying a lack of treatment infrastructure. According to WHO guideline (2004) and USEPA (1986), drinking water must be free from FC bacteria or *E.coli*. The great majority of pathogenic microorganisms are derived from fecal contamination from human and animal sources. Recently, Hasbani river has known for its problems with diseases originating from water, with large numbers of people consuming water that lacks adequate treatment.

3.6. Correlation relation between the physico-chemical parameters and the microbial pollution load

Statistical analysis was done to reveal the relation between the bacterial load and the physico-chemical parameters of the river water samples. Results shown in table 6, recorded that in January during winter season, total coliform and fecal coliform strongly correlated having $r=0.988$ at $p<0.001$. Total coliform showed non significant positive correlation with pH ($r=0.181$ at $p=0.445$), BOD ($r=0.245$ at $p=0.298$) and a non significant negative correlation with EC and TDS having $r=-0.121$ at $p=0.611$. However; fecal coliform showed a non significant positive correlation with pH($r=0.205$ at $p=0.387$), BOD($r=0.187$ at $p=0.431$) and a non significant weak negative correlation with EC ($r=-0.098$ at $p=0.68$) and TDS ($r=-0.098$ at $p=0.68$).

Data in table 7, revealed that in August during summer season total coliform and fecal coliform showed a strong positive correlation having $r=0.990$ at $p<0.001$. Total coliform showed negative

significant correlation with pH ($r=-0.461$ at $p=0.041$), strong positive significant correlation with BOD($r=0.606$ at $p=0.005$) and a non significant positive correlation with EC and TDS having $r=0.382$ at $p=0.097$. However; fecal coliform showed a negative significant negative correlation with pH ($r=-0.460$ at $p=0.041$), a strong positive significant correlation with BOD ($r=0.603$ at $p=0.005$) and a non significant positive correlation with EC and TDS having $r=0.397$ at $p=0.083$.

Data in table 8, revealed that in November during the olive period, total coliform and fecal coliform showed a strong significant positive correlation having $r=0.985$ at $p<0.0001$. Total coliform showed a non significant negative correlation with pH($r=-0.132$ at $p=0.58$) and a non significant positive correlation with BOD($r=0.141$ at $p=0.554$), EC ($r=0.162$ at $p=0.495$) and TDS($r=0.162$ at $p=0.495$). Moreover; fecal coliform showed a non significant negative correlation with pH ($r=-0.122$ at $p=0.608$), a non significant positive correlation with BOD($r=0.142$ at $p=0.55$), EC($r=0.165$ at $p=0.487$) and TDS($r=0.165$ at $p=0.487$).

3.7. Correlation relation between the inorganic ions and the microbial load

Data in table 9, revealed that during January, total coliform showed negative significant correlation with sodium ($r=-0.467$ at $p=0.038$), a non significant positive correlation with phosphate($r=0.273$ at $p=0.245$), sulfate($r=0.042$ at $p=0.86$) and potassium ($r=0.194$ at $p=0.412$) and a non significant negative correlation with chloride($r=-0.41$ at $p=0.072$), nitrate($r=-0.244$ at $p=0.299$), calcium($r=-0.319$ at $p=0.171$) and magnesium($r=-0.319$ at $p=0.171$). Moreover; fecal coliform showed a significant negative correlation with sodium($r=-0.447$ at $p=0.048$), a non significant positive correlation with phosphate($r=0.335$ at $p=0.148$), sulfate($r=0.066$ at $p=0.782$) and potassium($r=0.197$ at $p=0.404$) and a non significant negative correlation with chloride($r=-0.406$ at $p=0.076$), nitrate($r=-0.276$ at $p=0.239$), calcium($r=-0.323$ at $p=0.165$) and magnesium($r=-0.323$ at $p=0.165$).

