A MULTIFACTOR STATISTICAL MODEL FOR ANALYSING THE PHYSICO-CHEMICAL VARIABLES IN THE COASTAL AREA AT ST-LOUIS AND TAMARIN, MAURITIUS[1]

Vandna JOWAHEER

Department of Mathematics, Faculty of Science,
University of Mauritius, Mauritius

E-mail: vandnaj@uom.ac.mu

Varunah LALBAHADOOR

Department of Mathematics, Faculty of Science,
University of Mauritius, Mauritius

E-mail:

Roshan RAMESSUR

Department of Chemistry, Faculty of Science,
University of Mauritius, Mauritius

E-mail:

Lutchmee DOSORUTH

Department of Chemistry, Faculty of Science,
University of Mauritius, Mauritius

E-mail:

Abstract: *The coastal pollution is an issue of concern for Mauritius. Since the past two decades, agricultural activities have contributed to pesticide and fertilizer run off in coastal waters. Over the recent years, the major urban and industrial growth in Mauritius have also contributed to water pollution by indirect wastewater discharge containing contaminants into rivers. As polluted water is hazardous to both marine life and human beings, it is of national interest to analyse the levels of water pollutants and the factors effecting these levels. This paper aims at developing a statistical model to evaluate the extent of coastal pollution in urbanized and agricultural regions in Mauritius. The study was carried out at two stations: St-Louis River (an urbanized industrial area) and Tamarin River (an agricultural area). A multifactor statistical model was formulated and analysed for the experimental data on the chemical and physical variables collected at the two sites for the estuary and downstream at each station, during 2001 and 2005 randomly spread over summer and winter seasons. The model is highly efficient in depicting the independent as well as the interactive effects of seasonality, time-interval, strategic locations and activities on the levels of different variables. A series of interesting conclusions were drawn from the analysis of the model. One major derivation was that the seasonal factor and time-interval had a significant effect (p-values < 0.01) on the levels of chromium, lead and nitrates at both the stations. However, the direction and magnitude were different with respect to each variable over the strategic locations. Moreover, considerable interactive effect between various factors regarding salinity was detected. These conclusions among others raise concern.*

Key words: *Experimentation; Statistical modeling and analysis; Estuaries; Trace metals; Nutrients; Physical parameters*

1. Introduction

Mauritius, an island geologically with a total land area of about 1865 square kilometres is dotted with rivers and streams where most of them are sourced in the high rainfall regions of the central plateau and flow down slope towards the Indian ocean. Due to the fact that Mauritius is so small, all land based activities have an impact on the coastal zone , thus making the coastal waters prone to pollution. Over the past years, the agricultural activities, the increase in industrialization and pressure on land due to high population density have produced large volumes of waste matter which have been indirectly dumped into the surrounding marine environments. The main sources of water pollution are contamination of underground water by pesticides and fertilizers, indirect disposal of industrial waste into streams and rivers, and contamination of domestic water supplies by overflowing of sewage system. (Ramessur et al., 2009; Burnett et al., 2006).

For over 40 years, about 45% of the existing land area was covered with sugarcane plantation Over these years, a large amount of pesticides and fertilizers have been used in order to achieve a high yield but as side effects, these agricultural practices have represented particular risks to water sources. The fertilizers and pesticides have been penetrating the ground water sources and runoff during rainfall, thus adding to the level of contaminants in the surface waters. In addition, over the past two decades, several surface water bodies have been receiving industrial effluent discharges containing chemicals and trace of metals. Metal residues and textile slurries with high trace metal concentration have caused great deal of pollution. Hence there are strong reasons to believe that coastal waters of Mauritius may possibly be undergoing degradation of the water quality arising from the presence of biological and chemical pollutants. (Anon., 1998; Anon., 2005; Breward et al., 1998).

In order to study the physico-chemical activities in the coastal waters of Mauritius, several studies have been performed and the levels of various metals, nutrients, physical and chemical parameters were recorded (Ramessur *et al.,* 1998; Ramessur *et al.,* 2001; Ramessur 2004). These studies have shown the presence of the toxic metals such as chromium and lead. Since the pollution of rivers and estuaries is hazardous for both the marine life and human beings, it is important to find out whether the presence of toxic substances is significantly increasing due to the impact of industrial, agricultural activities, sewage and atmospheric pollution. The aim of this paper is to develop and analyse a multifactor statistical model to assess the extent of water pollution in the coastal areas of Mauritius where agricultural or industrial activities have been in practice over last few years.

