

REPUBLIC OF LEBANON
Council for Development and
Reconstruction
CDR
Beirut

FEDERAL REPUBLIC OF GERMANY
Federal Institute for Geosciences
and Natural Resources
BGR
Hannover



TECHNICAL COOPERATION

PROJECT NO.: 2008.2162.9

Protection of Jeita Spring

SPECIAL REPORT NO. 13

Assessment and Analysis of Micropollutants (2010-2011)

Goettingen
May 2012

Special Report No. 13: Assessment and Analysis of Micropollutants

Authors: Joanna Doummar¹, Dr. Tobias Knödler¹, Dr. Tobias Geyer¹,
Prof. Martin Sauter¹
Commissioned by: Federal Ministry for Economic Cooperation and Development
(Bundesministerium für wirtschaftliche Zusammenarbeit und
Entwicklung, BMZ)
Project: Protection of Jeita Spring
BMZ-No.: 2008.2162.9
BGR-Archive No.: xxxxxxxx
Date of issuance: May 2012
No. of pages: 48

¹ University of Goettingen/Germany

Special Report No. 13: Assessment and Analysis of Micropollutants

List of Reports prepared by the Technical Cooperation Project Protection of Jeita Spring

Report No.	Title	Date Completed
Technical Reports		
1	Site Selection for Wastewater Facilities in the Nahr el Kalb Catchment – General Recommendations from the Perspective of Groundwater Resources Protection	January 2011
2	Best Management Practice Guideline for Wastewater Facilities in Karstic Areas of Lebanon – with special respect to the protection of ground- and surface waters	March 2011
3	Guideline for Environmental Impact Assessments for Wastewater Facilities in Lebanon – Recommendations from the Perspective of Groundwater Resources Protection	November 2011
4	Geological Map, Tectonics and Karstification in the Groundwater Contribution Zone of Jeita Spring	September 2011
5	Hydrogeology of the Groundwater Contribution Zone of Jeita Spring	July 2013
6	Water Balance for the Groundwater Contribution Zone of Jeita Spring using WEAP including Water Resources Management Options and Scenarios	August 2013
7	Groundwater Vulnerability Mapping in the Jeita Spring Catchment and Delineation of Groundwater Protection Zones using the COP Method	February 2013
7b	Vulnerability Mapping using the COP and EPIK Methods	October 2012
Special Reports		
1	Artificial Tracer Tests 1 - April 2010*	July 2010
2	Artificial Tracer Tests 2 - August 2010*	November 2010
3	Practice Guide for Tracer Tests	Version 1 January 2011
4	Proposed National Standard for Treated Domestic Wastewater Reuse for Irrigation	July 2011
5	Artificial Tracer Tests 4B - May 2011*	September 2011

Special Report No. 13: Assessment and Analysis of Micropollutants

Report No.	Title	Date Completed
6	Artificial Tracer Tests 5A - June 2011*	September 2011
7	Mapping of Surface Karst Features in the Jeita Spring Catchment	October 2011
8	Monitoring of Spring Discharge and Surface Water Runoff in the Groundwater Contribution Zone of Jeita Spring	May 2013
9	Soil Survey in the Groundwater Contribution Zone of Jeita Spring	First Draft November 2011
10	Mapping of the Irrigation System in the Jeita Catchment	First Draft November 2011
11	Artificial Tracer Tests 5C - September 2011*	February 2012
12	Stable Isotope Investigations in the Groundwater Contribution Zone of Jeita Spring	October 2013
13	Micropollutant Investigations in the Groundwater Contribution Zone of Jeita Spring*	May 2012
14	Environmental Risk Assessment of the Fuel Stations in the Jeita Spring Catchment - Guidelines from the Perspective of Groundwater Resources Protection	June 2012
15	Analysis of Helium/Tritium, CFC and SF6 Tracers in the Jeita Groundwater Catchment*	June 2013
16	Hazards to Groundwater and Assessment of Pollution Risk in the Jeita Spring Catchment	October 2013
17	Artificial Tracer Tests 4C - May 2012*	October 2013
18	Meteorological Stations installed by the Project	October 2013
19	Risk estimation and management options of existing hazards to Jeita spring	October 2013
20	Project Exchange Meeting - Lessons learnt from Technical Cooperation in Jordan and Lebanon	November 2013
Advisory Service Document		
1	Quantification of Infiltration into the Lower Aquifer (J4) in the Upper Nahr Ibrahim Valley	May 2012

Special Report No. 13: Assessment and Analysis of Micropollutants

Report No.	Title	Date Completed
1 - 1	Addendum No. 1 to Main Report [Quantification of Infiltration into the Lower Aquifer (J4) in the Upper Nahr Ibrahim Valley]	June 2012
2	Locating the Source of the Turbidity Peaks Occurring in April - June 2012 in the Dbayeh Drinking Water Treatment Plant	June 2012
3	Locating the Pollution Source of Kashkoush Spring	September 2012
4	Preliminary Assessment of Jeita Cave Stability	April 2013
5	Preliminary Assessment of the Most Critical Groundwater Hazards for Jeita Spring	June 2013
6	Handover of Water Resources Monitoring Equipment and Stations Installed by the BGR Project	November 2013
Reports with KfW Development Bank (jointly prepared and submitted to CDR)		
1	Jeita Spring Protection Project Phase I - Regional Sewage Plan	October 2011
2	Jeita Spring Protection Project - Feasibility Study - Rehabilitation of Transmission Channel Jeita Spring Intake – Dbaye WTP	May 2012
3	Jeita Spring Protection Project - Environmental Impact Assessment for the Proposed CDR/KfW Wastewater Scheme in the Lower Nahr el Kalb Catchment	Draft June 2013 (BGR contribution)

* prepared in cooperation with University of Goettingen

PROTECTION OF JEITA SPRING - LEBANON -

- SPECIAL REPORT -

**ASSESSMENT AND ANALYSIS OF
MICROPOLLUTANTS (2010-2011)**

JOANNA DOUMMAR ⁽¹⁾ , KARSTEN NÖDLER, TOBIAS GEYER , MARTIN SAUTER

⁽¹⁾ Applied Geology, University of Göttingen, Goldschmidtstraße 3, 37077 Göttingen, Germany, jdoumma@gwdg.de

TABLE OF CONTENTS

TABLE OF CONTENTS.....	i
LIST OF FIGURES.....	iii
LIST OF TABLES.....	iv
LIST OF ABBREVIATIONS.....	v
1 Acknowledgement.....	6
2 Introduction.....	7
3 Field Site.....	8
4 Materials and methods.....	9
5 Results.....	13
5.1 Detected micropollutants.....	13
5.1.1 Stimulants and caffeine metabolites.....	13
5.1.2 Pharmaceuticals.....	14
5.1.3 Industrial and clinical micropollutants.....	15
5.2 Non detected micropollutants.....	16
5.3 Spatial distribution of micropollutants under various flow conditions.....	22
5.3.1 Campaign I: low flow periods.....	22
5.3.2 Campaign II: high flow periods with intermittent precipitation events.....	22
5.3.3 Campaign III: low flow periods.....	23
5.3.4 Campaign IV: intermediate flow periods.....	24
6 Discussion.....	25
6.1 Occurrence in Surface water.....	25
6.2 Fate of micropollutants within the Jeita cave.....	26
6.2.1 September 2011 (low flow periods; Figure 4).....	27
6.2.2 December 2012 (intermediate flow periods; Figure 5).....	28
6.3 Concentrations of micropollutants under various flow conditions in springs.....	30
7 Synopsis and conclusions.....	31

8 References34

9 APPENDIX A: Results36

LIST OF FIGURES

Figure 1	Main investigated catchments, springs, and rivers in the study area	9
Figure 2	Sampling locations during campaign I (a), II (b), III (C), IV (d)	12
Figure 3	Fate of MP along the Nahr El Kalb River since its origin in the Lebanese mountains until its outlet downstream to the Jeita spring	26
Figure 4	Behavior of benzoylecgonine and carbamazepine (mass flux and concentrations) in samples collected along the subsurface channel showing in some locations the input of additional compounds and/or effect of dilution (September 2011)	28
Figure 5	Behavior of benzoylecgonine and carbamazepine (mass flux and concentrations) in samples collected along the subsurface channel showing in some locations the input of additional compounds and/or effect of dilution (December 2011).....	29
Figure 6	Mass flux (g/d) of various compounds in Jeita and Qachqouch during different sampling periods (Low flow, high flow and Intermediate flow, when discharge measurements are available)	31

LIST OF TABLES

Table 1	Analytes and their application / origin.....	9
Table 2	Micropollutants detected in samples collected from spring water, surface water, and wastewater in the study area under various flow conditions (below DL: compound below detection limit)	17

LIST OF ABBREVIATIONS

BE	Benzoyllecgonine
BGR	Bundesanstalt fuer Geowissenschaften und Rohstoffe
CBZ	Carbamazepine
DL	Detection limit
GW	Groundwater
HF	High flow
LF	Low flow
STP	Sewage Treatment Plant
WWTP	Wastewater Treatment Plant

1 ACKNOWLEDGEMENT

The authors would like to thank Armin Margane and Jean Abi Rizk for assisting in the collection of the samples for the purpose of this study. Najib Najib and Ayman Ibrahim are deeply thanked for helping in the sampling logistics. Paul Souaid from the Dbayeh Water Treatment Plant is highly acknowledged for providing the laboratory facilities (Solid Phase Extraction (SPE) room and chemicals) for the extraction of the samples, as well as all the staff of the Dbayeh water treatment plant (Rajaa Mhanna, Roger Haddad, and Jihane Bedran).

2 INTRODUCTION

This report presents results of the micropollutants campaigns performed in the Framework of the Cooperation between the Institute for Geosciences and Natural Resources in Germany (BGR) and Georg-August Universität Göttingen as partial fulfillment of contract 10037409. The work undertaken is part of the German-Lebanese Technical Cooperation Project Protection of Jeita Spring funded by the German Ministry of Economic Cooperation and Development (BMZ) and implemented on the German side by BGR.

About 67% of the area in Lebanon consists of karstified (6,900 km²) rock sequences. The project area is the Jeita karst catchment drained by Jeita spring. It is considered one of the most important springs in Lebanon, which provides the capital Beirut with water for domestic use. Given its importance, it is primordial to secure a sustainable management of the spring resources and ensure its protection against potential sources of contamination. The risk assessment implies on the one hand the identification of the source of pollution present in a catchment area, and on the other hand, the understanding of the transport relationship between different water bodies existent in a catchment area, namely, surface water, groundwater, and other anthropogenic sources of water, e.g., wastewater. Various types of indicators for wastewater were identified and investigated. Wastewater markers are compounds introduced to a natural environment usually by anthropogenic activities; these include ionic species (e.g., chloride; Gasser et al., 2010), bacteriological species (*e-coli*form; Pronk et al., 2007) or micropollutants (pharmaceuticals, pesticides, or industrial compounds etc).