Data in table 10, revealed that during August, total coliform showed a significant positive correlation with nitrate($r=0.555$ at $p=0.011$) and a non significant positive correlation with phosphate($r=0.412$ at $p=0.071$), sulfate ($r=0.331$ at $p=0.154$), chloride($r=0.238$ at $p=0.313$), sodium($r=0.354$ at $p=0.125$), potassium($r=0.363$ at $p=0.115$), calcium($r=0.272$ at $p=0.247$) and magnesium($r=0.272$ at $p=0.247$). Moreover; fecal coliform showed a significant positive correlation with nitrate($r=0.514$ at $p=0.02$) and a non significant positive correlation with phosphate($r=0.408$ at $p=0.074$), sulfate($r=0.378$ at $p=0.1$), chloride($r=0.195$ at $p=0.409$), sodium($r=0.37$ at $p=0.108$) and potassium($r=0.381$ at $p=0.097$), calcium($r=0.259$ at $p=0.271$) and magnesium($r=0.259$ at $p=0.27$).

Data in table 11, revealed that during November, total coliform showed a non significant positive correlation with phosphate($r=0.141$ at $p=0.553$), sulfate($r=0.189$ at $p=0.424$), chloride($r=0.14$ at $p=0.555$), nitrate($r=0.213$ at $p=0.368$), sodium($r=0.153$ at $p=0.52$), potassium($r=0.154$ at $p=0.517$), calcium($r=0.184$ at $p=0.438$) and magnesium($r=0.192$ at $p=0.417$). Moreover; fecal coliform showed a non significant positive correlation with phosphate($r=0.132$ at $p=0.578$), sulfate($r=0.174$ at $p=0.463$), chloride($r=0.131$ at $p=0.581$), nitrate($r=0.204$ at $p=0.388$), sodium($r=0.15$ at $p=0.527$), potassium($r=0.151$ at $p=0.526$), calcium($r=0.178$ at $p=0.452$) and magnesium($r=0.189$ at $p=0.426$).

3.8. Correlation relation between trace metals and microbial load

Data in table 12, revealed that during January, total coliform showed a non significant positive correlation with zinc($r=0.361$ at $p=0.306$), lead($r=0.337$ at $p=0.341$), copper ($r=0.316$ at $p=0.373$), cobalt ($r=0.282$ at $p=0.429$) and cadmium($r=0.302$ at $p=0.397$). Moreover; fecal coliform showed a non significant positive correlation with zinc($r=0.356$ at $p=0.312$), lead($r=0.354$ at $p=0.315$), copper($r=0.313$ at $p=0.379$), cobalt ($r=0.297$ at $p=0.405$) and cadmium($r=0.28$ at $p=0.433$).

Data in table 13, revealed that during August, total coliform showed a non significant positive correlation with zinc ($r=0.48$ at $p=0.16$), lead ($r=0.591$ at $p=0.072$), copper($r=0.475$ at $p=0.165$) and cobalt($r=0.233$ at $p=0.517$) and a non significant negative correlation with cadmium having $r=-0.051$ at $p=0.89$. Moreover; fecal coliform showed a non significant positive correlation with zinc($r=0.468$ at $p=0.173$), lead($r=0.622$ at $p=0.055$), copper($r=0.42$ at $p=0.227$) and cobalt ($r=0.271$ at $p=0.449$) and a non significant negative correlation with cadmium having $r=-0.045$ at $p=0.902$.

Data in table 14, revealed that during November, total coliform showed a non significant positive correlation with zinc($r=0.361$ at $p=0.306$), lead($r=0.337$ at $p=0.341$), copper($r=0.316$ at $p=0.373$), cobalt($r=0.282$ at $p=0.429$) and cadmium($r=0.302$ at $p=0.397$). Moreover; fecal coliforms showed a non significant positive correlation with zinc($r=0.356$ at $p=0.312$), lead($r=0.354$ at $p=0.315$), copper($r=0.313$ at $p=0.379$), cobalt($r=0.297$ at $p=0.405$) and cadmium($r=0.28$ at $p=0.433$).

