An-Najah National University

Faculty of Graduate Studies

Establishment of Total Maximum Daily Loads (TMDLs) for Selected Pollutants at Various Segments of Wadi Al-fara'a

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Dedication

To my sweet mother (Nihad) and dear father (Reda) who always wish me continuous progress in my life.

To my husband Mahuob for his continuous support and love.

To my kids Hadi and Maher who were tolerant during my study.

To my Sisters Remaa, Thaeraa, Atheer, and Rewaa a and my brothers Mohammad and dear Ameer who always wish the best for me, I dedicate this work.

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My mother... whatever I spoke about you, I cannot give you your right. Thank you for your moral support, encouragement and patience. My Dear Husband many thanks for your support and love.

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Establishment of Total Maximum Daily Loads (TMDLs) for Selected Pollutants at Various Segments of Wadi Al-fara'a

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وإن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أية درجة عملية أو لقب علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's Name:	**اسم الطالب:** دعاء رضا أحمد دريدي
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List of Content

List of Table

List of Figures

Establishment of Total Maximum Daily Loads (TMDLs) for Selected Pollutants at Various Segments of Wadi Al-fara’a

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Abstract

Total Maximum Daily Load (TMDL) is both a quantitative assessment of the pollution sources and the pollutant reductions needed to restore and protect water resources.

In order to protect and restore impaired water bodies, the loads of pollutants that reach these water bodies need to be determined and controlled. To achieve this goal, the maximum amount of a pollutant that a water body can receive and still meet water quality standards (TMDL) should be determined.

Al-fara'a catchment which is located in the Northeastern region of the West Bank, is affected by many point pollution sources such as industrial facilities, and medical centres, and non-point pollution sources such as cesspits. So three heavy metals TMDLs had been done for three segments of Wadi Al-fara'a, three toxic organics TMDLs and two pharmaceutical compounds TMDLs had been done for other two segments of WadiAl-fara'a by this research.

The process of calculating and documenting the previous mentioned TMDLs involved a number of tasks, including characterizing the segments

of Wadi Al-fara'a, selecting and setting water quality targets for the detected pollutants that will be relied upon in TMDLs calculations for them, then identifying point and non-point sources for the detected pollutants, calculating the loading capacity (TMDLs), and identifying source allocations for them. finally implementing these TMDLs.

The analysis of the samples that were taken from the first sampling location which represent east Nablus wastewater. It has been shown, that in winter, the heavy metals concentrations increased in the water samples that were taken at this season compared with other seasons, due to the agricultural and urban runoff which represents another main source for heavy metals.

It was concluded that Al-fara'a stream has poor self-purification for Copper. However, the results of Chromium, Zinc, Nickel and Lead indicate that the stream self- purification for these metals was satisfactory.

The toxic organic Brommomethane which is a herbicide was detected at the tested locations at the stream, which indicates that it was still being used at the area as herbicide, in spite of the globally prohibition of using it.

High loadsreductions are required to be implemented for the selected segments at Wadi Al-fara'a due to the great gap between the estimated TMDLs and the current loads for these pollutants that reach the wadi.

The future East Nablus Wastewater Treatment Plant (ENWTP) will be the only point source to Wadi Al-fara'a for heavy metals, that it is not designated for a tertiary treatment, for that maximum limits (permits) for the detected heavy metals levels at the effluent of the prospective ENWTP were estimated as follows: 0.03 ppm for Copper, 0.065 ppm for Chromium, 0.01 ppm for Nickel, 0.032 ppm for Zinc, and 0.0002 ppm for Lead.

Chapter One

Introduction

1.1. General introduction

The West Bank basins are one of the most important ground water resources in the Middle East (Joint Venture, 1999). However, The West Bank is at the same time a region of increasing water scarcity in the renewable water sources. As a result of many factors like the arid- semiarid conditions in some areas, overexploitation, mismanagement, and the unequal sharing with the Israelis, only a minor share is available to the Palestinian population. The average daily per capita drinking water consumption for the Palestinians in the West Bank is less than 135 litters in the year 2011, compared to 353 litters per capita for the Israelis. (PCBS, 2011).

So the Palestinians ought to work on developing their water resources by compensating for the shortage in water supply and saving the available fresh water for domestic use. One of the most potential and promising alternative solutions is the reuse of treated wastewater for irrigation in agriculture (Haruvy, 1997).

However, in many areas in Palestine as Wadi Al-fara’a in the eastern part of Nablus, and for many decades, the raw wastewater from domestic use, industrial applications, and agricultural drainage has been discharged into Wadis (ephemeral streams) without any treatment; because of the lack in water resources, some of this raw wastewater is used for irrigating crops in agricultural areas near these Wadis. The rest of it infiltrates into ground water bodies and, consequently, pollutes the water resources in the catchment. Domestic, industrial and agricultural wastewater contains a large number of pollutants, a significant number of which is considered bio-toxic pollutants, and is subject to degradation by natural biological process or self- purification. Pollutants like heavy metals and toxic organics have negative health impacts, and may cause contamination to drinking water as well as agricultural products (Al-habash, 2003). Therefore, it is very crucial to study the existence and amounts of these toxic pollutants and to compare them with the national and international water standards in order to establish the maximum daily load in kg/day that the Wadi can receive from any specific pollutant and still meet the quality standards.

The use of untreated wastewater in irrigation is an established practice in Al-fara'a Catchment because it is a cheap resource and because there are no enforceable regulations to restrict the use of untreated wastewater (Abu baker, 2007). The eastern part of the City of Nablus, Balata, and refugee camps discharge near to 2.2 million cubic meters (mcm)/year, as domestic raw wastewater to the Wadi; in addition the eastern industrial zone of Nablus City discharges0.2 mcm/year as industrial untreated wastewater to the Wadi (Abu baker, 2007).

The water pollution comes from point and non-point sources. The non-point sources- which are diffuse sources- include wastewater discharged from houses, industrial sites, commercials facilities as well as urban and agricultural runoff. Pollutants which associate with these sources are pesticides, heavy metals and others. As for the point sources, they are discharged from wastewater treatment plants, and they include chemicals discharged from industry which flow directly into the receiving water body (Al-habash, 2003). In general, the point sources are easier to regulate and control by giving those permits for the maximum allowable daily loads for every discharged pollutant (Total Maximum Daily Loads TMDL).

The main objective for this thesis is to estimate the TMDLs for selected pollutants at Wadi Al-fara'a. The thesis focuses on heavy metals and toxic organics and pharmaceutical compounds at several locations along Wadi Al-fara'a. Consequently, current loads, total maximum daily loads, and load reductions were estimated for every detected pollutant for selected segments of Wadi Al-fara'a. Two scenarios were taken into consideration. The first scenario represents the current situation at Wadi Al-fara'a. While in the second scenario, the total maximum daily loads for the Wadi selected segments and proposed permits for the proposed Nablus East Wastewater Treatment Plant (ENWTP) were estimated. Finally, conclusions and recommendations about the TMDL implementation were provided.

1.2. Research objectives

The main objectives for this research are:

- To investigate the concentrations of selected heavy metals, selected toxic organics, and selected pharmaceutical compounds in Wadi Al-fara’a water, and to compare them with the national and international standards.

- To establish the Total Maximum Daily Loads (TMDL) for five heavy metals, three toxic organics and two pharmaceutical compounds in various segments of Wadi Al-fara’a.

- To estimate proposed permits for the previous mentioned pollutants for the Future ENWTP.

1.3. Research questions and motivation

1.3.1. Research questions

This research attempts to answer the following questions:

- What are the toxic pollutants that are found at the wadi and in which concentrations are they found?

- How does the investigated pollutants concentrations vary over space and time?

- What are the TMDLs for the investigated toxic pollutants?

- How much pollutants load reductions are required to preserve the catchment?

1.3.2. Motivation

- Wastewater is an important non-conventional water resource for the Palestinians. Therefore, it is important to determine its contents from toxic compounds and the maximum loads from these toxics that the Wadi can bear without being contaminated
- The effluent of industrial and domestic wastewater from the eastern parts of Nablus city is discharged to Wadi Al-fara'a without any treatment. No enforceable regulations on discharging toxic pollutants to the Wadi exist; therefore, it is very important to monitor its contents from toxics and to determine their amounts.

- The lack of studies about TMDLs estimation for Wadi Al-fara'a is yet another important motivating factor.

- The attained results of the TMDLs will support the decision-makers in their attempts to implement management strategies and practices which will attenuate pollution loads throughout the Wadi.

1.4. Expected outcomes

It is anticipated that the study will result in:

- Establishing the selected toxic pollutants concentrations in the area over space and time.

- Determining the TMDLs and loads reductions values for five heavy metals, three toxic organics and pharmaceutical compounds for selected segments from the Wadi.

- Proposing permits for the future ENWTP.

Chapter Two
Research Methodology

2.1. Sampling Methodology

Five Sampling points were selected at Wadi Al-fara'a to reflect the spatial variation in heavy metals concentration as shown in figure (2.1) and (2.2). These points were selected based on the following: accessibility to the sampling points, coverage of the upstream and downstream points as well as the focal points in the Wadi, and the dilution and mixing with other wastewater occurrence. The characteristics of the sampling locations are:

- Sampling location 1: The Azmout Junction (AJ) is selected to represent east Nablus municipal and industrial wastewater combined with east Nablus urban runoff. The AJ runs adjacent to the main road which joins Nablus with Jericho through Al-Bathan parks. Itwas chosen to represent the upstream of Wadi Al-fara'a, as it is shown in picture (2.1).

- Sampling location 2 (TWWBM): The Tawaheen wastewater is selected to represent the wastewater before it is mixed with Al-Bathan springs fresh water. This point is located right next to Tawaheen park and it represents wastewater stream that exits in AJ after it runs for 6 km and just before it is mixed with the freshwater from a group of springs in Al-Bathan village- See picture (2.2).

- Sampling location 3 (TWWAM): This location represents Tawaheen wastewater after it is mixed with Al-Bathan springs. This point represents the wastewater that exits in TWWBM after it runs for 100 m and just after it is mixed with the freshwater of Al-Bathan springs.

- Sampling location 4 (MB):The Malaqi Al-bathan is located nearby Al-malaqi transportable bridge, and it represents the wastewater stream that exits in TWWAM after it runs for 3 km and just after it is mixed with another water/wastewater stream composed of Al-fara'a spring and Al-fara'a refugee camp wastewater effluent- See picture (2.3).

- Sampling location 5 (SST): The Shibli stream represents the wastewater that exits in MB after it runs for 8 km and just after it is mixed with the freshwater from Shibli spring- See picture (2.4).

Two methods of sampling were performed: the first spatial and temporal sampling was conducted on monthly basis by taking one sample from every sampling location mentioned above. The sampling was done in the duration from December, 2010 to March, 2012 in order to evaluate the spatial and temporal variation impact on heavy metals concentration. The second method was composite sampling which was carried out at AJ location by taking one sample every two hours for 48 hours, from 8.30 AM 20/9/2012 to 6.30 AM 22/9/2012.

The sample size collected from each point was about 500 ml, enough to perform all necessary tests. For toxic organics and pharmaceutical compounds investigation, the sampling occurred for one time from three sampling locations: AJ, TWWBM, and TWWAM.

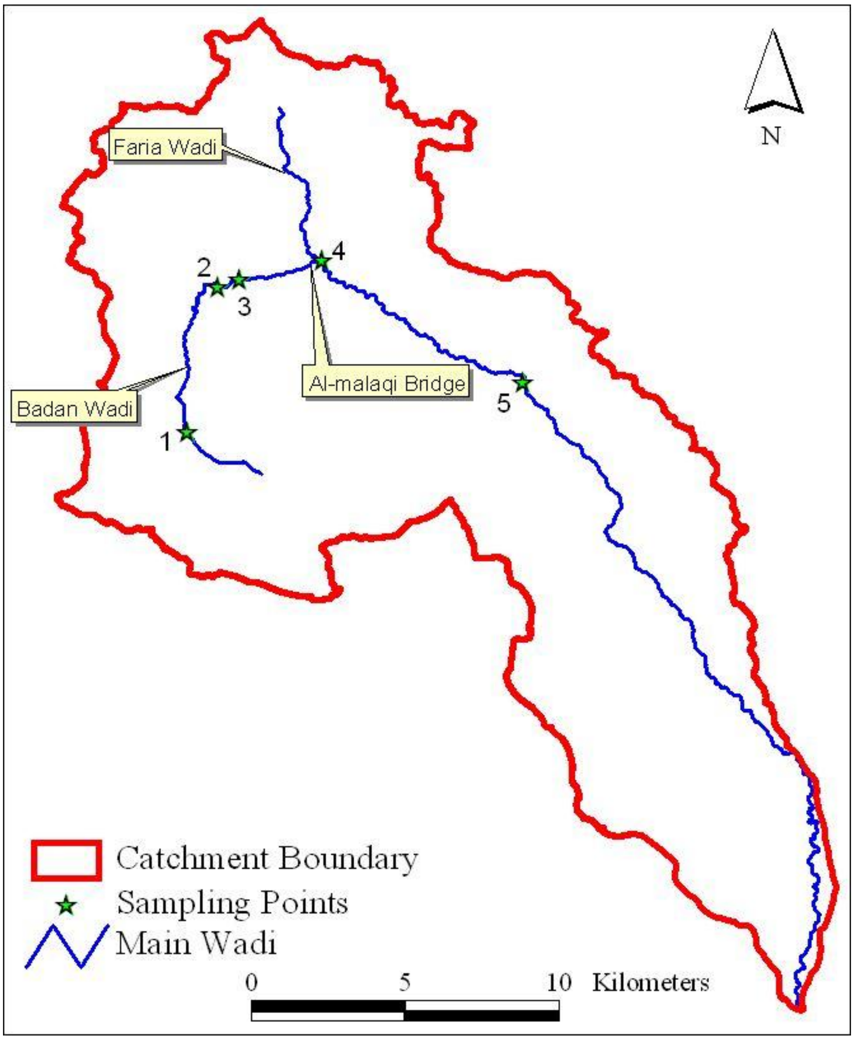

Figure (2.1): Sampling locations at Al-fara'a Catchment

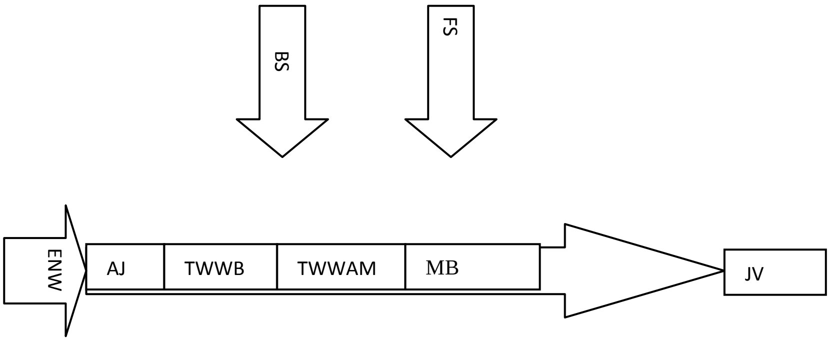

Figure (2.2): Al-fara'a stream [1]

Figure (2.3): Al-fara'a stream near Azmout (AJ location)

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[1] - ENW: East Nablus Wastewater
FS: Al-fara'a stream (it represents wastewater of A-fara'a camp mixed with Al-fara'a spring and run
off from Al-fara'a sup catchment in winter
BS: Al-bathan Springs freshwater (it represents Al-bathan springs freshwater after they mix together and flow in open channels)
SS: Shibli Stream (it represents MB after 8 km mixed with runoff from the part of lower Al-bathan
subCatchment in winter) a lot of water storage filling water from adjacent shibli spring, and near
shibli park
JV: Jordan Valley

Figure (2.4): Al-fara’a stream near Tawaheen Park

Figure (2.5): Malaqi Bathan (MB)

Figure (2.6): Shibli stream (SST)

2.2. Selection of segments from Wadi Al-fara'a

The TMDLs was estimated for five heavy metals in three segments of Wadi Al-fara'a:

Segment (1): starts from AJ sampling location and extends to TWWAM sampling location; it covers 6.1Km.

Segment (2): starts from TWWAM sampling location and extends to MB sampling location; this one covers 3Km.

Segment (3):starts from MB sampling location and extends to SST sampling location; segment 3 is 8Km long.

The TMDLs were estimated for three toxic organics and two pharmaceutical compounds in two segments of Wadi Al-fara'a:

Segment (1'): starts from AJ sampling location and extends to TWWBM sampling location, covering 6 Km.

Segment (2'): starts from TWWBM sampling location and extends to MB sampling location, covering 2.9 Km.

The average flow rate at every selected segment was determined by taking the average flow rate for the first and the final sampling locations; while, the average concentrations of the selected pollutants were determined for every segment.

2.3. Pollutants selection and quantification

2.3.1. Heavy metals selection and analysis

The heavy metals were chosen because of their toxicity and the high probability for them to be found at east Nablus industrial wastewater; they are difficult to be completely removed by secondary treatment in the proposed treatment plant which will be constructed in that area. Six heavy metals were selected to be quantified at the stream; these metals are Chromium (Cr), Copper (Cu), Zink (Zn), Nickel (Ni), Cadmium (Cd) and lead (pb). The samples were analysed using the Atomic Absorption flame Emission Spectrophotometer instrument (AA-6701, Shimadzu, Japan, 1995).

One blank and four standards were initially analyzed in order to initiate the calibration curve for selected heavy metals. These standards have the concentrations of 1, 2, 4, and 6 ppm. During the analysis, blank and quality control samples of 1ppm were analyzed in between every two samples to ensure the stability of the apparatus analysis.

2.3.2. Volatile organics selection and analysis

General scan analysis

One sample from AJ, the first sampling point at the Wadi, was taken since it is the location that less exposure to natural purification. This wastewater sample was analyzed for volatile organics using the gas chromatography-mass spectrometer GC-MS (Perkin Elmer, USA, 2010). The analysis was performed using the full scan mode on GC-MS, and the procedure came as follows: heating the sample to (70-90) °C; then the volatile organics evaporated and entered the chromatographic column where they were separated and detected as they arrived at the MS detector. The existing organics which have similar molecular weight appeared in one peak, while the higher concentration of one organic compound in the sample showed larger peak in the detector. Accordingly, three toxic organics and two pharmaceutical compounds were chosen from the larger result peaks, while still keeping in mind that the sources for these selected compounds could be found in the area. Further specific analysis for these elements was performed to determine their concentrations and observe their locations. The selected toxic organics were: Chloroacetic acid ($ClCH_2CO_2H$), Bromomethane (CH_3Br), and Naphthalene($C_{10}H_8$). All these compounds were detected in the largest peaks, and they are either pesticides as

Bromomethane or precursor for herbicides, pesticides and other chemicals as Naphthalene and Chloroacetic acid. It is expected that these components will be found in an agricultural area like Al-fara'a watershed. On the other hand, the selected pharmaceutical compounds were Batillol ($C_{21}H_{44}O_3$) and Phosphoromidic acid ($(HO)_2PONH_2$) the only found pharmaceutical compounds in the tested sample.

Specific analysis

Three samples were taken from different locations at Wadi Al-fara'a on 30/1/2012; these locations are AJ, TWWBM, and MB. They were analyzed by GC-MS (Perkin Elmer, USA, 2010) for the selected organics, which are: Chloroacetic acid ($ClCH_2CO_2H$), Bromomethane (CH_3Br), Naphthalene ($C_{10}H_8$), Batillol ($C_{21}H_{44}O_3$), and Phosphoromidic acid ($(HO)_2PONH_2$). The analysis was done using the SIM mode which allows for detection of specific materials with increased sensitivity relative to the full scan mode. In the SIM mode, the MS gathers data for masses of interest instead of searching for all masses over a wide range. Because the instrument is set to look for only masses of interest, it could allow for analysis of a particular material of interest.

2.4. Flow rates measurements at the selected locations

The major options for monitoring stream discharge are flumes, weirs, natural channels, or existing structures for Al-fara'a catchment. There is one flume at MB location which measures and stores the flow rate automatically every ten minutes at the wet months only. The flow rates measures taken by this flume for 2011- 2012 (WESI,2012) will be used in our calculation. The average flow rate for the day at which the sampling occurred will be measured, since; our methodology in estimating loads depends on estimating the pollutants loads throughout the day. For the MB location, the flume flowrates measures will be adopted for the months of January, February, March, April, December and November. For the other months, the flow rates were taken from another study that was implemented at the same time (Alawneh, 2013). Which used the estimated velocity of floating ball by measuring the time it takes to move a distance of about (15-25) m with water; she also measured stream depth and width, and calculated the stream flow rate using the following equations (USEPA, 2012):

$$\text{Flowrate} = \text{velocity} \times \text{cross section} \times 0.8 \tag{2.1}$$

$$\text{Velocity} = \text{distance} / \text{time} \tag{2.2}$$

$$\text{Cross section area} = \text{stream depth} \times \text{stream width} \tag{2.3}$$

The manually measured flow rates were used as average flow rates.

2.5. TMDL methodology

The methodology used in TMDL estimation was the load duration (USEPA, 2007. USEPA, 2008a).The USEPA maximum allowable concentrations of heavy metals for fresh water in natural streams (Chin, 2006) was adopted as the target for heavy metals; the USEPA standards for Halomethanes (USEPA, 1980) was adopted for Bromomethane; and, as the other organics do not have standards, the reference maximum permissible level for toxic organics was used as target for these organics (Labunska, 2011). The TMDL estimation was done for three segments of Wadi Al-fara'a as follows:

1. The TMDL was calculated for the selected pollutants using the following equation (EPA, 2007):

$$\mathrm{TMDL} = \mathrm{F} \times \mathrm{TC} \tag{2.4}$$

Where:

TMDL: is total maximum daily load for certain pollutant in (mg/day).

F: is the current flow rate at sampling point in L/day.

TC: is the target concentration of certain pollutant in mg/L.

2. The current pollutants loads were determined temporally at every sampling location. The average monthly concentration was multiplied by

the daily flow rate to estimate the daily loads for the month using following equation(EPA, 2007):

$$L = C \times F \quad (2.5)$$

Where:

L: is the current load of certain pollutant in mg/day.

C: is the current concentration of certain pollutant in mg/L.

F: is the current flow rate at sampling point in L/day.

3. The TMDLs and current loads for each pollutant were estimated for one day in each month over a period of one year (2011).

4. The load reductions necessary to achieve water-quality standards for each sampling location were calculated as follows: (Elshorbagy et al, 2005. Sohngen et al, 2006).

