AMERICAN UNIVERSITY OF BEIRUT

POLLUTANT LOAD ESTIMATION FOR RIVER MANAGEMENT STRATEGIES: A CASE STUDY OF BEIRUT RIVER

by SANIA EL NAKIB

A thesis

submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Sciences to the Interfaculty Graduate Environmental Science Program (Environmental Technology) of the Faculty of Engineering and Architecture at the American University of Beirut

> Beirut, Lebanon May 2018

AMERICAN UNIVERSITY OF BEIRUT

POLLUTANT LOAD ESTIMATION FOR RIVER MANAGEMENT STRATEGIES: A CASE STUDY OF BEIRUT RIVER

by SANIA EL NAKIB

Approved by:

Dr. Ibrahim Alameddine, Assistant Professor Civil and Environmental Engineering Department

Dr. May Massoud, Associate Professor Environmental Health Department

Advisø

Member of Committee

na

Dr. Majdi Abou Najm, Assistant Professor Civil and Environmental Engineering Department

Member of Committee

Date of thesis defense: May 3, 2018

AMERICAN UNIVERSITY OF BEIRUT

THESIS, DISSERTATION, PROJECT RELEASE FORM

| Student Name: | El Nakib | Sania | Khaled |
|---------------|----------|--------------------|---|
| | Last | First | Middle |
| Master's The | esis | O Master's Project | Doctoral Dissertation |

I authorize the American University of Beirut to: (a) reproduce hard or electronic copies of my thesis, dissertation, or project; (b) include such copies in the archives and digital repositories of the University; and (c) make freely available such copies to third parties for research or educational purposes.

I authorize the American University of Beirut, to: (a) reproduce hard or electronic copies of it; (b) include such copies in the archives and digital repositories of the University; and (c) make freely available such copies to third parties for research or educational purposes after : **One ----** year from the date of submission of my thesis, dissertation, or project.

14-05-2018

Signature

Date

ACKNOWLEDGEMENTS

This work would not have happened without the help and support of great people, friends, and family.

First of all, I dedicate my principal thankfulness and appreciations to my advisor, Dr. Ibrahim Alameddine who supported me with patience and knowledge despite his other academic and professional commitments. His coaching skills and knowledge inspired me and it was a great pleasure to work with him at AUB.

I would like to offer my deepest regards and appreciation to Dr. Majdi Abou Najm and Dr. May Massoud for their cooperation, suggestions, valuable comments and advices.

I also would like to thank the Litani River Authority, Lebanese Army, and the Weather Forecast team at the Beirut Rafic Hariri International Airport for providing me with relevant important data in order to conduct my study and analysis.

Moreover, I would like to thank all the professors and faculty staff at the Civil and Environmental Engineering department for their continuous help throughout my graduate studies.

I would like to extend my gratitude to my parents who provided me with moral support and bared my stress during the whole period, to my brother who supported and encouraged me to keep going on, and to my friends who always stand by my side. Their love, support and constant patience have taught me much about sacrifice, discipline and compromise.

AN ABSTRACT OF THE THESIS OF

<u>Sania El Nakib</u>

for <u>Master of Science, Environmental Sciences</u> <u>Major: Environmental Technology</u>

Title: <u>Pollutant Load Estimation for River Management Strategies: A Case Study of</u> <u>Beirut River</u>

Rivers are increasingly being subjected to increased anthropogenic pollution stresses that undermine their designated-uses and negatively affect sensitive coastal regions. The degradation of river water quality can be attributed either to point or non-point sources of pollution. While most developed countries have successfully reduced their point source loads and are now focused on managing their non-point sources, developing countries are still struggling with both types of pollution. In this study, we determine the relative contribution of point and non-point pollutant loads in the Beirut River basin, a poorly monitored seasonal Mediterranean river. Water quality samples were collected over two consecutive years (2016 and 2017) from four sampling sites that represent a gradient of increased urbanization. The spatio-temporal variability of the physiochemical and biological pollution levels were analyzed in an effort to better understand the relative contribution of point and non-point pollution sources. Flow-concentration statistical models were then developed to estimate the total nutrient and sediment loads reaching the different river segments. Loads were also estimated using the Beale's ratio method and compared with the loads generated from the regression-based models. Nonpoint source loads were also quantified using the Geographic Information System (GIS) enabled Open Nonpoint Source Pollution and Erosion Comparison Tool (OpenNSPECT). The model accounts for the landuse/landcover, overland flow, soil types, and adopted land-management practices in the river basin. Results showed significant seasonal variability in pollution levels across the river basin and a high correlation between the measured pollution loads and the measured river flows. Spatially, pollution levels appeared to correlate well with the urbanization levels observed all along the Beirut River watershed. Model results showed that point sources were the main cause of water quality impairment across the entire basin. The adopted modeling approach in this study provides an opportunity to better understand pollutant load dynamics in the basin and a mechanism to apportion pollution loads between point and non-point sources. It is hoped that this study will give decision makers a better understanding of the water quality situation in the Beirut River and thus facilitate the development of an integrated comprehensive and transparent river basin management plan.

Keywords: Water quality, Load estimation, Point sources, Non-point sources, Beirut River, Lebanon.

| ACKNOWLEDGEMENTS | v |
|---|----------|
| ABSTRACT | vi |
| LIST OF ILLUSTRATIONS | ix |
| LIST OF TABLES | X |
| Chapter pag | ge |
| 1. INTRODUCTION | .1 |
| 2. MATERIALS AND METHODOLGY | 6 |
| 2.1 Study area | .6 |
| 2.2 Water quality sampling | 12 |
| 2.3 River flows | 13 |
| 2.4 Load estimation | 15 |
| 2.4.1 Pollutant load estimation2.4.2 Non-point source load estimation: Open-NSPECT model | 15 19 |
| 2.4.3 Point load estimation | 22 |
| 2.5. Statistical Analysis | 22 |
| 3. RESULTS | 24 |
| 3.1 Spatial and temporal variation in water quality | 24 |
| 3.2. Total pollutant load estimation | 33 |
| 3.2.1 Regression based method | 33 37 |
| loads | 38 |
| 3.3. Non-point source loads | 39 |
| 3.4 Point source loads | 44 |

CONTENTS

| 4. | DISCUSSION | 46 |
|----|----------------------------|----|
| 5. | CONCLUSION AND FUTURE WORK | 52 |
| 6. | REFERENCES | 55 |

ILLUSTRATIONS

| igure Pag | ge |
|--|------------------|
| Map of the sub-catchments and the location of the sampling locations: (S1) Rwaysing El Ballout, (S2) Jaamani, (S3) Daychounyieh, and (S4) Jisr El Basha Land cover map of year 2010 Landuse and land cover in the vicinity of the sampling stations: (a) S1: the area is largely forested with no anthropogenic sources in its immediate vicinity, (b) S2: concrete masonry unit manufacturing facility along with a waste composting facility situated on the bank of the river | it . 8 . 9 |
| 4 Landuse and land cover in the vicinity of the sampling stations: (c) S3: the area at this station is agricultural and recreational with a large wastewater pipe discharge. (d) S4: heavily industrialized area with wastewater pipes discharging into the rive. | , r 11 |
| 5 Flow measurements across the four stations during the sampling period. Catchment areas are: S1= 49 Km ² ; S2= 126 Km ² ; S3= 213 Km ² ; and S4 = 216 Km ² 1 | ts 14 |
| 1 Spatial variation of temperature (Temp), pH and electric conductivity (EC) in Beirr River. Note that for pH the EU Class I,II and II standards are the same | ut 28 |
| ² Spatial variation of NO ₂ , NO ₃ , TN, PO ₄ , TP, SO ₄ , COD, BOD and TSS along the 4 stations in the Beirut River. Note that for SO ₄ and COD the EU Class I and II standards are the same | 1 28 |
| 3 Temporal variation of temperature (Temp), pH, and electric conductivity (EC) in Beirut River. Note that for pH the EU Class I II and II standards are the same | 31 |
| 4 Temporal variation of NO2, NO3, TN, PO4, TP, SO4, COD, BOD and TSS in the Beirut River. Note that for SO4 and COD the EU Class I and II standards are the same | 32 |
| -5 Spearman's rank correlations between the measured parameters during the wet and dry season. (a) Wet season; (b) Dry season | l 33 |
| 6 Comparison of the daily predicted and observed TN and TP concentrations at S1, S and S4 for the period between April 1, 2016 and November 30, 2017 | 53 36 |
| 7 Predictive regression-based distribution of TN and TP loads at S1, S3 and S4 | 37 39 |
| 9 Spatial distribution of the non-point TN, TP and TSS loads (tons/year) in the basin | 11 |
| 10 Spatial distribution of TN, TP and TSS local effects. S1B is the area draining into S1, S2B is the area draining into S2, S3B is the region between S1 and S2 on one hand and S3 on the other, S4B is the region between S3 and S4, SB5 is the region between S4 and the discharge point of the river | 42 nt |
| urban and forested areas for each of the 4 sub-catchments. Note that only at SB4 the area-averaged TP load was calculated from the regression-based load | 50 |

TABLES

| Table Page |
|---|
| 2-1 General description of the four sub-catchments along with the entire watershed9 Table 2-2 Adopted water quality analysis methods(Rice, Bridgewater, Water |
| Environment, American Water Works, & American Public Health, 2012) |
| 2-3 Pollutant coefficients for the given land cover classes (NOAA, 2014) |
| 2-4 Summary of input data used by OpenNSPECT |
| 2-5 TN, TP and TSS loads per capita. Source: (Henze & Comeau, 2008) |
| 3-1 Established regression-based flow-concentration equations at S1, S3 and S434 |
| 3-2 Pollutant load estimation using the Beale's method |
| 3-3 Summary of the non-point based TN, TP and TSS loads at the four sampling |
| locations over a year |
| 3-4 Summary of annual area averaged non-point pollutant loads at the sub-catchment level. S1B is the area draining into S1, S2B is the area draining into S2, S3B is the ragion between S1 and S2 on one hand and S3 on the other S4B is the ragion |
| between S3 and S4. SB5 is the region between S4 and the discharge point of the |
| river |
| 17001 + 44 |
| 3-5 Estimates of point source 1N, 1P and 1SS loads at the four sampling sites in the |
| Beirut River basin |
| 4-1 Percent contribution of point to non-point sources for TN, TP, and TSS |

CHAPTER I

INTRODUCTION

Anthropogenic induced alterations are the main drivers for modifying environmental systems and nutrient cycles, especially in freshwater bodies (Balter, 2013; Carpenter, Stanley, & Vander Zanden, 2011). Worldwide freshwater ecosystems, including rivers, have been degraded by the discharge of anthropogenic land-based sources of pollution (Da Silva & Sacomani, 2001; Meybeck, 2003; Vörösmarty et al., 2005; Vörösmarty et al., 2010). Surface water bodies, including lakes and rivers, are often used as the final destination for the discharge of wastes especially in developing countries. According to the United Nation, about 90% of domestic wastewater and 70% of industrial wastes are discharged untreated into water bodies in these countries (UN, 2003). Rivers provide key environmental services that include the provision of water for drinking, irrigation, and industrial purposes (Rissman & Carpenter, 2015) as well as habitats for invertebrates, fish, amphibian, and mammals. Yet, their ultimate use is often impaired by their water quality (Chapman, 1996). In an effort to preserve the functionality of rivers, environmental regulations, mainly across the developed world, have been developed with a focus on limiting and controlling the sources of river water pollution. These measures have resulted in a significant reduction in point source pollution. Nevertheless, diffuse sources of pollution, originating from agricultural runoffs and urban surfaces, remain a source of impairment across many freshwater systems (Schoumans et al., 2014).