3.9. Correlation relation between pesticides and microbial load

Statistical analysis was done to reveal the relation between the bacterial load and pesticides concentration of the river water samples. Data in table 15 revealed that, total coliform showed a non significant positive correlation with propoxur-1($r=0.238$ at $p=0.509$), diazinon($r=0.177$ at $p=0.626$), PCB 52($r=0.287$ at $p=0.422$), DDE($r=0.027$ at $p=0.941$) and endosulfanbeta($r=0.243$ at $p=0.499$) and a non significant negative correlation with hexachlorobenzene($r=-0.386$ at $p=0.271$). Similarly, fecal coliform showed a non significant positive correlation with propoxur-1($r=0.222$ at $p=0.538$), diazinon($r=0.167$ at $p=0.645$), PCB 52($r=0.294$ at $p=0.410$), DDE($r=0.095$ at $p=0.794$) and endosulfanbeta ($r=0.282$ at $p=0.429$) and a non significant negative correlation with hexachlorobenzene having $r=-0.371$ at $p=0.292$.

Table 1: Description of the physical parameters of the samples by period (N=20)

physical characteristics	January (2013)		August (2013)		November (2013)	
	mean(SD)	Range (Min;Max)	mean(SD)	Range (Min;Max)	mean(SD)	Range (Min;Max)
pH	7.83(0.11)	(7.4;7.9)	6.98(0.11)	(6.81;7.5)	5.32(1.67)	(4.01;7.72)
BOD	4.357(0.229)	(4.07;4.98)	5.898(0.369)	(5.07;6.41)	8.345(3.06)	(4.05;10.89)
EC	464.25(2.84)	(461;474)	516.25(7.44)	(498;529)	585.45(76.76)	(481;654)
TDS	301.76(1.85)	(299.65;308.1)	335.56(4.84)	(323.7;343.85)	380.54(49.89)	(312.65;425.1)

Table 2: Description of the trace metal concentration in the samples by period (N=10).

Physical characteristics (ppb)	January (2013)		August (2013)		November (2013)	
	Mean(SD)	Range (Min;Max)	Mean(SD)	Range (Min;Max)	Mean(SD)	Range (Min;Max)
Zinc	8.321(0.527)	(7.44;8.73)	14.637(0.239)	(14.01;14.83)	17.190(5.375)	(9.26;21.29)
Lead	1.785(1.072)	(0.12;3.17)	12.455(3.697)	(7.63;17.91)	13.079(6.839)	(2.04;19.48)
copper	2.297(0.803)	(1.50;3.89)	6.033(1.727)	(3.78;9.25)	11.487(6.696)	(1.59;17.52)
cobalt	0.778(0.165)	(0.42;0.97)	1.452(0.185)	(1.24;1.76)	2.803(1.369)	(0.53;3.82)
cadmium	0.093(0.108)	(0.00;0.27)	0.844(0.096)	(0.67;0.98)	1.872(1.062)	(0.23;2.89)

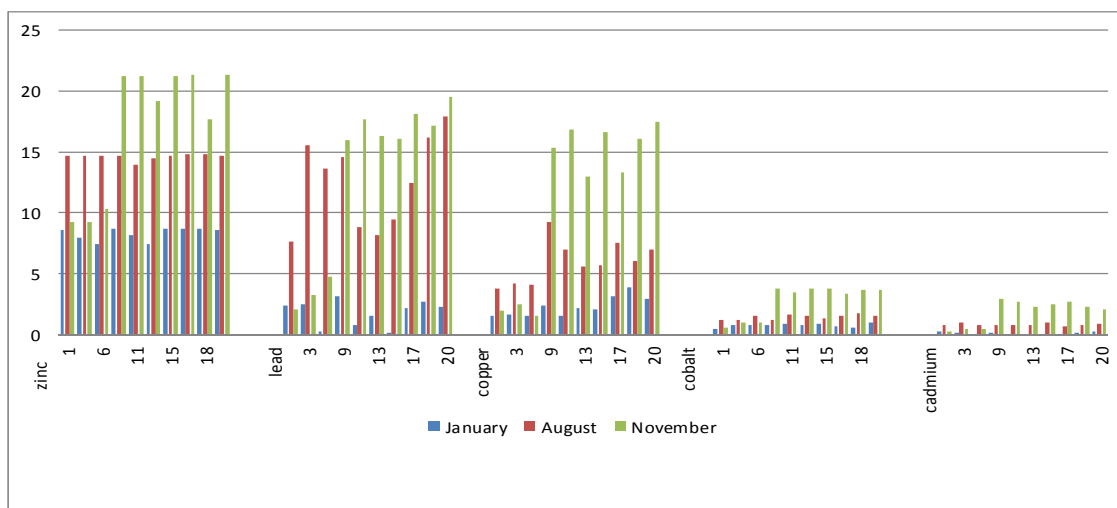


Fig.1: Trace metals variation during January, August and November 2013

Table 3: Description of inorganic ions in January, August and November by period (N=20)