Daily Load reduction = daily current load – TMDL (2. 6)

5. The pollutants source assessment was performed to determine possible point and non-point sources for each pollutant.

6. The current loads and TMDL were allocated between point sources and non-point sources.

The pollution loads from point and nonpoint sources and the TMDL for these sources were estimated as follows(EPA, 2000):

Total current load= Current point source load + nonpoint current load (2.7)

Total TMDL= Point source TMDL + non point current TMDL + margin of safety (2.8)

7. Based on the calculated results, suggestions to achieve pollutants load reduction were introduced.

Figure (2.7) summarizes the purposes and tools for TMLD methodology as follows:

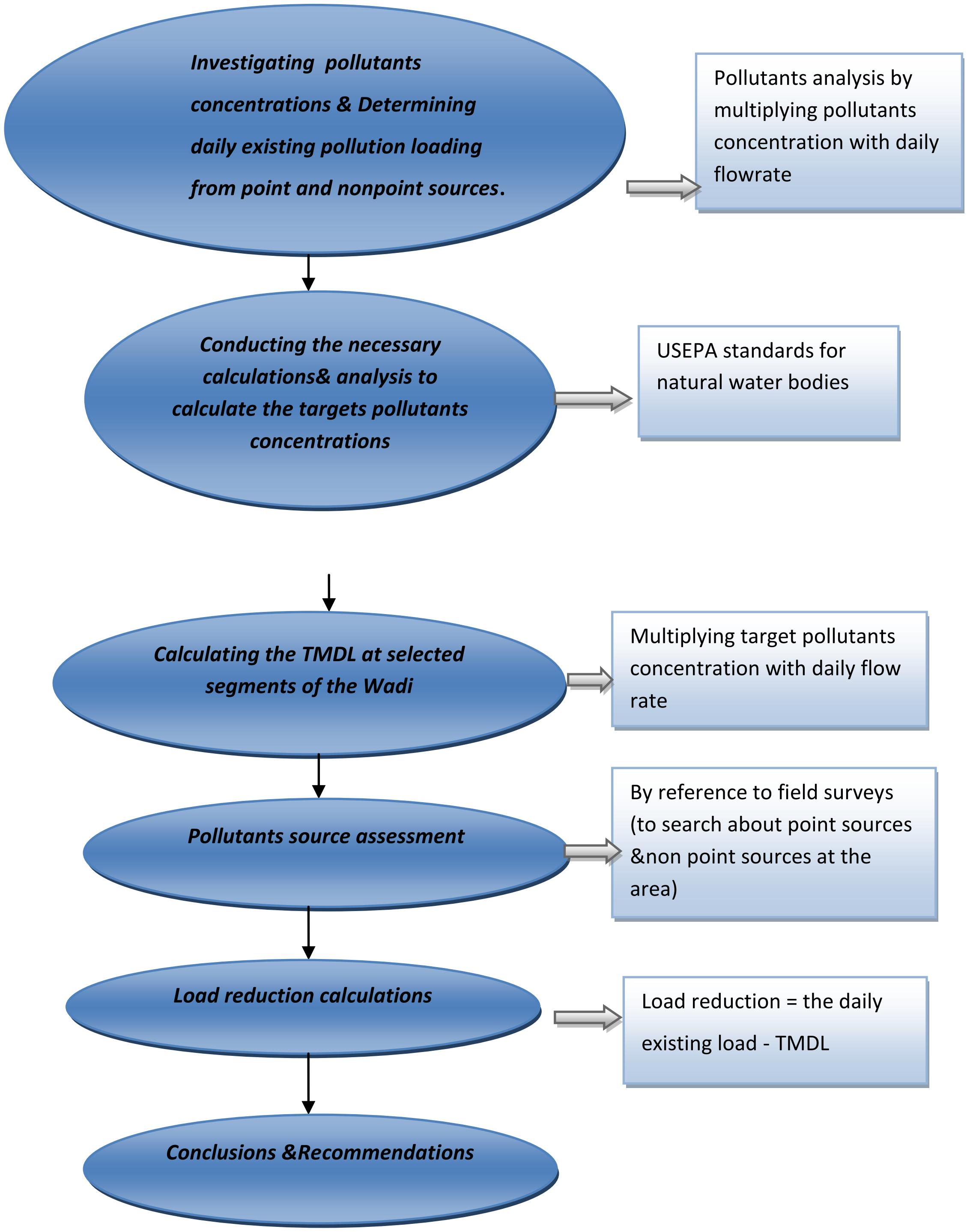

Figure (2.7): Flow chart for TMDL

Chapter Three

Literature Review

3.1. Introduction

This chapter gives background about heavy metals in wastewater; it provides important information about the heavy metals, toxic organics, and pharmaceutical compounds that had been found and investigated at Wadi Al-fara'a. It also makes reference to the national and international standards related to the investigated pollutants, total maximum daily loads (TMDLs), and TMDL case studies.

3.2. Heavy metals in wastewater

In geological terms, trace elements are defined as those occurring at 1000 ppm or less in the earth crust. The trace metals are divided into heavy (densities greater than $5g/cm^3$) and light (densities less than $5g/cm^3$). Trace metals with higher densities are named as heavy metals. They exist in water soluble as well as insoluble forms. The most common salts of heavy metal ions used in industrial operations are soluble in water, including chloride, sulphate and nitrates salts. As a dissolved salt, heavy metal ions exist in cationic form (Lewinsky, 2007).

Although severity and levels of pollution differ from place to place, the heavy metal pollution is a global problem. Heavy metals are harmful to humans due to their non- biodegradable nature, long biological half-lives, and the potential for them to accumulate in different body parts (Ackah et al, 2013). It is important to note that the metal species released are usually in a freely dissolved, bioavailable form (ICON, 2001).Variations in toxicity of the same metal are directly related to variations in water hardness, pH, content of suspended solids and the concentration of organic that can form complexes with the metal (Landner& Reuther, 2004).

Wastewater, and more specifically industrial wastewater, is known to be a major source of pollution with heavy metals. The disposal of raw wastewater creates the potential for heavy metals contamination (Jiries et al, 2002). The heavy metals transferred from liquid phase to solid phase by adsorption, precipitation, and biological uptake act like a sink for metals; however, various reactions, both microbiological and physicochemical, can transform and redistribute the metals within the sediments and to the water column (Mizyad, 2000. Daghrah, 2005).

When these metals are present in sediments, they reach the food chain through plants and aquatic animals; the vegetables take up metals by absorbing them from contaminated soil often in quantities high enough to cause clinical problems both to animals and human beings consuming these metals-contaminant plants (Zurera - Cosano et al. 1989. Ackah et al, 2013. Gupta et al, 2011).

More recent studies indicate that heavy metals have negative impact on the wastewater treatment process by damaging the DNA of effective microorganisms (EMs).This process leads to failure in the wastewater biological treatment and is listed as one key reason for failure of many treatment plants all over the world (Sheng, 2008).

One study conducted on Al- Bireh Treatment Plant (Mubarak, 2003) shows that the contents of a stabilized sludge from heavy metals decide the potential utilization of the sludge as agricultural fertilizer. Therefore, regulations on the pollution loads must be drafted and enforced on the sources of these pollutants.

The sources of heavy metals pollution in the wastewater system can be classified into three main categories: domestic, industrial and commercial, and urban runoff (ICON, 2001). Studies in the USA (Isaac et.al, 1997) and Europe (WRc, 1994) show that: the corrosion of the distribution-plumbing-heating networks contributes major inputs of heavy metals. Studies in the Scandinavian countries showed that the motor industry and vehicle workshops contribute most to the potentially toxic element load in urban wastewater. Vehicle washing was found to be an important source of potentially heavy metals contamination (ICON, 2001).

With regard to the urban runoff, the atmospheric inputs to the urban runoff depend on the nature of the surrounding industries. Road and roof runoff sources are particularly important during storm events, which will allow the flushing of potentially heavy metals from surfaces. None the less, these sources are very variable as they depend on changes in traffic, material and age of roofs, and meteorological and environmental conditions (ICON, 2001).

According to the previous studies, the sources of heavy metals vary; the main sources for copper are water pipes in buildings followed by motor vehicles; zinc comes mainly from motor vehicle tires followed by various galvanized materials. As for chromium and nickel, the main sources are road pavements followed by tires (Landner & Reuther, 2004).

The sections below give a brief description for selected heavy metals.

3.2.1. Zinc (Zn)

Zinc is the 23rd most abundant element in the Earth's crust. It degrades in the environment, and it can change from one form to another. Low solubility in water is reported for carbonates, oxides, and sulphides of Zinc; however, many of Zinc salts are highly soluble in water. Zinc adsorption by soil depends on the soil pH, organic matter, availability of minerals; while as for diffusion the Zn^{+2} ion can be adsorbed and transported into plants (Mizyad, 2000).

These industrial effluent wastewaters typically have high concentrations of Zn: electroplating, metal finishing and casting industries, rubber, plastics, paints and dying textile industries(IWS, 2004). In addition, the coal and fuel combustion mission Zn to the atmosphere will come down with the rainfall.

The major sources of Zinc in Industrial Runoff are motor oil and hydraulic fluid, tire dust, and galvanized metal surfaces(Davis et al, 2001. Golding, 2008); however, in urban runoff, Zn source comes mainly from road dust from tire abrasion (Davis et al, 2001).

There are some domestic and agricultural products that contain Zn. Examples on the domestic products aredetergents and personal care products such as sunscreens and anti-dandruff shampoo (Tjandraatmadja et al, 2008). Agricultural products like fertilizers, growth stimulant in animal husbandry, fungicides and insecticides contain Zn. Other Zn sources could be galvanized household water pipes and tanks, leachate from solid waste dump sites, and preservative wood against fungal rot and insects and storage batteries[2].

Previous studies show that the main sources of Zn in urban wastewater are the metal and electrical industries, goldsmiths and jewellery shops (ICON, 2001).Zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism. Extensive exposure to zinc chloride can cause respiratory disorders [(1)].

3.2.2. Chromium (Cr)

Chromium is rarely found as a free metal in nature. It does not corrode and that is why it retains its metallic sheen. Cr (III) oxide is among the ten most abundant compounds in the Earth’s crust (Jacobs et al, 2004).

[2] - http://www.lenntech.com/periodic/water/zinc/zinc-and-water.html

Chromium and its compounds are useful in common life. It is resistant to ordinary corrosive agents at room temperature, which is why it is used in electroplated, protective coating. It is also used in ferrous and nonferrous alloys; the ferrous alloys, mainly stainless steels, account for most of the consumption. These steels have a wide range of mechanical properties in addition to being corrosion and oxidation resistant. Chromium is also widely used in nonferrous alloys (nickel, iron-nickel, cobalt, aluminium, titanium and copper). Chromium chemicals are used in a variety of applications. The largest amount is consumed to manufacture pigments for use in paints and inks. Other applications include electroplating, leather tanning, metal corrosion inhibition, textile dyes, catalysts, and wood (Jacobs et al, 2004. Morning et al, 1980. EPA, 2000).

Chromium and its compounds originate in the environment mainly from anthropogenic sources (industry emissions, combustion processes) as from cement dust, tobacco smoke, copier servicing, glassmaking, paints/pigments porcelain and ceramics manufacturing, the welding of alloys or steel, and wood preservatives. A study in Finland has found out that the main sources of chromium in wastewater are from the metal, chemical and leather industries (Mukherjee, 1998).

Chromium can also originate naturally as leaching from topsoil and rocks which is the most important natural source of chromium entry into bodies of water. Solid wastes from chromate-processing facilities, when disposed of improperly in landfills, can be sources of contamination for groundwater, where the chromium residence time might be several years. Cr-containing particles in the atmosphere are carried over different distances by the wind before they fall or are washed out from the air onto the terrestrial and water surfaces. The efficient adsorption of metals by soils tends to limit the effects of atmospheric input of chromium (Bielicka et al, 2004)(ATSDR, 2008).

Most of the chromium in surface waters may be present in particulate form as sediment. Most of the soluble chromium in surface waters may be present as Cr (VI); a small amount may be present as Cr (III) organic complexes; Cr (VI) may be reduced to Cr (III) via organic matter present in water; and it may eventually deposit in sediments (EPA, 2009. Jacobs et al, 2004).

Chromium (VI) is much more toxic than Chromium (III). Severe and often deadly pathological changes are associated with excessive intake of Cr (VI) compounds. Inhalation and retention of materials containing Cr (VI) can cause perforation of the nasal septum, asthma, bronchitis, inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Skin contact of Cr (VI) compounds can induce skin allergies, dermatitis, and dermal corrosion (Bielicka et al, 2004) (EPA, 2000).

3.2.3. Lead

Nowadays, Lead contamination in an environment is a very important problem of worldwide concern due to its highly toxic and non-biodegradable nature. Lead has specific characteristics such as resistance to corrosion, conductivity, and the special reversible reaction between lead oxide and sulphuric acid (Khaoya et al, 2012), for these reasons lead was used from long ago in glass industry and as pigments for glazing ceramics; with the beginning of nineteen century, its uses had been increasing continuously. Particularly, it became a primary additive to petroleum products, building materials, paints and pigments (Lars Jarup, 2003).

It either reaches water system through urban runoff or discharges such as sewage treatment plants and industrial plants; however, the industrial production processes and their emissions are the primary sources for lead. Examples on these sources are paints pigments, paper, petrochemicals, refineries, printing, alloy, steel photographic materials, explosive manufacturing, ceramic, glass, and batteries industries; other sources are lead piping used in water distribution system, phosphate fertilizer, electronic, wood production, combustion of fossil fuel, forest fires, sewage wastewater, automotive (Lars Jarup, 2003. Singh, 2012)

A Swedish study (Palm Ostlund, 1996) has revealed that the largest amount of lead that finds its way to the Wastewater treatment plants is likely to be contributed by piping, followed lead jointed water pipes used outdoors (higher replacing rate), and PVC piping.

Lead is extremely toxic. In humans, it is absorbed directly into the blood stream and is stored in soft tissues, bones and teeth (Singh, 2012).It may also cause damage to the nervous system, kidney, organ, and the reproductive system. The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system, memory deterioration and reduced ability to understand. Recent data indicates that there may be neurotoxic effects of lead at lower levels of exposure than previously anticipated (Lars Jarup, 2003. Khaoya, 2012).

3.2.4. Nickel (Ni)

Nickel is a hard, silvery-white transition metal; it is an essential constituent in more than 100 minerals which have many industrial and commercial uses. It resists corrosion under ambient conditions, and, for that reason, it is used in the production of alloys including stainless steel, in battery manufacture and welding electrodes, and in the production of chemicals containing nickel like nickel sulphate, nickel chloride, and in catalysts, bathroom fittings, kitchen, electronics, food processing, textiles, and cables (Martin et al, 2009. Cempel et al, 2006).

Although Nickel occurs naturally in soils, particularly in igneous rocks, agricultural fertilisers, especially phosphates represent the main source of Nickel in the soil. Also, nickel can be highly concentrated in ash residues. Soil pH is the most important factor controlling nickel solubility, absorption and mobility with the clay. However, many nickel compounds are soluble at a pH less than 6.5, and it has been reported that plants can uptake nickel more readily in its simple ionic form ($Ni^{2+)}$ than as inorganic and organic complexes (Martin et al, 2009). It can be deposited in the sediment by such processes as precipitation and desorption on clay particles and via uptake by biota (Cempel et al, 2006).

From domestic sources, Nickelcan come from alloys used in food processing and sanitary installations; in industrial processes, Nickel is used in the production of alloys, electroplating, catalysts and nickel-cadmium batteries. The main emission of nickel is from corrosion of equipment from launderettes, electroplating shops and jewellery shops, and from paints. It also occurs in the catalysts hydrogenation of vegetable oils. Studies in Germany, Greece, and Italy have shown that the main sources of Ni in urban wastewater are metal and electrical industries and artisanal galvanic shops (ICON, 2001).

Nickel can cause allergic reaction in humans, and the ingestion of nickel can cause skin reactions in previously sensitised individuals; thus soluble nickel salts present in refinery dust are carcinogenic to the lung and nasal tissues in humans.

3.2.5. Copper (Cu)

Copper and its compounds are naturally present in the earth's crust; however the largest release of copper to the environment come from anthropogenic activities such as mining operations, agriculture, and sludge as well as from publicly-owned treatment works industrial solid waste. Copper is released to water as a result of the natural weathering of the soil and the discharges from industries. Also Copper compounds are often intentionally applied to water to kill algae[3]. Most copper that is refined in the U.S. is used in copper wire and rod; other Copper uses include: plumbing pipe, heat exchangers, jewellery, catalysts and coins, fertilizers, animal feed additives, motor vehicle components, pesticides, algaecides, fungicides, wood preservatives, and batteries.

Previous studies (Sorme & Lagerkvist, 2002) show that the urban runoff contributions from brake pads, tires, and asphalt were significant, while other sources were negligible. Though most of the copper which enters the environment is associated with particulate matter, other studies have shown that domestic waste water is the major anthropogenic source of copper in waterways (Nriagu & Pacyna, 1988).

Copper can accumulate in almost every organ of the body. Thus, copper toxicity contributes to many health problems such as: anorexia, fatigue, depression, anxiety, headaches, allergies, childhood hyperactivity and learning disorders[4].

3.3. Organic compounds in wastewater

A large number of organic pollutants from many sources can enter wastewater networks. A Stockholm-based study (Paxeus, 1996) mentioned over 137 organic compounds in the influent of the municipal wastewater plants, such as Polycyclic Aromatic Hydrocarbons, Polychlorinated

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[3] -http://www.atsdr.cdc.gov/toxprofiles/tp132-c6.pdf
[4] -http://www.arltma.com/Articles/CopperToxDoc.html

Biphenyls (PCBs), Anionic and Non-ionic Surfactants, food and household related products, Plasticisers and flame retardants, Preservatives and antioxidants, pesticides and herbicides, and pharmaceutical compounds (ICON, 2001).Other studies have shown that the sources of the main organic pollutants in sludge from WWTS were mainly from domestic and commercial sources. The soil is also another major source of organic matter and the urban and agricultural runoffs represent main sources of organic contamination in wastewater particularly for PAHs and pesticides (ICON, 2001).

The improper management and disposal of toxic organics and pharmaceutical compounds poses a threat to local and global environments; many of these substances can travel long distances and affect ecosystems and human populations far from the point of use or disposal.[5] For this reason, it is important to determine the existence and the amounts of these toxics in Wadi Al-fara'a and to estimate the maximum daily loads which can be disposed into the Wadi without causing contamination.

The following toxic organics and pharmaceutical compounds are detected in a rough Sample. They are selected according to their importance, environmental and health effects.

[5] - http://www.epa.gov/international/toxics

3.3.1. Chloroacetic acid ($ClCH_2CO_2H$)

It is one carboxylic acid used in drugs, dyes, and pesticides; it is the precursor to the herbicide glyphosate, caffeine, vitamin B and other pharmaceuticals. It is also used in veterinary medicine (IARC, 1995). It has white flakes appearance, while Chloroacetic acid is a potentially dangerous alkyl ting agent.

Since it is biodegradable and very soluble in water, it is not expected to adsorb to soil. Chloroacetic acid may enter the environment in emissions and wastewater from its production and use as chemical intermediate in the manufacture of herbicides (HSDB, 1996).

Chloroacetic acid easily penetrates skin and mucous membranes and interferes with cellular energy production. Initial dermal exposure to high concentrations (e.g., 80% solution) may not appear very damaging at first, however systemic poisoning may present within hours. Exposure can be fatal if greater than 6% body surface area is exposed to chloroacetic acid. The sodium salt does not penetrate the skin as well as the acid but can be as damaging given a longer duration and greater surface area of exposure.

3.3.2. Bromomethane (CH3Br)

It is hallo methane colourless gas used extensively as a pesticide until it was phased out by most countries because of its high toxicity (USEPA, 1980). It could cause major damage to the central and peripheral nervous system, mucosa, lung, kidney, liver, cardiovascular. It can cause death in the most severe cases[6].

3.3.3. Naphthalene ($C_{10}H_8$)

Naphthalene is moderately volatile, with a boiling point of 218 °C and low water solubility of 31.7 mg/L (20 °C).

It undergoes short-term bioaccumulation in tissues; the most familiar use of naphthalene is as a household fumigant. It is also used as dispersant for pesticides, a precursor for various dyestuffs, pigments rubber processing, chemicals and other miscellaneous chemicals and pharmaceuticals. Exposure to large amounts of naphthalene may damage or destroy red blood cells, a phenomenon known as anaemia. The symptoms include fatigue, lack of appetite, restlessness, and pale skin (EACAU, 2007). Naphthalene is on the list of priority substances under the Water Framework Directive (EC, 2001). Also, the International Agency for Research on Cancer classifies naphthalene as possibly carcinogenic to humans and animals(WHO, 2002).

3.3.4. Phosphoramidic acid

An example of a phosphorodiamidate is Morpholino which is used in molecular biology. Morpholinos are used as pharmaceutical therapeutics targeted against pathogenic organisms such as bacteria, and for

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[6] - http://www.chemyq.com/En/xz/xz1/3892galka.html

amelioration of genetic diseases. Its toxicity is represented by causing cell death in the central nervous system[7].

3.3.5. Batilol ($C_{21}H_{44}O_3$)

Main composition: Batilol, Chemical Name: 3- octadecyl alkoxyl-1,2-propylene glycol (alkyl glycerol). It is a drug for Leukopenia caused by various kinds of incidents, such as radioactivity. It has effects on resisting radioactive ray[8]. It is irritating to mucous membranes and upper respiratory tract[9].

3.4. National and International Standards

The industrial wastewater policy that is enacted by the Palestinian Water Authority (PWA) goes as follows: **"**Industries should be regulated through discharge permits from the PWA and they should comply with other Palestinian National Authority regulations (e.g., municipal, Ministry of Environmental Affairs). The discharge permits should include assurances that industrial effluents must have an acceptable quality for flows being discharged into water bodies or domestic wastewater systems, and they should not be discharged with contents of heavy metals or other toxic pollutants above given limits (HORIZON 2020, 2006). The Palestine Standards Institution (PSI) had developed standards (pS227) for treated industrial wastewater (PSI, 2010), which include the maximum

[7] -http://www.freebooknotes.com/wiki/Phosphoramidate
[8] -http://lekarstwo.ru/en/preparati/batilolum.html
[9] -http://www.chemicalbook.com/ProductMSDSDetailCB6280802_EN.htm

concentrations for many industrial pollutants, such as heavy metals that are allowed to be discharged in the industrial wastewater. The PSI standards for selected heavy metals are shown in table (3.1). These standards are designated for point sources like industries or treatment plants.