Pharmaceuticals prescribed in the medical sector are not completely metabolized by the human body, and are excreted unchanged or metabolized into the environment (Heberer, 2002). These products in addition to other industrial or agricultural micropollutants can leach into the soil, to surface water, and eventually to the unsaturated zone (Scheytt et al., 2006) to groundwater especially those which are not degraded under natural conditions. The detection of these substances in groundwater and surface water can give insights into the type of pollutants existing in the catchment area, especially in areas where wastewater is discharged without prior treatment. Despite that little is known about the potential infiltration of a drug to surface waters and the behavior of the micropollutants from the Sewage Treatment Plants (STPs) through soil, unsaturated zone and finally groundwater, due to the multitude of prescribed pharmaceuticals (Turner, 1998), it is still possible to estimate loads of substances consumed/discharged in a study area based on concentrations detected in water bodies.

The analysis of micropollutants is challenging in karst aquifers, given that they are characterized by a duality of recharge; diffuse or concentrated (dolines, sinkholes, etc.). Consequently, wastewater can be either transported by fast flow pathways and have short-term effects on groundwater or infiltrate into fractures and matrix and therefore have a long-term effect on the aquifer (Einsiedl et al., 2010).

An extensive campaign of micropollutant analysis undertaken in an investigated area believed to contribute to the Jeita spring in Lebanon in order to detect relationships between groundwater, surface water and wastewater and variation of these substances in water bodies over time. For this purpose, samples were collected from surface water, springs, wastewater and tap water under high, low and intermediate flow conditions over a total period of 2 years.

This report presents in details the results of the sampling campaigns. Section 2 provides a description of the study area, Section 3 discusses the methodology and description of the sampling campaigns, while Section 4 presents the results of the sampling campaigns. Section 5 consists of an elaborate discussion of the results. Finally Section 6 presents some conclusions and recommendations.

3 FIELD SITE

The investigated area will be mainly divided into three sub-zones (Figure 1):

- **Lower groundwater (GW) catchment:** consisting of the area upstream to Jeita and Qachqouch springs. The lithology in the latter is mainly composed of rocks of Jurassic age (mainly limestone and dolostone) and of Lower to Middle Cretaceous age (basal Cretaceous sandstones, Aptian limestone and Albian marly limestone rocks).
- **Upper groundwater (GW) catchment:** consisting of the area upstream to the Assal, Laban, Qana, and Afqa springs. The main lithology outcropping in the upper catchment is limestone of Middle Cretaceous age (Cenomanian).
- **The surface water catchment:** is the entire area drained by Nahr El Kalb River (Dog River), and its main tributaries. It extends from south to north from Metn to Keserwan districts. The two above groundwater catchments include partially the surface water catchment.

The **lower GW catchment** is drained partially or totally by Jeita and Qachqouch spring. The Jeita spring is an important karst spring located north to Beirut in Jounieh area. It constitutes the main water source for the Beirut Area for domestic use (about 1.5 million inhabitants). Governed by open channel flow, the Jeita Spring drains a catchment extending east in the Lebanese Mountains.

The Jeita cave is constituted of a subsurface channel developed in limestone of Jurassic age over a total length (excluding subsidiaries) of 5300 m. The Jurassic formation is mainly formed of limestone.

The Qachqouch spring is located at 60 m asl, it originates from limestones of upper Jurassic age (J6). It has a discharge varying between 0.2 and about 10 m³/s, where it is difficult to measure discharge in overflow periods. Qachqouch spring is diverted to the main channel fed by Jeita spring during the drought periods to supply water to Greater Beirut area. Qachqouch spring is conveyed partly to Nahr El Kalb River, especially if the main conveyor reaches its capacity in high flow periods.

The **upper GW catchment** area located above 1500 m asl, is drained mainly by four springs: Assal, Laban, Afqa and Qana Springs. The latter springs are believed to contribute to the Jeita Spring/Lower catchment.

Nahr El Kalb River is originating from the upper catchment mainly from springs like Laban and Assal, flowing through the lower catchment from east to west. It is mainly composed of two main tributaries joining the main river Nahr el Kalb before Daraya; Nahr El Salib river (north) (originating from Chabrouh, Assal and Laban) and Abu Mizane tributary (south) originating from the Metn area.

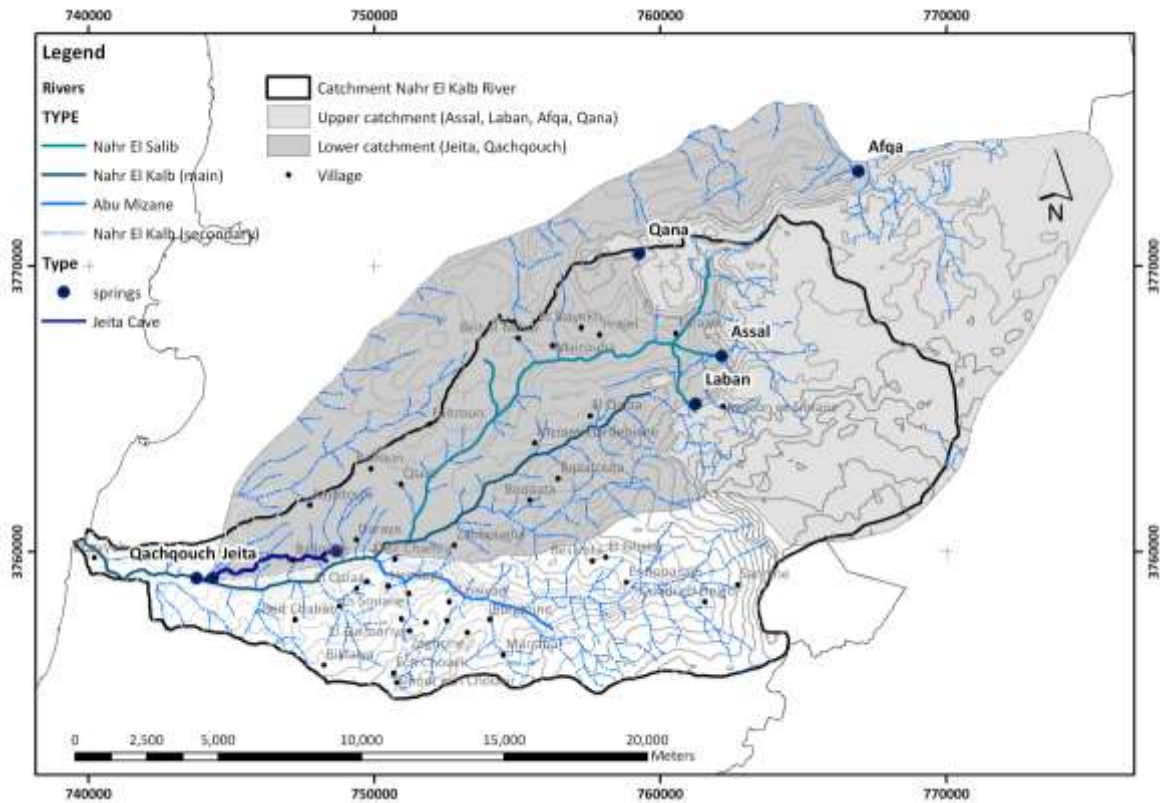


Figure 1 Main investigated catchments, springs, and rivers in the study area

4 MATERIALS AND METHODS

Four sampling campaigns were undertaken between September 2010 and January 2012, where major springs, rivers, and wastewater effluents were sampled (Figure 2). The various analyzed micropollutants are shown in Table 1. They consist of analgesics / anti-inflammatories, stimulants and caffeine metabolites, antihypertensive agents, iodinated contrast media, antibiotics, lipid regulators, antihistamines, anticonvulsants / sedatives, selective serotonin reuptake inhibitors, herbicides / herbicide metabolites, corrosion inhibitors, cocaine metabolite, and gastric acid regulator.

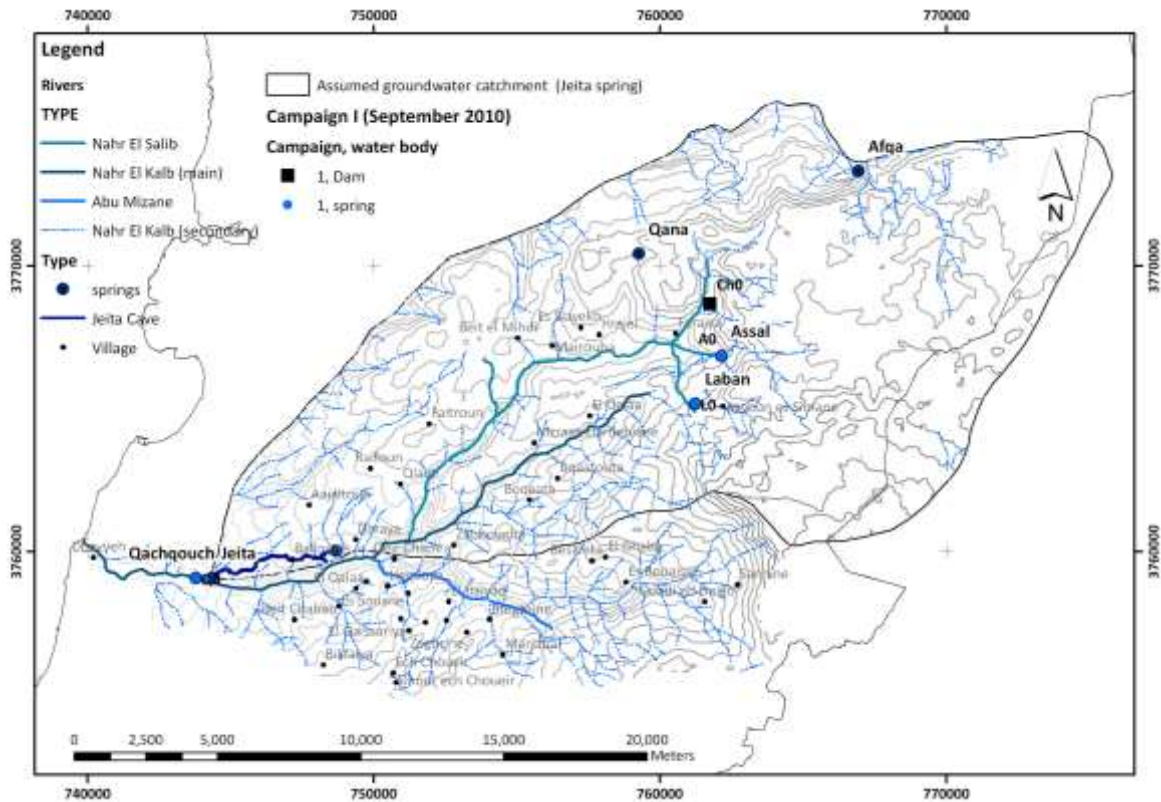
Table 1 Analytes and their application / origin

<i>Application or origin</i>	<i>Compound</i>	<i>Application or origin</i>	<i>Compound</i>
<i>Analgesics/Anti-inflammatories</i>	Diclofenac	<i>Lipid regulators</i>	Bezafibrate
	Ibuprofen		Clofibric acid
	Naproxen		Gemfibrozil
	Paracetamol	<i>Antihistamines</i>	Cetirizine
	Phenazone		Loratadine
	Caffeine		
Paraxanthine			
<i>Stimulants/Caffeine metabolites</i>	Theobromine		
	Theophylline		
	1-Methylxanthine		
	3-Methylxanthine		