Physical characteristics (ppm)	January (2013)		August (2013)		November (2013)	
	Mean(SD)	Range (Min;Max)	Mean(SD)	Range (Min;Max)	Mean(SD)	Range (Min;Max)
PO ₄ ³⁻	1.67(0.49)	(0.58;2.53)	7.54(1.42)	(5.05;10.95)	49.125(34.4)	(2.57;77.09)
SO ₄ ²⁻	9.34(1.13)	(7.82;11.82)	15.437(2.08)	(10.6;18.2)	35.76(17.24)	(12.69;55.08)
Cl ⁻	174.49(11.08)	(157.2;185.6)	230.24(4.62)	(223.6;239.8)	237.295(30.81)	(190.4;268.8)
NH ₄ ⁺	-	-	-	-	-	-
NO ₃ ⁻	65.92(26.67)	(13.53;90.72)	164.107(32.91)	(113.52;225.09)	262.48(103.14)	(88.63;352.86)
NO ₂ ⁻	-	-	-	-	-	-
Na ⁺	6.45(0.127)	(6.32;6.83)	8.102(0.698)	(7.59;9.37)	16.47(6.69)	(7.59;22.05)
K ⁺	1.028(0.004)	(1.02;1.03)	2.132(0.199)	(1.93;2.52)	5.52(2.75)	(1.77;7.7)
Ca ²⁺	94.1685(1.56)	(91.2;96.06)	118.196(2.215)	(113.09;120.38)	142.79(32.69)	(97.38;189.38)
Mg ²⁺	56.504(0.93)	(54.72;57.64)	70.916(1.33)	(67.85;72.23)	81.98(15.155)	(60.77;94.42)

-Not detected

Table 4: Description of pesticides concentration of the samples by period (N=10)

Pesticide (ng/L)	Mean (SD)	Range (min;max)
Propoxur1	2.833 (2.53)	(1.00;9.36)
Hexachlorobenzene	1.021 (0.685)	(0.17;2.70)
Diazinon	57.472 (56.311)	(1.41;210.58)
PCB 52	64.747 (32.035)	(35.43;121.61)
DDE	2.033 (1.174)	(1.12;4.99)
Endosulfanbeta	24.463 (32.29)	(3.26;107.39)

Table 5: description of bacterial counts in the river water samples by period (N=20)

Bacterial counts (CFU/100ml)	January (2013)		August (2013)		November (2013)	
	Mean (SD)	Range (min;max)	Mean (SD)	Range (min;max)	Mean (SD)	Range (min;max)
Total Coliform	466(339.07)	(210;1100)	835.5(334.35)	(290;1100)	700.5(377.88)	(240;1100)
Fecal Coliform	368.25(242.1)	(180;900)	658.2(251.19)	(240;900)	547.45(269.75)	(190;890)

Table 6: Correlation matrix between physical and bacteriological parameters during January (2013)

		pH	BOD (mg/L)	EC (μS/cm)	TDS (ppm)	Total coliform	Fecal coliform
pH	P correlation Sig. (2-tailed)	1					
BOD	P correlation Sig. (2-tailed)	.276 .239	1				
EC	P correlation Sig. (2-tailed)	-.712** .000	-.420 .065	1			
TDS	P correlation Sig. (2-tailed)	-.712** .000	-.420 .065	1.000** 0	1		
Total coliform	P correlation Sig. (2-tailed)	.181 .445	.245 .298	-.121 .611	-.121 .611	1	
Fecal coliform	P correlation Sig. (2-tailed)	.205 .387	.187 .431	-.098 .680	-.098 .680	.988** .000	1