However, non-point sources are not taken into consideration in these regulations. But the selected locations at Wadi Al-fara'a receive both point and non-point sources for many pollutants; hence theTMDL estimation includes all pollutant sources. Therefore, the USEPA standards for fresh water in natural water bodies (Chin, 2006) will be adopted in the total TMDL estimation, which are shown in table (3.2).The USEPA standards for Halomethanes will also be adopted for Bromomethane TMDL estimation, which equals zero for Bromomethane ;hence, its usage is prohibited (USEPA, 1980). Furthermore because the other organics do not have standards, the reference maximum permissible level for toxic organics (0.008 ppm) will be used in their TMDL estimation (Labunska et al, 2011).

Table (3.1): PSI standards for the selected heavy metals (PSI, 2010)

Heavy metal	Maximum allowable concentration (ppm)
Copper	1.5
Chromium	0.1
Nickel	0.2
Zink	5
Lead	0.2

Table (3.2): USEPA standards for the selected heavy metals (Chin, 2006)

Heavy metal	Maximum allowable concentration for natural water bodies (ppm)
Copper	0.065
Chromium	0.085
Nickel	0.052
Zink	0.12
Lead	0.003

3.5. Pollutants loads and TMDL

Pollutants loads are mainly estimated according to watershed land uses - urban or agricultural uses. Since contaminant input to a water body is mostly generated from activities within its watershed, control over the polluting activities and processes within a watershed is a fundamental component of the water-quality control. In agricultural watersheds, soils have the capacity to retain many pollutants in their particulate form, which is far less environmentally damaging than the dissolved form. The capacity of soils to retain and absorb pollutants depends on its composition and redox status(chin, 2006).

Another procedure in estimating loads is that since a pollutant load is the mass or weight of pollutant transported in a specified unit of time from pollutant sources to a water body, the loading rate or flux is taken to be the instantaneous rate at which the load is passing a point of reference on a river, such as a sampling station, and has units of mass/time such as grams/second or tons/day (USEPA, 2003).

The averaging period for loading estimates may be hourly, daily, monthly, or longer depending upon site-specific conditions and needs. The variability of loads within the average period of interest and the certainty with which water quality standards violations need to be documented will drive decisions regarding sampling design and frequency (USEPA, 2003).

Since the flux cannot be measured directly, it is often expressed as the product of concentration and flow. Thus the three basic steps for estimating pollutant load are:

- Measuring water discharge (e.g. cubic meters per second),
- Measuring pollutant concentration (e.g. milligrams per litre), and
- Calculating pollutant loads (multiplying discharge time concentration over the time frame of interest).

Human activities in a watershed may create point or nonpoint sources of water pollution. The point sources of pollution typically involve outfalls that discharge directly into streams; in other words, this is the wastewater that comes from factories, municipal and industrial wastewater treatment plants, urban storm sewers, and any other sources where polluted water is discharged through a pipe. This type of pollution is known as point source pollution. Because it is discharged through pipes or channels; this type can be easily monitored for quantity and water quality physical and chemical properties (FAO, 2013).

The non-point-source pollution can be produced by waters draining the land surrounding a water body; landuse activities such as road construction; mine drainage; rainwater runoff from city streets; runoff from agriculture and from many rural villages. All these sources produce water pollution that does not come from any specific pipe or channel but is dispersed across the landscape. This type has been recognized as a serious problem because it is typically associated with random hydrologic events, and it cannot be easily measured due to the 'diffuse' nature of these types of pollutants.

However, these point and non-point sources of pollution may degrade the health of the stream and render it impaired for certain uses (Elshorbagy. et al, 2005. Douglas, 2003).An impaired stream means the stream does not meet one or more of its designated uses. The designated uses may include supporting aquatic life, swimming, wading, drinking water supply use.

In order to protect and restore impaired water bodies, the loads of pollutants need to be determined and controlled. To achieve this goal, the maximum amount of a pollutant that a water body can receive and still meet water quality standards (TMDL) should be determined. In simple terms, a TMDL is a quantitative plan that determines the amount of a particular pollutant that a water body can receive and still meet its appropriate water quality standards. A TMDL is commonly expressed as a load, with units of mass per time (Sohngen and Yu Yeh, 2006). A TMDL is required mainly when a stream is assessed as being impaired.

In order to develop TMDLs, the calculated pollutant quantity is then distributed among all the pollutant sources. A TMDL is estimated using the following formula (USEPA, 2008b):

$$\mathrm{TMDL} = \mathrm{WLA} + \mathrm{LA} + \mathrm{MOS} \quad (3.1)$$

WLA: wasteload allocation; the portion of the TMDL allocated to existing or future point sources.

LA : load allocation; or the portion of the TMDL allocated to existing or future nonpoint sources and natural background.

MOS : margin of safety; or an accounting of uncertainty about the relationship between pollutant loads and receiving water quality.

It is important to note that the factors involved in TMDL development vary greatly from one study to another. Such differences are related to the waterbody type, the watershed size, the pollutants of concern, and the available data; the differences are also related to resources available for TMDL development including scheduling, available funds, and technical expertise. It is not possible to provide prescriptive instructions for translating loading expressions on the basis of specific waterbody types or pollutant types because there are simply too many possible combinations of pollutant, water body type and analytical techniques (USEPA, 2007).

The process of calculating and documenting a TMDL typically involves a number of tasks, including characterizing the impaired water body and its watershed; identifying point and non-point sources; setting water quality targets; calculating the loading capacity; identifying source allocations; preparing TMDL reports; and coordinating with stakeholders (Sohngen and Yu Yeh, 2006)(USEPA, 2008b).

3.6. TMDL case studies

The following table shows case studies of performing TMDL for different water bodies in the world:

Table (2.2): TMDL case studies

Case study Name	Year	Area	Pollutants that the TMDL was performed for	Outcome	Used methodology
Los Angeles Area Lakes TMDLs[10]	2011	Los Angeles, USA	Algae, Ammonia, Copper, DDT, Lead, Mercury, pH	Ten lakes in the area were assessed as impaired, and TMDLs for the previous pollutant developed	California Toxics Rule (CTR) for fresh water used to determine the mentioned pollutants targets concentrations.
Chollas Creek Dissolved metals TMDL[11]	2009	Sandiego, California state, USA	Copper, Zink, & Lead	Waste load allocations, TMDL for dissolved metals and implementation plan for sources reduction	California Toxics Rule (CTR) for fresh water used to determine the mentioned pollutants targets concentrations.
Total maximum daily load (TMDL) approach to surface water quality management: concepts, issues, &applications (Elshorbagy.et al, 2005)	2005	Canada	pH, Nutrients & pathogens	TMDL, loads reduction allocation and implementation guidelines	The current load is estimated by using the methodology described in section 2.5 used to estimate TMDLs for the mentioned pollutants
Two Total Maximum Daily Loads for Total Dissolved Solids and Sulfate in E.V. Spence Reservoir[12]	2003	Austin, Texas, USA	Total dissolved solids & Sulfate	Target concentrations , source analysis, evaluation of load reduction scenarios	Texas Surface Water Quality Standards (TSWQS) used to determine the mentioned pollutants targets concentrations. methodology described in section 2.5 used to estimate TMDLs for the mentioned pollutants

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[10] -http://www.epa.gov/region9/water/tmdl/la lakes/LaLakesTMDLsJune2010 PubMeet.pdf. Retrieved on July, 2011

[11] -http://www.sandiego.gov/stormwater/plansreports/chollas.shtml, Retrieved on septemper, 2011

[12] -http://www.tceq.state.tx.us/assets/public/implementation/water/tmdl/ 04spence/04 spence_final_2nd.pdf. Retrieved on october, 2011

Total Maximum Daily Load for Ammonia & NOx Rock Creek Clinton County, Iowa[13]	2000	USA, Low Moor	Amonia, & Nitrate TMDL,	TMDL, source assessment and implementation strategy plan	The current load is estimated by using the methodology described in section 2.5 used to estimate TMDLs for the mentioned pollutants
Cadmium, Lead, & Zink for 43 pokane river. (Pelletier &Merril, 1998)	1998	Washingt on, USA	Cadmium, Lead, & Zink	Waste load allocations, and calculations of TMDLs	California Toxics Rule (CTR) for fresh water is used to determine the mentioned pollutants targets concentrations.
Tar-Pamlico basin Douglas, (2003)	1998	Carolina, USA	Nitrogen & Phosphorus	Determination of the non-point loads and strategy of nutrients reduction was developed	methodology described in section 2.5 used to estimate TMDLs for the mentioned pollutants
Total maximum daily loads for Ten mile creek[14]	1998	West Virginia, USA	Aluminuim & Iron	Wasteload allocations and load allocations & needed reduction	The Hydrologic Simulation Program Fortran (HSPF), to simulate the runoff of pollutants from the watershed.
Keuka lake watershed study (Douglas, 2003)	1996	NewYork, USA	Sediment& Nutrients	Identify those sub watersheds with the greatest pollution potential and thus target areas for remedial action	A watershed model was used to estimate nonpoint-source loads of sediment and nutrients to Keuka Lake from agriculture

[13] -http://water.epa.gov/lawsregs/lawsguidance/cwa/tmdl/nutrients.cfm. Retrieved on May, 2011.

[14] -http://www.epa.gov/owow/tmdl/examples/metals/wv_tenmile.pdf. Retrieved on November, 2011

Chapter Four
Description of The Study Area

4.1. Location and Topography

A catchment or a watershed such as Al-fara'a watershed is an area that captures atmospheric precipitation (rain, snow) and drains the resulting surface runoff to a surface-water body. Al-fara'a catchment is located in the Northeastern region of the West Bank, the catchment extends from the ridges of Nablus Mountains down the eastern slopes to the Jordan River, and it lies over three districts of the west bank: Nablus, Tubas, and Jericho as shown in figure (4.1).The watershed is tee-shaped with an area of 320 km^2, which represents 6% of the total area of the west bank -5600 km^2- (Attallah, 2010). Part of the watershed that lies over the eastern hills of Nablus city is considered urban, while the rest of the watershed is mainly agricultural. The main sources of water in Al-fara'a Catchment are rainfall, springs and groundwater. The main use of water is for domestic and agricultural purposes. Al-fara'a Catchment accounts for 20% of the West Bank water resources and it provides more than 26% of the total West Bank food basket (Abu baker, 2007). Topography is a unique feature of Al-fara'a catchment since it starts at an elevation of about 920 meters above mean sea level in the Western edge of the catchment in Nablus Mountains and descends drastically to about 385 meters below mean sea level in the east at the confluence of the Jordan River over a distance of about 35 km. In less than 30 km there is a 1.25 km change in elevation. Such as elevation decline in a relatively short distance has considerable effects on the current meteorological conditions in the area(Shadeed, 2005).

4.2. Soil and land use

There are two main soil types that cover most of Al-fara'a catchment. These two types are Terra Rosa and Colluvial-Alluvial soils, together covering more than 60% of the total area (Abu baker, 2007). The texture of these soils mainly includes karastic formations such as alluvium, dolomite, and limestone (Abboushi, 2013). The land use of the catchment was classified into four classes: artificial surfaces, agricultural areas, forests and semi natural areas and water bodies as it is shown in figure (4.2).

1. The Artificial Surfaces

The artificial surfaces in the catchment are composed of refugee camps, urban fabrics, Israeli colonies and military camps. There are 20 Palestinian villages, living in built up area of about 9.5 km2, and 11 Israeli settlements in a total built up area of 5.1 km2. The artificial surfaces amount to 5.5 % of the catchment (Attallah, 2010).

2. Agricultural Areas

The agricultural land in the catchment is composed of arable land and heterogeneous agricultural areas(Shadeed, 2005). The arable land involves non-irrigated land, drip-irrigated land, olive groves, palm groves and citrus plantations. The heterogeneous agricultural areas involve irrigated and non-irrigated complex cultivated patterns and land principally occupied by agriculture with significant areas of natural vegetation (Attallah, 2010). The area of the agricultural part of Al-fara'a catchment represents 34.4% from the catchment, which is significantly greater than the populated area (5.5%); therefore the catchment is considered as an agricultural catchment. However, the agricultural activities can be one of the potential pollution sources of Wadi Al-fara'a, due to the unbalanced use of fertilizers and pesticides(Shadeed, 2008).

3. Forests and Semi-Natural Bodies

The forests and semi-natural bodies occupy an area which amounts to 60% of the total area. Most of the Israeli colonies are built in this area and take up much of the forest and semi natural areas (Shadeed, 2005).

4. Wetlands and water bodies

Most of the water courses are seasonal and there are few water bodies in the catchment near the Jordan River that are controlled by the Israeli occupation and are utilized for irrigation and fishing such as the Tirza reservoir (Shadeed, 2005).

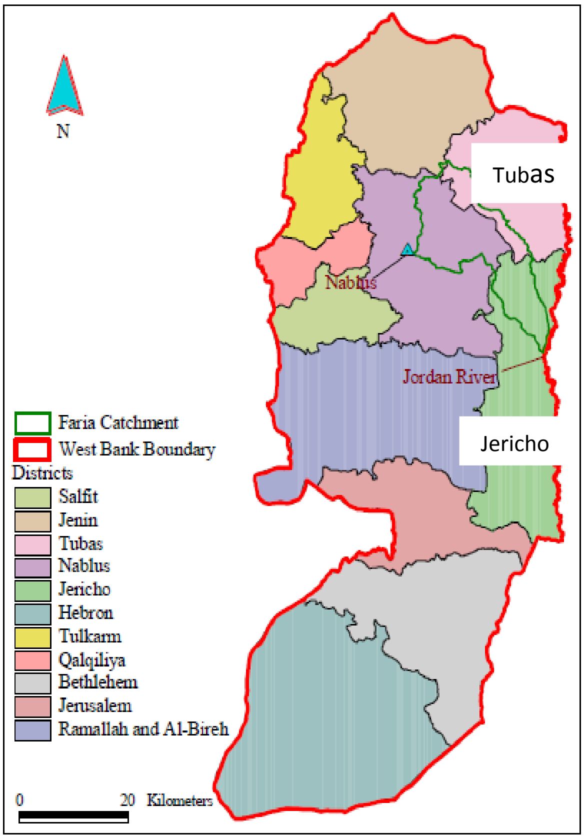

Figure (4.1): Al-fara'a catchment location in the west bank(Shadeed, 2005)

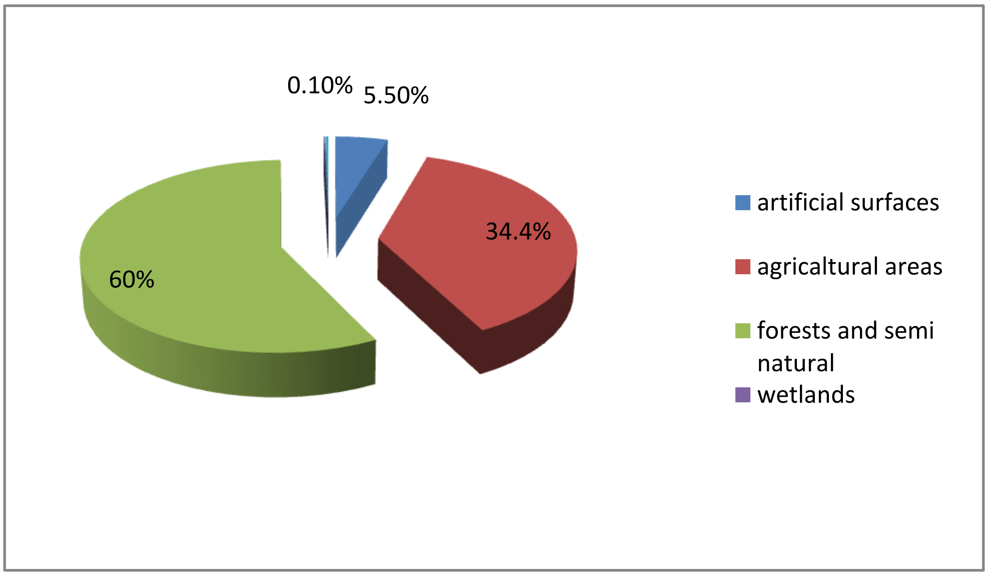

Figure (4.2): The land use classification at Al-fara'a catchment

None of the surveyed industries has on-site treatment, except the stone cutting, which has settling basins that are used for settling and reusing the cooling water, and the slaughter house, which has preliminary treatment for the produced wastewater.

4.3. Rainfall

The West Bank has the Mediterranean type climate. Regionally, the winter rainy season starts in October and ends in April in the catchment. Rainfall events predominantly occur in autumn and winter and they account for 90% of the total annual precipitation event (shadeed, 2005). Although the summer months are dry, some rain events occur occasionally. In winter, the North Atlantic high on North Africa and the Euro-Asian winter high over Russia are the primary cause of winter weather in the area. The steep gradient of the Jordan Valley greatly reduces the quantity of the rainfall in the Jordan Valley rift area. The rainfall distribution within Al-fara'a catchment ranges from 640 mm at the headwater to 150 mm at the outlet to the Jordan River (shadeed, 2005)

4.4. Water resources

There are 70 wells in Al-fara'a catchment of which 61 are agricultural wells, 4 are domestic and 5 are Israeli wells, as shown in figure (4.3)(Shadeed, 2005). There are 13 fresh water springs; most of them are located in the upper and middle parts of the catchment, as shown in figure (4.4). The annual discharge from these springs varies from 3.8 to 38.3 MCM (million cubic meters) /year with an average amount of 14.4

MCM/year (Ghanem, 1999). Some springs do not have effluent all the year and have it mainly in the spring season as Al-fara'a spring.

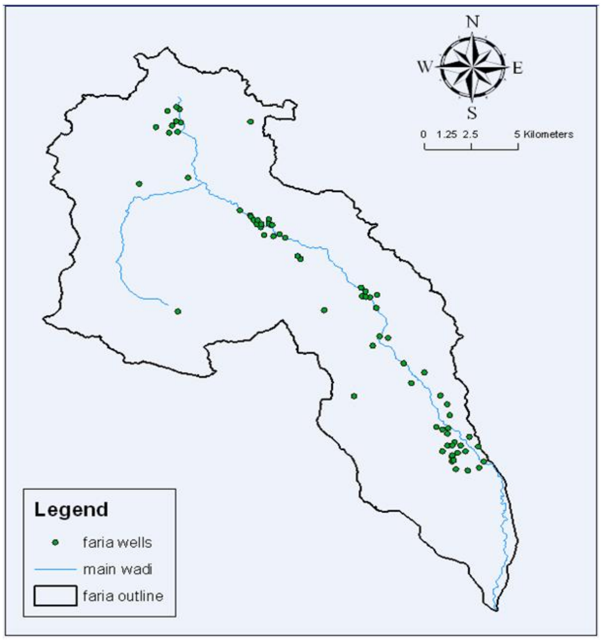

Figure (4.3): The distribution of the wells in Al-fara'a catchment area (shadeed, 2005)

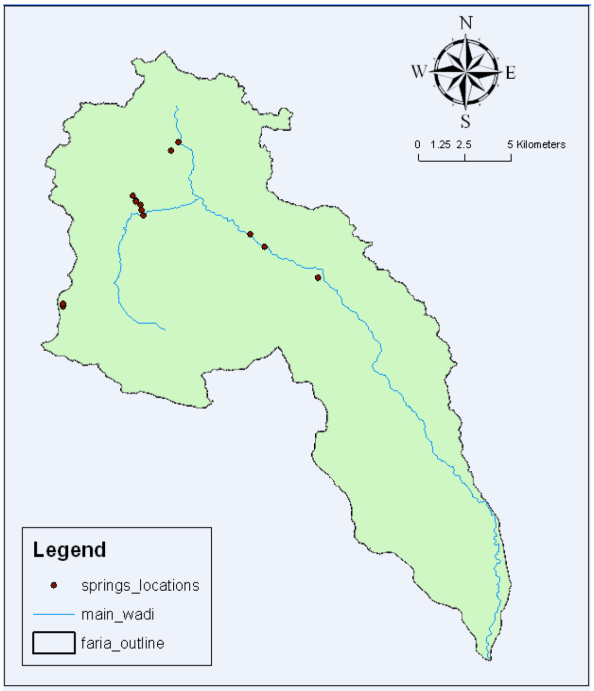

Figure (4.4): The distribution of the springs in Al-fara'a catchment area (shadeed, 2005)

Al-bathan and wadi Al-fara'a are the main wastewater streams in Al-fara'a catchment; there flow is composed of:

- Fresh water from springs.
- Runoff from winter storms.
- Untreated wastewater of the eastern part of Nablus and Al-fara'a camp(Shadeed, 2005)

4.5. Wastewater sources

About 2.2 MCM (million cubic meters) of wastewater are being generated from domestic sources by about 74000 Palestinians living in the eastern part of the city and in Al- Fara'a Camp. And 0.2 MCM are produced by industrial sources(Attallah, 2010). Besides, there is the discharging of evacuation tanks from surrounding villages, and the leachate from random dumping sites.

Wastewater collection network systems exist in Nablus City and Al-fara’a. Those sewage systems are combined systems for the collection of wastewater and storm water. The sewage system of Nablus City is divided into two major parts, one to the east and another one to the west. In the eastern side, the sewage pipeline discharges into Wadi Al-Sajoor where sewage flows through Wadi Al–fara’a and into the Jordan valley. Farmers use the untreated wastewater for irrigating vegetables (Abu baker, 2007).While the percolated amounts may leach down to pollute the underlying aquifer system. In the western side, the sewage pipelines discharge into Wadi Zeimar. The areas that are uncovered by sewage collection network systems use cesspits; these are most commonly used in villages (PCBS, 2000).Vacuum tanks are used to evacuate wastewater from cesspits and they subsequently empty their content either in Wad is or in open lands. Most of the cesspits are built without concrete linings in order to facilitate sewage infiltration and thereby to minimize emptying costs (Abu baker, 2007).

4.6. Pollution sources and environmental issues at Al-fara'a catchment

The Main Pollution sources and environmental issues at Al-fara'a catchment are listed bellow:

1. Raw wastewater from the eastern part of Nablus City and from Al-Fara'a Refugee

Camp discharged without treatment to the main wadi; these may infiltrate into the upper unconfined aquifer (Abboushi, 2013).

2. The use of untreated wastewater in irrigation is an ongoing practice (Abu baker, 2007).

3. Random solid waste dumping sites are widespread through the catchment; hence, the resulted leachate could pollute the Wadi (Abu baker, 2007).

4. Agricultural runoff that could result due to excess irrigation from the adjacent agricultural land which commonly use sprinklers and furrows as dominant irrigation methods. Agricultural runoff contains many pollutants due to the use of natural organic fertilizers (manure) and the use of artificial agrochemicals such as ammonia and sulphur fertilizers, pesticides, and herbicides (Abboushi, 2013).