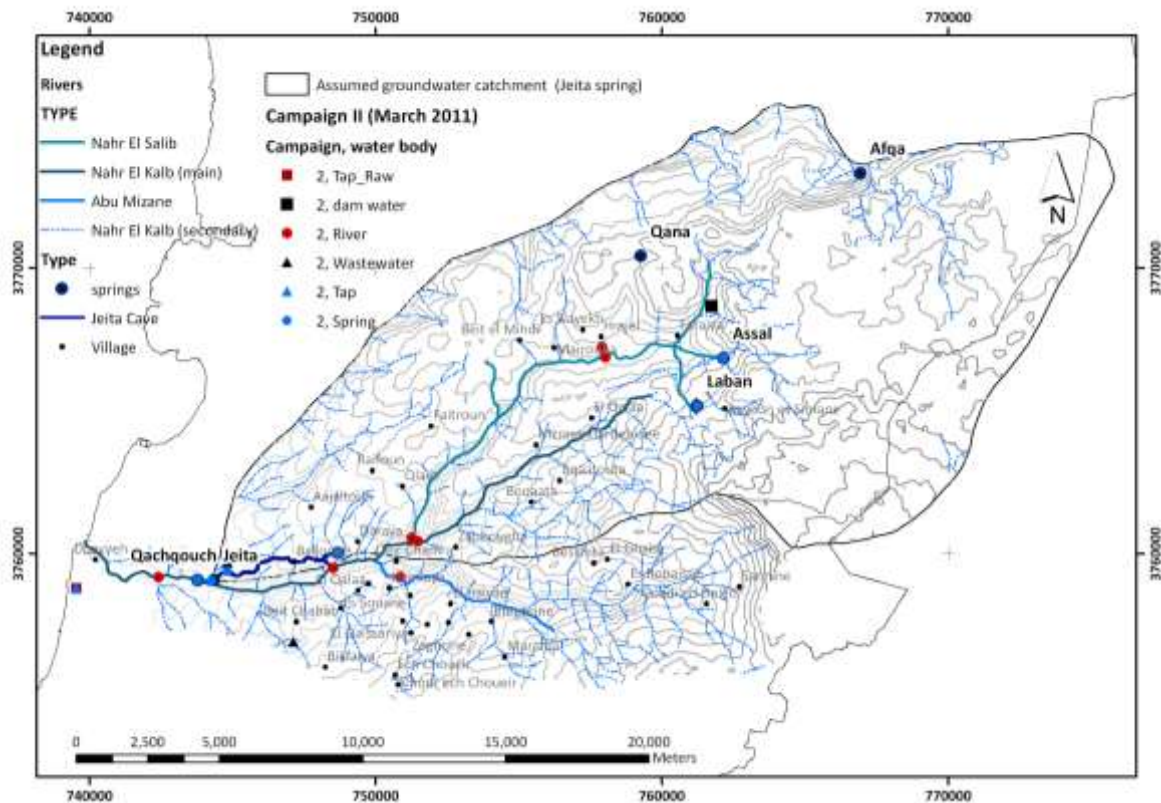
<i>Application or origin</i>	<i>Compound</i>	<i>Application or origin</i>	<i>Compound</i>
<i>Antihypertensive agents</i>	Atenolol Metoprolol Sotalol	<i>Anticonvulsants / Sedatives</i>	Carbamazepine Diazepam Primidone Tetrazepam
<i>Iodinated contrast media</i>	Iohexol Iomeprol Iopamidol Iopromide	<i>Selective serotonin reuptake inhibitors</i>	Citalopram Fluoxetine Sertraline
<i>Antibiotics</i>	Clarithromycin Erythromycin Roxithromycin Sulfamethoxazole Trimethoprim	<i>Herbicides / Herbicide metabolites</i>	Atrazine Desethylatrazine Desisopropylatrazine Diuron Isoproturon Mecoprop Metazachlor
<i>Gastric acid regulator</i>	Pantoprazole	<i>Corrosion inhibitors</i>	1H-Benzotriazole Tolyltriazole
		<i>Cocaine metabolite</i>	Benzoyllecgonine

A total of 100 samples were collected from different water bodies over the catchment (spring, rivers, and wastewater) under various flow conditions as follows:

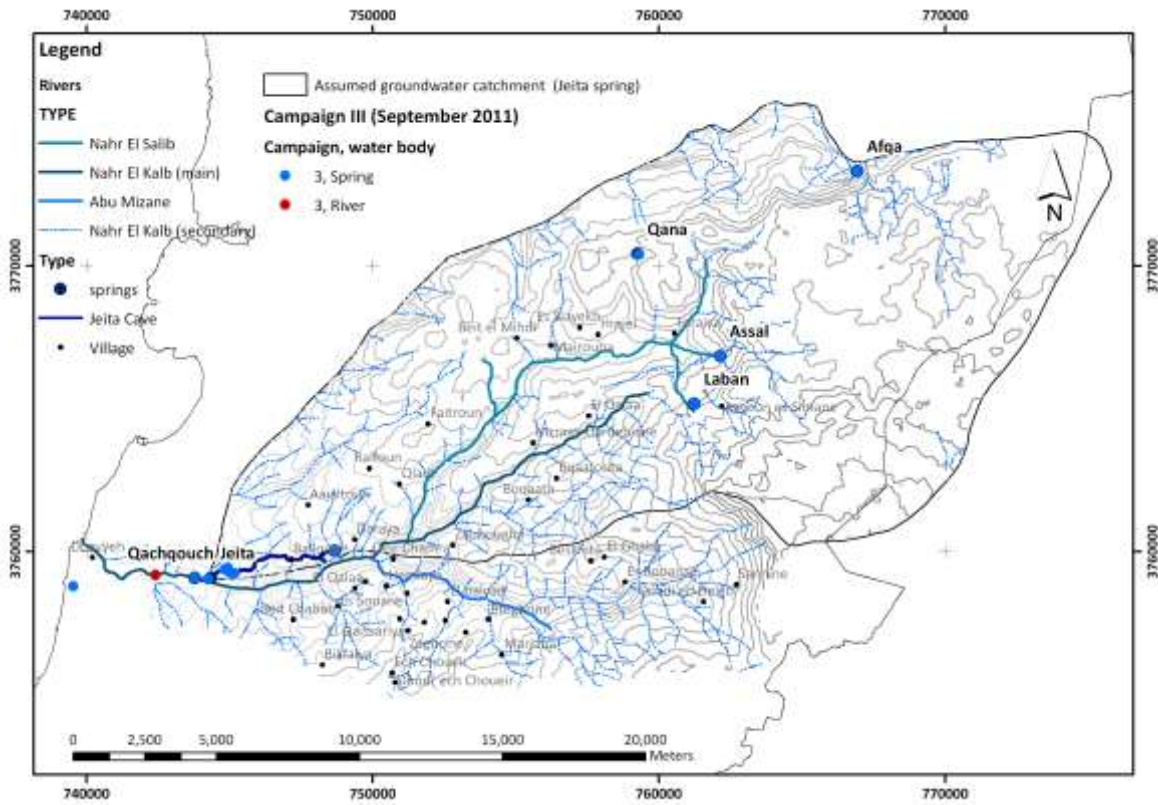
- Campaign 1: A pre-sampling campaign consisted of the sampling of the major springs (6 samples) in the catchment area on the 22nd of September 2010 during low flow periods.
- Campaign 2: A major campaign was undertaken in March 2011 during high flow periods, consisting of the sampling of the major springs, river branches (the Dog river), and wastewater effluents (51 samples).
- Campaign 3: This sampling campaign consisted of 16 samples and was undertaken during low flow period on September 2011. Major springs and flowing surface water were mainly sampled. Additionally samples were taken along the cave over the last 1000 m to assess the behavior of the different compounds along the course of the cave.
- Campaign 4: The last sampling campaign was performed in intermediate flow periods in December 2011 and January 2012 and consisted of the sampling of various river branches, and major springs. Additionally samples were taken along the cave over the last 1000 m to assess the behavior of the different compounds along the course of the cave.



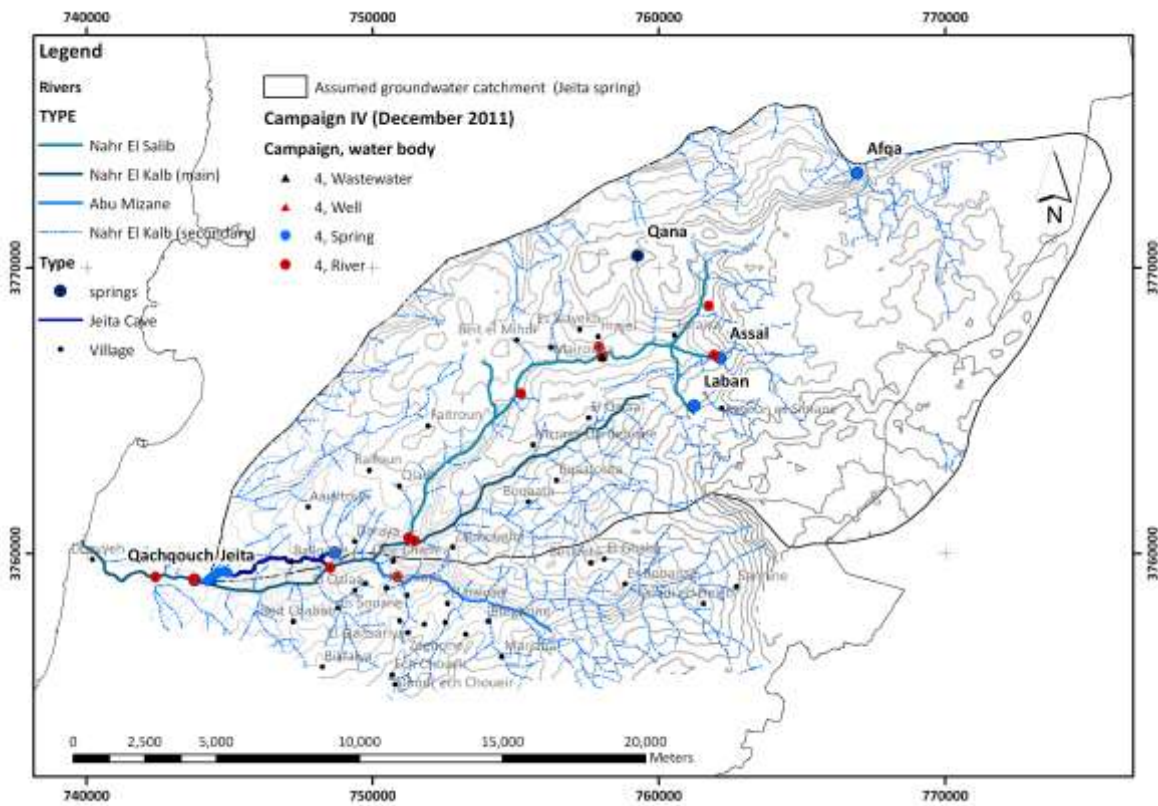
a



b



C



d

Figure 2 Sampling locations during campaign I (a), II (b), III (C), IV (d)

A total of 100 samples were retrieved each in 1L glass bottles during four sampling campaigns. The samples were stored at 4° C until extraction. Extraction was performed within 24 h. A multi- residue analytical method based on solid phase extraction (SPE) was performed on the samples for micropollutant analysis (Nödler et al., 2010) within not more than 24 hours following sampling. For springs and river samples, 500 mL were extracted, whereas only 10 mL and 20 mL of wastewater were extracted. The cartridges of the solid extract were stored at -19° C until analysis. Discharge rates for the major springs were either measured during sampling or retrieved from discharge curves of the spring under prevailing conditions.