The success of any waste reduction plan is contingent on the proper identification and quantification of the main sources of pollution responsible for the water quality impairment (Ding, Shen, Liu, Chen, & Lin, 2014; Novotny, 2003; Pellerin et al., 2014). Major sources of water pollution are often divided into two main categories, namely point and non-point source pollution. A point source enters the affected water body from a single well-identified location; examples of point sources include discharges from sewage treatment plants or industrial outfalls (Carpenter et al., 1998; Rissman & Carpenter, 2015). On the other hand, non-point pollution arise from multiple diffuse sources resulting largely from runoff over the landscape. Examples of non-point sources include storm-water runoff, agricultural runoff, and failed septic systems. While point sources are relatively easy to identify, quantify, and control (Albek, 2003; Carpenter et al., 1998), non-point sources are more challenging to manage as they cannot be traced back to a single origin or source (Novotny, 1999; Rissman & Carpenter, 2015). The estimation of non-point pollutant loads is often based on land cover/land use specific pollutant export coefficients (Bowes, Smith, Jarvie, & Neal, 2008; Pieterse, Bleuten, & Jørgensen, 2003). Most of the methods used to estimate diffused pollutant loads incorporate a Geographic Information System (GIS) component.

In the Mediterranean region, the discharge of polluted river water to the sea has been identified as a major stressor to the Mediterranean Sea (Bellos, Sawidis, & Tsekos, 2004; Nicolau, Galera-Cunha, & Lucas, 2006). Extensive studies on the impact of large Mediterranean rivers on sea water pollution have been conducted (Abril et al., 2002; Ludwig & Probst, 1998; Roy, Gaillardet, & Allegre, 1999); however, studies quantifying

and assessing the transfer of pollutants from the small Mediterranean rivers is still lacking (Dassenakis, Scoullos, & Gaitis, 1997; Stamatis, 1999). Unlike other rivers, Mediterranean rivers have unique chemical and physical characteristics. Their flow often fluctuates significantly across a given year and as such their chemical constituents show strong seasonal patterns (Nicolau et al., 2006). Back in 1978, the UNEP estimated that 320,000 tons of phosphorus, 800,000 tons of nitrogen, 60,000 tons of detergents, 12,000 tons of phenols, 100 tons of mercury, 3900 tons of lead, 2400 tons of chromium, 21,000 tons of zinc, 90 tons of organochlorine pesticides, and 120,000 tons of mineral oils entered the Mediterranean sea directly from the coastal zone or from rivers (UNEP, 1978). Since then several actions have been taken to reduce land-based pollution such as the Convention for the Protection of the Mediterranean Sea against Pollution (Gormley, 1976) and the Mediterranean Action Plan (UNEP/MAP, 2004). While these programs have been successful in reducing pollution loads in several regions, several recent studies across the Mediterranean have shown high anthropogenic loads of organic matter and nutrients entering Mediterranean rivers mainly from wastewater treatment plants and agricultural runoff (Bellos et al., 2004; Vega, Pardo, Barrado, & Debán, 1998).

In Lebanon there are 16 perennial rivers and 23 seasonal rivers that have a total annual flow of 3,900 million cubic meters (MCM) (MOE/UNDP/ECODIT, 2011). The water quality of these rives show high levels of microbiological pollution along with high levels of nitrates. The sources of pollution have been attributed to the discharge of untreated municipal wastewater and the excessive use of fertilizers (Houri & El Jeblawi, 2007; MOE/UNDP/ECODIT, 2011). A study conducted on the Damour River evaluated the

water quality of the river through the use of water quality indices. The study showed that the water quality in the studied river was degraded as a result of untreated wastewater discharges along with municipal solid waste disposal along the river banks (M. Massoud, 2012). Another study assessed how land use and anthropogenic activities influenced the water quality of the Abou Ali River in North Lebanon (M. A. Massoud, El-Fadel, Scrimshaw, & Lester, 2006b). The study concluded that the main sources of pollution were from wastewater discharges, livestock, and agricultural runoff. Moreover the water quality in the Upper Litani River Basin has been assessed by many studies (El-Fadel et al., 2003; ELARD, 2011; USAID, 2005). Results of the physio-chemical, biological and heavy metals tests showed that many of these parameters were above the national and international ambient water quality standards (Haydar et al., 2014).

In this study, the water quality of the Beirut River is assessed. Moreover, the pollutant loads reaching the different sections of the river are quantified and their sources identified. This study is the first study of its kind to be done on this seasonal river and it is hoped that this work will support and guide decision makers to take the necessary measures needed to protect this natural resource from anthropogenic pollution. For this purpose, a water quality sampling program was initiated whereby water quality samples were collected and analyzed at several locations along the river basin in an effort to identify the types and sources of pollution in the river. Moreover, the study estimated the total (point and non-point) pollutant loads at several locations along the river network, using flow and concentration measurements taken at the monitoring stations. Non-point source pollution loads within the basin were quantified using the GIS-based Open Nonpoint Source

Pollution and Erosion Comparison Tool (OpenNSPECT) model (NOAA, 2014). Finally, the point source loadings within the basin were estimated by comparing the total loads to the non-point source. The study concludes by proposing different mitigation measures that aim to reduce the different sources of pollution in an effort to help decision makers develop a river basin management plan for the Beirut River.

CHAPTER II

MATERIALS AND METHODOLGY

2.1 Study area

The Beirut River springs from the Western slopes of Mount Lebanon at an altitude of 1890 m. The river continues to flow westwards for about twenty kilometers. The river is also fed from the natural spring of Ain El Delbi. The river ultimately discharges into the Mediterranean Sea in the Karantina area. The total area of Beirut River watershed is 228 km². The basin is home to more than 200,000 people living in Beirut and its suburbs. The Beirut River separates Beirut city from its eastern urbanized suburbs, primarily Bourj Hammoud and Sin el Fil. Like most Lebanese rivers, the Beirut River is seasonal and dries out in the summer. The riverbed was large and wide until 1933, when Armenian refugees began to settle along its banks, hence narrowing the riverbed. As a result sediments started to accumulate causing an overflow in 1940. To control floods, concrete walls were constructed alongside the riverbed from starting from Karantini up to the Jisr al-Wati area. In 1988, the floodwalls were extended up to the Jisr al-Basha area (Frem, 2009).

In this study, four sampling locations S1 - Rwaysit El Ballout (33°49'50.4"N, 35°39'32.3"E), S2 - Jaamanni (33°51'48"N, 35°37'36"E), S3 - Daychounyieh (33°50'42"N, 35 °33'34"E), and S4 - Jisr El Basha (33°51'43"N, 35°32'28"E) were chosen along the Beirut River. The locations of the sampling station are represented in Figure 2-1, while a brief description of each of the local sub-catchments associated with the monitoring stations is summarized in Table 2-1. S1 is located in a pristine area dominated by pine forests.

Station S2 is located below Beit Meri. The site is in close proximity to a composting facility and a concrete masonry blocks plant. Station S3 is located near Anater Zbaydi. The area is largely agricultural with some touristic activities in its vicinity. Nevertheless, the station is just downstream of a wastewater effluent pipe collecting raw sewage from several suburban areas in the basin. The area in the vicinity of S4 (Jisr El Basha) is largely industrial and degraded. This section of the river is impacted by the open discharge of untreated wastewater and the open dumping of solid waste. Overall, the land cover of the watershed varies significantly with elevation; the headwaters of the basin are largely rural and heavily forested with some agricultural activity, while the lower sections are heavily urbanized and industrialized. A map illustrating the land cover of the study area is shown in Figure 2-2, along with photos taken at each of the 4 sampling stations (Figure 2-3 and 2-4).



Figure 2-1 Map of the sub-catchments and the location of the sampling locations: (S1) Rwaysit El Ballout, (S2) Jaamani, (S3) Daychounyieh, and (S4) Jisr El Basha

| Station | Sub-catchment area (Km ²) | Population | Agricultural area (Km²) | Urban area (Km²) |
|---------------------|---|------------|----------------------------|---------------------|
| S1 | 49 | 13,196 | 3.39 | 4.92 |
| S2 | 126 | 31,717 | 14.15 | 6.45 |
| S 3 | 38 | 26,488 | 2.87 | 4.32 |
| S4 | 3 | 11,762 | 0.75 | 1.83 |
| Beirut River | 228 | 199,419 | 22.27 | 25.85 |
| Watershed | | | | |

Table 2-1 General description of the four sub-catchments along with the entire watershed





Figure 2-2 Land cover map of year 2010





(a)



(b)

Figure 2-3 Landuse and land cover in the vicinity of the sampling stations: (a) S1: the area is largely forested with no anthropogenic sources in its immediate vicinity, (b) S2: concrete masonry unit manufacturing facility along with a waste composting facility situated on the bank of the river





(c)





(d)

Figure 2-4 Landuse and land cover in the vicinity of the sampling stations: (c) S3: the area at this station is agricultural and recreational with a large wastewater pipe discharge, (d) S4: heavily industrialized area with wastewater pipes discharging into the river

2.2 Water quality sampling

The water quality sampling stations were chosen to cover a wide range of landuse/landcovers within the watershed. The sampling was conducted between April 2016 and November 2017. Water samples from the four stations were collected on a weekly basis when the river was flowing. Concentrations of the physico-chemical and biological parameters were determined following the analytical methods shown in Table 2-2. Temperature, pH, and conductivity measurements were performed on site. Moreover, water quality samples were transported to the Environmental Engineering Research Center and Laboratories (EERC) at the American University of Beirut (AUB) and stored at 4 °C for further analysis. The analysis determined total suspended solids (TSS), nitrogen (as total nitrogen (TN) and nitrite and nitrate (NOx)), phosphorous (as total phosphate (TP) and as ortho-phosphate PO4), sulfates, chemical oxygen demand (COD), and biochemical oxygen demand (BOD5). Furthermore, biological tests were done to assess the total and fecal coliform concentrations at the four sites. Measured pollutants were compared to the ambient water quality standards set for rivers by the European Union (EU) as defined by the Water Framework Directive (WFD) (Buijs & Toader, 2007) and to the United States Environmental Protection Agency (USEPA) Ecoregion III (EPA, 2000).