5. More than 40% of the population in the Catchment lack water supply for drinking purposes (Almasri et al., 2005).

6. The estimated annual water gap between water needs and obtainable water supply is about 20 million cubic meters. This gap is increasing with time (Abu baker, 2007).

7. The unbalanced utilization of groundwater causes increasing salinity, especially in the south eastern part of the Catchment in proximity to the Jordan River (Almasri et al., 2005)

8. Water losses through evaporation and infiltration from the agricultural canals are high, and thus large quantities of water are not fully utilized.

9. Cesspools are major threats which may pollute the shallow groundwater.

4.7. The industial facillities at the eastern part of Nablus city

Suitable infrastructure facilities for the industries in Palestine in general are not found; the industrial wastewater produced from the industries in the eastern part of Nablus are discharged to the Wadi without sufficient treatment, which significantly contuributes to the Wadi contamination; hence, the industrial wastewater contains many persistence pollutants as heavy metals, toxic organics, salts, dyes, etc.(Al-habash, 2003)

There are 115 industries found in the eastern part of Nablus, most of them are considered small to medium in size and do not work 24 hours a day (Abu baker, 2007).There are three major industrial groups. The first one includes stone cutting and tiles which produce building materials; the second group is the food industry such as the tahina, dairy products, soft drinks, olive and vegtible oil processing and slaughter houses. The third group is metal finishing, chemicals, insecticides and veterinary medicines, detergents, paper, textile, and pharmaceuticals. Only cutting stone industries have on-site pretreatment which includes settling basins, while, the slaughter house has a preliminary treatment for the produced wastewater (Nablus Municipulity, 2006).

The generated quantities of wastewater from the eastern industrial zone are collected by the main network of domestic wastewater and discharged to Wadi Al-fara’a (Nablus Municipulity, 2006). Table (4.1) summarizes the type of industries, the total wastewater generated, and the constituents of the generated wastewater.

Table (4.1): the industries found at the eastern part of Nablus city, and related information (Al-habash, 2003) &(Nablus Municipulity, 2006).

Industry type	# of sources	Water consumption m3/month	Wastewater generation m3/month	Raw wastewater constituents	Wastewater collection method
Metal and furniture	12	86	76	Heavy metals	Network
Textile	2	9300	9300	Soap, sodium bisulfate anhydrous, enzyme, vinegar and NaOCl Arsenic and salt	
Tannery	1	430	430	Glycerin mono striate, white paraffin oil, citric acid, alcohol titanium dioxide and triethanol amine, heavy metals	Network
Carton	1	200	200		Network
Cosmetics	3	69	69		Network
Paints	1	105	11	Benzene, sulphonic acid, sodium laury, ether sulfate, sodium hypochlorite, diethanol amid, sodium chloride	Network
Soap	2	20	20		Network
Chemical	5	265	29		Network
Insecticide and veterinary medicines	3	67	Unknown	Antibiotics, pesticides, soda, acid, phenol and additives. toxic organics.	Network
Tiles	7	355	248	Cement and sand	Cesspit/septi c tank
Concrete	4	940	Few quantities	Domestic	network
Plastic	4	12	12	Domestic wastewater	Network
nylon	2	375	187	Ink, white acid and benzene	Network
Paper & printing industry	1	82	82	Domestic	Network
Shoes and rubber	1	3	3	Domestic	Network

Diapers	1	15	15	Domestic	Network
Stone cutting	17	905	634	Grains, dust and small Stones	Septic tank
Quarries and concrete	1	180	Few quantities	Cement and sand	Wadi
Tahina industry	7	1,295	1,295	High chloride load, salt	Wadi& network
Dairy products	1	3000	3000	High chloride, phosphoric acid, organic materials, whey protein and lactose	
Sweets, flour and soft drinks	4	390	55	Sugar, Sulfuric acid, soda	Network
Pickles	1	400	280	Salts and acetic acid	Network
Vegetable Ghee and Vegetable oil	1	2,020	2,020	Organic materials	Network
Olive oil mills	3	25	18	Phenols and other organics	Network
Luncheon meat	1	--	--	Organic materials, preservatives chemicals	Network
Slaughter house	1	300	300	High BOD, blood and organic materials	Wadi Sajoor
Closed facilities	25	--	--	--	--

4.8.The main medical facilities at the eastern part of Nablus city

There are mainly seven medical facilities at the eastern part of Nablus city, as shown in figure (4.5) (Nablus munucipility, 2014). The wastawter from these sites is being discharged to the public sewer netwerk without any treatment. Generally, in the West Bank, wastewater discharged from health and medical institutions is not treated separately and is discharged into domestic wastewater networks(EQA, 2010).

These health care and medical institutions are provided by three main operators:

1. The public sector: the responsibility for this sector lies on the Palestinian Ministry of Health (MOH)

2. UNRWA’s health department: the responsibility here lies on the United Nations Relief and Works Agency for Palestine Refugees (UNRWA)

3. The nongovernmental sector: involving local and international organizations. (ARIJ, 1996).

Figure (4.5): The main medical facilities at the eastern part of Nablus city (Habash, 2014)

Chapter Five

Results of Heavy Metals and Toxic Organics Analysis

5.1. Heavy metals analysis results and discussion

5.1.1. Introduction

Six heavy metals were selected to be quantified at the stream; these selected metals are Chromium (Cr), Copper (Cu), Zink (Zn), Nickel (Ni), Cadmium (Cd) and lead (pb). They were investigated at Wadi Al-fara'a in order to perform TMDL for the detected metals. The samples were analyzed by Atomic Absorption Flame Emission Spectrophotometer instrument (AA-6701, Shimadzu, Japan, 1995).

The sampling process was carried out at five locations in wadi Al-fara'a with the intention to cover the spatial and temporal variations in the tested parameters. Results are statically analyzed, discussed and compared by national and international standards; they are then presented by EXCELL program charts.

5.1.2. Results of temporal and spatial variation

In this type of analysis, a total of sixteen monthly raw wastewater samples were taken from every sampling location mentioned in the methods section above.Initially, one blank and four standards were analyzed in order to initiate calibration curve for every heavy metal before starting analysis for the samples. All the result calibration curves are linear with $R^2 > 0.99$ for most of them. The samples were analyzed for Chromium (Cr), Copper (Cu), Zink (Zn), Nickel (Ni), Cadmium (Cd) and lead (Pb).

a. Copper (Cu)

The following figure shows the monthly Copper concentration at AJ, TWWBM, TWWAM, MB, and SST for the duration from 27/12/2010 to 28/3/2012, and they are listed in table C.1 in Appendix C.

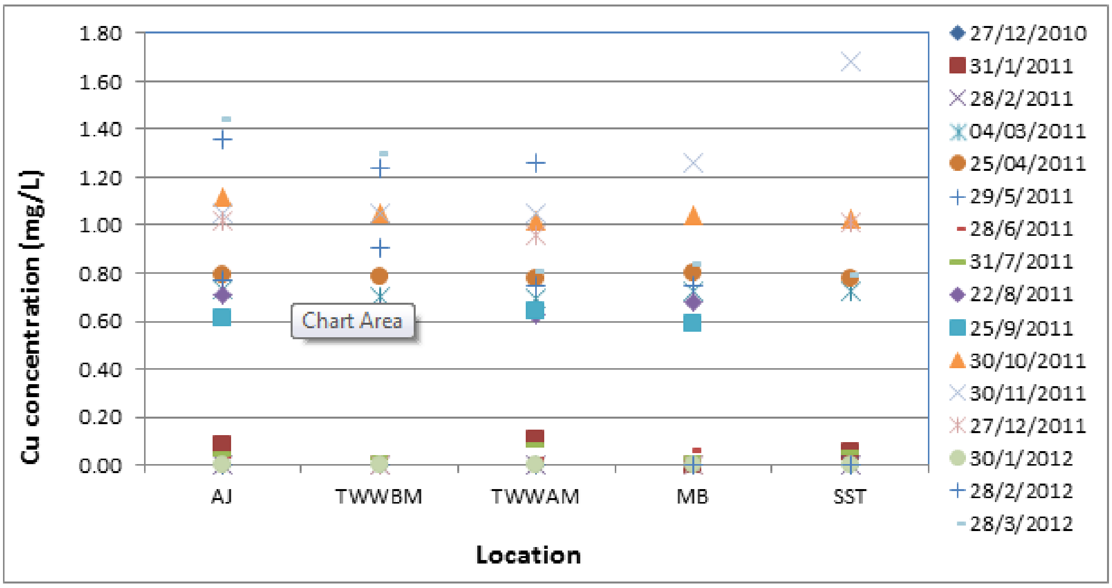

Figure (5.1): Copper concentrations at five sampling locations for sixteen months

As figure (5.1) shows, a decrease in Copper concentration is observed in 28/2/2012 and 28/3/2012 samples, while samples of 31/1/2011, 25/4/2011, 29/5/2011, 31/7/2011, 22/8/2011, 25/9/2011, and 30/10/2011 show almost constant concentration along the Wadi, indicating that weak purification occurs along the Wadi for Cu pollutant; these results may be attributed to the fact that over the years of Cu loading to the Wadi, its sediment became saturated with Cu. As mentioned previously, Cu has high affinity to associate with particulate matter.

27/12/2011 samples show a great fluctuation in Cu concentration along the Wadi. The variation may be attributed to the variation in the depth of sampling from site to site; Copper tends to attach with soil particles and then to precipitate, so the sampling depth is a crucial factor in this situation.

On 30/11/2011 the samples show a constant Cu level in AJ, TWBM, and TWWAM. From TWWAM to SST through MB the Cu level increased gradually, since this month is usually a wet month. The adjacent area to the stream from TWWAM to SST is an agricultural land, thus this month witnesses the beginning of land pesticide spraying to prepare the agricultural lands for cultivation. Accordingly, the runoff may flux the copper from the adjacent agricultural area to the stream, especially as mentioned earlier most of the pesticides are Cu based.

For every sampling location, the figure depicted the temporal variation in Cu concentration; it is clear that the concentration changes from month to month depending on the discharged quantities from domestic and industrial sources; the dilution with rain water happens in the winter season and with springs' water in the spring season.

Al-fara'a soil has little potency for adsorption heavy metals and other pollutants; accordingly, it has poor stream self-purification. This is the findings of a study conducted on the capacity of Al-fara'a soil for adsorption pollutants (Mezyed, 2000), and that is very clear in the previous results for Copper concentrations in the stream.

b. Chromium (Cr)

The following figure shows monthly Cr concentrations in (mg/l) at five sampling locations for six months and they are listed in table C.2 in Appendix C:

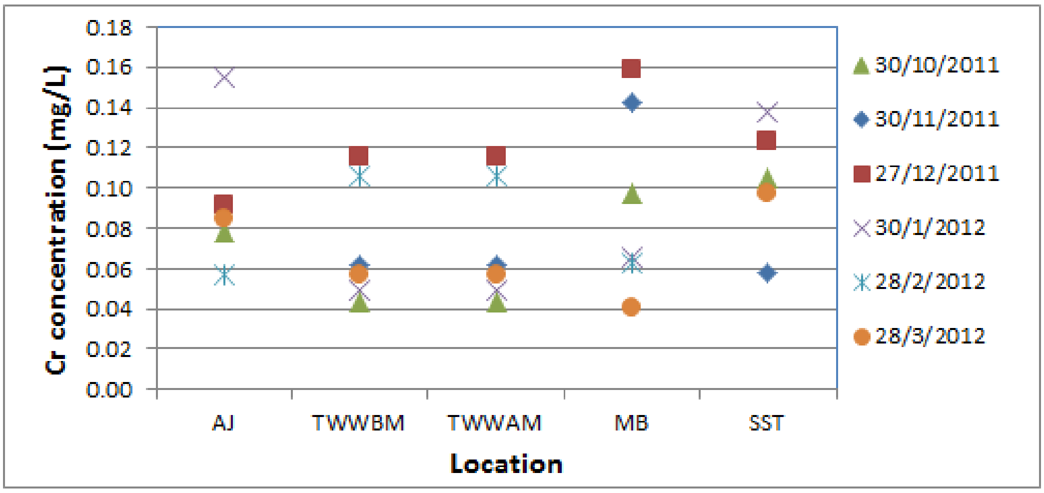

Figure (5.2): Cr concentrations at five sampling locations for six months

At AJ most samples show similar Cr concentrations about 0.08 ppm; the 30/1/2012 sample shows a higher Cr concentration because there is either a temporary Cr source in east Nablus industry as maybe an amount of paint or dye containing chromium was drained to the wastewater facility; or the physicochemical action can transform and redistribute the metals within the sediments to the water column as a vigorous flood (Daghrah, 2005).

At MB and SST Cr concentrations have a different pattern from the previous locations. The Cr concentrations differ from one sampling event to another and that can be attributed to the wastewater supply from Al-fara'a camp which reaches MB during rainy months. Only during winter, Al-fara'a camp wastewater reaches MB and mixes with the coming wastewater from TWWAM.

At TWWBM and TWWAM also most of the samples show similar concentrations of about 0.05 ppm, 27/12/2011 and 28/2/2011 samples show a higher Cr concentration of about 0.11 ppm; as mentioned previously, such increase can be linked to either to a temporary Cr source or a physicochemical action.

If we examine every sampling event over different locations for most of the sampling events, it is observed that the Cr concentrations become lower and lower as the Wadi flows until it reaches MB location, this decrease indicates that some form of purification has taken place - the chromium is likely to be adsorbed by soil and sediment. The MB samples, especially those taken at rainy months (30/10/2011, 30/11/2011, 27/12/2011, and 30/1/2012) show a higher chromium level than the samples of TWWBM, because of the runoff that come from Al-fara'a camp, which mixes with TWWBM wastewater at MB.

c. Zink (Zn)

The following figure shows monthly Zn concentrations in (mg/l) in five sampling locations over six months and they are listed in table C.3 in Appendix C:

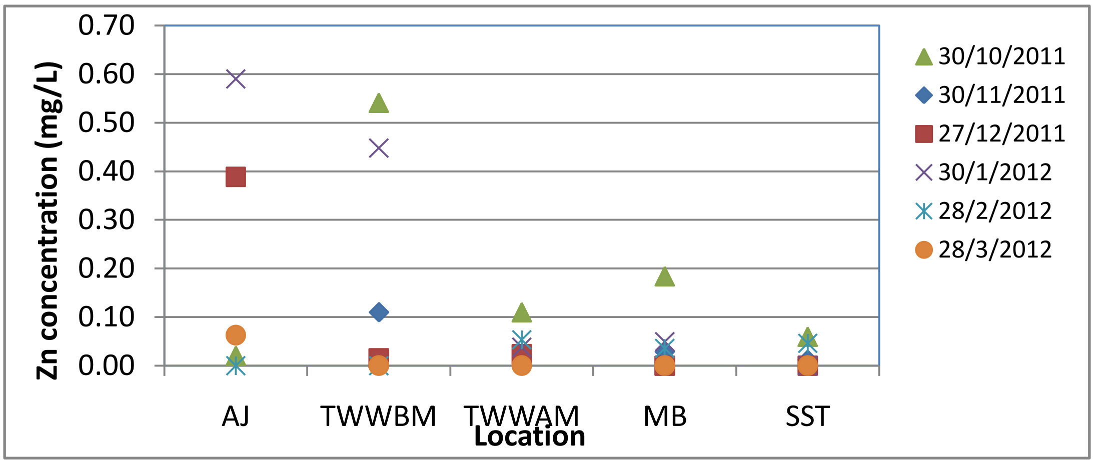

Figure (5.3): The Zn concentrations at five sampling locations for six months

At AJ location, high levels of Zn concentrations had been detected in the 27/12/2011 and 30/1/2012 samples. As mentioned in Zn source investigation, the urban and industrial runoff represents the main Zn source for the AJ segment. The high flow rates of 140.8 and 197.6 l/sec respectively were measured on these two sampling events, which happened shortly after rainy days; these figures are to be compared with 30/10/2011, 28/2/2012 and 28/3/2012, which have lower flow rates of 48.5, 73.1, and 84.6 l/sec respectively. The sampling in the latter cases happened during dry weather, and so the Zn concentrations were very low.

At TWWBM, the two samples have high concentrations of Zn on 30/10/2011 and 30/1/2012;asforthe30/1/2012 sample, it showed lower Zn concentration than the AJ sample for the same date. Again this may mean that some purification and dilution has occurred, especially if we examine the other samples of the same date taken at TWWAM, MB, and SST locations which show lower and lower Zn levels.

Nonetheless,the30/10/2011 TWWBM sample has a higher Zn concentration level than the AJ sample, which indicates that there is a temporary Zn source between AJ and TWWBM. The source could come from agricultural products such as fertilizers, growth stimulant in animal husbandry, fungicides and insecticides, or it could be linked to an amount of dry batteries thrown in the stream intentionally or accidentally which make Zn level increase so suddenly. For the other sampling dates, the Zn levels were low in the measured samples.

At TWWAM, all the samples have Zn concentrations lower than TWWBM samples. The reason could be attributed to the dilution from Al-Bathan springs.

At MB also most samples have Zn concentrations lower or similar to the concentrations of the TWWAM samples. The reason could be due to the fact that there is no significant Zn source at midway between the two locations. Nevertheless, the 30/10/2011 sample has a Zn level higher than the TWWAM sample. This increase can be linked to Zn concentrations in the wastewater from the TWWBM location, or to the fact that there is a temporary Zn source on the way to MB.

SST samples have Zn levels lower than MB samples, which may indicate that purification has happened along the way and that there is no significant Zn source reaching the stream.

By way of generalization it can be said that the Zinc concentrations decreased as the Wadi flows down its way. A decent level of purification is happening along the way.

d. Lead (Pb)

The following figure shows the monthly Pb concentrations in (mg/l) at five sampling locations for six sampling months and they are listed in table C.4 in Appendix C:

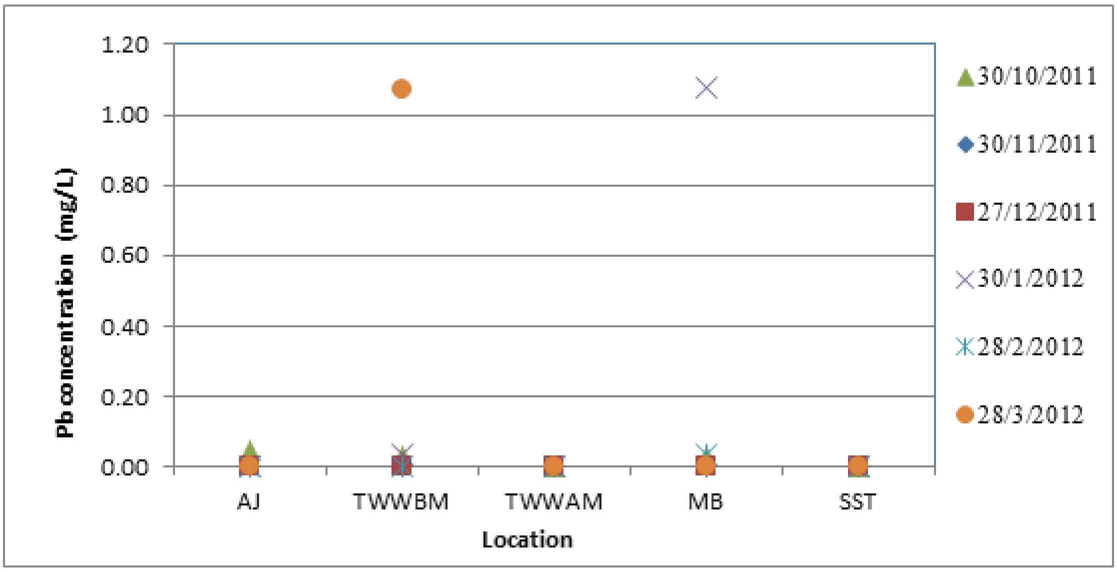

Figure (5.4): Pb concentrations at five sampling locations for six months

This figure shows that Pb had been detected in two samples only on 30/1/2011at MB and on 28/3/2012 at TWWBM; otherwise, the metal was not detected. This result can be attributed to the natural purification which may have occurred along the wadi, or it can be said that a temporary source of lead (paints, dry batteries, or gasoline) had been discharged to the wadi at these two dates.

e. Nickel (Ni)

The following figure shows the monthly Ni concentrations in (mg/l) at five sampling locations for ten months and they are listed in table C.5 in Appendix C:

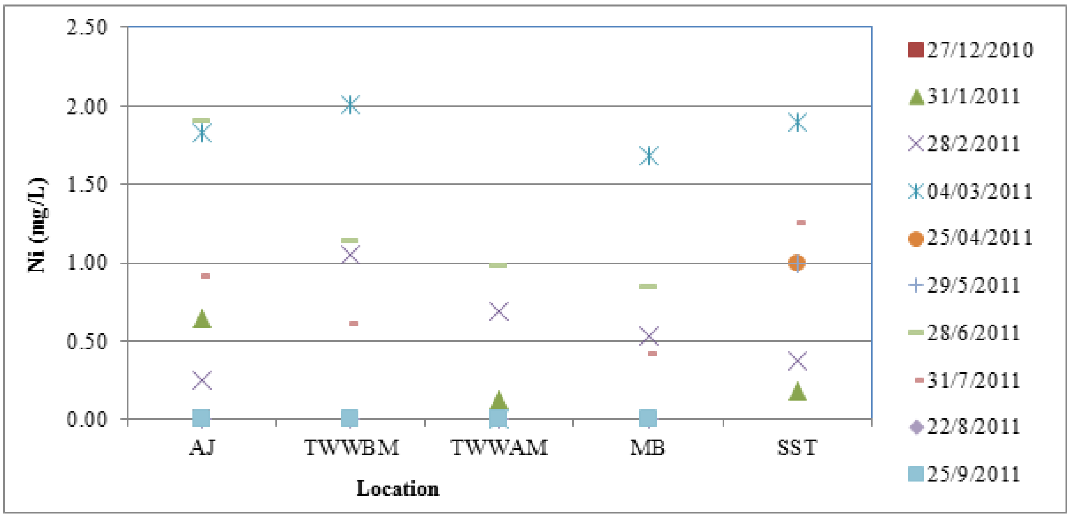

Figure (5.5): Ni concentrations at five sampling locations for ten months

For most of the sampling events, it is noticed that the AJ location which represent Nablus domestic and industrial wastewater has the highest Ni level compared with the next locations at which Ni level decreased gradually due to natural purification. However, Ni at TWWBM for the 28/2/2011 sample has a higher concentration than the AJ sample; this indicates that there may be a temporary Ni source between AZ and TWWBM waste dumping of dry batteries or alloys containing Ni. Another likely reason is that some types of Ni containing fertilizers were used by Al-Bathan village farmers in Feb/2011; it is well known that, at this month, the intensive agricultural season starts in the area.