Daily loads (mass flux) of micropollutants especially the persistent ones can be calculated as follows:

$$M = \frac{QC_i}{10^9}$$

Where M is the daily mass flux (g/d), Q is the daily discharge (l/d), C_i is the concentration (ng/l)

5 RESULTS

It is worth noting that all the concentrations of the detected micropollutants are in nanogram per liters and fall far below ranges of potential toxicity. Therefore the four sampling campaigns gave insights into the type of contaminants present on the catchment area. The results of the analysis can provide information about the following:

- An overview about micro pollutants present on the catchment area, along with concentrations in different water bodies,
- A brief overview about the fate of the micro pollutants as well as their occurrence in the study area in the three sub-investigated areas, mainly rivers, waste water tap water and the main sampled springs,
- Comparison between different micro pollutants concentrations and loads under high and low flow periods in the main springs when relevant,
- The variation of some indicator micro pollutants within the subsurface channel of the Jeita spring.

5.1 DETECTED MICROPOLLUTANTS

The detailed results of the campaigns are provided in Appendix A. This section shows the types of micropollutants present in the sampled water bodies (springs, rivers, dam, well, wastewater, and tap water). The micropollutants present in wastewater are discussed hereafter as well.

The types of micropollutants found in the samples are elaborated in the following section (Table 2).

5.1.1 Stimulants and caffeine metabolites

The stimulants caffeine and its metabolites paraxanthine, theobromine, and theophylline (Table 2) were found in the spring samples collected from the catchment, namely Jeita, Qachqouch, Laban, and Assal, Afqa and Qana springs. At instances, metabolites were not detected in Laban, Assal, Qana, and Afqa springs. These stimulants are easily degradable compounds and thus the presence of significant concentrations of these compounds is a strong indication for a contamination with untreated wastewater occurring in the catchment.

These same stimulants (paraxanthine, theobromine, and theophylline) in addition to other caffeine metabolites 1-methylxanthine and 3-methylxanthine were found in all the sections of the Nahr El Kalb River. These

stimulants found either in coffee or in other muscle relaxants or bronchodilators are usually excreted in the environment in urine, therefore they are believed to be wastewater indicators.

5.1.2 *Pharmaceuticals*

5.1.2.1 *Analgesics*

Analgesics and anti-inflammatory drugs (Table 1) are prescribed in large quantities in most of the countries (Herberer, 2002). However, they are mostly sold over the counter in large quantities in some countries where control is not reinforced. These products are metabolized by the human body and usually excreted by the urine; therefore they are also markers for wastewater contamination. The two products mostly detected in the spring and river samples are paracetamol and ibuprofen. Ibuprofen is readily degraded into its principal metabolites, which are usually removed in STPs to 96-99.9 % (Herberer, 2002). Paracetamol (also known as acetaminophen (Herberer, 2002)) is the most popular among analgesics that is found in Lebanon in about 80 type of medicine (syrups, tablets, suppository and drops; <http://www.pharmaguidelb.com>). Acetaminophen is easily degraded in Sewage Treatment Plants (STPs), however its degradation in natural environments is still controversial (Ternes, 1998a, Herberer, 2002). Diclofenac is also found in collected wastewater effluents. Ibuprofen is found in about 25 medicines in Lebanon. It is heavily metabolized in the human body and degraded in natural environment (e.g., surface waters; Buser et al., 1999) and in sewage treatment plants. Diclofenac and naproxen are only detected in wastewater effluents. Naproxen is detected at lower concentration than diclofenac, as the latter is prescribed in over 70 medicines in Lebanon. Both substances are removed in natural conditions by photolytic degradation (Buser et al., 1999, Tixier et al., 2003). Additionally, diclofenac was reported to undergo significant sorption and attenuation in the soil (Herberer 2002). Phenazone is prescribed in Lebanon only as ear drops, which explains why the latter is not detected in the analyzed samples.

5.1.2.2 *Lipid regulators*

Lipid regulators include three main analyzed compounds (Table 1). The compound gemfibrozil found in wastewater, groundwater, and surface water samples, is a lipid regulating agent (medicine: Lopid) used in Lebanon for treatment to reduce blood levels of cholesterol and triglycerides. This drug is excreted in urine or feces. Therefore, the presence of this drug in water samples indicates the presence of a wastewater contamination source on their catchment area. Gemfibrozil might be removed to a certain extent in wastewater treatment plants (up to 46%; Fang et al., 2012), however in the absence of WWTP, Gemfibrozil can only be removed by photodegradation or biological degradation (decay rate in loam 17-20 days), or delayed partially by sorption-desorption to soil (Fang et al., 2012).

5.1.2.3 *Anticonvulsants and sedatives*

Carbamazepine is an anti-epileptical drug used in most of the countries (Scheytt, 2005). It is also used for the treatment of manic-depressive illnesses. It was frequently detected in surface water as well as in effluents of sewage treatment plants, as less than 10% of carbamazepine are usually eliminated during sewage treatment and not attenuated during bank infiltration (Heberer, 2002). The body metabolizes about 98-99% of the

carbamazepine into metabolites (metabolite carbamazepine-10,11-epoxide) (Clara et al., 2004, Leclercq et al., 2009, Ternes, 1998, Frey and Janz 1985). According to other sources, only 3% of the carbamazepine is metabolized by the body (Ghauch et al., 2011). Carbamazepine is still considered to be fairly persistent in groundwater (Tixier et al., 2003), and is consequently regarded as an effective wastewater indicator because it is unlikely degradable or adsorbed. Therefore it can be present over detection limits in groundwater (Clara et al., 2004). In Lebanon, carbamazepine is known commercially by Tegretol (Ghauch et al., 2011) and is used as an antiepileptic, for treatment of schizophrenia, bipolar problems and alcohol withdrawal.

5.1.2.4 Cocaine Metabolite

Cocaine is considered as an illicit drug used worldwide to stimulate psychological effects and enhance the activity of the nervous system (Van Nuijs et al., 2009). Cocaine is directly either injected in the blood, inhaled directly through the nose or through smoking. The urine of a cocaine addict contains excreted cocaine as well as its metabolite benzoylecgonine. The latter allows tracing back the loads of metabolized cocaine (Zuccato et al., 2005).

5.1.3 *Industrial and clinical micropollutants*

5.1.3.1 Pesticides

Mecoprop is the sole type of pesticide found in the area, mostly in wastewater at very low concentrations not exceeding 20 ng/l. This type of herbicide used as a household weed killer or is widely used as a roof protection agent (Wittmer et al., 2010). Such concentrations are considered negligible and will be therefore not further elaborated.

5.1.3.2 Contrast media

Iodinated X- ray contrast media are widely used in hospitals and practical surgery; therefore they are indicators of clinical wastewater (Ternes and Hirsch, 2000). The sole substance detected in the analyzed samples (wastewater Hrajel, Nahr El Salib river and Jeita spring: upper catchment) is iopamidol. Other contrast media such as iohexol was only detected in wastewater whereas other products were not detected in the groundwater or wastewater mostly because they are not used in the catchment as they might not be available or approved in the local market (Ternes and Hirsch, 2000). Due to their high polarity, iodinated contrast media have a high chemical stability, i.e., a low likelihood for sorption (Ternes and Hirsch, 2000). Additionally, they are characterized by a low degradation potential, therefore, they are considered as highly persistent in the aquatic environment and easily leaching to groundwater (Heberer, 2002). This substance, discharged into clinical waste water into rivers might have infiltrated to the aquifer especially that it is persistent under environmental conditions or discharged directly through sinkholes or open pits in the aquifer.

5.1.3.3 Corrosion inhibitors

1-H Benzotriazole is present in the Jeita spring in Daraya and Jeita sections during low flow periods. This compound is a corrosion inhibitor that is found in dish washing liquids and cooling fluids. It generates from domestic wastewater where such products are released. These compounds are persistent and relatively resistant to biodegradation (Voutsas et al., 2006). Benzotriazole 1-H is present exclusively in river branches and

wastewater present on the northern part of the catchment in Hrajel area, whereas it is absent in the springs located in the upper catchment areas, namely, Laban, Assal, Afqa, and Qana springs.

5.2 NON DETECTED MICROPOLLUTANTS

Some of the analyzed compounds were not detected in any of the samples in the catchment, because they are either not used locally, or at relatively insignificant loads or degrade at a high rate in the natural conditions. The absent micropollutants are as follows:

- Antihistamines (Loratadine)
- SSRI (Selective Serotonin Reuptake Inhibitor; Citalopram, Fluoxetine, Sertraline)
- Pesticides and pesticide metabolites (Atrazine, Desisopropylatrazine, Diuron, Isoproturon, Metazachlor)
- Proton pump inhibitor (Pantoprazole)

Table 2 Micropollutants detected in samples collected from spring water, surface water, and wastewater in the study area under various flow conditions (below DL: compound below detection limit)

	Spring	Micro-pollutants			
		09-2010 (LF)	09-2011 (LF)	03-2011 (HF)	12-2011 (HF)
Springs	Laban	- Caffeine and metabolites	- Caffeine and metabolites	- Caffeine and metabolites - Tolyltriazole	-
	Assal	- Caffeine and metabolites	- Caffeine and metabolites	- Caffeine and metabolites	-
	Afqa	not analyzed	- Caffeine and metabolites	-	-
	Qana	not analyzed	- Caffeine and metabolites	not analyzed	not analyzed
	Qachqouch	- Caffeine and metabolites - Sulfamethoxazole - Carbamazepine - 1H-Benzotriazole - Cocaine metabolite (Benzoylecgonine) - Gemfibrozil	- Caffeine and metabolites - Sulfamethoxazole - Carbamazepine - 1H-Benzotriazole - Cocaine metabolite (Benzoylecgonine) - Gemfibrozil	- Caffeine and metabolites - Carbamazepine	- Caffeine and metabolites - Carbamazepine - Cocaine metabolite (Benzoylecgonine) - Gemfibrozil
	Jeita spring (entrance)	- Caffeine and metabolites - Sulfamethoxazole - Carbamazepine - 1H-Benzotriazole - Cocaine metabolite (Benzoylecgonine)	- Caffeine and metabolites - Sulfamethoxazole - Carbamazepine - Gemfibrozil - Iopamidol - 1H-Benzotriazole - Cocaine metabolite (Benzoylecgonine)	- Caffeine and metabolites - Carbamazepine - Sulfamethoxazole	- Carbamazepine - Cocaine metabolite (Benzoylecgonine)