| | Quality indicators | Method | Method number | |
|------------|------------------------------|---------------------------|---------------|--|
| | рН | Electrometery | 4500-H+B | |
| Physical | Conductivity | Electrometery | 9050-A | |
| | Total suspended solids (TSS) | Filtration | 2540-В | |
| | Chemical oxygen demand | Reactor digestion | 5220-D | |
| | Biochemical oxygen demand | Respirometry | 5210-В | |
| | Nitrate | Colorimetry | 4500-NO3-B | |
| Chaminal | Nitrite | Colorimetry | 4500-NO2-B | |
| Chemical | TN (Total Nitrogen) | TNT Persulfate Digestion | 10071 | |
| | Phosphate | Colorimetry | 4500-P.B | |
| | TP (Total Phosphorus) | Acid Persulfate Digestion | 4500-P.B&E | |
| | Sulfate | Spectrophotometrically | 10200 H.2 | |
| Biological | TC/TF | Membrane filtration | 9222B/9222D | |

Table 2-2 Adopted water quality analysis methods(Rice, Bridgewater, Water Environment, American Water Works, & American Public Health, 2012)

2.3 River flows

Flow measurements for the Beirut River dating back to 2009 were provided by the Litani River Authority (LRA). LRA provided flow measurements for three points (S2, S3 and S4), while the flow at S1 was measured concurrently with the water quality sampling efforts using an electromagnetic flow meter, the Hach FH950 flow meter. The choice of the FH950 was based on its ability to measure flow in streams with shallow depth as is the case for the Beirut River in the dry season. Flows were estimated based on the ISO 748:2007 standards for the mid-section method. Note that a regression equation was developed to estimate the flow at S1 from the flow recorded at S2 (Equation 1). The model was able to predict 80 % of the variability in the observed flow at S1. It is worth mentioning that

between May and October there was no flow in the river at all four stations. Figure 5 presents the flow measurements across the four stations during the sampling period.



Figure 2-5 Flow measurements across the four stations during the sampling period. Catchments areas are: $S1=49 \text{ Km}^2$; $S2=126 \text{ Km}^2$; $S3=213 \text{ Km}^2$; and $S4=216 \text{ Km}^2$

$$\sqrt{Q_{S1}} = 0.25 + 0.55\sqrt{Q_{S2}} + \cos\left(\frac{2\pi Tsample}{365}\right) + \varepsilon$$
 (1)

Where:

 $\sqrt{Q_{S1}}$: Square root transformation of flow at S1 $cos(2\pi T sample/365)$: Seasonal factor determined as a function of the cosine of the time

of sampling; T is the sampling date starting with April 1 2016 (April 1 2016 = 1)

 ε : Residual error of the model; $\varepsilon \sim N(0, 0.21)$

2.4 Load estimation

2.4.1 Pollutant load estimation

River pollutant loads were estimated based on the data collected from the in situ water quality monitoring programs. Given that the water quality data are often limited as compared to flow data, flow-concentration relationships were developed in an effort to estimate total pollutant loads and impute missing pollutant concentration (Bowes et al., 2008; Dolan, Yui, & Geist, 1981; Ferguson, 1987; Haggard, Soerens, Green, & Richards, 2003; Koch & Smillie, 1986; Malan & Day, 2003; Pellerin et al., 2014; Phillips, Webb, Walling, & Leeks, 1999; Smith & Croke, 2005). Statistical approaches, such as regression models, are typically used to impute missing pollutant concentrations. This is done by developing regression models that predicts pollutant concentration from flow data (Dolan (Cohn, 1995; Dolan et al., 1981; Park & Engel, 2014; Richards, 1998). The functional form of these flow-concentration models are often represented by single or multiple linear regression equations with logarithmic transformation (Brezonik & Stadelmann, 2002; Gilroy, Hirsch, & Cohn, 1990). Software used to estimate pollutant loads in rivers and streams depend on the adopted regression equations. LOADEST and FLUXMASTER are two software programs developed by the United States Geological Survey (USGS) to estimate water pollutant loads reaching rivers and streams (Lee et al., 2016). Each of these software has several models that includes different types of parameters depending on the data set of pollutant concentrations and discharge used (Runkel, Crawford, & Cohn, 2004; Schwarz, Hoos, Alexander, & Smith, 2006).

In this study, multiple linear regression models were developed for each station to predict TN, TP and TSS pollutant concentrations as a function of the flow measurements, water temperature, and seasonality (Equation 2) (Haggard et al., 2003; Lee et al., 2016). Final models were fit using the R software (R Core Team, 2017) based on the stepwise selection procedure that eliminates insignificant variables. The total annual loads were estimated by summing the daily loads as shown in Equation 3.

$$Trans(C_x) = \beta_0 + \beta_1 \log(Q) + \beta_2 (\log(Q))^2 + \beta_3 \cos(2\pi T/365)$$

+ $\beta_4 \sin(2\pi T/365) + \beta_5 (Temp) + \varepsilon$ Equation 2

Where:

Trans(C_x): Transformed concentration for each pollutant (x : TP, TN or TSS) log(Q): Logarithmic transformation of flow (m^3 /sec)

 $\cos\left(\frac{2\pi T}{365}\right)$: Seasonal factor determined as a function of the cosine of the time of sampling; *T* is the sampling date starting with April 1 2016 (April 1 2016 = 1)

 $\sin\left(\frac{2\pi T}{365}\right)$: Seasonal factor determined as a function of the sine of the time of sampling; *T* is the sampling date starting with April 1 2016 (April 1 2016 = 1)

Temp: Temperature in °C

 ε : Residual error of the model; $\varepsilon \sim \text{Norm}(0, \sigma^2)$

$$\hat{L}_{\tau} = \Delta t \sum_{i=1}^{NP} (Q\hat{C})_i = \Delta t \sum_{i=1}^{NP} \hat{L}_i$$
 Equation 3

Where:

 $\hat{L}_i = [(Q\hat{C})_i]$: Estimate of instantaneous load

\hat{L}_{τ} : Estimate of total load

NP: Number of discrete points in time when Q>0

Δt : Time interval represented by instantaneous load (1 day)

The Beale's ratio (BR) estimator method was also used to estimate pollutant loads (Equation 4). This methods has been found to outperform the regression-based approach when the flow-concentration relationship is not log linear or has high variance (Preston, Bierman, & Silliman, 1989) and when the number of flow data is large as compared to concentration data (Quilbé et al., 2006). Nevertheless, the ratio method needs a larger number of samples as compared to the regression method to achieve the same level of accuracy (Lee et al., 2016; Preston et al., 1989; Richards & Holloway, 1987). The Beale's ratio load estimation approach assumes a positive correlation between load and flow and has been utilized extensively in the estimation of pollutant loads in the Great Lakes area and other regions of the United States (Richards & Holloway, 1987). Moreover, Dolan et al. (1981) used the Beale's ratio estimator method to estimate annual total phosphorous loads entering Lake Michigan from the Grand River. Another study conducted by Quilbé, et al. (2006) chose the ratio estimator method after evaluating several estimation methods to calculate sediment and nutrient loads to the Beaurivage River watershed. In the Beale's method, the total pollutant loads are estimated by summing up the daily sampled daily loads with the product of the estimated Beale's ratio multiplied by the total flow for all days when the pollutants were not sampled and for which there was a flow measurement

(Equation 5). Moreover in this study, differences between regression based loads and those estimated by the Beale's ratio method were explored and discussed.

$$BR = \hat{R} \left(\frac{1 + \frac{1 - f}{n} c_{LQ}}{1 + \frac{1 - f}{n} c_{QQ}} \right)$$
 Equation 4

Where:

 $\hat{R} = \bar{l}/\bar{q}$: Ratio of the sample means of load and flow f = n/N: Ratio of the number of samples, *n*, to the total number of days (sampled or unsampled) in the prediction period, N (when Q>0)

 $c_{LQ} = \frac{s_{LQ}}{(\bar{l}\bar{q})}$: Ratio of the sample covariance between load and flow, s_{LQ} , to the product

of the sample means of load and flow

 $c_{QQ} = \frac{s_Q^2}{\bar{q}^2}$: Ratio of the sample variance of flow to the square of the sample mean of flow

$$L_t = \sum_{i=1}^{n} C_i \times Q_i + BR \times \sum_{j=n+1}^{NP} Q_j$$
 Equation 5

The uncertainty in the regression-based load predictions was quantified using a Monte Carlo simulation. The predictive distribution of each of the pollutant concentrations (transformed or untransformed) was described by a conditional normal distribution with a mean given by the simulated coefficients of each variable and the simulated standard error for each linear model. The Monte Carlo simulations were done using the sim function in the arm package in R (Gelman et al., 2016). One thousand simulations were conducted. The function returns a vector of simulated residual standard deviations and a matrix of simulated regression coefficients. We used these simulations to generate the predictive distribution for each pollutant. These distributions account for the model uncertainties in the multiple regression model. Note that the use of Monte Carlo simulations helps address re-transformation biases (Qian, 2016). In this work, potential biases can be associated with the logarithmic or cubic root transformation applied to the pollutant concentrations.

2.4.2 Non-point source load estimation: Open-NSPECT model

Non-point source pollutant loads contribute part of the total pollutant loads reaching the river. The OpenNSPECT model was used to estimate the annual TP, TN and TSS nonpoint loads reaching the Beirut River. The OpenNSPECT software is a model developed by the National Oceanic and Atmospheric Administration (NOAA) Office for Coastal Management to examine non-point pollution loads at the watershed level based on the landuse/landcover, elevation, soil types, precipitation, and adopted best-practices. The model has been successfully used to assess the effect of landuse modifications in several places in the Unites States, including the Deep River watershed area in Indiana and Ko⁴olaupoko in Hawaii (Viswanathan & Karim, 2015). OpenNSPECT has also been used to assess the effects of wildfire on non-point source pollutants reaching sensitive oceanic ecosystems (Morrison & Kolden, 2015). Moreover, the model has been used to recommend non-point source management practices in areas with high levels of pollutant (KBAC, 2007).