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 7: Correlation matrix between physical and bacteriological parameters during August (2013)

		pH	BOD (mg/L)	EC (μS/cm)	TDS (ppm)	Total coliform	Fecal coliform
pH	P correlation Sig. (2-tailed)	1					
BOD	P correlation Sig. (2-tailed)	-.698**	1				
EC	P correlation Sig. (2-tailed)	-.716**	.601**	1			
TDS	P correlation Sig. (2-tailed)	-.716**	.601**	1.00**	1		
Total coliform	P correlation Sig. (2-tailed)	-.461*	.606**	.382	.382	1	
Fecal coliform	P correlation Sig. (2-tailed)	-.460*	.603**	.397	.397	.990**	1

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 8: Correlation matrix between physical and bacteriological parameters during November (2013)

		pH	BOD (mg/L)	EC (μS/cm)	TDS (ppm)	Total coliform	Fecal coliform
pH	P correlation Sig. (2-tailed)	1					
BOD	P correlation Sig. (2-tailed)	-.995**	1				
EC	P correlation Sig. (2-tailed)	-.995**	.990**	1			
TDS	P correlation Sig. (2-tailed)	-.995**	.990**	1.000**	1		
Total coliform	P correlation Sig. (2-tailed)	-.132	.141	.162	.162	1	
Fecal coliform	P correlation Sig. (2-tailed)	-.122	.142	.165	.165	.985**	1

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 9: Correlation matrix between inorganic ions and bacteriological parameters during January (2013)

		PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	NO ₃ ⁻	NO ₂ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	TC	FC
PO ₄ ³⁻	P correlation Sig.(2-tailed)	1											
SO ₄ ²⁻	P correlation Sig.(2-tailed)	.079	1										
		.740											
Cl ⁻	P correlation Sig.(2-tailed)	.083	-.037	1									
		.729	.879										
NH ₄ ⁺	P correlation Sig.(2-tailed)	-	-	-	1								
		-	-	-									
NO ₃ ⁻	P correlation Sig.(2-tailed)	-.170	-.045	.189	-	1							
		.473	.850	.425	-								
NO ₂ ⁻	P correlation Sig.(2-tailed)	-	-	-	-	-	1						
		-	-	-	-	-							
Na ⁺	P correlation Sig.(2-tailed)	.095	-.020	.056	-	.213	-	1					
		.691	.932	.814	-	.367	-						
K ⁺	P correlation Sig.(2-tailed)	-.303	-.192	-.047	-	-.052	-	.015	1				
		.194	.417	.844	-	.828	-	.949					
Ca ²⁺	P correlation Sig.(2-tailed)	-.224	.186	.229	-	.083	-	-.026	-.187	1			
		.343	.432	.331	-	.726	-	.914	.430				
Mg ²⁺	P correlation Sig.(2-tailed)	-.223	.190	.237	-	.086	-	-.025	-.188	.999**	1		
		.345	.421	.315	-	.720	-	.917	.427	.000			
TC	P correlation Sig.(2-tailed)	.273	.042	-.410	-	-.244	-	-.467*	.194	-.319	-.319	1	
		.245	.860	.072	-	.299	-	.038	.412	.171	.170		
FC	P correlation Sig.(2-tailed)	.335	.066	-.406	-	-.276	-	-.447*	.197	-.323	-.323	.988**	1
		.148	.782	.076	-	.239	-	.048	.404	.165	.165	.000	

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 10: Correlation matrix between inorganic ions and bacteriological parameters during August (2013)

		PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	NO ₃ ⁻	NO ₂ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	TC	FC
PO ₄ ³⁻	P correlation	1											
	Sig.(2-tailed)												
SO ₄ ²⁻	P correlation	.304	1										
	Sig.(2-tailed)	.193											
Cl ⁻	P correlation	.122	-.228	1									
	Sig.(2-tailed)	.609	.333										
NH ₄ ⁺	P correlation	-	-	-	1								
	Sig.(2-tailed)	-	-	-									
NO ₃ ⁻	P correlation	.285	-.174	.235	-	1							
	Sig.(2-tailed)	.223	.463	.318	-								
NO ₂ ⁻	P correlation	-	-	-	-	-	1						
	Sig.(2-tailed)	-	-	-	-	-							
Na ⁺	P correlation	.368	.489*	.256	-	-.042	-	1					
	Sig.(2-tailed)	.111	.029	.277	-	.860	-						
K ⁺	P correlation	.447*	.540*	.267	-	-.003	-	.965**	1				
	Sig.(2-tailed)	.048	.014	.256	-	.992	-	.000					
Ca ²⁺	P correlation	-.022	.480*	-.068	-	.066	-	.432	.524*	1			
	Sig.(2-tailed)	.926	.032	.774	-	.783	-	.057	.018				
Mg ²⁺	P correlation	-.022	.480*	-.069	-	.066	-	.432	.524*	1.00**	1		
	Sig.(2-tailed)	.926	.032	.773	-	.783	-	.057	.018	.000			
TC	P correlation	.412	.331	.238	-	.555*	-	.354	.363	.272	.272	1	
	Sig.(2-tailed)	.071	.154	.313	-	.011	-	.125	.115	.247	.247		
FC	P correlation	.408	.378	.195	-	.514*	-	.370	.381	.259	.259	.990**	1
	Sig.(2-tailed)	.074	.100	.409	-	.020	-	.108	.097	.271	.270	.000	

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 11: Correlation matrix between inorganic ions and bacteriological parameters during November (2013)

		PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	NO ₃ ⁻	NO ₂ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	TC	FC
PO ₄ ³⁻	P correlation Sig.(2-tailed)	1											
SO ₄ ²⁻	P correlation Sig.(2-tailed)	.986**	1										
		.000											
Cl ⁻	P correlation Sig.(2-tailed)	.990**	.970**	1									
		.000	.000										
NH ₄ ⁺	P correlation Sig.(2-tailed)	-	-	-	1								
		-	-	-									
NO ₃ ⁻	P correlation Sig.(2-tailed)	.985**	.974**	.980**	-	1							
		.000	.000	.000	-								
NO ₂ ⁻	P correlation Sig.(2-tailed)	-	-	-	-	-	1						
		-	-	-	-	-							
Na ⁺	P correlation Sig.(2-tailed)	.997**	.982**	.990**	-	.983**	-	1					
		.000	.000	.000	-	.000	-						
K ⁺	P correlation Sig.(2-tailed)	.998**	.981**	.989**	-	.984**	-	.999**	1				
		.000	.000	.000	-	.000	-	.000					
Ca ²⁺	P correlation Sig.(2-tailed)	.983**	.978**	.975**	-	.967**	-	.984**	.981**	1			
		.000	.000	.000	-	.000	-	.000	.000				
Mg ²⁺	P correlation Sig.(2-tailed)	.992**	.977**	.988**	-	.983**	-	.997**	.996**	.975**	1		
		.000	.000	.000	-	.000	-	.000	.000	.000			
TC	P correlation Sig.(2-tailed)	.141	.189	.140	-	.213	-	.153	.154	.184	.192	1	
		.553	.424	.555	-	.368	-	.520	.517	.438	.417		
FC	P correlation Sig.(2-tailed)	.132	.174	.131	-	.204	-	.150	.151	.178	.189	.985**	1
		.578	.463	.581	-	.388	-	.527	.526	.452	.426	.000	

** Correlation is significant at the 0.01 level (2-tailed)/ *Correlation is significant at the 0.05 level (2-tailed)

Table 12: Correlation matrix between trace metals and bacteriological parameters during January (2013)

		Zinc	Lead	Copper	Cobalt	Cadmium	TC	FC
Zinc	P correlation	1						
	Sig. (2-tailed)							
Lead	P correlation	.414	1					
	Sig. (2-tailed)	.234						
Copper	P correlation	.533	.495	1				
	Sig. (2-tailed)	.113	.146					
Cobalt	P correlation	-.217	-.358	-.110	1			
	Sig. (2-tailed)	.546	.309	.761				
Cadmium	P correlation	.378	.654*	.269	-.313	1		
	Sig. (2-tailed)	.281	.040	.453	.378			
TC	P correlation	.361	.337	.316	.282	.302	1	
	Sig. (2-tailed)	.306	.341	.373	.429	.397		
FC	P correlation	.356	.354	.313	.297	.280	.988**	1
	Sig. (2-tailed)	.312	.315	.379	.405	.433	.000	