	Spring	Micro-pollutants			
		09-2010 (LF)	09-2011 (LF)	03-2011 (HF)	12-2011 (HF)
Spring	Jeita spring (Daraya)	not analyzed	<ul style="list-style-type: none"> - Caffeine and metabolites - Sulfamethoxazole - Carbamazepine - Iopamidol - 1H-Benzotriazole - Cocaine metabolite (Benzoylecgonine) 	<ul style="list-style-type: none"> - Caffeine and metabolites - Carbamazepine 	<ul style="list-style-type: none"> - Carbamazepine - Cocaine metabolite (Benzoylecgonine)
	Nahr El Kalb	Southern Branch (Abou Mizane- R3)	dry	dry	<ul style="list-style-type: none"> - Caffeine and metabolites - Ibuprofen/Paracetamol - Atenolol - Gemfibrozil - Carbamazepine - Cocaine metabolite (Benzoylecgonine)
Middle Branch (low-R2)		dry	dry	<ul style="list-style-type: none"> - Ibuprofen - Caffeine and metabolites - Gemfibrozil - Atenolol 	<ul style="list-style-type: none"> - Caffeine and metabolites - Gemfibrozil
northern Branch (high- Laban)		dry	dry	below DL	<ul style="list-style-type: none"> - Caffeine
Northern Branch (Assal Chabrouh)		dry	dry	below DL	<ul style="list-style-type: none"> - Paracetamol - Caffeine and metabolites - Cocaine metabolite (Benzoylecgonine)-(Assal side)

	Spring	Micro-pollutants			
		09-2010 (LF)	09-2011 (LF)	03-2011 (HF)	12-2011 (HF)
Nahr El Kalb	Northern Branch (Hrajel)	dry	dry	below DL	<ul style="list-style-type: none"> - Ibuprofen - Caffeine and metabolites - Gemfibrozil - Iopamidol - Carbamazepine - Cocaine metabolite (Benzoyllecgonine)
	Northern Branch (R1)	dry	dry	<ul style="list-style-type: none"> - Ibuprofen - Caffeine and metabolites - Gemfibrozil - Atenolol - Carbamazepine - Cocaine metabolite (Benzoyllecgonine) 	<ul style="list-style-type: none"> - Ibuprofen - Caffeine and metabolites - Gemfibrozil - Carbamazepine - Cocaine metabolite (Benzoyllecgonine)
	Daraya (RD)	dry	dry	<ul style="list-style-type: none"> - Caffeine and metabolites - Ibuprofen - Paracetamol - Atenolol 	<ul style="list-style-type: none"> - Gemfibrozil - Carbamazepine - Cocaine metabolite (Benzoyllecgonine) - + Desethylatrazine (12-2011)
	At Qachqouch	dry	dry	not analyzed	<ul style="list-style-type: none"> - Caffeine and metabolites - Ibuprofen - Paracetamol - Atenolol - Gemfibrozil - Carbamazepine - Cocaine metabolite (Benzoyllecgonine)

	Spring	Micro-pollutants			
		09-2010 (LF)	09-2011 (LF)	03-2011 (HF)	12-2011 (HF)
Nahr El Kalb	Mokhada	not analyzed	<ul style="list-style-type: none"> - Caffeine and metabolites - Iopamidol - Sulfamethoxazole - Carbamazepine - 1H-Benzotriazole 	<ul style="list-style-type: none"> - Caffeine and metabolites - Carbamazepine 	<ul style="list-style-type: none"> - Caffeine and metabolites - Carbamazepine
	Wastewater northern part-Hrajel	not analyzed	not analyzed	not analyzed	<ul style="list-style-type: none"> - Diclofenac, Paracetamol - Ibuprofen, Naproxen - Caffeine and metabolites - Atenolol - Iohexol - Iopamidol - Gemfibrozil - 1H-Benzotriazole - Cocaine metabolite (Benzoylecgonine)
Wastewater	Wastewater southern part- Metn-Beit Chabab		not analyzed	<ul style="list-style-type: none"> - Diclofenac and Ibuprofen - Paracetamol - Caffeine and metabolites - Gemfibrozil and Cetrizine - Carbamazepine - Cocaine metabolite (Benzoylecgonine) - Mecroprop 	not analyzed
	Wastewater Jeita	not analyzed	not analyzed	<ul style="list-style-type: none"> - Diclofenac Ibuprofen - Naproxen - Caffeine and metabolites - Gemfibrozil and Cetirizine - 1H-Benzotriazole- Tolytriazole 	not analyzed

	Spring	Micro-pollutants			
		09-2010 (LF)	09-2011 (LF)	03-2011 (HF)	12-2011 (HF)
Wastewater	Wastewater northern part-Hrajel	not analyzed	not analyzed	<ul style="list-style-type: none"> - Diclofenac, Ibuprofen - Paracetamol - Caffeine and metabolites - Iohexol, Iopamidol - Atenolol - Gemfibrozil and Cetirizine - 1H-Benzotriazole - Cocaine metabolite (Benzoylecgonine) 	not analyzed
Tap water	Tap water	not analyzed	<ul style="list-style-type: none"> - Caffeine - Carbamazepine - 1H-Benzotriazole - Cocaine metabolite (Benzoylecgonine) 	<ul style="list-style-type: none"> - Caffeine - Carbamazepine 	not analyzed

5.3 SPATIAL DISTRIBUTION OF MICROPOLLUTANTS UNDER VARIOUS FLOW CONDITIONS

5.3.1 Campaign I: low flow periods

During low flow periods, the only compound found in the springs (Assal, Laban, Chabrouh) located in the upper catchment (Cretaceous aquifer) is caffeine. The loads of caffeine in Laban are 0.065 g/d and in Assal 0.06 g/d given the discharge rates estimated for the date of sampling.

In the lower catchment (Jurassic aquifer), given the measured concentrations under prevailing flow rates, daily loads (grams) of carbamazepine (3.7, 1), sulfamethoxazole (0.5, 0.25), benzoylecgonine (0.85, 0.19) and 1H-benzotriazole (0.8, 0.21) can be found respectively in Jeita and Qachqouch springs.

5.3.2 Campaign II: high flow periods with intermittent precipitation events

5.3.2.1 Groundwater: upper catchment

Only caffeine is found in the springs (Assal and Laban) of the upper catchment. This period cannot be considered a high flow period, as both springs do not reach their maximum discharge at this time of the year rather after the snow melt event at the end of April. Therefore the results of the Upper catchment are representative of intermediate flow periods.

5.3.2.2 Groundwater: lower catchment

Only caffeine and carbamazepine are found in the springs of the lower catchment, namely Jeita and Qachqouch. The load of carbamazepine in baseflow during high flow periods is about 7.5 g/d in the Jeita spring and 2.16 g/d in Qachqouch spring. The absence of the other compounds is due to the high dilution effect resulting from a high discharge rate (e.g., 8000 l/s in Jeita).

5.3.2.3 Surface Water: Nahr El Kalb River

Carbamazepine and benzoylecgonine are introduced in surface water (Nahr El Salib) at the level of Hrajel village, where concentration of both compounds increase drastically downstream to the Hrajel wastewater outlet. Between Hrajel and the intersection of Nahr El Salib with the two other southern branches (R3 and R2) and Nahr El Kalb at Daraya, concentrations of benzoylecgonine and carbamazepine tend to decrease gradually due to dilution. Downstream to Jeita and Qachqouch in Mokhada channel, carbamazepine concentrations increase due to inflow of carbamazepine rich waters from Jeita and Qachqouch springs, while benzoylecgonine tends to decrease drastically because of dilution with benzoylecgonine free spring (Jeita and Qachqouch) water.

5.3.2.4 Wastewater and Tap Water

All the collected wastewater samples contain high concentrations of caffeine (6000-38000 ng/l) and its metabolites. Additionally, analgesics and anti-inflammatories were also detected at high concentration in all of the wastewater samples except the sample collected downstream to Laban spring.

- Lower catchment Jeita

Wastewater originating from the Village of Jeita evacuated in the river contains gemfibrozil, and 1H-benzotriazole. Carbamazepine and benzoyllecgonine are both absent in this wastewater sample.

- Southern catchment: Metn area

Carbamazepine, benzoyllecgonine, mecoprop, and gemfibrozil are present in the collected wastewater sample from Beit Chabab area.

- Upper northern catchment: Hrajel

Carbamazepine, benzoyllecgonine, mecoprop, and gemfibrozil are found in the wastewater discharged from the village of Hrajel and neighbouring areas.

- Upper middle catchment: Laban

Only 1H-benzotriazole and mecoprop are found in the wastewater discharging downstream to Laban.

- Tap water: Dbayeh treatment plant

Upon comparison between Jeita raw water and the treated water of Dbayeh, it can be deduced that carbamazepine concentration is constant and is not removed upon processing at the Dbayeh treatment plant. Other micropollutants are heavily diluted under high flow conditions, therefore they are mostly absent in the Jeita raw water and the Dbayeh treated water.

5.3.3 Campaign III: low flow periods

5.3.3.1 Groundwater: upper catchment

As observed in September 2010, the only compound found in the springs (Assal, Laban, Chabrouh, Assal and Qana) located in the upper catchment (Cretaceous aquifer) is caffeine.

The loads of caffeine in Laban are 0.08 g/d and in Assal 0.4 g/d given the discharge rates estimated for the date of sampling.

5.3.3.2 Groundwater: lower catchment

Caffeine, iopamidol, sulfamethoxazole, carbamazepine, 1-H Benzotriazole, and benzoyllecgonine are found in Qachqouch and Jeita Springs. With respect to results obtained in September 2010 for both springs, loads of benzoyllecgonine decreased by about 60%, whereas loads of carbamazepine and 1-H benzotriazole remained almost the same in both springs. The presence of iopamidol in the Jeita spring may suggest that hospital wastewater is also discharged on the Jeita spring catchment.

5.3.3.3 Surface Water: Nahr El Kalb River

The fate of the micropollutants downstream to the Jeita Spring and Mokhada channel was based on the comparison of the samples collected from Qachqouch and Jeita springs and the sample collected at Mokhada spring. An increase of concentrations of caffeine, iopamidol and benzoylecgonine is observed; whereas concentrations of sulfamethoxazole, carbamazepine and 1-H Benzotriazole decrease implying that additional wastewater mostly from hospital use is also discharged along this section.

5.3.3.4 Tap Water

During low flow periods, water from Jeita and Qachqouch springs is diverted at the Mokhada dam to the Dbayeh water canal coming from Jeita. Therefore, a comparison between the Jeita-Dbayeh canal at Mokhada and the treated water at Dbayeh plant enable to detect the fate of the micropollutants following treatment. The concentrations of sulfamethoxazole, iopamidol, and caffeine metabolites decrease to below detection limits, whereas caffeine concentration decreases by a factor of 10. Concentrations of carbamazepine, benzoylecgonine and 1-H Benzotriazole remain the same in the treated water. Benzoylecgonine and 1-H Benzotriazole are for the first time detected in tap water, mostly due to low flow conditions and low dilution effect.

5.3.4 *Campaign IV: intermediate flow periods*

5.3.4.1 Groundwater: upper catchment

The analysis of samples collected from Assal, Laban, and Afqa show that no micropollutants are present above detectable limits in the sampled springs.