The model estimates pollutant loads (TN, TP and TSS) by generating pollutant concentration grids from assigned load contribution coefficients based on land cover classes (Table 2-3). When these grids are multiplied by the accumulated runoff volume

raster, the product will be grids of the pollutant mass produced at each cell. Note that when the flow direction grid is used, accumulated pollutant mass grids are generated that take into account contributions from upstream cells. For the purpose of removing the effect of upstream cells, OpenNSPECT can also produce local effect grids using runoff and pollutant concentrations grids generated at each cell rather than including the cumulative effects of upstream cells in the basin.

| Land Cover Class | Total Nitrogen (mg/L) | Total Phosphorus (mg/L) | Total Suspended Solids (mg/L) |
|-----------------------------|--------------------------|----------------------------|----------------------------------|
| Water | 0.00 | 0.00 | 0.00 |
| High Intensity Developed | 2.22 | 0.47 | 71.00 |
| Bare Land | 0.97 | 0.12 | 70.00 |
| Mixed Forest | 1.25 | 0.05 | 11.00 |
| Sedge Herbaceous | 0.00 | 0.00 | 0.00 |
| Cultivated Land | 2.68 | 0.42 | 55.30 |

Table 2-3 Pollutant coefficients for the given land cover classes (NOAA, 2014)

Water routing for the model is based on the Digital Elevation Model (DEM) for the watershed. In this study, the DEM for the study area had a resolution of 10m and was generated from 1m contours provided by the Department of Geographic Affairs in the Lebanese Army. As such, the Spatial Analyst toolbox under ArcGIS 10.5 was used to generate the flow direction, flow accumulation, length slope (Equation 6) and to determine the watershed boundary. Moreover, the erodibility factor (k) and the hydrologic soil group fields were generated and used to develop the soil database needed to run the model. The erodibility factor was established based on the soil texture (clay, loamy sand, silty clay ... etc) and its organic matter content (Stewart, Woolhiser, Wischmeier, Caro, & Frere, 1975). As for the hydrologic soil group, this data was developed based on the infiltration rate of each

soil type (NOAA, 2014). Note that the 2006 national soil map developed by the National Center for Scientific Research (NCSR) was used to identify the soil types and texture in the study area.

$$ls = \left(\frac{[Flowacc] * resolution}{22.1}\right)^{0.4} * \left(\frac{\sin([slope] * 0.01745)}{0.09}\right)^{1.4} * 1.4$$
 Equation 6

Where:

Flowacc: A raster generated by ArcGIS 10.5 showing the accumulated flow into each cell.

resolution: A 10m resolution raster was used

slope: It is the gradient, or rate of maximum change in z-value generated from each cell of a raster surface (DEM). Note that the slope is calculated in degrees and the raster was generated using the slope tool under Spatial Analyst toolbox in ArcGIS 10.5.

The main input datasets used for calculating the non-point pollutant loads for the Beirut River Watershed are summarized in Table 2-4.

| Layer | Description | File type and resolution |
|---------------|--|--------------------------|
| Land cover | Land use and development of the study area | Raster; 10m |
| Elevation | Digital elevation data of the study area | Raster; 10m |
| Precipitation | Annual precipitation data for the study area for 2016 and 2017 | Raster; 10m |
| Soil | Type and characteristics of the soil in the study area | Vector |

Table 2-4 Summary of input data used by OpenNSPECT

OpenNSPECT outputs include both accumulated and local effect grids. These grids present the mobilization and accumulation of pollutants through the landscape as well as the amounts of pollutants originating from each cell in the watershed area. These grids include the accumulated runoff, pollutant concentration, accumulated pollutant loads, runoff local effect, and pollutant local effect (NOAA, 2012).

2.4.3 Point load estimation

In an effort to estimate the point pollutant loads reaching the Beirut River, the calculated non-point pollutant loads were subtracted from the total estimated pollutant loads. These estimates were compared with the maximum pollutant loads that can be generated from the discharge of raw wastewater into the river without attenuation. The maximum loads were calculated by multiplying the total population within each catchment with their wastewater generation rate and the daily TN, TP and TSS loads per capita. Given that there is no national data on the domestic wastewater pollutant loads per capita in Lebanon, Egyptian loads were used as a reference (Table 2-5). The comparison between the two estimates provides a rough assessment of river attenuation and/or the contribution of non-domestic point sources.

| Parameter | Load per capita (kg/capita.year) |
|-----------|-------------------------------------|
| TN | 4 |
| TP | 0.5 |
| TSS | 20 |

Table 2-5 TN, TP and TSS loads per capita. Source: (Henze & Comeau, 2008)

2.5. Statistical Analysis

Correlations (Spearman's rank correlation) between the different water quality parameters were first determined and assessed for their statistical significance.

Additionally, repeated measure ANOVA was performed to test for the significance of spatial variability in the observed water quality parameters. Note that all concentrations were log transformed to achieve normality. This was followed by a multiple comparison test using Tukey's method to identify statistically significant differences between pollutant concentrations and sampling stations. The variation in the observed pollutant variances across the four stations was also analyzed using the Flinger-Killeen test. As for the temporal variation, the parametric t-test and the non-parametric Wilcoxon test were used to assess observed variation between the dry and wet season. A two-way ANOVA was conducted to investigate concurrently the effects of both spatial and temporal variations on pollutant concentration. The potential for an interaction between location and seasons was also assessed. As for the assessing the similarity between the pollutants loads estimated from both load estimation methods, this was conducted through the use of the parametric ttest on log transformed loads. Furthermore, the Levene test was conducted to assess if the variance around each estimate were similar. Note that all the statistical tests were conducted at the 95% confidence level (α =0.05). All statistical analysis were performed using the R software (R Core Team, 2017).

CHAPTER III

RESULTS

3.1 Spatial and temporal variation in water quality

Most of the water quality parameters tested at the four sampling stations were in violation of the EU Class I standards defined for undisturbed rivers and the USEPA Ecoregion III standards, except for SO₄ as shown in Figures 3-1 and 3-2. As can be seen in the figures, concentrations tended to increase moving from the upstream sections of the river down to the downstream sections. The highest concentrations of most parameters were observed at S4 and/or S3. The median levels of TN at S4 exceeded the EU Class I water quality standards (1.5 mg/L) by approximately 3 times and the USEPA standards (0.38 mg/L) by approximately 12 times. The median TN concentrations at S1 and S2 were found to exceed the EU class I and USEPA standards by 1.4 and 5 times respectively. At S3 and S4 approximately 30% of the observed TN concentrations exceeded the Class III EU standards (8 mg/L) that expects a serious negative impact on aquatic life. The median TN concentrations was found to statistically differ across the four stations (ANOVA, pvalue 0.01). According to the Tukey multiple comparison test, statistical differences were observed between S1 and S4 and between S1 and S3 (Tukey, p-value 0.002 and 0.04 respectively). TN concentrations at S4 and S3 were approximately two times greater than those observed at S1. Similarly, the measured TP concentrations were found to exceed EU Class I and the USEPA standards consistently across the four sampling stations. The

median levels of TP at S4 and S3 were 3 times higher than the EU Class I standard limits (0.1 mg/L), and 18 times higher than the USEPA standard (0.0218 mg/L). At S1 and S2, median TP concentrations exceeded the EU Class I and USEPA standard limits by approximately 1.6 and 10 times respectively. At S3 and S4 approximately 22% and 17 % of the observed TP concentrations exceeded the Class V standard limits set by the EU standards (1 mg/L), respectively. Exceeding Class V standards indicates that the water body is in a bad status and its use is impaired and only available for no-quality demanding purposes. Moreover at S3 and S4, 27% and 39% of the observed TP concentrations respectively were between Class III and IV (0.4 mg/l - 1 mg/L). This range identifies the water quality as deteriorated for aquatic life and insufficient for quality usage purposes. The observed TP concentrations didn't show a significant difference across the four stations (ANOVA, p-value 0.1). As for TSS levels, the highest levels were recorded at S3 with a median concentration of 77 mg/L. This value was approximately 3 times larger than the median values recorded at S1 and S2. This is due to the sudden change in landuselandcover around that station, where the basin transitions from a heavily forested region into a densely urban landuse. However, TSS concentrations were not found to be significantly different across the four stations (ANOVA, p-value 0.08). This is due to the large within group variability in TSS levels at each site. Sulfate concentrations didn't exceed the water quality standards at all sampling occasions. Yet, difference in sulfate concentrations was noted across the stations (ANOVA, p-value <0.05). Levels at S4, S3, and S1 were found to be significantly higher than those recorded at S2 when performing the

multiple comparison test (Tukey, p-values < 0.05). This is most likely attributed to the natural presence of sodium sulfate and magnesium sulfate deposits at these sites.

COD concentrations at S3 and S4 were 0.9 and 3 times higher than the EU Class I water quality standard (7 mg/L) respectively. Median COD levels at the uppermost stations (S1 and S2) marginally exceeded the EU Class I water quality standards. Moreover, 63% and 42% of the measured COD concentrations at S4 and S3 respectively were above EU Class IV standard limit (20 mg O₂/L), however only 13% of the observed concentrations were above this limit at S1. Note that the area surrounding S3 and S4 is heavily industrialized and open dumping of wastes is a common practice. The difference in concentration between the four stations was significantly different (ANOVA, p-value <0.05). Levels at S4 were found to be significantly higher than those recorded at S1, when performing the multiple comparison test (Tukey, p-values = <0.05). This is to be expected as the area around S4 is heavily industrialized, with many factories dumping their wastewater effluents untreated immediately upstream of that site. With respect to BOD, the median level at S4 was 7 mg O_2/L , which exceeds the Class I standard level (3 mg O_2/L) set by the EU. Note that even in the upper sections of the river (S1 and S2), the median BOD levels exceeded the standard. The percentages of observed concentrations that exceeded Class IV were 11%, 33%, 44% and 52% at S1, S2, S3 and S4 respectively. No significant difference of BOD concentrations across the four sampling sites was shown (ANOVA, p-value 0.4). This highlights that municipal wastewater pollution is a problem common to all sections of the river basin. The strong impact of wastewater discharge on the river water quality was further highlighted by the fact that the total and fecal coliform

bacteria counts across the 4 stations were found to be too numerous to count and exceeded the EU Class V standards even when 1:100 dilution was implemented.

Significant difference in water temperature were observed across the stations (ANOVA, p-value <0.05). Mean water temperature at S1 (upper southernmost station) was found to be higher than the temperatures at S2 (upper northernmost station) due to the fact that flows in S1 were consistently lower than those observed at S2. Moreover, water depths at S2 tended to be very shallow. The median temperature at S4 was 16 °C, which was about 1.5 times higher than that recorded at S1. This significant increase in temperature (Tukey, p-value 0.001) is both due to the drop in elevation as well as increased discharge of wastewater all along the river. The pH values ranged from 6.97 to 11.38. Levels of pH showed no significant difference across the four stations (ANOVA, p-value 0.08). As for the electric conductivity measurements, they ranged between 3 to 1,170 μ S/cm. No statistical difference was noted across the four stations (ANOVA, p-value 0.9). The observed variance for all pollutants (Flinger-Killeen, p-value <0.05) were found to statistically differ across the 4 stations, except for temperature, pH, NO₃ and TSS (Flinger-

Killeen, p-value >0.05).