2. Materials and methods

2.1. Study Sites

The 2 sites along the western coast of Mauritius extending from St Louis to Tamarin are shown in Figure 1.

St Louis Catchment urban estuaries (stations 1 and 2)

The Grand River Bay estuary receives urban runoff indirectly from the St.Louis River, which flows through Pailles and Plaine Lauzun industrial and urban area. The GRNW, which discharges south of Port Louis, has a catchment area of 116 km^2 and is fed by small southern tributaries from Upper Plaines Wilhems and Moka district and runs adjacent to the M1 motorway.
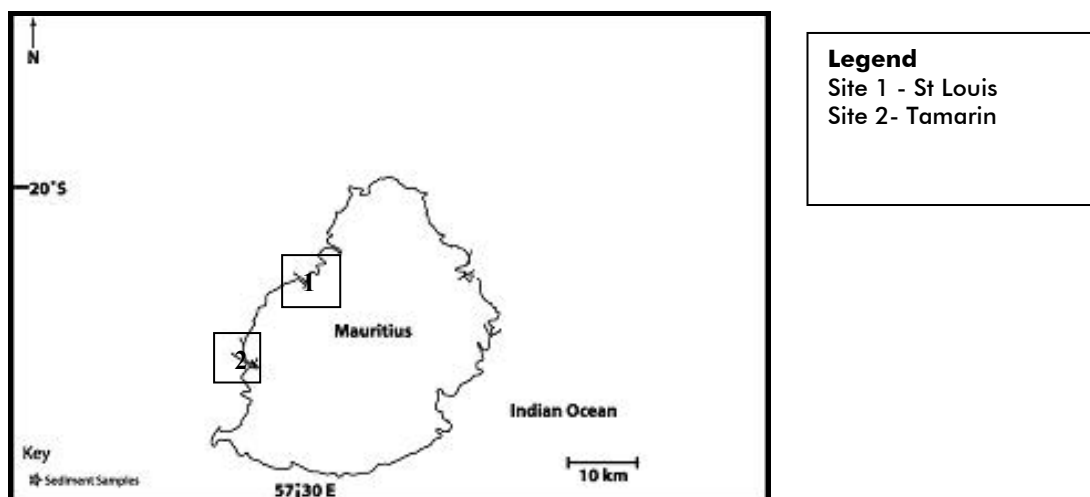
Figure 1. Sampling stations along 2 sites on the western coast of Mauritius
Note. Urban–site 1; Rural–site 2

Tamarin estuaries (stations 3 and 4)

The Tamarin estuary is unique in its kind where the topology of the sandy beach might change overnight. Sand deposits often block the mouth of the river such that water is trapped in the estuary forming a sort of basin. Anthropogenic activities that are near the estuary are mainly related to the tourism industry and also from human settlements upstream.

2.2. Experimental Data

Physical variables --- pH (v_1) & Salinity (v_2)

Salinity was recorded in the different compartments along the St Louis River using a Bellingham and Stanley field refractometer with a precision level of 0.2%. Replicate measurements of pH and temperature in situ the river were done using a Whatman pH portable meter A270. Replicate measurements of dissolved oxygen (D.O) were made in situ using a portable D.O meter Jenway Model 9071 consisting of a 'Clark' type polarographic oxygen electrode after calibration using a solution of 2% sodium sulphite.

Trace metal analysis in surface sediments ---- Pb (v_3) & Cr (v_4)

Cr and Pb were determined in the extracted solution from surface sediments collected along the 2 estuaries in 2001 and 2005 using a UNICAM 929 Atomic Absorption Spectrometer (AAS) (Analytical Technology Inc. 1993). Standards used for calibration for trace metal determination in sediments were prepared from standard 1000 mg L^{-1} stock solution. The working solutions (10 mg L^{-1}) of each Pb and Cr were prepared by diluting the stock solution in a 100 mL volumetric flask with deionised water. Standards were then prepared in the range of 1.0-4.0 mg L^{-1} for Pb and 1.0-5.0 mg L^{-1} for Cr. Flame AAS used for trace metal analysis in surface sediments involved the use of a mixture of acetylene and nitrous oxide for Cr at a wavelength of 357.9 nm and an air-acetylene flame for Pb at a wavelength of 217.0 and 213.9 nm respectively. The sample of carrier gas flow rate was maintained between 200-500 mL min^{-1}.