For the 4/3/2011 samples, the TWWBM has a slightly higher concentration than AJ, due to physiochemical actions which may have occurred in the stream near TWWBM. Then at TWWAM the Ni disappeared, a fact which indicates the occurrence of a great dilution in the stream. At this point the Al-Bathan springs fresh water mixes with the TWWBM wastewater. Also in March the springs yield is higher than any other season. As is shown in the figure above, Ni appeared gain in MB because of the evaporation which has happened along the distance between TWWAM and MB.

At 25/9/2011 the Ni disappeared from the stream, either due to the large amount of freshwater discharged to the stream for cleaning purposes at this date which causes great dilution or no source for Ni was at this date. The soil condition is also suitable for Ni absorption because of its pH, organic content. Since September is a dry month in the area, so it is suggested that there are no aggressive actions in the stream which may allow Ni precipitation to take place.

For every sampling location, the figures revealed temporal variation in Ni concentrations; the concentration changes from month to month depending on the discharged quantities from domestic and industrial sources and dilution with rain water in the winter season and with the springs' water in spring season.

5.1.2. Statistical measures for heavy metals results in each location

a. The Azmout Junction (AJ) location

Table (5.1) gives general statistical measures computed for heavy metals results at AJ location,which represents the domestic and industrial wastewater of east Nablus; Ni has the highest mean and maximum concentrations compared with other heavy metals, as shown in table (5.1).The source for Ni is very likely the industries found inthe industrial area of east Nablus. The factories that reproduce detergents, and they release 265 $m^3$of wastewater monthly (Abu Baker, 2007). While Ni is detected in 67% of the tested samples, 100% of the detected samples have concentrations higher than the US EPA standard for Nickel. Copper is detected in 81% of the tested samples; 68.8% of the detected samples have concentrations higher than the US EPA standard for Copper which is 0.065 ppm. Copper has the highest median and the second highest maximum and mean concentrations which indicate that there are Copper resources in the area. As mentioned in the literature review, the Copper sources are plumbing pipe, heat exchangers, jewellery industry, catalysts and coins, motor vehicle components, Pesticide (algaecide, fungicide, wood preservative, bactericide), and batteries. All of these goods are either produced or used in the eastern side of Nablus.

With regard to Cr and Zn, they are detected in 100% and 80 % of the tested samples with a means of 0.09 and 0.21 ppm respectively. This result may indicate that there are some sources for them in the area; the sources can be either domestic or industrial as mentioned previously in the literature review and elsewhere in the study. Zn and Cr are found in 50% and 33.3% of the detected samples with concentrations above the US EPA standards for Zn and Cr respectively.

Pb has the lowest mean and maximum concentrations compared with the other detected heavy metals. It was detected in only one sample with concentrations higher than the US EPA standard. This result may indicate low presence for Pb sources at the area.

Table (5.1): Statistical data for heavy metals concentrations at AJ location

	Cu	Cr	Ni	Zn	Pb
Mean (ppm)	0.54	0.09	0.77	0.21	0.01
Minimum (ppm)	0.0	0.06	0.0	0.0	0.0
Maximum (ppm)	0.0	0.16	1.9	0.59	0.05
Median (ppm)	0.66	0.08	0.65	0.06	0.0
Number of samples	16	6	9	5	5
Number of detected samples	13	6	6	4	1
Percent of detected samples (%)	81.25	100	66. 67	80	20
US EPA standards (ppm)	0.065	0.085	0.052	0.12	0.003
Number of samples above US EPA standards	11	2	6	2	1
Percent of samples above US EPA standards (%)	68.75	33.33	100.00	50.00	100.00

b. The Tawaheen Waste Water before Mix (TWWBM) location

Table (5.2) gives general statistical measures computed for heavy metals testing results at TWWBM location, which represents the wastewater of AJ after 6 Km of flowing in an open stream, often mixing in winter with runoff from adjacent agricultural and urban areas. For this reason, the location is not considered as a point source, rather it can be considered as a natural water body receiving both point and non point sources; accordingly the US EPA standards for fresh water are applicable in this location.

Like at AJ location, Ni has the highest mean and maximum concentrations; it was detected in 63% of the tested samples, all of which have concentrations above EPA standards. Likewise, Copper has the highest median, the second highest mean and maximum concentrations; it was detected in73% of the tested samples, 82% of which are above the US EPA standards for Copper. Cr and Zn also have similar mean concecnetrations to the AJ location, a result which may indicate that no purification happened between the two locations inspite of the long distance separating them. Also,we may conclude that there are no significant sources for these metals located between the two locations.

Otherwise, Lead has higher mean and maximum concentrations than in the AJ location; it was detected in 50% of the tested samples with concentrations higher than US EPA standards. We may reasonably conclude that there are lead sources on the way between the two locations. These Lead concentrations come from solidwaste dumping sites in the area which often has dry battaries and domestic solidwaste;additionally,the combustion of fossil fuel and wood are also common practices in this rural area.

Table (5.2): Statistical data for heavy metals concentration at TWWBM location

	Cu	Cr	Ni	Zn	Pb
Mean (ppm)	0.52	0.12	0.70	0.19	0.19
Minimum (ppm)	0.00	0.05	0.00	0.00	0.00
Maximum (ppm)	1.30	0.14	2.01	0.54	1.07
Median (ppm)	0.63	6	0.61	0.06	0.01
Number of samples	15	6	8	6	6
Number of detected samples	11	6	5	4	3
Percent of detected samples (%)	73.33	100	62.5	66.67	50.00
US EPA standards (ppm)	0.065	0.085	0.052	0.12	0.003
Number of samples above EPA standards	9	5	5	2	3
Percent of samples above EPA standards (%)	81.82	83.33	100	33.33	50.00

c. The Tawaheen Waste Water after Mix (TWWAM) location

Table (5.3) gives general statistical measures computed for heavy metals results at TWWBM location, which represents TWWBM after it mixes with spring water. As shown in the table below, Copper has the highest mean, median and maximum concentrations compared with other heavy metals. Cu was detected in 81% of the tested samples, 92% of which have concentrations higher than the US EPA standards. These measures for Cu concentration are similar to those for the TWWBM location. Apparently, the dilution with spring water did not have any effect; an even worse scenarios that the spring water carries Cu to the stream as it flows through dirt in an open channel. However, the other heavy metals measures for the

TWWAM location are lower than those for the TWWBM location due to the dilution with spring water.

Table (5.3): Statistical data for heavy metals concentration at TWWAM location.

	Cu	**Cr**	**Ni**	**Zn**	**Pb**
Mean (ppm)	0.52	0.07	0.29	0.05	0.00
Minimum (ppm)	0.00	0.04	0.00	0.02	0.00
Maximum (ppm)	1.26	0.12	0.98	0.11	0.00
Median (ppm)	0.64	0.06	0.06	0.04	0.00
Number of samples	16	6	9	6	5
Number of detect samples	13	6	4	5	0
Percent of detected samples (%)	81.25	100.00	44.44	83.33	0.00
US EPA standards (ppm)	0.065	0.085	0.052	0.12	0.003
Number of samples above EPA standards	12	2	4	0	0
Percent of samples above EPA standards (%)	92.31	33.33	100.00	0.00	0.00

d. The Malaqi Bathan (MB) location

Table (5.4) gives general statistical measures computed for heavy metals results at the MB location, which represents the TWWAM after 3 km and after mixing with Al-fara'a camp wastewater. As the table shows, Ni has the highest mean and the maximum concentrations. These measures are similar to those at the TWWBM; despite the long distance, the water springs which mix with the stream at TWWAM have dried out. On the other hand, Cu still has mean and maximum concentrations close to the previous locations. Clearly, poor purification has occurred for Cu. Lead was detected in 60% of the samples with concentrations higher than the

EPA standards. This is due to Al-fara'a camp wastewater which is likely to carry lead to the Wadi; and as lead is found on the roads as transportation fuel exhaust, it can go as runoff to the Wadi in winter time.

Table (5.4): Statistical data for heavy metals concentration at MB location

	Cu	Cr	Ni	Zn	Pb
Mean (ppm)	0.43	0.09	0.57	0.05	0.23
Minimum (ppm)	0.00	0.04	0.00	0.00	0.00
Maximum (ppm)	1.26	0.16	1.69	0.18	1.08
Median (ppm)	0.36	0.08	0.42	0.03	0.03
Number of samples	16	6	8	6	5
Number of detect samples	12	6	4	4	3
Percent of detected samples (%)	75.00	100.00	50.00	66.67	60.00
US EPA standards (ppm)	0.065	0.085	0.052	0.12	0.003
Number of samples above EPA standards	9	3	4	1	3
Percent of samples above EPA standards (%)	75.00	50.00	100.00	25.00	100.00

e. The Shibli Stream (SST) location

Table (5.5) gives general statistical measures computed for heavy metals results at the SST location, which represents the wastewater after 8 km from the MB location. As the table shows Ni has the highest mean, max and median concentrations in all the tested samples with concentrations higher than the EPA standards. This result indicates that there are Ni sources on the way to the SST location. If we keep in mind that no point sources are discharging into the wadi, and that the lands adjacent to the wadi are used for crop cultivation, then these high concentrations must come from the fertilisers that are used in large amounts in this area. As mentioned in the literature review; fertilisers, especially phosphates, represent the main source of Nickel in agricultural soils. Otherwise, Cu has concentrations similar to the previous locations, a fact which may indicate that weak purification is happening along the wadi.

Table (5.5): Statistical data for heavy metals concentration at the SST location

	Cu	**Cr**	**Ni**	**Zn**	**Pb**
Mean (ppm)	0.56	0.10	0.94	0.02	0.00
Minimum (ppm)	0.00	0.06	0.18	0.00	0.00
Maximum (ppm)	1.68	0.14	1.90	0.06	0.00
Median (ppm)	0.72	0.11	1.00	0.01	0.00
Number of samples	11	5	5	6	5
Number of detect samples	8	5	5	3	0
Percent of detected sample (%)	72.73	100.00	100.00	50.00	0.00
US EPA standards (ppm)	0.065	0.085	0.052	0.12	0.003
Number of samples above EPA standards	6	4	5	0	0
Percent of samples above EPA standards (%)	75.00	80.00	100.00	0.00	0.00

5.1.3. Composite sampling results

One sample **e**very two hours was taken from the AJ location; the sampling occurred in the duration between8:30 PM of 20/9/2012till 6:30 PM of 22/9/2012. Thursday and Friday were chosen for sampling days to show the heavy metals concentration variation between holidays and working days. The twenty four samples were analyzed for Cu, Cr, Zn, and Pb; however, samples were not analyzed for Ni due to technical problems in the apparatus. The analysis was performed using the Atomic absorption apparatus. One blank and four standards samples were analyzed initially in order to set off the calibration curve for Cu, Cr, Zn, and Pb. The result calibration curves were linear with R^2=0.97, 0.99, 0.99, and 0.99, respectively. During the analysis blank and quality control samples of 1ppm were analyzed between every two samples to ensure the satiability of the apparatus analysis.

a. **Copper results**

Figure (5.6) shows the results of Cu concentrations in relation to sampling time. The second series shows the USEPA standard concentration for Cu which equals 0.056 ppm. Cr had been detected in all the samples with an average concentration close to 0.7 ppm except one sample in which there was no trace of Cr at all. This sample was taken at 8:30 PM on 21/9/2012; thus it was excluded. The relative standard deviation for Cu results equals 2.5%, showing low variety in the Cu concentrations throughout the two days.

The Copper concentrations in the stream at AJ location are nearly stable in working days and in holidays, at midday and during the night. As it is mentioned in the literature review, previous studies (Some and Lagerkvist, 2002) have shown that the urban runoff contributions from brake pads, tires, and asphalt were significant, while the other sources were negligible. However, other studies have shown that domestic wastewater is the major anthropogenic source of copper in waterways (Nriagu and Pacyna

1988).Since the sampling occurred in September which is a relatively dry month, thus, the domestic wastewater is the potential main source for Cu; this is especially true if we account for the fact that there is no significant difference in Cu concentration between industrial working days and holidays, a fact which reduces the potential contribution of industrial sources in Copper loading in the stream.

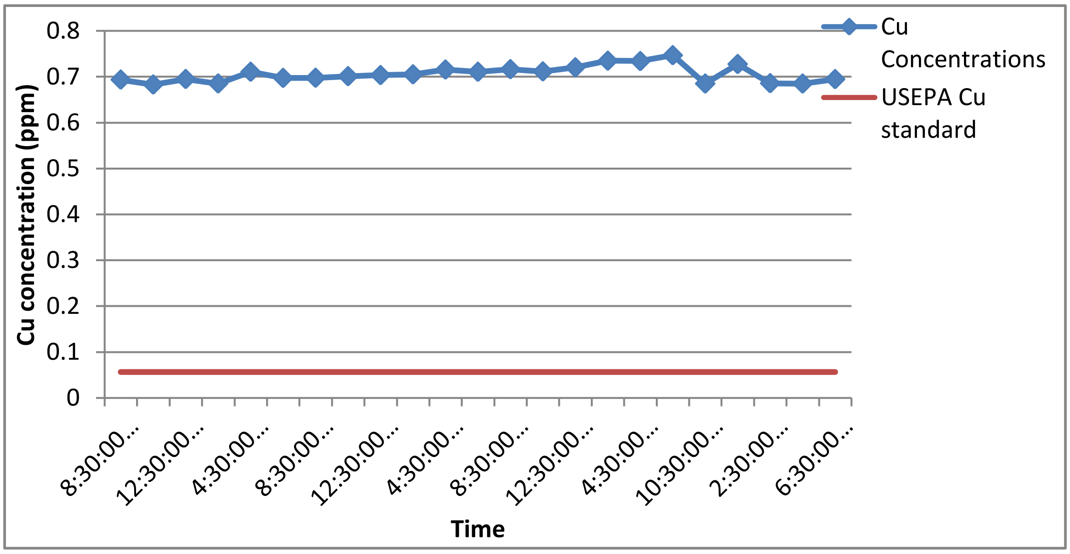

Figure (5.6): Cu concentrations versus time for the composite samples

b. Chromium results

The first series in Figure (5.7) shows the results for Cr concentrations versus time, while the second series shows the USEPA standard concentration for Cr which stands at0.085 ppm. Cr had been detected in all the samples with concentrations ranging between 0.08 and 0.4 ppm. Most samples have higher Cr concentration than the USEPA standard. The relative standard deviation for the Cr results equals 39%, which indicates high variance in Cr concentrations throughout the two days. On Thursday, a normal working day in the industrial facilities, it was noticed that the samples of the midday have Cr concentrations ranging from 0.1 to 0.2 ppm, but between 6:30 PM and 12:30 PM, the Cr concentrations were stable at 0.22 ppm; from then until 10:30 PM, the Cr concentrations increased gradually to reach nearly 0.4 ppm. The sudden drop in the Cr level occurred at 10:30 PM, while in last samples taken during Saturday night, the Cr began to increase gradually reaching 0.44 ppm at 6:30 AM Saturday morning.

As mentioned in the literature review, paints, textile dyes industries, in addition to metal corrosion are the main sources of Cr in the wastewater. Likewise, the sampling results have shown that the Cr concentration increased during the industrial working hours from 0.13 ppm at 8:30 AM to 0.226 ppm at 6:30 PM. These figures confirm the potential industrial contribution of loading Cr in the stream.

Through the night the Cr level remained stable; however; around midday Friday the Cr level started to increase reaching 0.38 ppm. A likely explanation for such increases that a Cr source is contributing to the increase. The increase could be caused by the coating and rehabilitation works for the paints houses. The drop that occurred after that might be a result of the potential dilution in fresh water.

The Chromium level increased again through the night to reach close to its level at midday, because usually there is less water consumption during the night; so the Cr concentration shores up one more time.

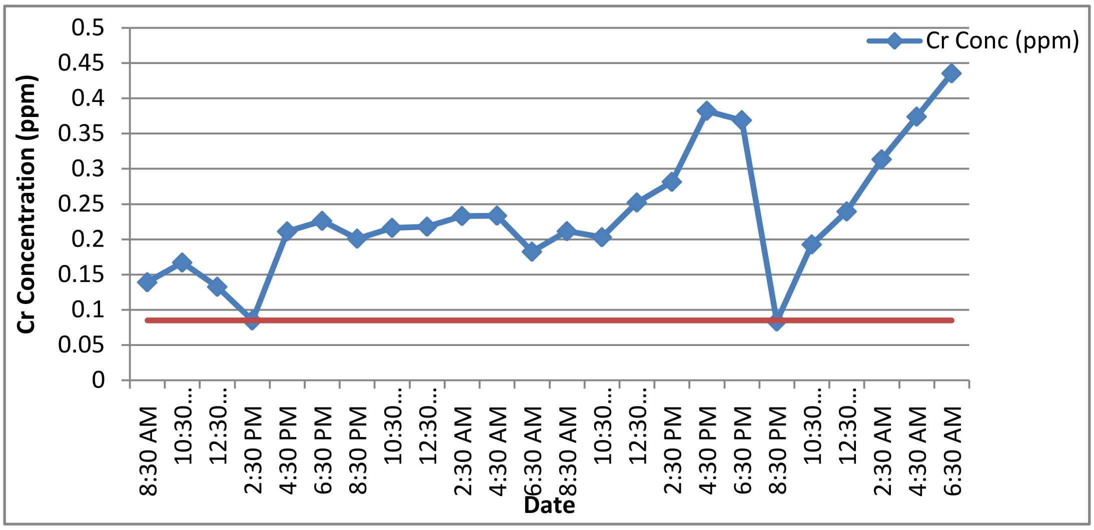

Figure (5.7): Cr concentrations versus time for the composite samples

c. Lead results

The first series in Figure (5.8) shows the results of Pb concentrations versus time, while the second series shows the USEPA standard concentration for Pbat 0.003 ppm. No Pb concentrations had been detected in the first day samples on Thursday, except for the first sample taken at 8:30 Am where Pb had been detected at 0.11 ppm concentration. In contrast, Pb had been detected in most of the second day samples at concentrations in ranges from 0.003 ppm to 0.09 ppm. The highest concentration is related to the sample taken at 12:30 PM on Friday. These results indicate that there were some activities occurring in the area on Friday that emit lead to the environment. After studying the potential lead sources in the area, it was noticed that the AJ are located near to the main road which connects Nablus and Al-bathan recreation areas; a lot of people come for picnicduring holidays, causing high traffic emissions on the main road. On the contrary, in the Thursday samples Pb was almost non-existent, a fact which may indicate that there are no significant industrial lead sources in the area.

d. Zinc results

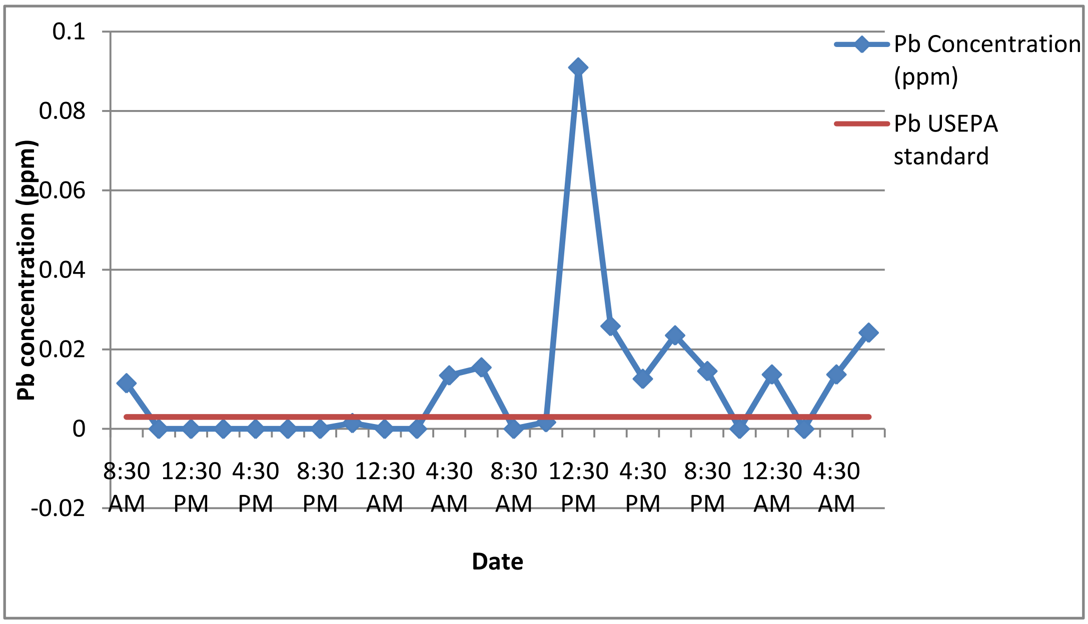

Figure (5.8): Pb concentrations versus time for the composite samples

Figure (5.9) shows the results of Zn concentrations versus time in the first series, while the second series shows the USEPA standard concentration for Zn, which equals 0.12 ppm. Zn had not been detected in most of the tested samples except for only two samples. The first one is the sample taken at 12:30 PM on Thursday, where Zn existed at 0.2 ppm concentration; and the second sample is the one taken at 2:30 PM on Friday, with 0.028 ppm concentration. The high concentration on midday Thursday can be attributed to discharges from an industrial Zn source at this time. The Friday sample had very small, rather insignificant concentrations if compared to the USEPA standards.

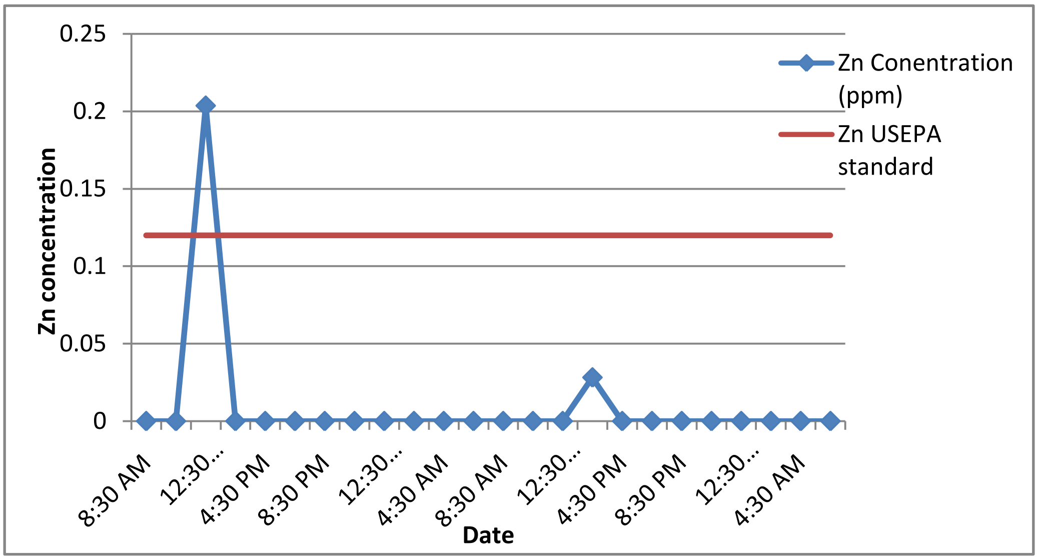

Figure (5.9): Zn concentrations versus time for the composite samples.