Figure 3-1 Spatial variation of temperature (Temp), pH and electric conductivity (EC) in Beirut River. Note that for pH the EU Class I,II and II standards are the same



Figure 3-2 Spatial variation of NO₂, NO₃, TN, PO₄, TP, SO₄, COD, BOD and TSS along the 4 stations in the Beirut River. Note that for SO₄ and COD the EU Class I and II standards are the same

Seasonal variations in pollution levels within the Beirut River basin were assessed by comparing concentrations between the wet and dry seasons (Figure 3-3 and 3-4). Overall most of the physiochemical and biological parameters were found to be higher in the dry season as compared to the wet season. Water temperatures exhibited a significant seasonal cycle (t test, p-value <0.05), whereby the highest value (28 °C) was recorded at S3 and S4 during the dry season and the lowest value (6 °C) was measured at S1 and S2 in February during the wet season. As for pH measurements, no significant variability was detected between the two seasons. The median for EC concentrations in the dry season was 449 μ S/cm, which was around 2 times higher than the median recorded during the wet season. This variation between seasons was significant (Wilcoxon, p-value <0.05) and is to be expected as flows in the dry season tend to be low and heavily influenced by anthropogenic discharges. Similarly, the difference in TN levels between the two seasons was significant (Wilcoxon, p-value <0.05), with the highest TN concentration (29.1 mg/L) measured at S4 in November during the dry season and the lowest concentration (0.01 mg/L) recorded at S1 in March during the wet season. The median TN concentration during the dry season was almost 5 times higher than the median recorded for the wet season. A similar seasonal pattern was observed for TP concentrations, with the highest concentration (4.92 mg/L)measured at S4 on the 2nd of June (dry season) as compared to the lowest concentration (0.01 mg/L), which was recorded at S2 on the 12th of December in the wet season. Sulfate concentrations ranged between 60 and 88 mg/L during the dry season and between 20 and 70 mg/L in the wet season. TSS values were also found to be significantly higher (t test, pvalue 0.04) during the dry season as compared to the wet season. Similarly, the

concentrations of COD exhibited a significant seasonal pattern (Wilcoxon, p-value 0.001), whereby the median concentration in the dry season was 6.5 times higher than the median concentration of COD during the wet season. On the other hand, the seasonal pattern of the BOD concentrations was less evident (Wilcoxon, p-value 0.02) as compared to that associated to COD levels, however the median BOD concentration during the dry season was 6 times higher than that associated with the wet season. The fact that all pollution levels dropped in the wet season as compared to the dry season indicates that dilution in the Beirut River plays a dominant role in modulating pollution.

To further analyze for a possible interaction between space and time on the measured pollution levels, a two-way ANOVA was performed for each tested parameter. It was noted that for all the tested parameters (TN, TP, TSS, Temperature, BOD, COD, and electrical conductivity) no significant interaction was observed. Only pH levels were found to be affected by a spatio-temporal interaction (p- value for interaction < 0.05), whereby pH levels were similar across the 4 stations in the wet season but showed large variability in the dry season, with station S4 showing a significantly higher pH level as compared to the remaining three stations during the dry season.

The correlations between the different pollutants and flow was assessed for both the wet (A) and the dry (B) seasons (Figure 3-5). While most parameters exhibited a negative correlation with flow in the wet season, an indication of pollutant dilution, only TSS showed a positive correlation. This is probably attributed to the higher erosion rates following high intensity rain events. In the dry season, pH, TN, NO₂, and SO₄ exhibited a positive correlation with flow. A significant (p-value 0.001) positive correlation was found

between TN and TP in the wet season; yet the correlation weakened in the dry season. This is indicative that the pollution sources of both TN and TP are similar during the wet season; yet the pollutant loads and/or uptake appear to differ in the dry season.



Figure 3-3 Temporal variation of temperature (Temp), pH, and electric conductivity (EC) in Beirut River. Note that for pH the EU Class I,II and II standards are the same



Figure 3-4 Temporal variation of NO2, NO3, TN, PO4, TP, SO4, COD, BOD and TSS in the Beirut River. Note that for SO4 and COD the EU Class I and II standards are the same



Figure 3-5 Spearman's rank correlations between the measured parameters during the wet and dry season. (a) Wet season; (b) Dry season

3.2. Total pollutant load estimation

The annual total loads of TN, TP and TSS were estimated at each sampling site, using both the regression-based method as well as the Beal's ratio approach.

3.2.1 Regression based method

The use of the regression-based approach was only possible for the estimation of TN and TP loads at S1, S3 and S4. No statistical relationships between TN and TP concentrations on one hand and flow on the other were found at S2. Moreover, the correlation between TSS and flow proved to be weak across all stations and as such no significant regression models could be fit. Table 3-1 shows the regression equations used to estimate the daily concentrations by station. The results show that both TN and TP concentrations exhibited a significant negative relationship with river flow across the three

monitoring stations (S1, S3 and S4). This indicates that pollutant dilution rather than pollutant wash-off is the dominating process controlling pollutant loading into the basin. This negative relationship also implies a dominance of point source pollution sources as compared to non-point sources.

| Station | Pagression model equation | Adjusted | Total loads | |
|------------|---|----------------|-------------|--|
| Station | Regression model equation | R ² | (Tons/year | |
| | $\log(C_{TN}) = 1.29 - 0.47 \log(Q)$ | 0.41 | 25.22 | |
| S 1 | $\varepsilon \sim \operatorname{Norm}(0, \sigma^2) 0.5728$ | 0.41 | 23.22 | |
| 51 | $log(C_{TP}) = -1.6 - 0.53 \log(Q)$ | 0.42 | 2.45 | |
| | $\varepsilon \sim \operatorname{Norm}(0, \sigma^2) \ 0.6551$ | 0.42 | 5.45 | |
| | $log(C_{TN}) = 1.72 - 0.21 \log(Q)$ | 0.20 | 173 16 | |
| \$3 | $\varepsilon \sim \operatorname{Norm}(0, \sigma^2) 0.4053$ | 0.29 | 175.10 | |
| 05 | $\sqrt[3]{C_{TP}} = 0.84 - 0.16 \log(Q)$ | 0.58 | 13.89 | |
| | $\varepsilon \sim \operatorname{Norm}(0, \sigma^2) 0.2064$ | 0.50 | | |
| S4 | $log(C_{TN}) = 2.03 - 0.33 \log(Q) - 0.83 \cos(2\pi T/365)$ | 0.59 | 282.96 | |
| | $\varepsilon \sim \operatorname{Norm}(0, \sigma^2) 0.6739$ | 0.59 | 202.90 | |
| | $\sqrt[3]{C_{TP}} = 0.18 - 0.14 \log(Q) - 0.14 \sin(2\pi T/365): \log(Q)$ | 0.66 | 22.82 | |
| | ε ~Norm(0, σ^2) 0.1869 | 0.00 | 22.82 | |

| Table 2 1 Established | magnagian has | and flow come | antrotion agric | tions at C1 C | 2 and CA |
|------------------------|-----------------|---------------|-----------------|----------------|-----------|
| Table 5-1 Established | regression-das | sed now-conce | entration equa | lions al ST. S | oo and 54 |
| 1 doite e 1 Boudomonio | - iegiession ow | | | | |

The regression model for the square root of TN at S1 had a slope of -0.47 on the natural logarithm of flow and had an adjusted R^2 of 0.41, which indicates that the model explains more than 40% of the observed variability in the TN concentrations. The TP model for S1 was able to account for 42% of the variance in the observed data. Moreover, the model predicts that for every 10% increase in flow, the TP concentration was expected to drop by 5.3%. Moving downstream to Station S3, the regression model for TN concentration was able to explain around 30% of the observed variability. The model

predicts that for every 10% increase in stream flow, the TN concentration was expected to drop by 2.1%. Regarding the model that was used to predict TP concentrations at S3, the slope indicated that the cubic root of TP concentration is expected to drop by 0.21 for every 1 m³/sec increase in flow; the model was able to explain around 58% of the variance in the data. With regards to the regression models for station S4 both TN and TP concentrations were found to be affected by both flow and seasonality. With regards to the TN model, the lowest and highest TN concentrations were expected to occur in April and in October respectively. As for the effect of flow, the model predicts that for every 10% increase in flow measurement, TN concentration was expected to drop by 3.3%. The TN model for S3 had an adjusted R² of 60%. As for the TP regression model that was established for S4, the model structure showed a significant interaction between flow and season. The model was able to explain 66% of the variability in the data.

The performance of the regression-based models as compared to the observational data can be seen in Figure 3-6, where the predicted values are compared against the observed daily TN and TP concentrations at S1, S3 and S4 over time. Overall, the regression models appear to be providing good estimates of the observed concentrations.



Figure 3-6 Comparison of the daily predicted and observed TN and TP concentrations at S1, S3 and S4 for the period between April 1, 2016 and November 30, 2017

The regression equations established for TN and TP at S1, S3 and S4 were used to simulate 1000 pollutant concentration realizations for each day during the sampling period. These simulations were used to generate the predictive distributions for TN and TP loads at S1, S3 and S4 (Figure 3-7). Estimates of TN and TP total loads across the stations showed

that the highest TN and TP loads were recorded at S4. However the lowest TN and TP loads estimated were recorded upstream at S1. TN load at S4 was approximately 12 times the load at S1. As for TP load estimates, a 600% increase in total load was noted as we moved downstream from the northern uppermost station (S1) to the Jisr El Basha area (S4). Also it is worth mentioning that TN total loads were always higher that TP total loads at all three stations.



Figure 3-7 Predictive regression-based distribution of TN and TP loads at S1, S3 and S4 **3.2.2** *Beale's ratio based method*

The Beale's ratio estimator method was also used to estimate total pollutant loads across the four stations. In addition to the mean load estimates for each pollutant (TP, TN, and TSS), the standard deviation (SD) around each load estimate was calculated (Table 6). Similar to the regression-based analysis, the Beale's ratio results showed that all pollutant loads exhibited an increasing trend moving from the upstream to the downstream sections of the river (Table 6). The highest mean TN load was recorded at S4 and it was around 10 times larger than the estimated load at S1. In addition, the mean TP load at S4 was 3 times larger than the load estimated at S1. Similarly, TSS loads were found to increase as one moved from the upstream sections of the river down to the downstream stations. This is largely due to the fact that the headwaters of the river are still heavily forested, which protects against soil erosion.

| | TN | | ТР | | TSS | |
|------------|------------------|-------|------------------|-------|------------------|----------|
| | Load (Tons/year) | SD | Load (Tons/year) | SD | Load (Tons/year) | SD |
| S 1 | 21.84 | 9.5 | 2.60 | 1.35 | 1007.28 | 1033.60 |
| S2 | 42.38 | 8.96 | 3.28 | 0.88 | 2538.91 | 1364.92 |
| S 3 | 158.41 | 66.23 | 14.72 | 6.22 | 9521.33 | 10129.08 |
| S4 | 204.38 | 86.29 | 7.97 | 14.99 | 23407.62 | 25862.65 |

Table 3-2 Pollutant load estimation using the Beale's method

3.2.3 Comparison between the Regression-based loads and the Beale's Ratio loads

Differences were apparent between the total pollutant loads estimated by the regression-based method and those based on the Beale's ratio across the four stations (Figure 3-8). Predicted mean TN and TP loads at S1, S2 and S4 were found to be within the same order of magnitude in both methods. Yet, their means were still found to be statistically different (p-value <0.05) except for TP at S3 (p-value=0.08). It is worth mentioning that the regression based method consistently over-predicted the Beale's estimates across all stations except for the TP load at S3. Moreover, the variances of each method were found to be statistical different (Levene test, p-value <0.05), with the exception of TN loads at S3 (Levene test, p-value =0.4). The variance of the TN load using the regression based method at S4 was higher than that based on the Beale's. This was not the case at S1 where the

variability around the load was higher for the Beale's ratio estimate. For TP loads, the Beale's estimated loads were associated with higher variability at S3 and S4.