Nutrients --- Nitrate (v_5), Nitrite (v_6) and Phosphate (v_7)

Replicate samples of water were collected in 200ml plastic bottles (dissolved nitrate) and glass bottles (reactive phosphate) in the coastal area in St Louis and Tamarin. Samples were stored at 4°C and analysed within 24h. The concentration of dissolved nitrite, dissolved nitrate, and dissolved phosphate were determined using standard spectrophotometric methods (Parsons et al., 1984) at 543nm and 882nm respectively using a PU 8710 spectrophotometer and a UNICAM 8700 Series UV/VIS spectrometer following calibration using known standard solutions. Quality control was achieved by analysing an internal reference independently prepared from the standard and the standard curves were verified after 10 successive runs by analysis of one standard solution within the linear range for each nutrient.

In the presence of mineral acids nitrites reacted with amines to give diazonium salts which in turn reacted with an organic amine to give a pink azo dye after 10min. The amount of azo dye produced was measured by its absorption of light at 543nm in a 10cm cuvette.

Dissolved nitrate in the samples were reduced almost quantitatively to nitrite by running samples and standards through a column containing commercially available cadmium granules coated with metallic copper. The nitrite produced were determined by diazotising with sulphanilamide and coupling with N-(1-naphthtyl)-ethylenediamine dihydrochloride to form a highly coloured azo dye which was measured spectrophotometrically in 10 cm cuvettes at 543nm after 15 min. The reduction efficiency of the Cd column was determined by comparing the amount after reduction with the calculated amount supplied to the column. A correction was made for the nitrite present in the sample by analysing without the reduction step. The precision of nitrate determination was at the 1 mmol L^{-1}

Samples for reactive phosphate analysis were immediately filtered after collection. In a suitably acidified solution, phosphate reacted with molybdate to form molybdo-phosphoric acid, which was then reduced to the intensely coloured molybdenum blue complex after 5min. The absorbance of the latter was measured at 882nm in a 10cm cell. The precision was at the 0.1 mmol L^{-1}.

Quality Control

The accuracy and precision of the method was evaluated using three replicate determination of Standard Reference Material SRM 1646a Trace Elements in Estuarine Sediments from National Institute for Science and Technology (Colorado, U.S.A) which yielded 25.6 ± 1.8 mg kg^{-1} (Cr); 8.7 ± 1.3 mg kg^{-1} (Pb) compared to certified values of 40.9 ± 1.9 mg kg^{-1} (Cr) and 11.7 ± 1.2 mg kg^{-1} (Pb) respectively (mean and standard deviation) as determined using ICP MS by NIST with % recovery as 62.8%, 82.8% and 74.4% for Cr and Pb respectively. The main causes of losses were during the digestion procedure and also included random and systematic sources of uncertainty during analysis using the atomic absorption spectrometer. Necessary corrections were made accordingly. The detection limits were 2.3, 2.2 and 1.2 mg kg^{-1} for Cr and Pb respectively. (The limits of detection were taken as 3σ of three replicates of the procedural blank digested filter paper (3x standard deviation about the mean).

2.3. Multifactor Statistical Model

We formulate a 2^4 factorial model following Montgomery (1997), to investigate the effect of sites (A), years (B), stations (C) and seasons (D) each with two categories over each variable. The model equation is given by

$$y_{ijklr}^{v_m} = \mu + \alpha_i + \beta_j + \gamma_k + \delta_l + (\alpha\beta)_{ij} + (\alpha\gamma)_{ik} + (\alpha\delta)_{il} + (\beta\gamma)_{jk} + (\beta\delta)_{jl} + (\gamma\delta)_{kl} + (\alpha\beta\gamma)_{ijk} +$$
$$(\alpha\beta\delta)_{ijl} + (\alpha\gamma\delta)_{ikl} + (\beta\gamma\delta)_{jkl} + (\alpha\beta\gamma\delta)_{ijkl} + \varepsilon_{ijklr} \; ; \qquad i,j,k,l = 1,2 \; ; \; r = 1,2, ..., n \; ;$$

where $y_{ijklr}^{v_m}$ is the response from r^{th} sampling unit of mth variable v_m $(m = 1, ... , 7)$ for the ith, j^{th}, k^{th} and l^{th} categories of the factors A, B, C and D respectively; μ is the overall mean effect; $\alpha_i, \beta_j, \gamma_k$ and δ_l are the main effects; $(\alpha\beta), (\alpha\gamma), (\alpha\delta), (\beta\gamma), (\beta\delta) \& (\gamma\delta)$ are two-way interaction effects; $(\alpha\beta\gamma), (\alpha\beta\delta), (\alpha\gamma\delta)$ and $(\beta\gamma\delta)$ are three-way interaction effects; $(\alpha\beta\gamma\delta)$ is the effect of interaction between all the four factors and ε_{ijklr} is the error component corresponding to y_{ijklr} such that ε_{ijklr} are mutually independent and normally distributed with mean zero and variance σ^2. The model fitting is done using the software SPSS 14.