5.2. Toxic organics and pharmaceutical compounds analysis and discussion

Two types of analysis were conducted using GC-Ms apparatus; the first one was done by scanning the sample taken from the AJ location to determine the volatile organics which may exist in the sample. The most toxic organics were chosen for the second type of analysis. Accordingly, the second type of specific analysis was performed on the samples taken from different locations at the stream for the previously selected organics using the GC_MS SIM mode. This analysis is based on searching for determined molecular weight.

a. Results of the general scan analysis

Figure (A.1)in appendix A shows the GC-MS instrument output for the AJ sample after labelling the significant peaks. Table (A.2) shows the peaks sorted from highest to smallest, noting that the highest peak indicates higher concentration. The organics detected by the MS detector as explained by the instrument library are shown in the first two columns of table (A.1).The materials selected for analysis include Chloroacetic acid ($ClCH_2CO_2H$), BromoMethane (CH_3Br), Naphthalene ($C_{10}H_8$), Batillol ($C_{21}H_{44}O_3$), and Phosphoromidic acid ($(HO)_2PONH_2$).The samples were analyzed for the purpose of quantifyingthe concentrations of these materials in the Wadi. The selection of these materials was based on their toxicity, availability of their potential sources at the area, and peak height at which the proposed organic could be found. Priority in the selection was given for higher peaks.

b. Results of the specific analysis

Table (5.6) shows the results of the analysis for the samples taken from different locations in the Wadi on 30/1/2012. The terms detected here show that the concentration for the tested organic ranges between0.01 and 0.05 ppb. The average concentration result came at 0.03 ppb. As the table shows all the tested organics were detected in the tested samples.

Table (5.6): Results of the toxic organics analysis Chloroaceticacid ($ClCH_2CO_2H$)analysis results

	AJ	**TWWBM**	**MB**
Chloroacetic acid	Detected	Detected	Detected
Naphthalene	Detected	Detected	Detected
Bromo methane	Detected	Detected	Detected
Batillol	Detected	Not measured	Not measured
Phosphoromidic acid	Detected	Not measured	Not measured

GC-MS instrument outputs for the analysis of AJ, TWWBM, and MB samples, respectively for chloroacetic acid, indicate that chloroacetic acid was detected in concentration near to 0.03 ppb. This value is higher than the maximum permissible limit for toxic organics which stands at 0.008 ppb. Apparently, there are sources for chloroacetic acid in the area. As explained in the literature review, the chloroacetic acid is the precursor to the herbicides and pesticides. Since, Al-fara'a is an agricultural area, the herbicides and pesticides are considered potential sources for chloroacetic acid in the area, especially if we note that the sampling occurred during a rainy month.

Naphthalene ($C_{10}H_8$) analysis results

GC-MS instrument outputs for the analysis of AJ, TWWBM, and MB samples for Naphthalene, indicate that Naphthalene was detected in the tested samples at concentrations near to 0.03 ppb. This result is clearly higher than the toxic organics maximum permissible limit (0.008 ppb).It was mentioned in the literature review that the most familiar use for naphthalene is as a household fumigant. It is also sometimes used as dispersants for pesticides and precursor for various pigments and other chemicals. All these sources could be found in the area. Also, it is widely known that farmers in this area use Naphthalene pellets to keep the snakes and insects away from their homes.

Bromomethane (CH3Br)analysis results

GC-MS instrument outputs for the analysis ofAJ and MB samples for Bromomethane indicates that Bromomethane was detected in the tested samples at concentrations near to 0.03 ppb. This result is clearly higher than the maximum permissible limit which is zero because it's use is forbidden. This organic was measured at these locations since it is a herbicide, and these sites are located near to agricultural lands. Its detection indicates that it was still used as a herbicide in the area, in spite of the fact that it had been phased out by most countries because of its high toxicity(1).

Batillol($C_{21}H_{44}O_3$) results analysis

GC-MS instrument output for analysis of the sample taken from AJ location for the pharmaceutical compound Batillol, indicates that Batillol was detected in the tested sample at concentrations near to 0.03 ppb. This result is clearly higher than the toxic organics maximum permissible limit (0.008 ppb). As mentioned in literature review, Batillol is antitumor drug, so its source is most likely from medical centres or hospitals found at the eastern part of Nablus.

Phosphoromidic acid ($(HO)_2PONH_2$)

GC-MS instrument output for the analysis of the sample taken from AJ location for the pharmaceutical compound Phosphoromidic acid, indicates that Phosphoromidic acid was detected in the sample at concentration near to 0.03 ppb. This result is clearly higher than the toxic organics maximum permissible limit (0.008 ppb). It was mentioned in the literature review that Phosphoromidic acid is used to combat pathogenic organisms such as bacteria or viruses. Accordingly, its source is most likely from the medical centres or hospitals found at the eastern part of Nablus.

Chapter Six

Estimations of Total Maximum Daily Loads

6.1. Introduction

A TMDL is both a quantitative assessment of the pollution sources and the pollutant reductions needed to restore and protect water. It essentially provides a quantitative estimate of what it takes to achieve stated water quality goals. The TMDL sets the maximum amount of pollution a waterbody can receive without violating water quality standards, including safety margin to account for seasonal variations and uncertainties in the calculations. It also provides scientific calculations of how much pollutant loads need to be reduced to meet water quality standards.

Depending on the monthly measured concentrations for heavy metals and toxic organics and using the daily modified flow rates, the current loads in four selected segments were calculated for the months of Jan/2011, Feb/2011, Mar/2011, Apr/2011, May/2011, Jun/2011, Sep/2011, Oct/2011, Nov/2011, Dec/2011and Jan/2012. The selected segments are: AJ segment near to AJ location, TWWBM segment near to TWWBM location, TWWAM near to TWWAM location, and MB segment near to MB location. Every segment was around 20 m.

By using the USEPA standards for fresh water in rivers and natural streams and the daily modified flow rates, the Total Maximum Daily Loads (TMDLs) were estimated for every selected segment in the previous months. The USEPA guidelines for reclaimed wastewater were used to estimate the TMDLs for East Nablus Wastewater Treatment Plant point source. Loads reductions in amounts and percentages were also estimated by calculating the difference between the current loads and the TMDLs. For comparison purposes, the current loads, the TMDLs and the loads reductions were graphed using the EXCEL program.

The margin of safety (MOS) was not considered in the calculation of the TMDLs because USEPA standards for detected pollutants were adopted in the calculation. The American standards have fewer values than the Palestinians specifications for point sources; thus the safety factor was implicitly accounted for.

6.2. Potential sources of heavy metals and toxic organics at Al-fara'a catchment

An important part of the TMDL analysis is accomplished through the identification of pollutant source categories, individual sources for each pollutant in the catchment, and the amount of pollutant loading contributed by each of these sources. The sources are classified into point and nonpoint sources. The former are discharges to surface waters via confined and discrete conveyance, while the nonpoint sources are diffuse sources of pollution associated with everyday human activities, including runoff from urban land uses, agriculture, and mining (USEPA, 2008b).

6.2.1. Point sources

Currently, there are no point sources contributing heavy metals and toxic organic contamination for Wadi Al-fara'a. Nevertheless, with the beginning of 2016, it is expected that the East Nablus Wastewater Treatment Plant will be installed on a piece of land near the main road that joins Nablus with Jericho. The plant's exact location is between Salem and Azmout villages, very near to the AJ location. Thus it will represent a prospective point source for heavy metals and toxic organics, since the treatment plant processes are not designated for heavy metals treatment (Nablus Municipality, 2014).

The toxic organics are persistent in the environment and are rather difficult to treat; accordingly, this point source is taken into consideration in the TMDL allocation later. When the Treatment Plant is in operation, it will be necessary to monitor its effluent by periodic analysis for heavy metals and toxic organics. It is crucial for water quality that this source is periodically monitored to ensure that it functions in accordance with the heavy metals and toxic organics TMDLs permits.

6.2.2. Non-point sources

In the Western countries, the point source pollution is well controlled, yet water pollution remains a problem in many rivers and lakes. The United States, one country which regularly monitors and reports upon the status of water quality in rivers and lakes, has found out that agriculture is the principal cause of surface water pollution (FAO, 2013).As it is shown in chapter five, the insecticides Naphthalene, the herbicide Bromomethane, and the precursor for pesticides and other chemicals Chloroaceticacidare found at all the tested locations along the Wadi, indicating that the agricultural activities like fertilizing and irrigation and using herbicides and pesticides are among the main contributorsin the contamination of Wadi Al-fara'a. Additional loading may come from atmospheric conditions, especially in the case of Bromomethane which is a gas herbicide. Since Phosphoromidic acid and Batillol are pharmaceutical compounds, it is claimed that their sources are the medical and health centres that are found at east of Nablus.

With respect to heavy metals, their sources are different and diverse. As it is shown in chapter five, and in most of the sampling events ,the AJ location has higher concentrations of heavy metals, which indicates that the main sources for heavy metals are the industrial effluent. Clearly, the monitoring and law enforcement practiced by the Environmental Quality Authority (EQA) and the Ministry of Industries (MOI) for the industries at the Eastern Part of Nablus is not efficient. A second potential source for heavy metals detection at the AJ location is the urban runoff which appears only in wet season; in addition there is the agricultural runoff whose impact appeared clearly in a number of sampling events where some heavy metals are detected in high concentrations as in the MB and the SST.

As shown previously in the literature review, some types of fertilizers and pesticides contain heavy metals. Many of the sampling events occurred at the cultivation seasons. Other sources of heavy metals appear to be temporal sources, since they appeared in one location for one time only and then they disappeared in other locations due to either dilution with fresh water or to being absorbed by sediments. An example on these temporal sources is the leachate reaching the Wadi from solid waste disposal site. The disposal of amounts of industrial or building rehabilitation waste directly into the Wadi increases the likelihood that these wastes containing one type or more from heavy metals would contribute to lowering the water quality in this area. Composite sampling results show that some heavy metals like Copper have constant concentration over time in the Wadi, which indicates that its sediment becomes saturated with Copper.

6.3. Flow rates measurements

The flow rates were measured at all the sampling locations manually for 2011;since these measurements do not represent the average flow through the day, the flow rates measures taken by the flume at the MB for 2011-2012 (WESI, 2012) were used to modify the flow rates. The calculation was made by finding the ratio between the manually measured and the flume flow rate at the MB location for every sampling event. The manually measured flow rates at the other locations were then multiplied with this ratio, assuming that all the sampling locations will have the same modification ratio, especially through the wet days; at this time, the flood passing through the sampling locations lasted for a relatively short period due to the steep nature of the Wadi (see Appendix B shows the manually measured rates as well as the estimated flowrates for the five sampling locations). The average flow rate at every selected segment was determined by taking the average flow rate for the first and the final sampling locations.

6.4. TMDLs estimation results

TMDLs were estimated based on two scenarios; the first scenario represents the current situation at which, there is no point sources discharging its effluent to the Wadi. The second scenario represents the future situation when the Nablus Eastern Wastewater Treatment Plant will be operating; it is anticipated that this plant will act as a point source for many pollutants to Wadi Al-fara'a.

6.4.1. Scenario one

This scenario represents the current situation at which no specific pollutants point sources discharge their effluent to the Wadi which can be monitored and given permits. Thus, no permits for point sources will be estimated here.

a. TMDL for heavy metals

The current loads, TMDLs, and loads reductions were estimated for three segments of Wadi Al-fara'a for five heavy metals.

TMDL for Copper

The statistical measures for current loads, TMDLs, and loads reductions for Cu are shown in table (6.1); as shown in this table and in figure (6.1), the highest mean for the current loads of Copper is for segment (3). It also has the highest maximum current load which was detected in November/2011 (46.59 Kg/day); in this month, the highest Cu concentration and the highest flow rate were detected for MB location- the final location at the segment. This month is usually a wet month during which the MB location receives urban runoff from Al-fara’a camp mixed with the camp wastewater in addition to agricultural runoff from the adjacent agricultural lands. Copper was not detected in some samples which resulted in current loads of zero. As for TMDL, the only variable parameter is the flow rate. For all the segments, the TMDL for Copper ranged between 0.04-2.06 Kg/d. The highest mean and the highest maximum for Cu TMDL was for segment (3), which occurred in November/2011. In winter the Wadi receives wastewater and runoff from Al-fara’a Camp and the adjacent lands thus recording the highest maximum flow rate in comparison with the other segments, and accordingly it has the highest maximum Cu TMDL.

As mentioned earlier, the load reduction is taken as the difference between the current loads and the TMDLs. For all the tested segments, Cu must be reduced in the range of (86-93) % from the current load in order to match the TMDL. This can be achieved by applying many management practices at the watershed. Since the MB location receives additional wastewater from Al-fara'a Camp, it has the highest mean load reduction as shown in figure (6.1). This result will mean effective management practices will need to be applied in the area to reduce the Copper loads in the MB segment and in the other segments as well.

Table (6.1): Current loads, TMDLs, and loads reductions for Cu at selected segments for Wadi Al-fara'a

Segment	**Current load (kg/d)**				**TMDL (kg/d)**				**Load reduction(kg/d)**	
	Min	Max	Mean	Median	Min	Max	Mean	Median	Mean	%
Segment (1)	0.00	11.32	3.35	1.13	0.08	1.17	0.47	0.42	2.88	86.00
Segment (2)	0.00	26.28	3.80	1.38	0.06	1.48	0.41	0.26	3.39	89.27
Segment (3)	0.00	46.59	5.97	0.72	0.04	2.06	0.42	0.18	5.55	92.97

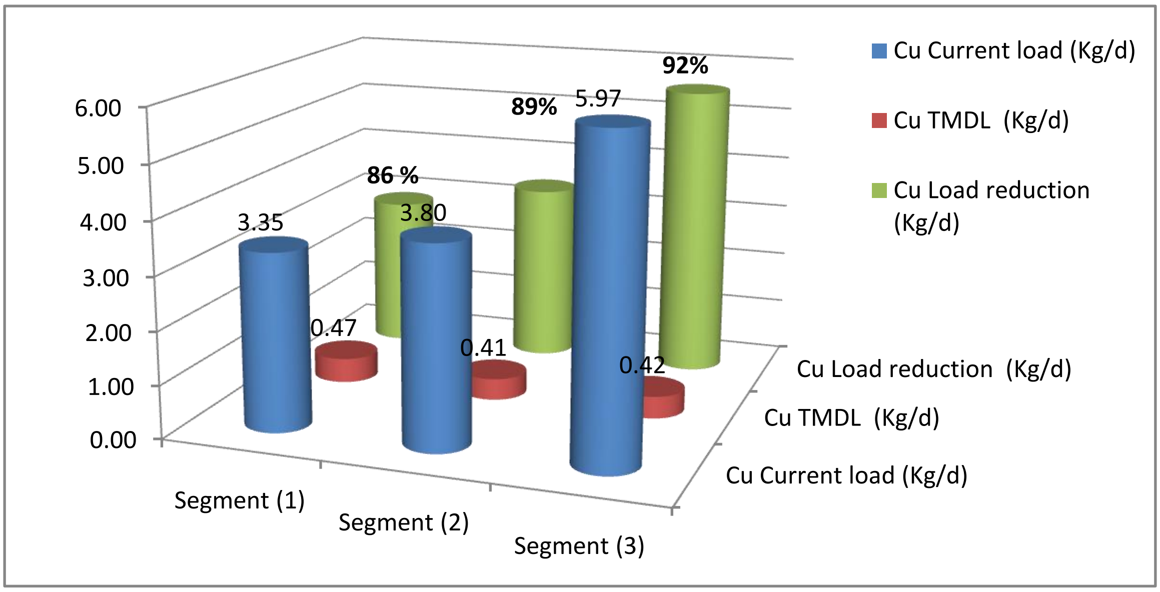

Figure (6.1): Column chart for Current loads, TMDLs, and loads reductions means for Cu at selected segments at Wdai Al-fara'a

TMDL for Chromium

The statistical measures for current loads, TMDLs, and load reductions for Cr are shown in table (6.2). As shown in this table and in figure (6.2), the highest mean for the current loads of Cr is for segment (3); this segment also has the highest maximum due to the incoming wastewater from Al-fara'a Camp in addition to urban and agricultural runoff which reach the MB segment in winter. However, segment (2) has the highest median, the second mean and the maximum current loads, a result which may indicate that this segment receives Cr load from sources located between AJ and TWWAM. My observations showed that there are random solid waste disposal sites between these two segments. However, the minimum current load for the three segments is relatively high (0.1 - 0.17 Kg/day), a result which indicates that Cr was found at all the tested samples.

Segment (3) has the highest maximum and mean for TMDL due to the fact that the MB location has the highest flow rates.

Load reduction is needed urgently for segments 2 and 3 by 12 and 17 % respectively as it is clearly shown in figure (6.2).

Table (6.2): Current loads, TMDLs, and loads reductions for Cr at selected segments for Wadi Al-fara'a

Segment	**Current load (kg/d)**				**TMDL (kg/d)**				**Load reduction(kg/d)**	
	Min	Max	Mean	Median	Min	Max	Mean	Median	Mean	%
Segment (1)	0.10	0.78	0.38	0.31	0.08	0.87	0.37	0.27	0.005	1.31
Segment (2)	0.10	2.33	0.71	0.20	0.07	1.93	0.62	0.24	0.083	11.78
Segment (3)	0.17	3.17	1.01	036	0.14	2.69	0.84	0.26	0.173	17.10

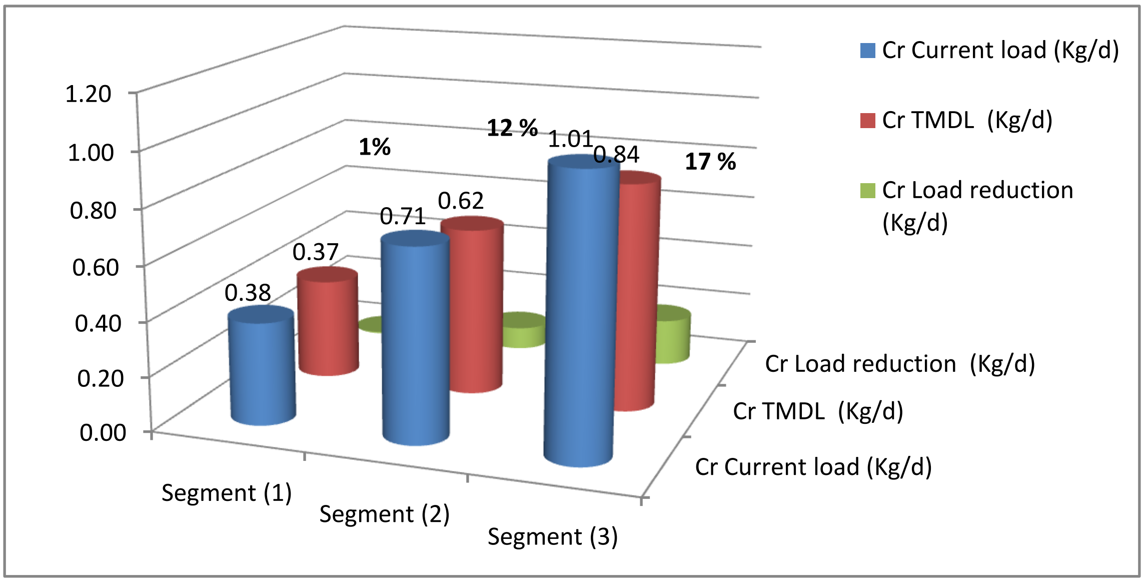

Figure (6. 2): Column chart for Current loads, TMDLs, and load reductions for Cr at selected segments at Wdai Al-fara'a

TMDL for Nickel

The statistical measures for current loads, TMDLs, and load reductions for Ni are shown in table (6.3). As shown in the table and in figure (6.3), the highest mean, max and median for the current loads of Ni came for segment (1). This result indicates that the main source of Ni comes from East Nablus wastewater which contains industrial wastewater taken to be the most probable source for Ni. The minimum is zero for all the locations since Ni was not detected in some samples. Load reductions in the Ni loads must be performed in the range of 83-90% from the current loads. The highest Ni load reduction must be done for segment (1) by 90%. Consequently, a great effort is required in order to achieve these high reductions in Ni loads.

Table (6.3): Current loads, TMDLs, and loads reductions for Ni at selected segments for Wadi Al-fara'a

Segment	Current load (kg/d)				TMDL (kg/d)				Load reduction(kg/d)	
	Min	Max	Mean	Median	Min	Max	Mean	Median	Mean	%
Segment (1)	0.00	12.31	4.31	5.08	0.08	0.73	0.44	0.43	3.87	89.82
Segment (2)	0.00	4.64	1.71	1.63	0.10	0.71	0.29	0.26	1.41	82.76
Segment (3)	0.00	3.27	2.33	2.89	0.09	0.95	0.36	0.25	1.96	84.44

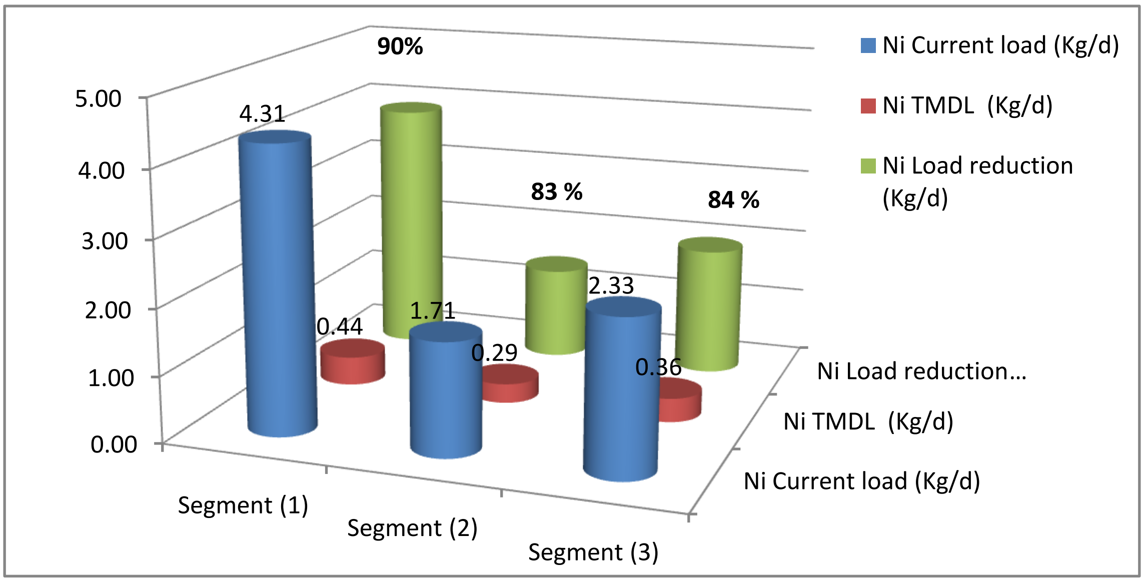

Figure (6. 3): Column chart for Current loads, TMDLs, and loads reductions for Ni at selected segments at Wdai Al-fara'a

TMDL for Zinc

The statistical measures for current loads, TMDLs, and load reductions for Zn are shown in table (6.4). As shown in the table and in figure (6.4), the highest mean, median and max for the current loads of Zn are for segment (1). This result indicates that the main source of Zn is coming from East Nablus wastewater which contains industrial wastewater. Load reduction is needed only for segment (1) by 17% from the current load.