Figure 3-8 Regression-based and Beale's ratio – based loads for TN, TP and TSS at the four sampling sites

3.3. Non-point source loads

Non-point source-based loads over the study period (April 1, 2016 to November 30, 2017) were predicted using the Open-NSPECT model. Table 3-3 summarizes the total non-point TN, TP and TSS loads reaching the Beirut River at each of the four sampling station in tons per year. Figure 3-9 maps the accumulation of the pollutants as they move

downstream from the headwaters down to station S4. The accumulated non-point TN and TSS loads at S4 were around 4 times higher than the loads estimated at S1. As for TP, the estimated non-point loads at S4 were approximately 3 times higher than the loads reaching station S1.

| | | 2 | |
|----|-------------|-------------|-------------|
| | TN | TP | TSS |
| | (tons/year) | (tons/year) | (tons/year) |
| S1 | 3.11 | 0.61 | 106.31 |
| S2 | 6.08 | 1.04 | 259.68 |

1.92

2.02

407.36

421.61

10.51

10.96

S3 S4

Table 3-3 Summary of the non-point based TN, TP and TSS loads at the four sampling locations over a year

In an effort to determine the pollution hotspot areas that contributed the highest nitrogen and phosphorus loads to the river, spatially localized loading maps were generated for the basin. These maps take into account both the effective pollutant concentration associated with the dominating LULC along with the generated volume of runoff for that region. Hotspot areas thus represent the areas within the basin that are vulnerable to a high runoff volume while also having a high non-point source (Figure 3-10). The areas contributing the highest amounts of nitrogen and phosphorus were mainly found to be the agricultural lands in the headwaters as well as the dense urban areas in the lower sections of the basin. Both of these regions were associated with a high effective pollutant concentrations. Moreover, urban and bare lands were also found to be hotspots for the release of TSS, given the high volume of runoff passing through these locations.



Figure 3-9 Spatial distribution of the non-point TN, TP and TSS loads (tons/year) in the basin



Figure 3-10 Spatial distribution of TN, TP and TSS local effects. S1B is the area draining into S1, S2B is the area draining into S2, S3B is the region between S1 and S2 on one hand and S3 on the other, S4B is the region between S3 and S4, SB5 is the region between S4 and the discharge point of the river

Table 3-4 summarizes the non-point pollutant loads entering each of the 5 sub catchments of the Beirut River in Tons/km². Note that the Beirut River basin was subdivided into the two headwater sub-catchments (S1B and S2B), the S3B sub-catchment which stretches between S1 and S2 on one hand and S3 on the other, S4B that stretches between S3 and S4, as well as S5B that stretches between S4 and the discharge point to the Mediterranean Sea. Standardizing by area allows for the identification of the regions contributing the most with regards to nonpoint pollutant loads at the sub-catchment level. The data in the table below clearly indicates that sub-catchments S4B and S5B had the highest non-point pollutant loads per Km². Although these two sub basins have relatively small areas, their relative contributions to the non-point pollution load were very high. As a matter of fact, the average non-point TN load/Km² at SB5 was found to be 2.7 to 3.4 times higher than that of S1B and S2B respectively. Similarly, the non-point TP load/Km² at S5B was approximately 2.8 to 4.1 times bigger than S1B and S2B respectively. As for the area averaged non-point TSS load, the load at S5B was around 2.4 times higher than the loads at S1B and S2B. These findings indicate that the highly urbanized regions (mostly in S5B and S4B) of the basin are contributing the most non-point source pollutants per Km². Note that sub basin SB1 had the lowest area averaged load of non-point source pollutants; that subbasin is still dominated with dense forests that decrease the transportation of non-point source pollutant and reduce runoff.

Table 3-4 Summary of annual area averaged non-point pollutant loads at the sub-catchment level. S1B is the area draining into S1, S2B is the area draining into S2, S3B is the region between S1 and S2 on one hand and S3 on the other, S4B is the region between S3 and S4, SB5 is the region between S4 and the discharge point of the river

| | Total TN load (Tons) | Total TP load (Tons) | Total TSS load (Tons) | Area (km ²) | Area average TN load (Tons/km ²) | Area average TP load (Tons/km ²) | Area average TSS load (Tons/km ²) |
|-------|-------------------------|----------------------------|--------------------------|----------------------------|--|--|---|
| S1B | 3.11 | 0.60 | 106.20 | 49 | 0.063 | 0.012 | 2.167 |
| S2B | 6.07 | 1.04 | 259.35 | 126 | 0.048 | 0.008 | 2.058 |
| S3B | 1.31 | 0.26 | 41.40 | 38 | 0.034 | 0.006 | 1.089 |
| S4B | 0.44 | 0.089 | 14.27 | 3 | 0.146 | 0.029 | 4.756 |
| S5B | 1.95 | 0.41 | 62.77 | 12 | 0.162 | 0.034 | 5.230 |
| Total | 12.91 | 2.43 | 484.01 | 228 | 0.056 | 0.01 | 2.122 |

3.4 Point source loads

The contribution of the point source loads in the Beirut River basin were estimated by subtracting the total estimated loads from the corresponding estimated non-point loads. Table 3-5 represents the estimated TN, TP and TSS point source estimated loads based on the regression-based and Beale's ratio estimation methods. The estimated point source TN loads were found to increase by one order of magnitude moving downstream from S1 to S4 (Table 3-5). As for the estimated point source TP loads, the regression-based method and the Beale's ratio approach diverged with regards to their prediction. The estimates based on the regression model predicted that the highest point source loads were at S4, with loads 7 times higher than those calculated for S1 (Table 3-5). TP point source loads based on the Beale's ratio predicted that the highest load would occur at S3 (Table 3-5). Estimated point source loads of TSS were predicted to be highest at S4, with a load 25 times higher than the point source predicted loads at S1 (Table 3-5). The increasing point source loads observed moving downstream in the basin is expected given that lower sections of the river are

industrial, heavily populated, and lack functional wastewater treatment plants.

Table 3-5 Estimates of point source TN, TP and TSS loads at the four sampling sites in the Beirut River basin

| | Regression based point sources | | Beale's ratio based point sources | | | |
|------------|--------------------------------|-------------|-----------------------------------|-------------|-------------|--|
| | TN | TP | TN | TP | TSS | |
| | (Tons/year) | (Tons/year) | (Tons/year) | (Tons/year) | (Tons/year) | |
| S 1 | 22.10 | 2.85 | 18.72 | 1.98 | 900.97 | |
| S2 | | | 36.29 | 2.23 | 2279.22 | |
| S 3 | 162.64 | 11.96 | 147.89 | 12.79 | 9113.96 | |
| S 4 | 271.99 | 20.79 | 193.42 | 5.95 | 22986.02 | |

A comparison between the estimated point-source loads at each of the 4 sub-catchment (Figure 3-5) and the maximum potential wastewater loads, shows that the estimates were consistently lower. This is probably attributed to natural uptake and pollutant attenuation as well as the fact that many villages use cesspools in the study area and thus do not discharge directly into the river. However, the estimated point source loads for TSS at S4 were found to exceed the maximum loads associated with wastewater discharge by 14 times. This is mainly due to the heavy industrial wastewater effluent discharge in that section. Note that several concrete batching plants are directly located on the river banks at S4.

CHAPTER IV

DISCUSSION

The two adopted pollutant load estimation methods showed divergence in their estimates. This is in agreement with the conclusions of Lee et al. (2016) who evaluated several load estimation methods in streams and rivers. A closer look at the estimated loads generated by the regression-based load estimation method and the Beale's method shows that the latter's estimates of the TP and TN loads were consistently higher as compared to those estimated by Beale's. This could be attributed to the seasonal variation in the pollutants that causes the heteroscedasticity of the model residuals. Pollutant seasonal variability is a result of heavy rain events and periodic application of fertilizers (Hirsch, 2014; Stenback, Crumpton, Schilling, & Helmers, 2011). Given the sparsity of the available water quality monitoring data, it is not possible to assess which of the two approaches produced more accurate and unbiased estimates of loads in our targeted river basin. Increasing the sampling frequency with an emphasis on capturing high discharge events will help to minimize the errors associated with both load estimation methods (Haggard et al., 2003; Lee et al., 2016).

In the Beirut River Basin, TN and TP exhibited a statistical significant negative flow-concentration relation across 3 of the 4 sampling stations (S1, S3, and S4). TSS levels on the other hand appeared to be statistically independent of the recorded flows across all 4 stations during the sampling period. This indicates that with regards to the nutrient loads (TN and TP), point source pollution dominated at S1, S3, and S4. While at S2, it appears

that the impact of dilution is limited in reducing nutrient loading. This is probably due to the low flows observed at S2. Sediment loading also appears to be weakly modulated by dilution across the 4 stations as TSS concentrations tended to increase with flow. Table 4-1 shows the percent contribution of point to non-point sources for TN, TP, and TSS. It is clear from the table below that point source pollution is a common problem for the four stations. The lowest percent contribution of point to non-point source of pollution was recorded at S1 and S2 (Table 4-1). The similar contribution at these two stations is attributed to the forested land cover at upstream areas. At the lower section of the basin, the importance of point sources increases as the basin becomes more urban and industrial.

| ~ · | Point/non-point (%) | | | | |
|------------|---------------------|-----|------|--|--|
| Station | TN | ТР | TSS | | |
| S 1 | 600 | 325 | 847 | | |
| S2 | 596 | 213 | 878 | | |
| S 3 | 1406 | 663 | 2237 | | |
| S4 | 1763 | 294 | 5452 | | |