3. Results and discussions

As depicted in Figure 2, exploratory analysis of experimental data indicates that the levels of lead and chromium are much higher in St-Louis as compared to Tamarin at both the sites and for both the time points. This can be attributed to the fact that since St-Louis river flows through Plaines Lauzan, an industrial zone, it may be receiving lots of industrial waste water which elevates the level of metal content in this river.
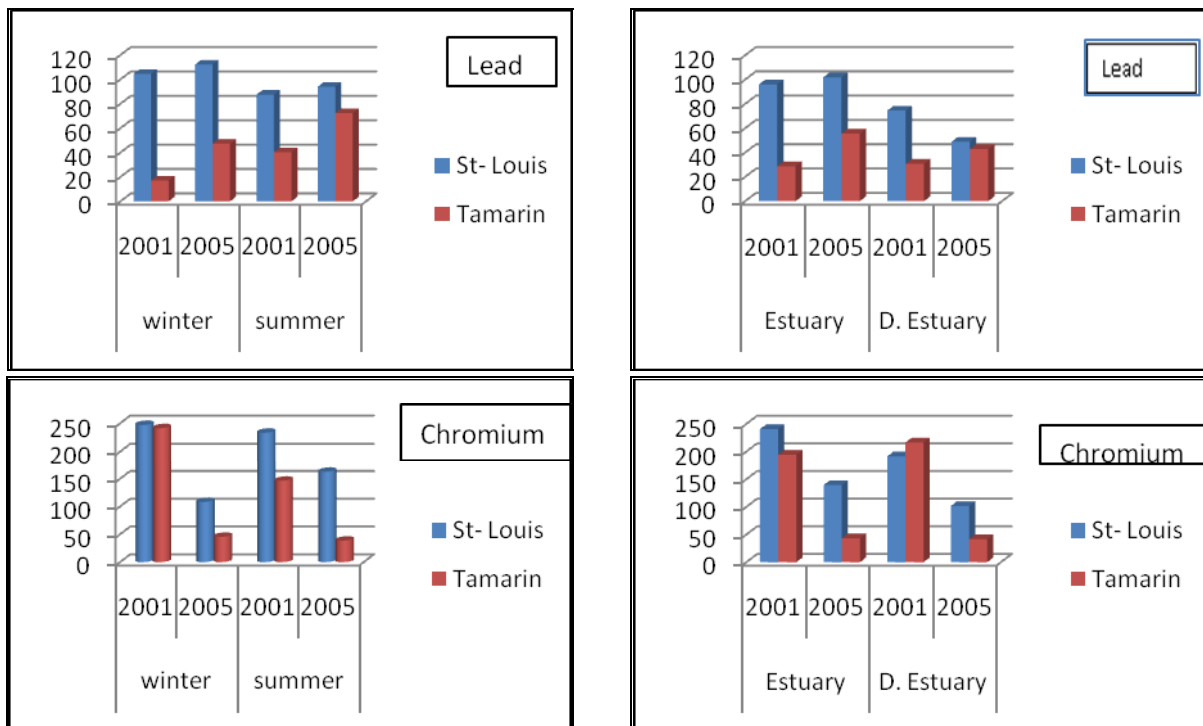

Figure 2. Distribution of Metal Contents

We also notice that in winter, the level of lead is higher at both the sites. From 2001 to 2005, there has been an increase in lead content and a decrease in chromium content at Tamarin. Moreover, estuaries have comparatively higher levels of lead than in downstreams.