5.3.4.2 Groundwater: lower catchment

Only benzoylecgonine and carbamazepine are found in the springs of the lower catchment, namely Jeita and Qachqouch. Gemfibrozil, and caffeine and its metabolites are additionally found in Qachqouch spring. The load of carbamazepine is about 3.1 g/d in the Jeita spring and 4.3 g/d in Qachqouch spring. The absence of the other compounds (except for stimulants and analgesics) in Jeita spring is believed to be due to the high dilution effect resulting from a high discharge rate (e.g., 5700 l/s in Jeita). The loads of carbamazepine are similar to that observed during low flow periods. Only loads of benzoylecgonine appear to increase in both Jeita and Qachqouch springs.

5.3.4.3 Surface Water: Nahr El Kalb River

In consistence with campaign II, benzoylecgonine, gemfibrozil, caffeine, paracetamol, ibuprofen, and iopamidol are discharged in surface water (Nahr El Salib) at the level of Hrajel village, where concentration of both compounds increase drastically downstream to the Hrajel wastewater outlet. The ratio of discharged effluent to river water can be estimated by a simple mixing relationship between concentration of the effluent and concentrations before the effluent and after the effluent. The volume of discharged wastewater is about 0.045 (4.5%) the discharge of the river. The presence of iopamidol is an indicator of clinical wastewater at this level. carbamazepine is found in

the sample collected at Kfar Debbiane Bridge, which implies the presence of a source of carbamazepine from wastewater before the bridge. Between the Kfarzebiane Bridge and the intersection with the two other southern branches in Deir Chemra, a dilution of all compounds is observed, where concentrations decrease to 20-60 % of original concentrations. Desethylatrazine is present in the surface water sample collected at Daraya, resulting from the presence of this pesticide metabolite in the Nahr el Kalb river branch extending east to Abou Mizane.

At Daraya concentrations of carbamazepine, benzoylecgonine and ibuprofen decrease because of dilution with the middle and lower branch of the river (R2 and R3), whereas paracetamol, caffeine and gemfibrozil increase.

Downstream of Qachqouch, carbamazepine concentration increases due to the inflow of carbamazepine rich Qachqouch waters. At the Jeita- Dbayeh canal at Mokhada, carbamazepine continues to increase because of the effect of Jeita and Qachqouch waters, whereas dilution of all other compounds takes place, namely benzoylecgonine, caffeine, paracetamol, and gemfibrozil.

5.3.4.4 Wastewater, upper northern catchment: Hrajel

Caffeine, benzoylecgonine, iopamidol, ibuprofen, gemfibrozil and paracetamol are found in the wastewater discharged from the village of Hrajel and neighbouring areas. Those compounds are indicators for both domestic and clinical wastewater (iopamidol).

6 DISCUSSION

6.1 OCCURRENCE IN SURFACE WATER

Surface water was analyzed during high flow periods (March 2011) and intermediate flow periods (December 2011), where the Nahr el Kalb River is active (Figure 3). Both campaigns show the same results. Carbamazepine and benzoylecgonine are introduced in surface water (Nahr El Salib) at the level of Hrajel village, where concentration of both compounds increase drastically downstream to the Hrajel wastewater outlet until Kfarzebiane Bridge. Between the bridge and the intersection of Nahr El Salib with the two other southern branches (R3 and R2), a decrease in the concentration of benzoylecgonine, carbamazepine and caffeine is observed.

Between the river intersection and Nahr El Kalb River at Daraya, concentrations of benzoylecgonine and carbamazepine tend to decrease or relatively remain constant due to dilution. Caffeine concentration increases because the inflowing branches (R2 and R3) are characterized by high concentration of caffeine with respect to the other two compounds.

Downstream to Jeita and Qachqouch in Mokhada channel, carbamazepine concentrations increase due to inflow of carbamazepine rich waters from the Jeita springs, while benzoylecgonine tends to decrease drastically because of dilution with benzoylecgonine and caffeine free spring (Jeita) water.

The three compounds benzoylecgonine, carbamazepine, and caffeine follow generally the same trend throughout the river course, except for carbamazepine that is persistently introduced to the surface water system through overflowing groundwater from the Jeita spring.

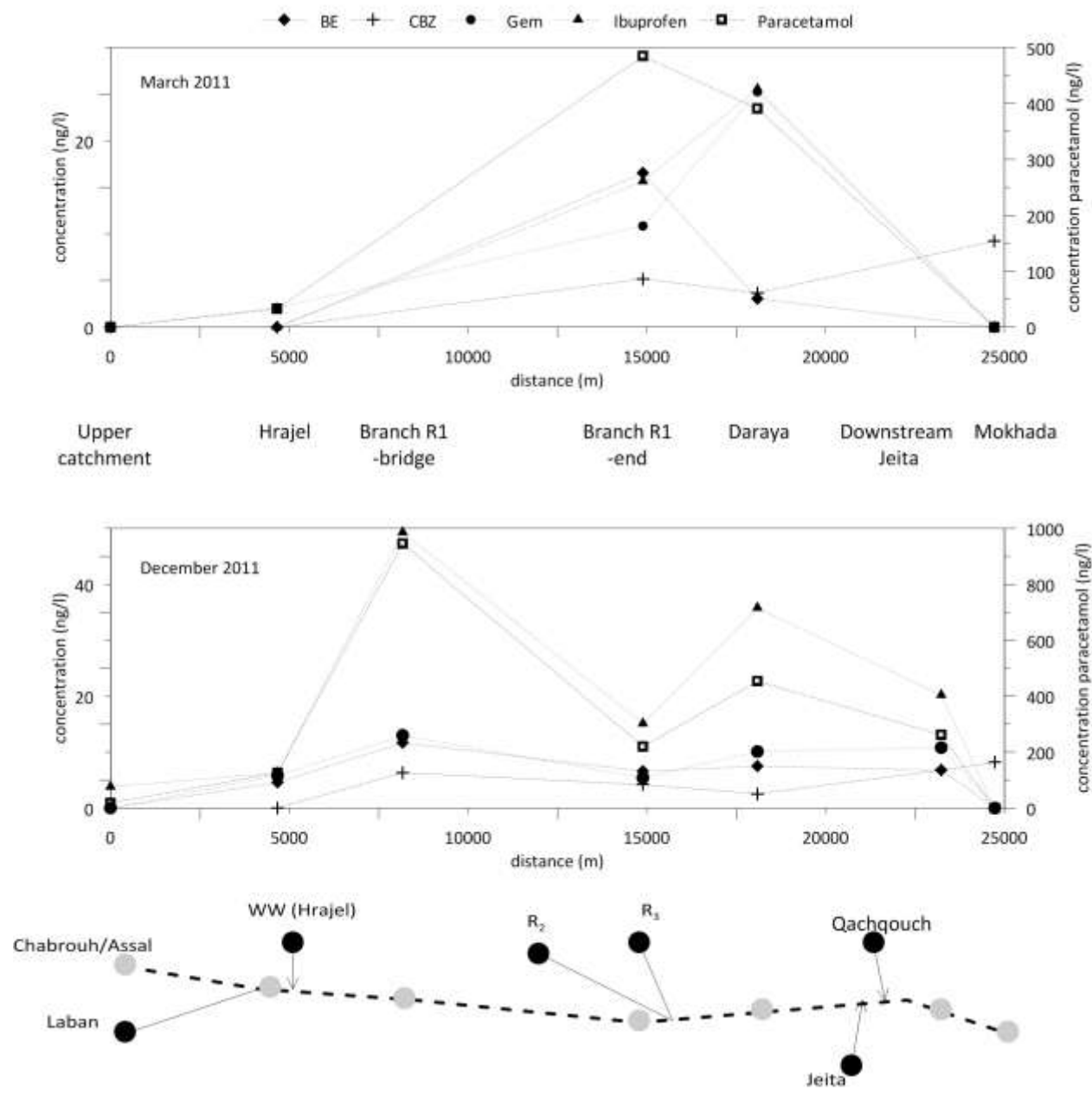


Figure 3 Fate of MP along the Nahr El Kalb River since its origin in the Lebanese mountains until its outlet downstream to the Jeita spring

6.2 FATE OF MICROPOLLUTANTS WITHIN THE JEITA CAVE

Samples were taken in September 2011 (Figure 4) and in December 2011 (Figure 5) in the subsurface channel over a total distance of 5300 m starting from the last accessible point on the cave (Daraya tunnel) to the spring outlet in potential accessible locations. Concentrations (ng/l) and loads (g/d) of benzoylecgonine and carbamazepine were plotted against distance in September and December 2011. Dilution tests were performed during sampling for discharge estimation at each point of sampling. As shown in Figure 4 and Figure 5, an inflow of water converging

to the subsurface channel at about 4620 m affects locally the mass fluxes of the investigated compounds. The amount of the inflow is about 240 l/s (1/6 of total flow) in September 2011 and 1500 l/s during December 2011 (about ¼ of the total flow).

6.2.1 September 2011 (low flow periods; Figure 4)

Benzoyllecgonine and carbamazepine remain constant generally constant over the channel. Variations in the mass fluxes can be observed locally as follows:

- About 16-17% increase of mass flux occurs between Daraya (5300 m) and 3800 m downstream to it, the increase amounts to 0.47 and 0.05 g/d for carbamazepine and benzoyllecgonine respectively.
- A dilution effect is observed following the inflow location. The inflow located at 4620 m contains loads of carbamazepine (about 0.43 g/d), whereas it contains no detectable traces of benzoyllecgonine. Therefore after inflow location, mass fluxes of carbamazepine increase, while concentrations of benzoyllecgonine decreases due to dilution.