Table 4-1 Percent contribution of point to non-point sources for TN, TP, and TSS

The negative impact of increased urbanization on the river water quality of the Beirut River can be clearly seen by comparing the area-normalized total pollutant loads across the four stations with the percent urban area within each sub-catchment (Figure 4-1). Annual area-average TN loads at the two upper sub basins, namely SB1 and SB2, were similar (0.44 and 0.33 Tons/km² respectively); however the annual area-averaged loads at SB1 and SB2 were found to have increased by one to two orders of magnitudes (2.47 and 15.32 Tons/km²). As for TP, the lowest annual area-average load was identified at S1B (0.053 Tons/km²). Downstream at SB4, TP area-averaged loads were found to be 55 times higher than the S1B loads. The spatial loading pattern for TSS was also similar, with TSS area-averaged loads at SB4 being 225 times higher than the area-average load at S2B. While the negative impact of urbanization on water quality has been shown in many other watersheds (Brodie, 2013; Bu, Tan, Li, & Zhang, 2010; Chang, 2008; Chen, Hu, Wang, Guo, & Dahlgren, 2016; Wu & Chen, 2013), the dramatic scale of the deterioration observed in the study area is a direct result of the compounded effect that the discharge of untreated domestic and industrial wastewater has on the river. Moreover, the urbanized regions in the basin tend to occur in regions of high slopes and as such soil erosion is magnified. Given the fast rate of urbanization in the basin, it is expected that future urban growth will further aggravate the water quality issues, particularly that urbanization is occurring in regions where sewerage networks and domestic wastewater treatment plant are either non-existent, under-construction, or not operational. During the study period, high levels of BOD as well as fecal coliforms were recorded along the entire watershed, which highlighted that the discharge of untreated wastewater is not just an urban problem but also an issue in the more rural sections of the basin. Interestingly, when the ratio of BOD to COD is computed and compared across the 4 stations, it becomes apparent that the upstream areas had a ratio around 0.45, while the lower two stations (SB3 and SB4) had ratios below 0.2. This clearly shows the high negative impact that the industrial areas in the lower sections of the basin have. On the other hand, the positive role that forests play with regards to improving the water quality can be seen by the negative correlation between TSS levels and forested areas in each of the sub-catchments (Spearman's r = -0.8). This can be also shown in Figure 4-1 that represents a decreasing trend in area-averaged total pollutant

loads as the percentage of forest areas increase. Note that despite the large pollutant loads that reach S3, the S3B sub-catchment had a relatively small pollutant load contribution per area. This can be attributed to the high percentage of forested areas in that section. As a matter of fact, it is probable that most of the load in this section is produced just above station S3, where the area shifts from forested to urban.

The water quality in the river showed strong seasonality. The river water quality was found to be particularly dire during the dry season due to the high contamination levels observed and the low river flows during this period. Although, the observed pollutant levels still exceeded the ambient water quality standards during both seasons, the levels of exceedance tended to be lower during the wet season as a result of the dilution effect. Similar observations have been recorded in other point-source dominated rivers systems (Alberto et al., 2001; Chang, 2008; M. A. Massoud, El-Fadel, Scrimshaw, & Lester, 2006a; Vega et al., 1998).



Figure 4-1 Annual area-average pollutant loads across the four stations as a function of percent urban and forested areas for each of the 4 sub-catchments. Note that only at SB4 the area-averaged TP load was calculated from the regression-based load

Form the results obtained it is clear that Beirut River watershed is subject to excessive loads of point source pollutants. Among these sources, the discharge of domestic and industrial wastewater appear to be the leading sources of nutrient and sediment loads reaching the river. As such, there is a need to survey the entire watershed and to identify the major domestic and industrial outfalls discharging into the river. Moreover, there is a need to accelerate the implementation of the national wastewater treatment plan that envisions building new wastewater treatment stations within the study region which should collect and treat the wastewater generated from most of the urbanized regions of the river. Up until these stations are constructed and made operational, concerned municipalities should reduce the number of new building permits given in an effort to control the rate of urbanization in the Beirut River basin. As for the management of the industrial effluents, there is an urgent need to issue and implement laws and regulations that both adopt the principle of the polluter pays while also providing incentives to encourage industries to manage and reduce their generated wastes and wastewater (Higgins, 2017; M. A. Massoud et al., 2006b). Concerning the management of diffused sources, it was clear that the role of the agricultural runoff in the basin is comparatively small. Yet, there is a need to start implementing best management practices all along the river such as establishing riparian buffer zones, encouraging terracing, embracing green infrastructure, managing irrigation and nutrient application, as well as using soil erosion control measures (Bowes et al., 2008).

CHAPTER V

CONCLUSION AND FUTURE WORK

This study represents a first attempt towards fully characterizing the water quality and pollution sources within the Beirut River, a poorly monitored Mediterranean seasonal river. The estimated pollution loads will help stakeholders to develop and test different management strategies that aim to mitigate pollution along the river. From the results obtained, the following conclusions can be drawn:

- The Beirut River water quality is in violation of most ambient water quality standards and as such its designated uses are compromised.
- The deterioration of the water quality across the basin showed a strong spatial pattern, with the water quality getting consistently worst moving from the headwaters down to the discharge point. This also highlights that the river has a major negative impact on the coastal water quality around its discharge point.
- While all tested water quality parameters exceeded the standard limits during both the wet and dry season, the highest levels of pollution were consistently observed during the dry season, when the flow in the river was low.
- The regression-based method was capable of estimating the TN and TP loads at S1, S3 and S4. The correlation between TSS and flow proved to be weak and as such no significant regression models were found across the 4 stations. The observed negative relationship between flow and the different measured pollutants indicates that the main sources of pollution in the Beirut River are point sources emerging from anthropogenic activities all

along its watershed. Among these sources, the discharge of domestic and industrial wastewater appear to be the leading sources of impairment all along the river.

- Among the two pollutant load estimation methods adopted, the regression based method consistently over predicted TP and TN total pollutant loads across all stations except for the TP load at S3.
- The comparison of the area-normalized pollutant loads with the percent urban area within each sub-watershed showed the negative impact of increased urbanization on the river water quality of the Beirut River.
- Accumulated nonpoint TN, TP and TSS loads at S4 were around 3-4 times higher than the loads estimated at S1. A closer look at the local effect non-point loads showed that the areas contributing the highest amounts of nitrogen and phosphorus were mainly found to be the agricultural lands in the headwaters as well as the dense urban areas in the lower sections of the basin. Urban and bare lands were found to be hotspots for the release of TSS.
- Point source loads also exhibited an increasing trend moving downstream in the basin.
- There is an urgent need to develop and implement a basin-wide management plan that aims to limit the fast and unplanned urbanization of the Beirut River while also implementing the national wastewater treatment plan that has been proposed by the Ministry of Energy and Water.

In the future, the following work is proposed:

• Develop a long-term and well-designed sampling program for the Beirut River watershed.

- Survey the entire watershed to identify the major domestic and industrial outfalls discharging into the river.
- Focus on developing a detailed water quality model for the basin so as to further characterize and map pollutant hotspots all along the basin.

REFERENCES

- Abril, G., Nogueira, M., Etcheber, H., Cabeçadas, G., Lemaire, E., & Brogueira, M. (2002). Behaviour of organic carbon in nine contrasting European estuaries. *Estuarine, coastal and shelf science,* 54(2), 241-262.
- Albek, E. (2003). Estimation of point and diffuse contaminant loads to streams by nonparametric regression analysis of monitoring data. *Water, Air, and Soil Pollution, 147*(1-4), 229-243.
- Alberto, W. D., del Pilar, D. a. M. a., Valeria, A. M. a., Fabiana, P. S., Cecilia, H. A., & de los Ángeles, B. M. a. (2001). Pattern Recognition Techniques for the Evaluation of Spatial and Temporal Variations in Water Quality. A Case Study:: Suquía River Basin (Córdoba–Argentina). *Water research*, 35(12), 2881-2894.
- Balter, M. (2013). Archaeologists say the 'Anthropocene'is here—but it began long ago. *Science*, *340*(6130), 261-262.
- Bellos, D., Sawidis, T., & Tsekos, I. (2004). Nutrient chemistry of river pinios (Thessalia, Greece). *Environment international*, *30*(1), 105-115.
- Bowes, M. J., Smith, J. T., Jarvie, H. P., & Neal, C. (2008). Modelling of phosphorus inputs to rivers from diffuse and point sources. *Science of the Total Environment,* 395(2-3), 125-138.
- Brezonik, P. L., & Stadelmann, T. H. (2002). Analysis and predictive models of stormwater runoff volumes, loads, and pollutant concentrations from watersheds in the Twin Cities metropolitan area, Minnesota, USA. *Water Research*, *36*(7), 1743-1757.
- Brodie, J. E. (2013). 2013 Scientific Consensus Statement: Land Use Impacts on the Great Barrier Reef Water Quality and Ecosystem Condition: Reef Water Quality Protection Plan Secretariat.
- Bu, H., Tan, X., Li, S., & Zhang, Q. (2010). Temporal and spatial variations of water quality in the Jinshui River of the South Qinling Mts., China. *Ecotoxicology and Environmental Safety*, *73*(5), 907-913.
- Buijs, P., & Toader, C. (2007). Support for Convergence with EU Water Quality Standards in Moldova. Retrieved from <u>http://www.oecd.org/env/outreach/38120922.pdf</u>
- Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N., & Smith, V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological applications*, *8*(3), 559-568.
- Carpenter, S. R., Stanley, E. H., & Vander Zanden, M. J. (2011). State of the world's freshwater ecosystems: physical, chemical, and biological changes. *Annual review of Environment and Resources*, *36*, 75-99.
- Chang, H. (2008). Spatial analysis of water quality trends in the Han River basin, South Korea. *Water research*, *42*(13), 3285-3304.
- Chapman, D. V. (1996). Water quality assessments: a guide to the use of biota, sediments, and water in environmental monitoring.

- Chen, D., Hu, M., Wang, J., Guo, Y., & Dahlgren, R. A. (2016). Factors controlling phosphorus export from agricultural/forest and residential systems to rivers in eastern China, 1980–2011. *Journal of Hydrology*, *533*, 53-61.
- Cohn, T. (1995). Recent advances in statistical methods for the estimation of sediment and nutrient transport in rivers. *Reviews of Geophysics, 33*(S2), 1117-1123.
- Da Silva, A. M. M., & Sacomani, L. B. (2001). Using chemical and physical parameters to define the quality of Pardo River water (Botucatu-SP-Brazil). *Water Research*, *35*(6), 1609-1616.
- Dassenakis, M., Scoullos, M., & Gaitis, A. (1997). Trace metals transport and behaviour in the Mediterranean estuary of Acheloos River. *Marine Pollution Bulletin*, 34(2), 103-111.
- Ding, X., Shen, Z., Liu, R., Chen, L., & Lin, M. (2014). Effects of ecological factors and human activities on nonpoint source pollution in the upper reach of the Yangtze River and its management strategies. *Hydrology and Earth System Sciences Discussions, 11*(1), 691-721.
- Dolan, D. M., Yui, A. K., & Geist, R. D. (1981). Evaluation of river load estimation methods for total phosphorus. *Journal of Great Lakes Research*, 7(3), 207-214.
- El-Fadel, M., Maroun, R., Bsat, R., Makki, M., Reiss, P., & Rothberg, D. (2003). Water quality assessment of the Upper Litani river basin and Lake Qaraoun— Lebanon. Integrated Water and Coastal Resources Management-Indefinite Quantity Contract. Bureau for Asia and the Near East. US Agency for International Development. 77p.
- ELARD. (2011). *Business plan for combating pollution of the Qaraoun Lake* Retrieved from Lebanon: Beirut.:
- EPA, U. (2000). Ambient Water Quality Criteria Recommendations Information Supporting the Development of State and Tribal Nutrient Criteria Rivers and Streams in Nutrient Ecoregion IX. *Washington, DC: Office of Water*.
- Ferguson, R. (1987). Accuracy and precision of methods for estimating river loads. *Earth surface processes and landforms*, *12*(1), 95-104.
- Frem, S. (2009). *Nahr Beirut: projections on an infrastructural landscape.* Massachusetts Institute of Technology.
- Gelman, A., Su, Y.-S., Yajima, M., Hill, J., Pittau, M. G., & Kerman, J. (2016). arm: Data analysis using regression and multilevel/hierarchical models. 2015. URL <u>https://CRAN</u>. R-project. org/package= arm. R package version, 1.9-3.
- Gilroy, E., Hirsch, R., & Cohn, T. (1990). Mean square error of regression based constituent transport estimates. *Water Resources Research*, *26*(9), 2069-2077.
- Gormley, W. P. (1976). Convention for the protection of the mediterranean sea against pollution. *Environmental Policy and Law, 2*(1), 45-47.
- Haggard, B., Soerens, T., Green, W., & Richards, R. (2003). Using regression methods to estimate stream phosphorus loads at the Illinois River, Arkansas. *Applied Engineering in Agriculture, 19*(2), 187.
- Haydar, C. M., Nehme, N., Awad, S., Koubaissy, B., Fakih, M., Yaacoub, A., . . . Hamieh, T. (2014). Water Quality of the upper Litani River Basin, Lebanon. *Physics Procedia*, 55, 279-284.