Table (6.4): Current loads, TMDLs, and loads reductions for Zn at selected segments for Wadi Al-fara'a

Segment	**Current load (kg/d)**				**TMDL (kg/d)**				**Load reduction(kg/d)**	
	Min	Max	Mean	Median	Min	Max	Mean	Median	Mean	%
Segment (1)	0.13	0.91	0.63	0.74	0.11	1.22	0.53	0.39	0.11	16.90
Segment (2)	0.02	0.59	0.30	0.30	0.10	2.73	0.88	0.34	0.00	0.00
Segment (3)	0.00	0.64	0.29	0.27	0.20	3.80	1.19	0.37	0.00	0.00

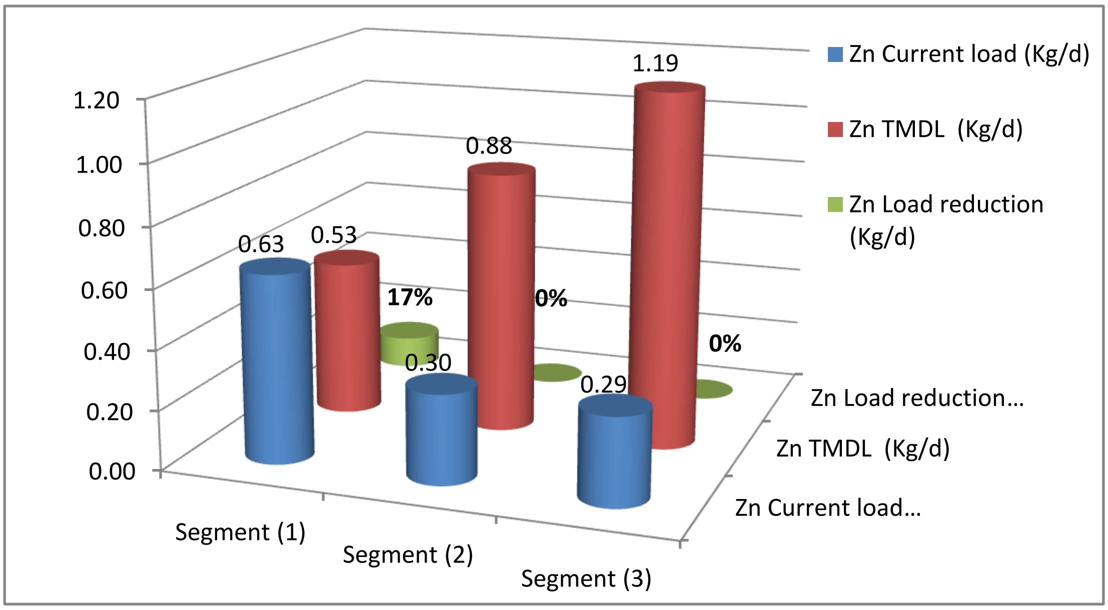

Figure (6. 4): Column chart for Current loads, TMDLs, and loads reductions for Zn at selected segments at Wdai Al-fara'a

TMDL for Lead

The statistical measures for current loads, TMDLs, and load reductions for Pb are shown in table (6.4). As shown in the table and in figure (6.4), the highest mean, max and median for the current loads of Pb came for segment (2). The load reduction has high values for segments 2 and 3 at 90% and 87 % of the current loads respectively due to the high current loads at these segments. Since Lead is considered a very toxic heavy metal, practical and effective management practices must be put in place as soon as possible in order to reduce the current load of Lead and make it match with the TMDLs.

Table (6.5): Current loads, TMDLs, and load reductions for pb at selected segments for Wadi Al-fara'a

Segment	Current load (kg/d)				TMDL (kg/d)				Load reduction(kg/d)	
	Min	Max	Mean	Median	Min	Max	Mean	Median	Mean	%
Segment (1)	0.00	0.10	0.03	0.01	0.00	0.03	0.01	0.01	0.02	60.28
Segment (2)	0.00	0.91	0.24	0.03	0.00	0.07	0.02	0.01	0.22	90.93
Segment (3)	0.00	0.88	0.23	0.03	0.00	0.10	0.03	0.01	0.20	87.32

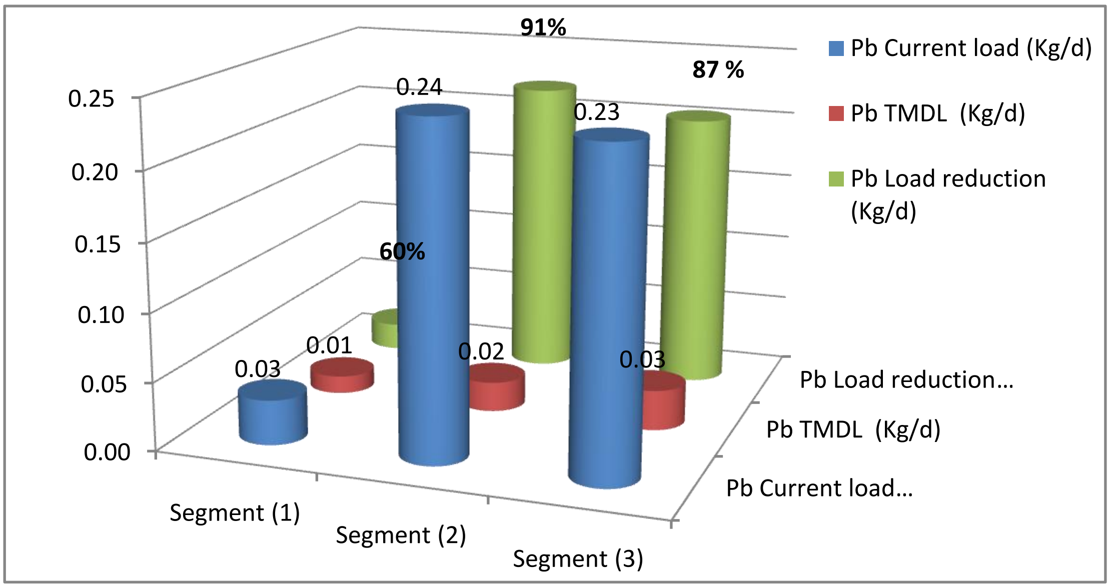

Figure (6. 5): Column chart for Current loads, TMDLs, and loads reductions for Pbat selected segments at Wdai Al-fara'a

b. TMDL for organic materials

Chloroacetic acid, Naphthalene, Batillol, and Phosphoromidic acid had been detected in the tested locations with nearly the same concentration-about 0.03 ppb. Since they have the same maximum permissible limit (0.008 ppb), so they will have the same current loads, TMDLs, and load reductions; these are listed in table (6.6) for segments (1') and (2**'**). The two segments show nearly similar parameters. The current loads for these toxic organics must be reduced by 73 % from their current loads. Effective management practices and periodic monitoring on the medical facilities effluent wastewater must be implemented in order to achieve these high load reductions.

Table (6.6): Current loads, TMDLs, and loads reductions for several detected toxic organics for selected segments at Wadi Al-fara'a

Segment	Current load (g/d)	TMDL (g/d)	Load reduction (g/d)	Percent of load reduction (%)
Segment (1')	0.081	0.021	0.059	73
Segment (2')	0.077	0.021	0.057	73

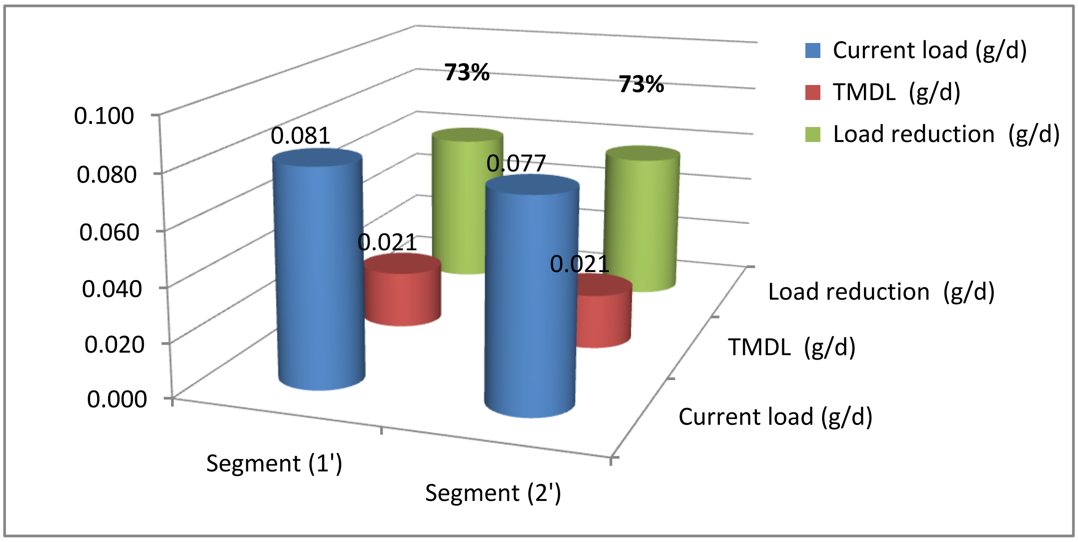

Figure (6.6): Column chart for Current loads, TMDLs, and loads reductions for several detected toxic organics for selected segments at Wadi Al-fara'a

Similarly, Bromomethane was detected in the tested samples with concentration near to 0.03 ppb and Since; using Bromomethane is forbidden, it has a maximum permissible limit equal to zero (USEPA, 1980). Accordingly, the TMDL should be equal to zero as shown in table (6.7). Thus, all the current loads at the selected segments must be reduced to zero. This target could be achieved by preventing the supply of the herbicide Brommethane to the Palestinian farmers.

Table (6.7): Current loads, TMDLs, and loads reductions for Bromomethane for selected segments at Wadi Al-fara'a

Segment	Current load (g/d)	TMDL (g/d)	Load reductution (g/d)	Percent of load reductution (%)
Segment (1')	0.081	0	0.081	100
Segment (2')	0.077	0	0.077	100

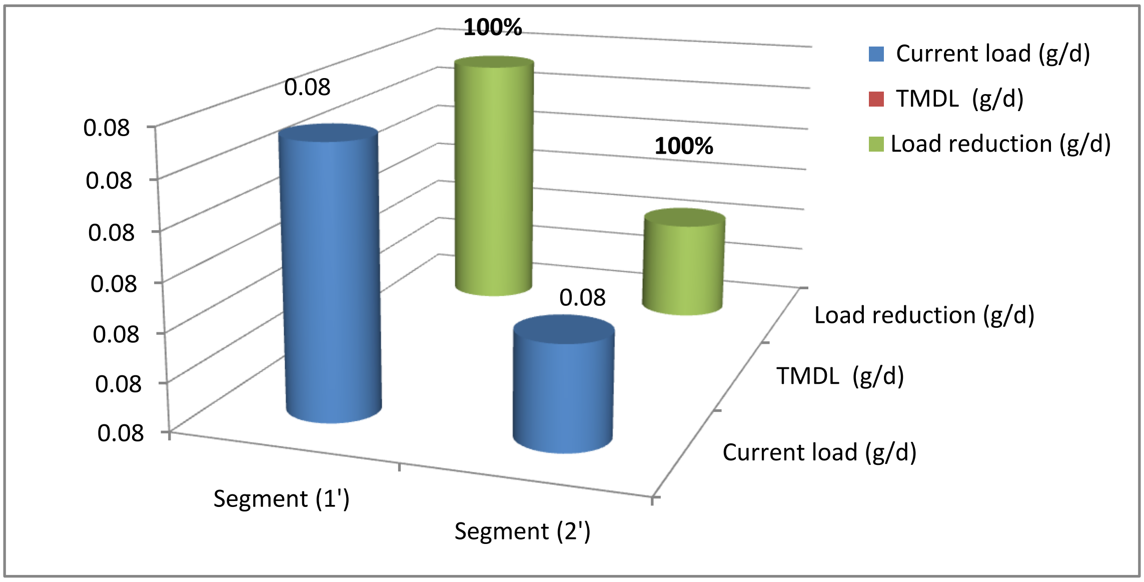

Figure (6.7): Column chart for Current loads, TMDLs, and loads reductions for Bromomethane for selected segments at Wadi Al-fara'a

6.4.2. Scenario two

This scenario represents the future situation when the Eastern Nablus Wastewater Treatment Plant (ENWTP) is in operation. The estimated TMDLs and the proposed permits concentrations are given below. For toxic organics, it was not possible to estimate the TMDLs for the proposed ENWTP because of insufficient data.

a. TMDLs and TMDLs allocations for heavy metals

The term TMDL addresses waste load allocations in addition to load allocations. The waste load allocation refers to the pollutant load allocated to current and the future point sources, while, load allocations refer to the non-point sources.

For the first segment, it is expected that there will be one point source which is the ENWTP (potential point source for many pollutants). This source is expected to discharge 14000 m^3/d. This amount will form the main flow in the stream, and it expected that it will be reduced after being exposed to percolation underground and evaporation to reach 11190, 9710.5, and 11441 m^3/d as average flow rates in segments (1), (2) and (3) respectively. In order to estimate the TMDLs (permits) for this point source, the non-point sources contribution for every heavy metal must initially be estimated by taking the average difference between the current loads upstream (AJ location) and the loads downstream (TWWBM location).

Accordingly, the permit for the ENWTP will be estimated by conducting mass balance for every segment (taking the difference between the current loads upstream and the downstream loads in the segment); thus, equation (2.8) in the methodology section will be applied (USEPA, 1992):

$$\text{TMDL for point source} = \text{total TMDL} - \text{TMDL for nonpoint sources}$$

Copper

Table (6.8) shows the Copper total TMDL and TMDLs for point and non-point sources. For segment (1), there is one point source which is the ENWTP where the permitted effluent concentration and total maximum daily load (TMDL) of Copper must not exceed 0.03 ppm 0.407 Kg/day. This includes the total TMDL for the segment (0.727 Kg/d) and the TMDL for non-point source (0.32 Kg/d). However, the Palestinian specifications for Copper in the reclaimed industrial wastewater place the value at 1.5 ppm (PSI, 2010). Therefore, the TMDL for a point source according to this specification will reach 21 Kg/d. This value is much higher than the total average TMDL of the segment, which adds a great Cu load upon the segment and subsequently the Wadi as a whole. Thus, it could make the Wadi impaired and contaminated with Copper. With regard to segments (2) and (3), the results show that they do not receive any discharges from point sources, and that the total TMDLs for them equals 0.63 and 0.65 (Kg/d) respectively.

Table (6.8): Cu TMDLs allocations

Segment	Total TMDL (Kg/d)	TMDL Non Point sources (Kg/d)	TMDL Point source - ENWTP- (Kg/d)	Permit concentration for ENWTP (ppm)
Segment (1)	0.727	0.320	0.407	0.03
Segment (2)	0.63	--	--	--
Segment (3)	0.65	--	--	--

Chromium

Table (6.9) shows Chromium total TMDL and TMDLs for point and non-point sources. Segment (1) has one point source (ENWTP). Its permitted effluent concentration and total maximum daily load (TMDL) of Chromium must not exceed 0.065 ppm and 0.91 Kg/day respectively. This includes the total TMDL for the segment (0.95 Kg/d) and the TMDL for non-point source (0.04 Kg/d) –low contribution from non point sources. However, the Palestinian specification for Chromium in the reclaimed industrial wastewater is set at to 0.1 ppm (PSI, 2010). Accordingly, the TMDL for a point source will reach 1.4 Kg/d, which is higher than the total average TMDL for the segment as shown in the table below. This result makes it clear that there is a great Cr load upon the segment and the Wadi as a whole. The total TMDLs for segments (2) and (3) equal0.83 and 1.07 (Kg/d) respectively.

Table (6.9): Cr TMDLs allocations

Segment	Total TMDL (Kg/d)	TMDL Non Point sources (Kg/d)	TMDL Point source - ENWTP- (Kg/d)	Permit concentration for ENWTP (ppm)
Segment (1)	0.95	0.04	0.91	0.065
Segment (2)	0.83	--	--	--
Segment (3)	1.07	--	--	--

Nickel

Table (6.10) shows Nickel the total TMDL and TMDLs for point and non-point sources. As shown in the table, there is a high Ni contribution from non-point sources (0.54 Kg/d) in segment (1), which leads to small TMDL (permit) for the point source; for the ENWTP (0.14 Kg/d) its effluent permitted concentration must not exceed 0.01 ppm of Ni. However, the Palestinian specification for Ni in the reclaimed industrial wastewater equals 0.2 ppm (PSI, 2010).Accordingly, the TMDL for a point will reach 2.8 Kg/d, which is higher than the total average TMDL for the segment (0.68 Kg/d). This result makes it clear that there is a great Ni load upon the segment and the Wadi as a whole. The total TMDLs for segments (2) and (3) equal to 0.46, and 0.56 (Kg/d) respectively.

Table (6.10): Ni TMDLs allocations

Segment	**Total TMDL (Kg/d)**	**TMDL Non Point sources (Kg/d)**	**TMDL Point source** - ENWTP- **(Kg/d)**	**Permit concentration for** ENWTP (ppm)
Segment (1)	0.68	0.54	0.14	0.01
Segment (2)	0.46	--	--	--
Segment (3)	0.56	--	--	--

Zinc

Table (6.10) shows Zinc the total TMDL and TMDLs for point and non-point sources. As shown in the table, there is a high Zn contribution from non-point sources (0.85 Kg/d) in segment (1), which leads to small TMDL (permit) for the point source; for the ENWTP (0. 45 Kg/d), its effluent permitted concentration must not exceed 0.032 ppm of Zn. However, the Palestinian specification for Zn in the reclaimed industrial wastewater is set high at 5 ppm (PSI, 2010). Therefore, the TMDL for a point source upon this specification will reach 70 Kg/d, which is much higher than the total average TMDL for the segment (1.3 Kg/d).The result makes it clear that there is a great Zn load upon the segment and the Wadi as a whole. The total TMDLs for segments (2) and (3) equal to 1.17 and 1.5 (Kg/d) respectively.

Table (6.11): Zn TMDLs allocations

Segment	Total TMDL (Kg/d)	TMDL Non Point Sources (Kg/d)	TMDL Point Source - ENWTP- (Kg/d)	Permit concentration for ENWTP (ppm)
Segment (1)	1.3	0.85	0.45	0.032
Segment (2)	1.17	--	--	--
Segment (3)	1.5	--	--	--

Lead

Table (6.12) shows Lead total TMDL and TMDLs for point and non-point sources .The table shows that for segment (1) there is a high Pb contribution from non-point sources (0.03 Kg/d), which leads to small TMDL (permit) for the point source. For the ENWTP (0. 002 Kg/d), its effluent permitted concentration must not exceed 0.0002 ppm of Pb. However, the Palestinian specification for Zn in the reclaimed industrial wastewater is very high and equals 0.2 ppm (PS227, 2010). Accordingly, the TMDL for a point source will reach 2.8 Kg/d, which is much higher than the total average TMDL of the segment (0.032 Kg/d). It is again clear from this result that there is a great Pb load upon the segment and the Wadi as a whole. The total TMDLs for segments (2) and (3) equal to 0.029 and 0.037 (Kg/d) respectively.

Table (6.12): PbTMDLs allocations

Segment	Total TMDL (Kg/d)	TMDL Non Point sources (Kg/d)	TMDL Point source - ENWTP- (Kg/d)	Permit concentration for ENWTP (ppm)
Segment (1)	0.032	0.03	0.002	0.0002
Segment (2)	0.029	--	--	--
Segment (3)	0.037	--	--	--

6.5. Implementation of the TMDL

Notifications must be given for industries, medical centres, and other facilities that its discharge could carry potential toxics to the public sewer. These permits should include every toxic pollutant, especially those that were detected in this project. The main goal remains to limit the pollutants loads at their sources before they reach the prospective ENWTP. It is recommended that the loads should be limited at the proposed TMDLs (Permits).

Much effort should be directed at restoring Wadi A-fara’a to a healthy condition, which will in turn reflect positively on the surrounding environment. Otherwise, the heavy metals which are found in the stream are known to have harmful effects on the biological waste water treatment process, including destroying the DNA for effective microorganisms (Sa’idi M, 2010).

One study has shown the effective microorganisms bacteria maximum tolerant concentrations of some heavy metal ions are at 0.5 ppm for Cr and Cu, and 1 mg/L for Pb and Zn (Zhou, 2008).

The permitting of storm water discharges differs from the permitting of most wastewater point sources because storm water discharges as non-point sources cannot be centrally collected, monitored, and treated. They are not subject to the same types of effluent limitations as wastewater facilities; instead they are required to meet a performance standard of providing treatment to the maximum extent through the implementation of Best Management Practices (BMPs), which include schedules of activities, prohibitions of practices, maintenance procedures, and other management practices. BMPs also include operating procedures and practices to control plant site runoff, spillage or leaks, sludge or waste disposal (USEPA, 1996).

Chapter Seven
Conclusions and Recommendations

7.1. Conclusions

The first conclusion to be made is that the concentrations of heavy metals varied temp orally from month to month depending on the discharged quantities from domestic and industrial sources besides the agricultural and urban runoff and dilution with fresh rain water and springs water. More specific conclusions are given below:

1. It has been observed that the AJ location has the highest concentrations of many heavy metals, which indicates that the industries in east Nablus represent the main source for heavy metals in this location.