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 13: Correlation matrix between trace metals and bacteriological parameters during August (2013)

		Zinc	Lead	Copper	Cobalt	Cadmium	TC	FC
Zinc	P correlation	1						
	Sig. (2-tailed)							
Lead	P correlation	.434	1					
	Sig. (2-tailed)	.210						
Copper	P correlation	-.185	.256	1				
	Sig. (2-tailed)	.608	.475					
Cobalt	P correlation	-.229	.148	.198	1			
	Sig. (2-tailed)	.524	.684	.583				
Cadmium	P correlation	.146	.242	-.270	-.539	1		
	Sig. (2-tailed)	.688	.501	.451	.108			
TC	P correlation	.480	.591	.475	.233	-.051	1	
	Sig. (2-tailed)	.160	.072	.165	.517	.890		
FC	P correlation	.468	.622	.420	.271	-.045	.990**	1
	Sig. (2-tailed)	.173	.055	.227	.449	.902	.000	

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 14: Correlation matrix between trace metals and bacteriological parameters during November (2013)

		Zinc	Lead	Copper	Cobalt	Cadmium	TC	FC
Zinc	P correlation Sig. (2-tailed)	1						
Lead	P correlation Sig. (2-tailed)	.971**	1					
Copper	P correlation Sig. (2-tailed)	.960**	.971**	1				
Cobalt	P correlation Sig. (2-tailed)	.961**	.971**	.971**	1			
Cadmium	P correlation Sig. (2-tailed)	.973**	.948**	.942**	.961**	1		
TC	P correlation Sig. (2-tailed)	.361	.337	.316	.282	.302	1	
FC	P correlation Sig. (2-tailed)	.356	.354	.313	.297	.280	.985**	1
		.312	.315	.379	.405	.433	.000	

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Table 15: Correlation matrix between pesticides and bacteriological parameters

		propoxur1	Hexachlorobenzene	Diazinon	PCB 52	DDE	Endosulfanbeta	TC	FC
propoxur1	P correlation Sig.(2-tailed)	1							
Hexachlorobenzene	P correlation Sig.(2-tailed)	.212	1						
Diazinon	P correlation Sig.(2-tailed)	.911**	.298	1					
PCB 52	P correlation Sig.(2-tailed)	-.391	-.686*	-.480	1				
DDE	P correlation Sig.(2-tailed)	-.326	.357	-.162	-.326	1			
endosulfanbeta	P correlation Sig.(2-tailed)	-.278	-.380	-.114	.492	-.075	1		
TC	P correlation Sig.(2-tailed)	.238	-.386	.177	.287	.027	.243	1	
FC	P correlation Sig.(2-tailed)	.222	-.371	.167	.294	.095	.282	.990**	1
		.538	.292	.645	.410	.794	.429	.000	

** Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

The chemicals studied in the present study adhere to the water surface. Some of them are potentially toxic that are taken up by plankton and benthos animals, most of which are either deposit or filter feeders. However; the toxins are concentrated upward within aquatic food chains. Many particles combine chemically in a manner highly depletive of oxygen. Toxic metals can also be introduced into the aquatic food webs. These can cause changes to tissue matter, biochemistry, behavior, reproduction and suppress growth in aquatic life. Also, many animal feed have a high fish meal or fish hydrolysate content. In this way, toxins in river can be transferred to land animals, and appear later in meat and in dairy products. The process by which a contaminant increases in concentration as it rises in the food chain (phytoplankton- zooplankton- fish) is known as biomagnifications (Doworth, 2009).

4. CONCLUSION

Results of the present study reflect a continuous exposure of Hasbani river to various types of contaminants resulting from, mostly, domestic and agricultural activities. As, the water quality profile, metal and pesticide speciation are expected to impact the quality of water's river, aquatic organisms and consequently human health. Thus, it is critical to implement recommended interventions plans to safe the "Hasbani River" in accordance with international treaties and conventions.

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