Figure 3 reveals that salinity and pH levels are in general higher in Tamarin estuary and especially during the summer season, there appears to be a significant difference between the two sites concerning these two physical variables. However, in winter salinity is higher in St-Louis than in Tamarin over both the years. For both the sites, pH and salinity are much higher in downstream waters than in estuaries at both the time points. It is interesting to remark that pH levels have increased over years at both the stations of St-Louis whereas these levels show a decrease over years at both the stations of Tamarin.
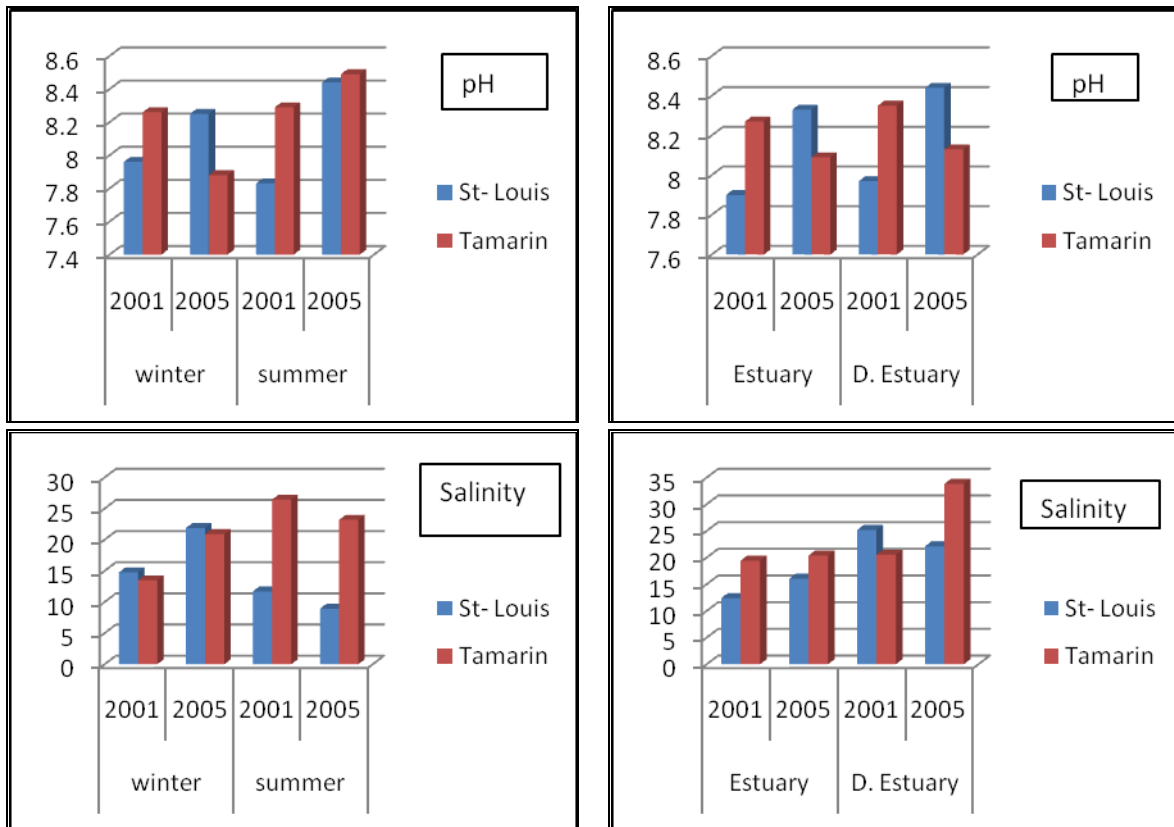

Figure 3. Distribution of Physical Variables

Concerning the level of nutrients, it is obvious from Figure 4, that the nitrate and nitrite contents at both sites have decreased drastically over the years. At St- Louis, this may be because industries are filtering their wastes before discharging into the river while at Tamarin, the decrease may be attributed to the fact that land being cleared for construction purposes, there is lesser cultivation, thus less use of fertilizers. It is observed that the phosphate content at St- Louis is higher except for winter 2005. Also, from 2001 to 2005 at Tamarin, we notice that there has been a general increase in the phosphate level.