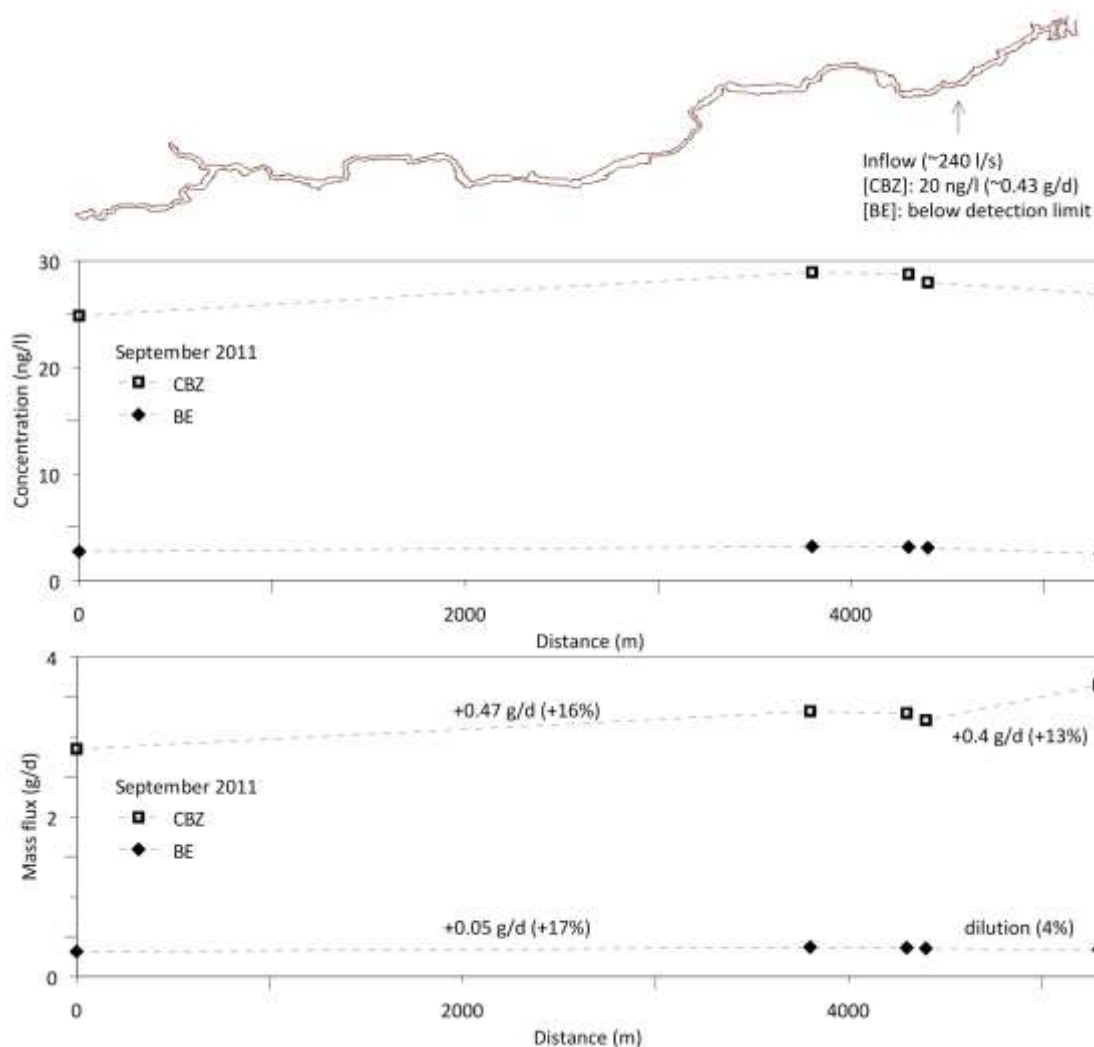


Figure 4 Behavior of benzoylecgonine and carbamazepine (mass flux and concentrations) in samples collected along the subsurface channel showing in some locations the input of additional compounds and/or effect of dilution (September 2011)

6.2.2 December 2012 (intermediate flow periods; Figure 5)

A different behaviour of both benzoylecgonine and carbamazepine is observed under intermediate flow with respect to low flow periods:

- About 15-18% increase of mass flux occurs between Daraya (5300 m) and 3800 m downstream to it, the increase amounts to 0.34 and 0.24 g/d for carbamazepine and benzoylecgonine respectively.
- Downstream to the inflow located at 4620 m, mass fluxes increase of 15% for carbamazepine (+0.44 g/d) and 33 %for benzoylecgonine (+0.67 g/d). Based on a simple mixing model, the concentration of the inflow is estimated to be 3.4 ng/l and 5.2 ng/l respectively.
- The mass fluxes of both benzoylecgonine and carbamazepine remain constant over the last 500 m.

- In December concentrations of caffeine in the Jeita spring are below detection limits, this could be explained by either a high degradation of caffeine, or high dilution of relatively low concentrations of caffeine present in the system from low flow periods.

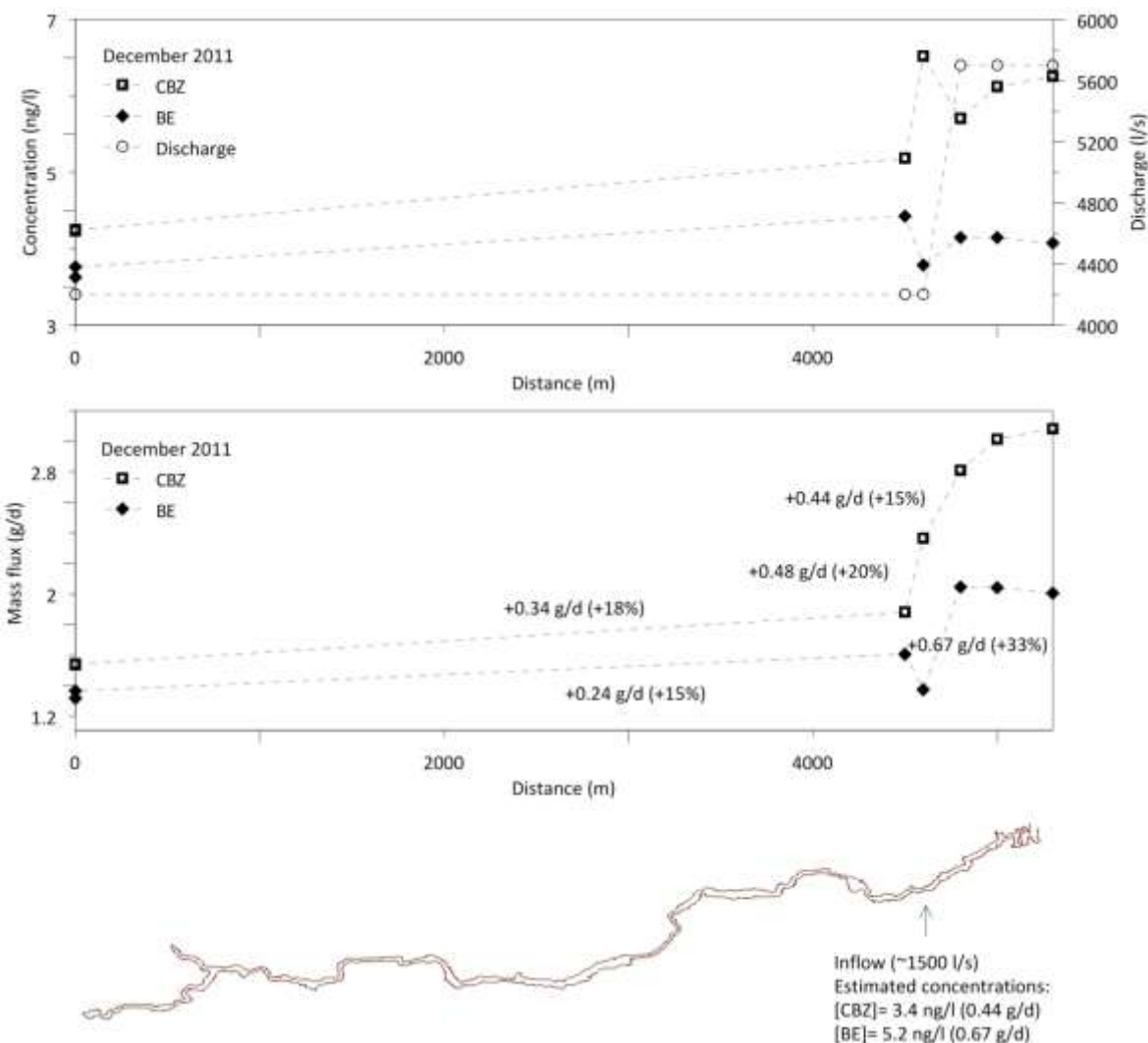


Figure 5 Behavior of benzoylecgonine and carbamazepine (mass flux and concentrations) in samples collected along the subsurface channel showing in some locations the input of additional compounds and/or effect of dilution (December 2011)

Since benzoylecgonine and carbamazepine are found at the beginning of the channel (at Daraya location) in both sampling campaigns (September 2011, December 2011), a major source of wastewater exist upstream to this location. Additionally, the concentration of benzoylecgonine and carbamazepine increases between Daraya and the next sampling locations (about 3800 m) downstream. An increase of those compounds can only be enhanced by wastewater; therefore, this implies that additional sources of carbamazepine/benzoylecgonine exist between the two points, if the quantity of wastewater is considered negligible with respect to the discharge of the spring (concentrated wastewater).

The inflow converging to the main cave is characterized by a constant mass flux of carbamazepine (0.47 g/d) in September and December 2011. Benzoyllecgonine is only found under intermediate flow periods in this same inflow (0.67 g/d), equivalent to 1.5 g/d street cocaine.

Concentrations of benzoyllecgonine fall below detection limits under low flow periods.

6.3 CONCENTRATIONS OF MICROPOLLUTANTS UNDER VARIOUS FLOW CONDITIONS IN SPRINGS

As shown in Figure 6, the concentration of carbamazepine remains constant under low flow periods (2010-2011), it is thought that the increase of carbamazepine loads with respect to background concentrations is only due to the concentrated infiltration of carbamazepine rich wastewater during events in high flow periods (Doummar, 2012). The presence of a background value could be explained by a continuous source of carbamazepine (waste water) existing on the catchment mainly upstream to Daraya. In high flow periods, most of the micropollutants (sulfamethoxazole and 1-H benzotriazole) are diluted except for carbamazepine. The loads of benzoyllecgonine have increased between 2010 and 2011; this value can only be explained by an increase in the usage of this type of drug. This increase in benzoyllecgonine loads is also observed in the Qachqouch spring between 2010 and 2011. One additional micropollutant indicator of clinical wastewater (iopamidol) was detected in the Jeita spring in December 2011.