2. It has also been observed that the concentrations of heavy metals increased after the MB location to be higher than the heavy metals concentrations of TWWAM location, which indicates that Al-fara'a camp wastewater and runoff represents main source for many heavy metals at this point.

3. In winter, the heavy metals concentrations increased due to the agricultural and urban runoff which represents another main source for heavy metals in the wet season.

4. Al-fara'a stream has poor self-purification for Copper. However, the results of Chromium, Zinc and Nickel analysis indicate that the stream self-purification for these metals was satisfactory.

5. Some toxic organics were detected at the area including pharmaceutical compounds which contaminate the Wadi.

6. Brommomethane was detected at the tested locations, which indicates that it is still being used at the area as herbicide, in spite of the prohibition globally on using it.

7. The composite sampling of Cu and Cr results show that there is no great variation between their level over 24 hours (one day) or during normal working days and holidays.

8. Many non-point sources contribute to the loading of heavy metals and toxic organics into Wadi Al-fara'a such as urban and agricultural runoff and solid waste dumping sites.

9. High load reductions for heavy metals and toxic organics are required for the selected segments at Wadi Al-fara'a due to the great gap between the estimated TMDL and the current loads.

10. The resultant permits for heavy metals levels at the effluent of the prospective ENWTP must not exceed the following: 0.03 ppm for Cu, 0.065 ppm for Cr, 0.01 ppm for Ni, 0.032 ppm for Zn, and 0.0002 ppm for Pb.

11. The Palestinian Standards for heavy metals in the treated industrial wastewater effluent (point sources) are very great when compared with the US EPA standards or the resultant permits from the estimated TMDLs.

This will negatively affect both of the efficiency of prospective ENWTP and the Wadi Al-fara'a water quality.

7.2. Recommendations

The study presents important recommendations to the authorities concerned with water quality in Palestine:

- One important recommendation for relevant Palestinian authorities is to put in place, monitor and enforce environmental standards and laws for discharging heavy metals and toxic organics into the environment.
- It is also recommended that the competent authorities apply the ENWTP TMDLs (Permits) to the prospective ENWTP.
- Using the toxic organic Bromomethane should be prohibited in Palestine due to its high toxicity as is the case with most of the countries in the world.
- Since heavy metals and toxic organics affect the wastewater treatment process negatively, it is recommended that the resultant pollutants loads reductions be implemented at their sources, and before the pollutants reach the prospective ENWTP.
- It is recommended that a wastewater treatment plant be constructed to treat Al-fara'a Camp wastewater which pollutes Wadi Al-fara'a with many toxic organics.

- It is recommended to implement some management practices to reduce the loading of heavy metals and toxic organics from non-point sources such as closure of the random dumpsites that are found at the area and replacing the usage of chemical pesticides and herbicides with organic ones.

- Since pesticides and herbicides represent main source for many heavy metals and toxic organics, it is important to use them rationally.

- The concerned Authorities should not give permits for any point source which likely to discharge any pollutants before conducting reliable TMDLs studies for these pollutants.

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Appendices

Appendix (A): Results of Toxic organics analysis

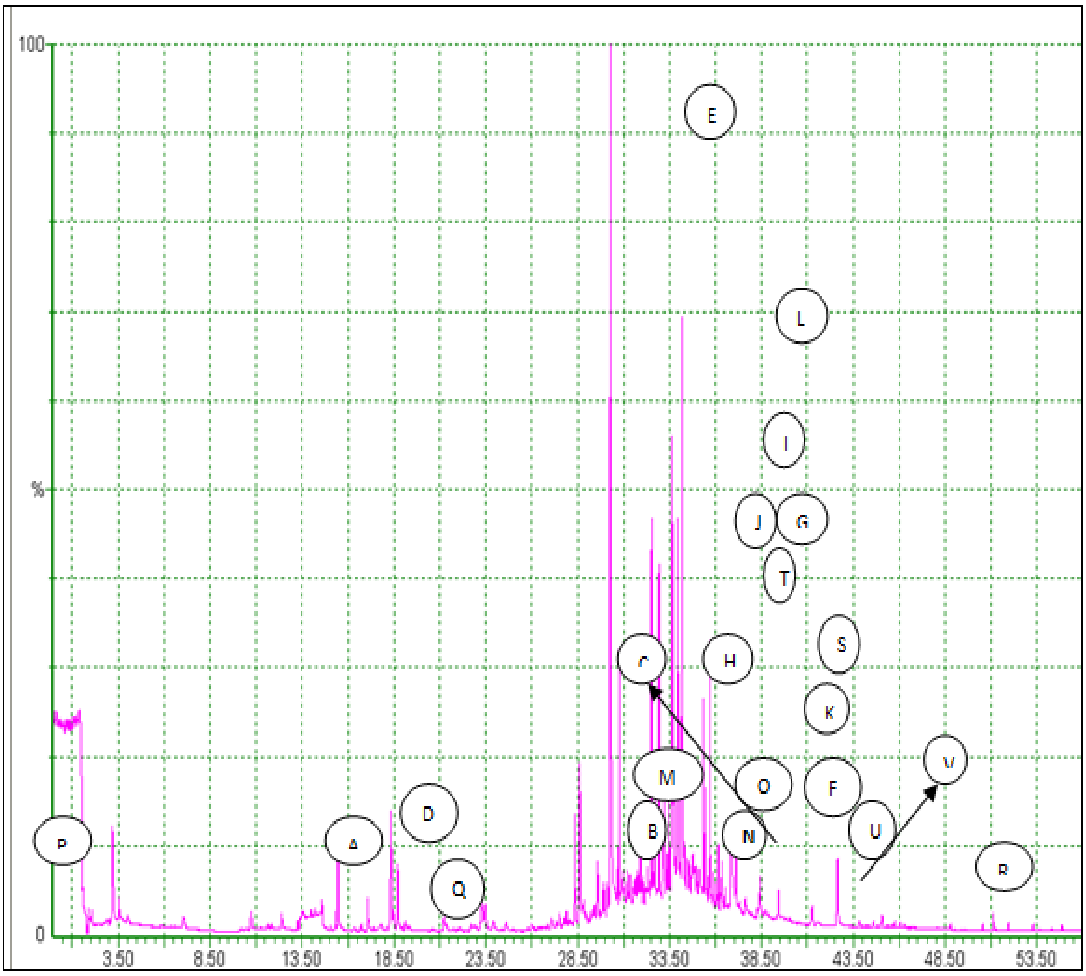

Figure (A.1): GC-MS instrument output for wastewater sample from AJ sampling location

Table (A.1): organics found in the AJ wastewater sample, sorted by priority

Material found	Material	Peak
fluoroacetic acid, dodecyle ester	fluoroacetic acid (FCH_2COOH)	(E)(I)
Chloroacetic acid, dodecyle ester/Chloroacetic acid, tetradecyl ester/Chloroacetic acid, pentadecyl/ Chloroacetic acid, chloro-, octadecyl ester/	Chloroacetic acid ($ClCH_2CO_2H$)	(E)(I)
Cyclododecane,	Cyclododecane $C_{12}H_{24}$	(E)(I)
Acetic acid, chloro-octadecyl ester/ Acetic acid, chloro-decyl ester	Acetic acid CH_3COOH	(E)(I)
Hexadecane (G)/ Hexadecane,2,6,10,14-tetramethyl(K)/ Hexadecane,7-methyl-(K)/ Hexadecane,2,6,11,15-tetramethyl-(K)	Hexadecane $C_{16}H_{34}$	(G)(J) (M)(Z)(F)(N)(K)(C)
Methane, bromo	Methane, bromoCH_3Br	(A)
phosphoramidic acid, dimethyl	phosphoramidic acid $(HO)_2PONH_2$	(A)
Oxirane, tridecyl/ oxiranetetradecyl	Ethylene oxide, also called oxirane, C_2H_4O.	(D)
Camphene	Camphene ($C_{10}H_{16}$)	(B)
(*p*-Menth- 1-en-8-ol)	Terpineol(*p*-Menth- 1-en-8-ol) (CH_{10} O_{18})	(B)
Ocimene	Ocimene ($C_{10}H_{16}$)	(B)
Boric acid, ethyl-, didecyl ester (M,G)	Boric acid (H_3BO_3)	(G)(M)
Galaxolide	Galaxolide (C18H26O.)	(T)
Isopropyl myristate (O)	Isopropyl myristate $C_{17}H_{34}O_2$	(O)
Decanoic acid	Decanoic acid $CH_3(CH_2)_8COOH$	(O)
dica cionanoN	Nonanoicacid $CH_3(CH_2)_7COOH$.	(O)
Naphthalene, decahydro-1,4A-dimethyl-7-(1-methylethyl)	Naphthalene $C_{10}H_8$	(H)
Cyclohexane, 1-ethanol, 1-hydroxymethyl	Cyclohexane	(H)
Dimethyl Disulfide	Dimethyl Disulfide ($C_2H_6S_2$)	(A)

enasocie,2,6,10,14,18-pentamethyl/ enasocie,2,6,10,14,19-pentamethyl	Icosane(enasocie) $_{42}H_{20}C$	(K)
Octadecane, 2,6,10,14-tetramethyl	Octadecane ($C_{18}H_{38}$)	(K)
Heptadecane/ Heptadecane,3-methyl/ Heptadecane,2,6,10,15-tetramethyl	Heptadecane $C_{17}H_{36}$	(F)(N)
Cyclododecanol	Cyclododecanol C13H24O	(D)
(Tridecane,2,5-dimethyl)/ (Tridecane, 6-cyclohexyl)	Tridecane $C_{13}H_{28}$	(F)(C)
Undecane ,3,9-methyl/ Undecane , 3,6-dimethyl/ Undecane , 5,5-dimethyl	Undecane $CH_3(CH_2)_9CH_3$	(C)
Tetradecane/ Tetradecane, 2,5-dimethyl	Tetradecane $C_{14}H_{30}$	(C)
Decane, 2,3,5-trimethyl/ Decane, 3,8-dimethyl	Decane $C_{10}H_{22}$	(C)
Squalane	Squalane $_{62}H_{30}C$	(K)
Batilol (3- octadecyl alkoxyl-1,2-propylene glycol)	Batilol $C_{21}H_{44}O_3$	(Q)

Table (A.2):peaks order from the highest to the lowest

E	L	I	J	G	T	S	H	K	M	O	F	N	D	B	C	A	U	P	R	Q	V

Appendix B: results of the streams flow rate measurements

Table (B1): flow rates at MB location

Date	Manually measured flow rate (l/s)	Estimated ratio (flume/measured)	MB flume Measured flow rate (l/s)
31/1/2011	0.00	--	210.40
28/2/2011	50.00	1.43	71.30
04/03/2011	90.82	0.39	35.00
25/4/2011	20.96	2.37	49.60
29/5/2011	--	--	--
28/6/2011	53.57	--	--
31/7/2011	NM	--	--
22/8/2011	NM	--	--
25/9/2011	103.63	--	--
30/10/2011	47.71	--	--
30/11/2011	366.84	--	--
27/12/2011	157.66	0.10	15.10
30/1/2012	174.55	0.12	20.20

Table (B2): flow rates at AJ location

Date	Manually measured flow rate (l/s)	Ratio of MB (flume/measured)	Estimated flume flow rate (l/s)
31/1/2011	198.87	--	198.87
28/2/2011	73.17	1.43	104.35
04/03/2011	84.62	0.39	32.61
25/4/2011	55.25	2.37	130.72
29/5/2011	141.57	--	--
28/6/2011	174.40	--	--
31/7/2011	not measured	--	--
22/8/2011	not measured	--	--
25/9/2011	208.90	--	--
30/10/2011	48.52	--	--
30/11/2011	73.82	--	--
27/12/2011	140.83	0.10	13.49
30/1/2012	197.64	0.12	22.87

Table (B2): flow rates at TWWBM location

Date	Manually measured flow rate (l/s)	Ratio of MB (flume/measured)	Estimated flume flow rate (l/s)
31/1/2011	183.85	1.97	183.85
28/2/2011	84.86	1.43	121.00
04/03/2011	33.66	0.39	12.97
25/4/2011	52.13	2.37	123.35
29/5/2011	57.80	--	--
28/6/2011	79.95	--	--
31/7/2011	not measured	--	--
22/8/2011	not measured	--	--
25/9/2011	115.24	--	--
30/10/2011	48.52	--	--
30/11/2011	120.38	--	--
27/12/2011	131.48	0.10	12.59
30/1/2012	339.86	0.12	39.33

Table (B4): flow rates at TWWAM location

Date	Manually measured flow rate (l/s)	Ratio of MB (flume/measured)	Estimated flume flow rate (l/s)
31/1/2011	106.98	1.97	106.98
28/2/2011	35.30	1.43	50.33
04/03/2011	25.50	0.39	9.83
25/4/2011	15.05	2.37	35.61
29/5/2011	27.41	--	--
28/6/2011	63.49	--	--
31/7/2011	not measured	--	--
22/8/2011	not measured	--	--
25/9/2011	72.53	--	--
30/10/2011	44.70	--	--
30/11/2011	159.83	--	--
27/12/2011	51.02	0.10	4.89
30/1/2012	165.00	0.12	19.09

Table (B5): flow rates at SST location

Date	Manually measured flow rate (l/s)	Ratio of MB (flume/measured)	Estimated flume flow rate (l/s)
31/1/2011	0	1.97	0
28/2/2011	44.8	1.43	63.9
04/03/2011	18	0.39	6.93
25/4/2011	11.4	2.37	26.97
29/5/2011	Not measured	--	--
28/6/2011	31.54	--	--
31/7/2011	Not measured	--	--
22/8/2011	Not measured	--	--
25/9/2011	Not measured	--	--
30/10/2011	Not measured	--	--
30/11/2011	Not measured	--	--
27/12/2011	347.7	0.10	33.3
30/1/2012	151.6	0.12	17.54

Appendix C: results of heavy metals analysis

Table C.1: Copper results

Cu (mg/L)					
Date/Location	**AJ**	**TWWBM**	**TWWAM**	**MB**	**SST**
12/14/2010	NA	0.10	0.11	0.13	0.00
27/12/2010	0.00	0.00	0.00	0.00	0.00
31/1/2011	0.08	NA	0.11	0.00	0.06
28/2/2011	0.00	0.00	0.00	0.00	0.00
3/4/2011	0.73	0.70	0.70	0.73	0.72
4/25/2011	0.80	0.79	0.77	0.80	0.78
29/5/2011	0.77	0.91	0.75	0.75	NA
28/6/2011	0.04	0.03	0.02	0.06	NA
31/7/2011	0.05	0.03	0.08	0.03	0.05
22/8/2011	0.71	0.64	0.62	0.68	NA
25/9/2011	0.61	0.63	0.64	0.59	NA
30/10/2011	1.12	1.05	1.02	1.04	1.03
30/11/2011	1.05	1.05	1.05	1.26	1.68
27/12/2011	1.02	0.00	0.96	0.00	1.01
30/1/2012	0	0.00	0.00	0.00	0.00
28/2/2012	1.36	1.24	1.26	0.00	0.00
28/3/2012	1.44	1.30	0.81	0.84	0.79
Avg	0.61	0.56	0.55	0.42	0.51

Table C.2: Chromium results

Cr (mg/L)					
Date/Location	**AJ**	**TWWBM**	**TWWAM**	**MB**	**SST**
30/10/2011	0.08	0.04	0.04	0.10	0.11
30/11/2011		0.06	0.06	0.14	0.06
27/12/2011	0.09	0.12	0.12	0.16	0.12
30/1/2012	0.16	0.05	0.05	0.07	0.14
28/2/2012	0.06	0.11	0.11	0.06	NA
28/3/2012	0.08	0.06	0.06	0.04	0.10
29/4/2012	0.00	0.00	0.00	0.00	0.00
29/5/2012	0.00	0.00	0.00	0.00	0.00
Avg	0.07	0.05	0.05	0.07	0.07

Table C.3: Zinc results

Zn (mg/L)					
Date/Location	**AJ**	**TWWBM**	**TWWAM**	**MB**	**SST**
30/10/2011	0.02	0.54	0.11	0.18	0.06
30/11/2011	NA	0.11	0.02	0.03	0.01
27/12/2011	0.39	0.02	0.02	0.00	0.00
30/1/2012	0.59	0.45	0.04	0.05	0.00
28/2/2012	0.00	0.00	0.05	0.04	0.05
28/3/2012	0.06	0.00	0.00	0.00	0.00
Avg	0.21	0.19	0.04	0.05	0.02

Table C.4: Lead results

Pb (mg/L)					
Date/Location	**AJ**	**TWWBM**	**TWWAM**	**MB**	**SST**
30/10/2011	0.05	0.03	0.00	0.03	0.00
30/11/2011	0.00	0.00	0.00	0.00	0.00
27/12/2011	0.00	0.00	0.00	0.00	0.00
30/1/2012	0.00	0.04	0.00	1.08	0.00
28/2/2012	0.00	0.00	0.00	0.03	0.00
28/3/2012	0.00	1.07	0.00	0.00	0.00
Avg	0.01	0.19	0.00	0.19	0.00

Table C.5: Nickel results

Ni (mg/L)					
Date/Location	**AJ**	**TWWBM**	**TWWAM**	**MB**	**SST**
12/14/2010	NA	1.12	0.48	1.67	NA
27/12/2010	0.00	NA	NA	NA	NA
31/1/2011	0.65	NA	0.13	NA	0.18
28/2/2011	0.25	1.05	0.69	0.53	0.38
3/4/2011	1.83	2.01	0.00	1.69	1.90
4/25/2011	0.00	0.00	0.00	0.00	1.00
29/5/2011	1.38	0.35	0.60	0.00	NA
28/6/2011	1.90	1.15	0.98	0.85	NA
31/7/2011	0.92	0.61	0.00	0.42	1.26
22/8/2011	0.00	0.00	0.00	0.00	NA
25/9/2011	0.00	0.00	0.00	0.00	NA
30/10/2011	0.00	0.00	0.00	0.00	0.00
30/11/2011	0.00	0.00	0.00	0.00	0.00
27/12/2011	0.00	0.00	0.00	0.00	NA
Avg	0.58	0.47	0.20	0.32	0.67

جامعة النجاح الوطنية
كلية الدراسات العليا

إنشاء إجمالي الحدود القصوى من الأحمال اليومية (TMDLs) لمجموعة مختارة من الملوثات في مقاطع مختلفة من وادي الفارعة

إعداد

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إشراف

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في هندسة المياه والبيئة، بكلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس – فلسطين.

2015

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الملخص

إجمالي الحد الأقصى للحمل اليومي (TMDL) يشمل تقييم كمي لمصادر التلوث بالإضافة لتقدير الكمية المطلوب تخفيضها لاستعادة وحماية المصادر المائية. من أجل حماية واستعادة المسطحات المائية المتضررة، يجب تحديد كميات الملوثات التي تصلها والسعي للسيطرة عليها، لتحقيق هذا الهدف يجب تحديد أقصى كمية من الملوث التي يستطيع المسطح المائي استيعابها ويبقى يحقق المعايير المطلوبة لجودة المياه.

حوض الفارعة الذي يقع في المنطقة الشمالية الشرقية من الضفة الغربية البالغ مساحته 320 كيلومتر مربع، يتأثر بالعديد من مصادر التلوث المحددة المنشأ منها كالمنشآت الصناعية والمراكز الطبية وغير محددة المصدر كما الحفر الامتصاصية. لهذا قد تم في هذا البحث إنشاء إجمالي الحدود القصوى للملوثات التالية: خمس معادن ثقيلة في ثلاث مقاطع من وادي الفارعة و ثلاث مركبات عضوية سامة ومركبين دوائيين في مقطعين من وادي الفارعة.

وقد شملت عملية تقدير وتوثيق كميات إجمالي الحدود القصوى للأحمال اليومية (TMDLs) للملوثات المذكورة على عدد من المهام وهي: تحديد خصائص المقاطع المختارة من وادي الفارعة، وتحديد ووضع معايير جودة المياه بالنسبة للملوثات التي تم الكشف عن وجودها والتي سيتم الاعتماد عليها في حساب كميات إجمالي الحدود القصوى للأحمال اليومية (TMDLs) لهذه الملوثات، و تحديد مصادر هذه الملوثات، ومن ثم حساب كميات إجمالي الحدود القصوى

للأحمال اليومية (TMDLs) وتوزيعها على مصادرها. وأخيرا محاولة تطبيقها واقتراح مجموعة من الإجراءات للتنفيذ.

تظهر نتائج تحليل العينات المأخوذة من الموقع الأول الذي يمثل المياه العادمة القادمة من شرق نابلس أنها الأعلى تركيزا بالمعادن الثقيلة مما يشير إلى أن المصانع الواقعة في شرقي مدينة نابلس تمثل المصدر الأساسي للمعادن الثقيلة في المنطقة. وقد تبين أن تراكيز المعادن الثقيلة قد زادت في العينات التي تم أخذها في فصل الشتاء عنها في فصول أخرى وهذا يعود إلى مياه الصرف الزراعي والحضري الذي يمثل مصدرا آخرا للمعادن الثقيلة.

وقد تم الاستنتاج أن وادي الفارعة لديه قدرة ضعيفة على التنقية الذاتية بالنسبة للمعدن الثقيل النحاس وفي الوقت ذاته لديه قدرة مقبولة على التنقية الذاتية بالنسبة للمعادن الثقيلة التالية: الكروم، الزنك، النيكل، والرصاص.

تم الكشف عن وجود المركب العضوي البروموميثان وهو عبارة عن مبيد عشبي في المواقع التي تم فحصها في الوادي مما يدل على أنه ما زال يستعمل بالمنطقة المحيطة على الرغم من المنع الدولي لاستعماله.

يجب العمل على تخفيض الأحمال الكبيرة من المعادن الثقيلة والمواد العضوية التي تصل وادي الفارعة، بسبب الفجوة الكبيرة ما بين إجمالي الحدود القصوى للأحمال اليومية لمقاطع مختارة من الوادي والأحمال الحالية والتي تم حسابها لهذه الملوثات.

ستكون محطة نابلس المستقبلية لتنقية المياه العادمة هي المصدر الوحيد المحدد للمعادن الثقيلة في وادي الفارعة بسبب أنه ليس من المتوقع أن تقوم بتنقيته لأنه يحتاج إلى تقنية خاصة للمعالجة ولذلك تم حساب الحدود القصوى للمعادن الثقيلة في المياه الخارجة من المحطة المستقبلية هي كالتالي: 0.03، 0.065، 0.01، 0.032، 0.0002 جزء من المليون للنحاس و الكروم النيكل والزنك والرصاص على التوالي .