Furthermore, the nitrate and nitrite content are higher at St- Louis at each station as compared to Tamarin over both years. Also, these nutrients at each site are higher at the estuaries. It is observed that the phosphate content at both stations was higher in St- Louis region in 2001 while at both stations in 2005, the phosphate content is higher at Tamarin. Overall, we notice that from 2001 to 2005, the phosphate content at St- Louis has fallen down while at Tamarin, there has been an increase. We also note that, the phosphate content at the estuary of each station is higher than that at downstream estuary.
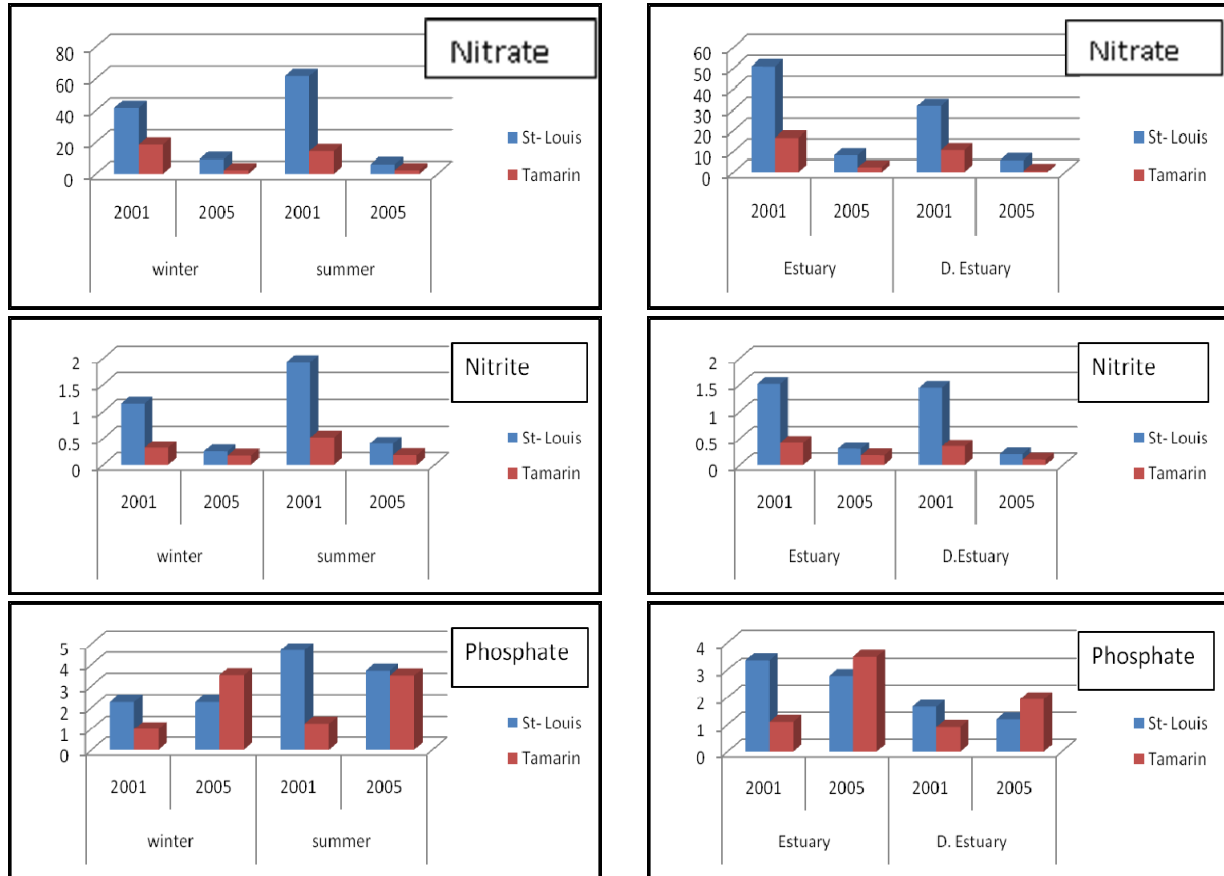
Figure 4. Distribution of Nutrients

With respect to the model fitting, all the assumptions of the model equation given in Section 2.3. are well satisfied by the data and the results obtained from model fitting are summarized in terms of p-values for the significant main factors as well as the interaction effects for all the variables under study and represented in Table 1.

Table1. Significant p-values

Sources	Pb	Cr	pH	Salinity	NO_3^-	NO_2^-	PO_4^{3-}
A	0.000	0.001	-	0.000	0.000	0.000	-
B	-	0.000	0.003	0.036	0.000	0.000	-
C	0.009	-	-	0.000	0.016	-	0.014
D	-	-	-	0.016	-	-	-
AB	-	0.01	0.000	0.003	0.000	0.002	0.034
AC	-	0.034	-	-	-	-	-
AD	-	0.038	0.004	0.000	-	-	-
BD	-	0.005	0.001	0.000	-	-	-
ABC	-	-	-	0.000	-	-	-

There is a significant difference between the lead contents for sites St- Louis and Tamarin. Between the stations also, we observe a significant difference at 5%. The model analysis shows that St-Louis estuary exhibits greater levels of lead as compared to Tamarin estuary. Among the treatment combinations for chromium, we notice that there is a significant difference between the chromium content for the sites and for the different years. A significant interaction is found between sites and years, stations and sites, sites and seasons, years and seasons with respect to chromium.