- Henze, M., & Comeau, Y. (2008). Wastewater characterization. *Biological wastewater treatment: Principles modelling and design*, 33-52.
- Higgins, T. E. (2017). *Hazardous Waste Minimization Handbook: 0*: CRC Press.
- Hirsch, R. M. (2014). Large Biases in Regression Based Constituent Flux Estimates: Causes and Diagnostic Tools. *JAWRA Journal of the American Water Resources Association, 50*(6), 1401-1424.
- Houri, A., & El Jeblawi, S. W. (2007). Water quality assessment of Lebanese coastal rivers during dry season and pollution load into the Mediterranean Sea. *Journal of water and health*, *5*(4), 615-623.
- KBAC. (2007). *Ko'olaupoko Watershed Restoration Action Strategy*. Retrieved from Hawai'i's Department of Health:
- Koch, R. W., & Smillie, G. M. (1986). BIAS IN HYDROLOGIC PREDICTION USING LOG -TRANSFORMED REGRESSION MODELS. JAWRA Journal of the American Water Resources Association, 22(5), 717-723.
- Lee, C. J., Hirsch, R. M., Schwarz, G. E., Holtschlag, D. J., Preston, S. D., Crawford, C. G., & Vecchia, A. V. (2016). An evaluation of methods for estimating decadal stream loads. *Journal of Hydrology*, *542*, 185-203.
- Ludwig, W., & Probst, J.-L. (1998). River sediment discharge to the oceans; presentday controls and global budgets. *American Journal of Science, 298*(4), 265-295.
- Malan, H., & Day, J. (2003). Linking flow, water quality and potential effects on aquatic biota within the reserve determination process. *Water SA*, *29*(3), 297-304.
- Massoud, M. (2012). Assessment of water quality along a recreational section of the Damour River in Lebanon using the water quality index. *Environmental monitoring and assessment, 184*(7), 4151-4160.
- Massoud, M. A., El-Fadel, M., Scrimshaw, M. D., & Lester, J. N. (2006a). Factors influencing development of management strategies for the Abou Ali River in Lebanon II: Seasonal and annual variation. *Science of the total environment, 362*(1-3), 31-41.
- Massoud, M. A., El-Fadel, M., Scrimshaw, M. D., & Lester, J. N. (2006b). Factors influencing development of management strategies for the Abou Ali River in Lebanon: I: Spatial variation and land use. *Science of the Total Environment*, *362*(1), 15-30.
- Meybeck, M. (2003). Global analysis of river systems: from Earth system controls to Anthropocene syndromes. *Philosophical Transactions of the Royal Society B: Biological Sciences, 358*(1440), 1935-1955.
- MOE/UNDP/ECODIT. (2011). SOER (State of the Environment).Chapter 3: Water Resources. Retrieved from Lebanon:
- Morrison, K. D., & Kolden, C. A. (2015). Modeling the impacts of wildfire on runoff and pollutant transport from coastal watersheds to the nearshore environment. *Journal of environmental management*, *151*, 113-123.
- Nicolau, R., Galera-Cunha, A., & Lucas, Y. (2006). Transfer of nutrients and labile metals from the continent to the sea by a small Mediterranean river. *Chemosphere*, *63*(3), 469-476.

- NOAA. (2012). Tutorial for OpenNSPECT, Version 1.1: Example Analyses for the Waianae Region of Oahu, Hawaii. Retrieved from
- NOAA. (2014). *Technical Guide for OpenNSPECT, Version 1.2*. Retrieved from
- Novotny, V. (1999). Integrating diffuseinonpoint pollution control and water body restoration into watershed management. *JAWRA Journal of the American Water Resources Association*, *35*(4), 717-727.
- Novotny, V. (2003). *Water quality: diffuse pollution and watershed management*: John Wiley & Sons.
- Park, Y. S., & Engel, B. A. (2014). Use of pollutant load regression models with various sampling frequencies for annual load estimation. *Water*, *6*(6), 1685-1697.
- Pellerin, B. A., Bergamaschi, B. A., Gilliom, R. J., Crawford, C. G., Saraceno, J., Frederick, C. P., . . . Murphy, J. C. (2014). Mississippi River nitrate loads from high frequency sensor measurements and regression-based load estimation. *Environmental science & technology*, 48(21), 12612-12619.
- Phillips, J., Webb, B., Walling, D., & Leeks, G. (1999). Estimating the suspended sediment loads of rivers in the LOIS study area using infrequent samples. *Hydrological processes*, *13*(7), 1035-1050.
- Pieterse, N., Bleuten, W., & Jørgensen, S. (2003). Contribution of point sources and diffuse sources to nitrogen and phosphorus loads in lowland river tributaries. *Journal of Hydrology*, *271*(1-4), 213-225.
- Preston, S. D., Bierman, V. J., & Silliman, S. E. (1989). An evaluation of methods for the estimation of tributary mass loads. *Water Resources Research*, *25*(6), 1379-1389.
- Qian, S. S. (2016). *Environmental and ecological statistics with R*: CRC Press.
- Quilbé, R., Rousseau, A. N., Duchemin, M., Poulin, A., Gangbazo, G., & Villeneuve, J.-P. (2006). Selecting a calculation method to estimate sediment and nutrient loads in streams: application to the Beaurivage River (Québec, Canada). *Journal of Hydrology*, 326(1-4), 295-310.
- R Core Team. (2017). *R: A Language and Environment for Statistical Computing.* Retrieved from Vienna, Austria:
- Rice, E. W., Bridgewater, L., Water Environment, F., American Water Works, A., & American Public Health, A. (2012). *Standard methods for the examination of water and wastewater* (Vol. 22nd). Washington, D.C: American Public Health Association.
- Richards, R. P. (1998). Estimation of pollutant loads in rivers and streams: A guidance document for NPS programs. *Project report prepared under Grant X998397-01- 0, US Environmental Protection Agency, Region VIII, Denver*, 108.
- Richards, R. P., & Holloway, J. (1987). Monte Carlo studies of sampling strategies for estimating tributary loads. *Water Resources Research*, *23*(10), 1939-1948.
- Rissman, A. R., & Carpenter, S. R. (2015). Progress on nonpoint pollution: Barriers & opportunities. *Daedalus*, 144(3), 35-47.
- Roy, S., Gaillardet, J., & Allegre, C. (1999). Geochemistry of dissolved and suspended loads of the Seine river, France: anthropogenic impact, carbonate and silicate weathering. *Geochimica et cosmochimica acta*, *63*(9), 1277-1292.

- Runkel, R. L., Crawford, C. G., & Cohn, T. A. (2004). *Load Estimator (LOADEST): A FORTRAN program for estimating constituent loads in streams and rivers* (2328-7055). Retrieved from
- Schoumans, O., Chardon, W., Bechmann, M., Gascuel-Odoux, C., Hofman, G., Kronvang, B., . . . Dorioz, J.-M. (2014). Mitigation options to reduce phosphorus losses from the agricultural sector and improve surface water quality: a review. *Science of the Total Environment*, 468, 1255-1266.
- Schwarz, G., Hoos, A., Alexander, R., & Smith, R. (2006). The SPARROW surface waterquality model: theory, application and user documentation. *US geological survey techniques and methods report, book, 6*(10), 248.
- Smith, C., & Croke, B. (2005). Sources of uncertainty in estimating suspended sediment load. *IAHS-AISH publication*, 136-143.
- Stamatis, G. (1999). The chemical composition of the surface system of Peneos river, Thessaly/Central Greece. *Environmental geology*, *38*(2), 126-140.
- Stenback, G. A., Crumpton, W. G., Schilling, K. E., & Helmers, M. J. (2011). Rating curve estimation of nutrient loads in Iowa rivers. *Journal of Hydrology*, *396*(1-2), 158-169.
- Stewart, B., Woolhiser, D., Wischmeier, W., Caro, J., & Frere, M. (1975). Control of water pollution from cropland, volume 1: US Environmental Protection Agency. *Washington, DC*.
- UN. (2003). *Water: A Matter of Life and Death.* Retrieved from Fact sheet. International Year of Freshwater 2003:
- UNEP. (1978). Pollutants from Land-based Sources in the Mediterranean. Retrieved from
- UNEP/MAP. (2004). Guidelines For The Application Of Best Available Techniques (Bats) And Best Environmental Practices (Beps) In Industrial Sources Of Bod, Nutrients And Suspended Solids For The Mediterranean Region. Retrieved from Athens:
- USAID. (2005). *Litani water quality management project: rapid review report.* Retrieved from
- Vega, M., Pardo, R., Barrado, E., & Debán, L. (1998). Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water research*, *32*(12), 3581-3592.
- Viswanathan, C., & Karim, M. (2015). *Non Point Source Pollution Modeling Using NSPECT Model to Facilitate Watershed Planning.* Paper presented at the World Environmental and Water Resources Congress 2015.
- Vörösmarty, C. J., Lévêque, C., Revenga, C., Bos, R., Caudill, C., Chilton, J., . . . Balvanera, P. (2005). Fresh water. *Millennium ecosystem assessment, 1*, 165-207.
- Vörösmarty, C. J., McIntyre, P. B., Gessner, M. O., Dudgeon, D., Prusevich, A., Green, P., . . . Liermann, C. R. (2010). Global threats to human water security and river biodiversity. *Nature*, 467(7315), 555-561.
- Wu, Y., & Chen, J. (2013). Investigating the effects of point source and nonpoint source pollution on the water quality of the East River (Dongjiang) in South China. *Ecological Indicators*, *32*, 294-304.