Further, the level of chromium content for 2005 at St- Louis downstream estuary during summer significantly exceeds than that at Tamarin downstream estuary during summer.

We also note that there is a significant difference between the pH values for years. Moreover there is significant interaction between sites and years, sites and seasons, years and seasons, with respect to pH.

For salinity we can conclude that there is a significant difference between sites, years, stations and seasons. Moreover, there is significant interaction between sites and years, sites and seasons, year and seasons, and, stations, years and sites with respect to salinity. There is a significant increase in salinity during winter, both in estuaries as well as downstream estuaries and the levels are comparatively higher in St-Louis.

With respect to nitrate levels there is a significant difference between sites, years and stations. Also a significant interaction between sites and years is observed. The model analysis confirms that as compared to Tamarin, St-Louis has higher levels of nitrates at both the stations. However, when compared over years, the levels are lower in 2005 than in 2001. The same scenario is observed for the nitrate levels. Phosphate levels had been significantly higher in St-Louis river than at Tamarin in 2001 but the situation was reverse in 2005, which implies that phosphate levels have been considerably brought down at St-Louis over years.

4. Conclusions

The analysis demonstrate the potential for Pb concentrations in estuarine sediments at St Louis to exceed contamination limits. The contamination of sediments with Pb at St louis was significant showing an increasing trend over the years which could be considered to arise from accumulation and the heavy use of leaded petrol and potentially constitute a health hazard. However, storm runoff during flash floods in summer could cause a significant decrease in the levels of Cr in the rural estuary due to dilution with cleaner background sediments comparable. Excessive nutrients at St Louis and Tamarin can promote algal blooms, leading to oxygen depletion and severe deterioration of water quality as well as fish mortality. It can be argued that agricultural, urbanization and tourism activities have contributed to an increase in anthropogenic activities and hence have increased the potential for increased land and urban runoff in the two areas.

5. References

1. Anon **Mauritius Neap II: Environmental Strategy option report**, Environmental Resources Management London, 1998, pp. 173
2. Anon **Assessment and Management Implications of Submarine Groundwater Discharge into the Coastal Zone**, ICAM-IHP-IAEA, 2005, pp. 52
3. Breward, N. *et al.* **Manual for contaminant flux assessment in tropical coastal environments. Volume 1: Guidelines**, British Geological Survey, Overseas Geology Series, Technical report WC/98/41, 1998, pp. 56
4. Burnett, W.C. *et al.* **Quantifying Submarine Groundwater Discharge in the Coastal Zone via Multiple Methods**, Science of the Total Environment, Vol. 367, 2006, pp. 498–543
5. Montgomery, C. D. **Design and Analysis of Experiments**, 4th ed., John Wiley & Sons Inc, 1997, pp. 228-240
6. Parsons, T., Maita, Y. and Lalli, C. M. **Chemical and Biological methods for seawater analysis,** Pergamon Press, 1984

7. Ramessur, R. T. *et al.* **Statistical comparison between consecutive winter and summer concentrations in zinc and lead from sediments in a tropical urban estuary in Mauritius. Environmental Monitoring and Assessment**, DOI: 10.1007/s10661-009-1118-z, 2009

8. Ramessur, R. T., Parry, S. J. and Jarvis, K. E. **Characterization of some trace metals from the Export Processing Zone and a coastal tourist area in Mauritius**, Environment International 326, Vol. 24, No.7, 1998, pp. 773-781

9. Ramessur, R. T., Parry S. J. and Ramjeawon, T. **The relationship of dissolved Pb to some dissolved trace metals (Al, Cr, Mn and Zn) and to dissolved nitrate and phosphate in a freshwater aquatic system in Mauritius**, Environment International, Vol. 26 No. 4, 2001, pp. 223-230

10. Ramessur, R. T. and Ramjeawon, T. **Determination of Pb, Cr and Zn from an urbanized river in Mauritius**, Environment International, Vol. 28 No. 4, 2002, pp. 315-324