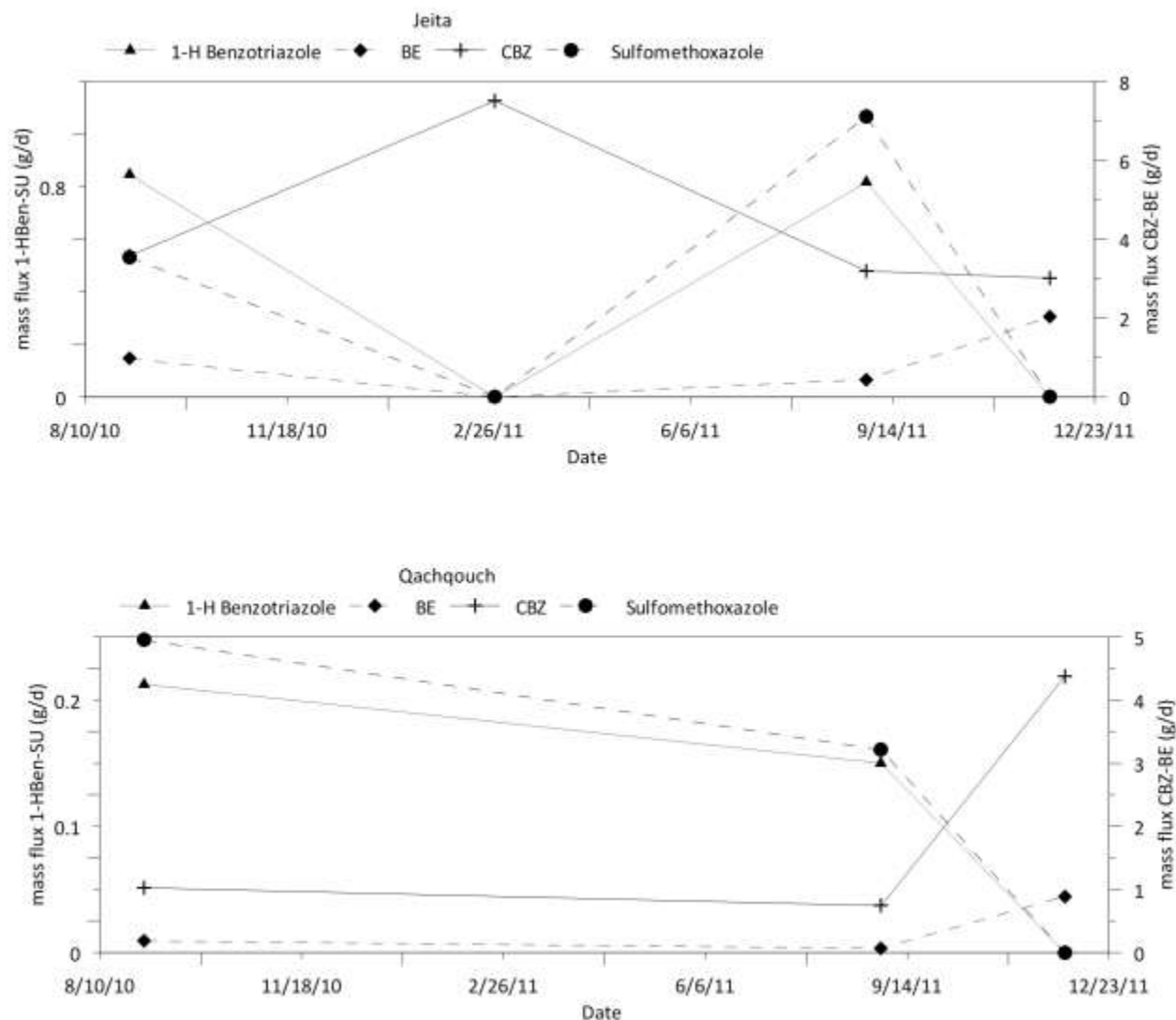


Figure 6 Mass flux (g/d) of various compounds in Jeita and Qachqouch during different sampling periods (Low flow, high flow and Intermediate flow, when discharge measurements are available)

7 SYNOPSIS AND CONCLUSIONS

The analysis of micropollutants gave insights into the type of contaminants existing in the investigated area namely in surface water and groundwater (Jeita, Qachqouch, Afqa, Laban and Assal springs). Locations where wastewater (domestic, clinical, agricultural or industrial) is being discharged in the Nahr El Kalb River where delineated. Based on masses fluxes, the variation of loads of various contaminants were compared under various flow conditions. Additionally, variations of mass fluxes of persistent compounds were tracked along the Jeita cave to depict potential locations of wastewater discharge in the catchment. A summary of the results is presented as follows:

1. Surface water- Nahr El Kalb

- Indication of contamination of surface water by wastewater from Hrajel area with persistent compounds (carbamazepine), caffeine, and benzoylecgonine. Dilution of the latter occurs further downstream before the level of the Jeita spring.
 - i. **Northern branch** (Nahr El Salib; R1) shows evidence of point source wastewater contamination and clinical wastewater between Hrajel and Kfarzebiane.
 - ii. **The middle branch** (R2) is characterized by limited concentration of micropollutants if any, it plays therefore a role in the dilution of the micropollutants in the northern branch
 - iii. **Southern branch** (R3) shows evidence of domestic wastewater; however it plays a minor role in changing the mass fluxes because of its relatively low discharge.
- Nahr El Kalb River is characterized by a downstream dilution of most of the compounds, except carbamazepine, which is introduced to the surface water from the groundwater component discharging into it (mainly Jeita) downstream to Jeita spring.

2. Groundwater- Jeita Spring

Three sources of carbamazepine and benzoylecgonine, i.e., *wastewater* exists upstream to Daraya, and within the subsurface channel as portrayed by the following:

- i. Presence of carbamazepine and benzoylecgonine in Daraya implies that a continuous source of wastewater leaching to the aquifer is discharged upstream to Daraya even during low flow periods.
- ii. Increase of concentrations of both compounds between Daraya and a location about 3500 m downstream to it, suggests that an additional inflow of carbamazepine and benzoylecgonine rich waters is responsible for the increase of concentration and mass fluxes (from 4.2 ng/l to 5 ng/l), as processes like dilution and potential degradation will result in a decrease of the concentrations.
- iii. Carbamazepine is also found in the inflow to the phreatic cave, implying the discharge of wastewater (0.43 g/d) from northern recharge areas/ villages. This mass flux remains constant under low and intermediate flow periods. Benzoylecgonine is detected in this inflow only in December with mass fluxes equivalent to 1.5 g/d of street cocaine.

Mass fluxes of carbamazepine and benzoylecgonine in the Jeita Spring are constant during low flow periods (2010, 2011). Different behaviours are observed during high flow periods:

- i. Effective dilution of benzoylecgonine concentrations (to below detection limits) are due to the high discharge rates and the low concentration of this compound.
- ii. The concentration of carbamazepine remains constant under low flow periods (2010-2011). It is thought that the increase of carbamazepine loads with respect to background concentrations is due to the

concentrated infiltration of carbamazepine following precipitation events (Doummar, 2012). The presence of a background value could be explained by a continuous source of carbamazepine (waste water) existing on the catchment mainly upstream to Daraya. It can also be assumed that given that it is highly persistent, the source of carbamazepine is present in the karst system (fissured matrix, epikarst or fast flow pathways).

- iii. Caffeine shows the same patterns as carbamazepine in groundwater; concentrations increase with an increase of discharge implying that additional loads of caffeine are further introduced to the system through infiltration of raw wastewater under high flow conditions. However it is to be noted that caffeine concentrations fall below detection limits under intermediate flow periods outside event responses.
3. The interaction between surface water and groundwater occurs downstream to Jeita, where micropollutants concentrations in surface water increase because of the inflow of spring waters into surface water. This however does not exclude the likelihood of surface water infiltration upstream to Daraya.

8 REFERENCES

- Buser, H., Poiger, T., and Muller, M. 1999. Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater. *Environmental Science and Technology*. 33: 2529-2535
- Clara, M., Strenn, B., and Kreuzinger, N. 2004. Carbamazepine as a possible anthropogenic marker in the aquatic environment: investigation on the behavior of carbamazepine in wastewater treatment and during groundwater infiltration, *Water Resources*. 38: 947-954
- Einsiedl, F., Radke, M., and Maloszewski, P. 2010. Occurrence and transport of pharmaceuticals in a karst groundwater system affected by domestic wastewater treatment plants. *Journal of Contaminant Hydrology*. 117:26-36
- Fang, Y., Karnjanapiboonwong A., Chase, D. A., Wang, J. Morse A. N., and Anderson, A. T. 2012. Occurrence, fate, and persistence of gemfibrozil in water and soil. *Environmental Toxicology and Chemistry*. 31 (3): 550-555
- Frey and Janz, 1985. H.H. Frey, D. Janz (Eds.), *Antiepileptic Drugs*, Springer Verlag, Berlin-Heidelberg (1985)
- Gasser, G., Rona, M., Voloshenko, A., Shelkov, R., Tal, N., Pankratov, I., Elhanany, S., and Lev, O. 2010. Quantitative evaluation of tracers for quantification of wastewater contamination of potable water sources. 44: 3919-925
- Ghauch, A., Baydoun H., and Dermesropian P. 2011. Degradation of aqueous carbamazepine in ultrasonic /Fe⁰/H₂O₂ systems. *Chemical Engineering Journal*. 172: 18-27
- Heberer, T. 2002. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. *Toxicol. Lett.* 131: 5–17
- Heberer, T. 2002b. Tracking persistent pharmaceutical residues from municipal sewage to drinking water. *Journal of Hydrology*. 266: 175-189
- Leclercq, M., Mathieu, O., Gomez, E., Casellas, C., Fenet, H. and Hillarie-Buys, D. 2009. Presence and fate of carbamazepine, oxcarbazepine, and seven of their metabolites at wastewater treatment plants, *Arch. Environ. Contam. Toxicol.* 56: 408-415
- Nödler, K., Licha, T., Bester, K., and Sauter, M. 2010. Development of a multi-residue analytical method, based on liquid chromatography–tandem mass spectrometry, for the simultaneous determination of 46 micro-contaminants in aqueous samples. *J. Chromatography. A* 1217: 6511-6521
- Pronk M., Goldscheider, N., and Zopfi J. 2007. Particle-size distribution as indicator for fecal bacteria contamination of drinking water from karst springs. *Environmental Science & Technology*. 41: 8400-8405.
- Scheytt, T., Mersmann, P., Lindstaedt, R., and Heberer, T. 2005 Determination of sorption coefficients of pharmaceutically active substances carbamazepine, diclofenac, and ibuprofen, in sandy sediments. *Chemosphere*. 60: 245-253

- Scheytt, T.J., Mersmann, P., and Heberer, T. 2006. Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible- displacement experiments. *J. Contaminant Hydrology*. 83: 53-69
- Ternes, T.A. 1998. Occurrence of drugs in German sewage treatment plants and rivers. *Water Resources* 32: 3245-3260
- Ternes, T. A. and R. Hirsch. 2000. Occurrence and Behavior of X-ray Contrast Media in Sewage Facilities and the Aquatic Environment. *Environmental Science & Technology*. 34: 2741-2748
- Tixier, C., Singer, H.P. Oellers, S., and Müller, R.R. 2003. Occurrence and fate of carbamazepine, clofibrac acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters, *Environmental Science & Technology*. 37:1061-1068
- Van Nuijs, ALN., Pecceu, B., Theunis, L., Dubois, N., Charlier, C., and Jorens, PG. 2009b. Can cocaine use be evaluated through analysis of wastewater? A nation-wide approach conducted in Belgium. *Addiction* 2009c; 104: 734–41
- Voutsas, D., Hartmann, P., Schaffner, C. and Giger, W. 2006. Benzotriazoles, alkylphenols and bisphenol a in municipal wastewaters and in the Glatt River, Switzerland. *Environmental Science Pollution Research International*. 13(5): 333–341
- Wittmer, K., Bader, H.-P., Scheidegger, R., Singer, H., Lück, A., Hanke, I., Carlsson C., Stamm C. 2010. Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. *Water Res.*, 44: 2850-2862
- Zuccato, E., Chiabrando, C., Castiglioni, S., Calamari, D., Bagnati, R., Schiarea, S. 2005. Cocaine in surface waters: a new evidence-based tool to monitor community drug abuse. *Environmental Health* 4:14.

9 APPENDIX A: RESULTS

Campai			Elevation_						
Sample	gn	Coding	Name	Longitude	Latitude	m	Sampling_date	Source	Type_of_water
1	1	1_1	Ch0	34.026046	35.834777	1565	22.9.11 0:00	Chabrouh	Dam
2	1	1_2	J01	33.943878	35.643877	90	22.9.11 0:00	Jeita	spring (entrance)
3	1	1_3	J02	33.943878	35.643877	90	22.9.11 0:00	Jeita	spring (entrance)
4	1	1_4	Q0	33.943974	35.637827	55	22.9.11 0:00	Qachqouch	spring
5	1	1_5	A0	34.009523	35.838656	1538	22.9.11 0:00	Assal	spring
6	1	1_6	L0	33.994732	35.828338	1643	22.9.11 0:00	Laban	spring
7	2	2_1	Q1	33.943974	35.637827	55	21.3.11 10:20	Qachqouch	spring (entrance)
8	2	2_2	R1	33.57394	35.43317	596	21.3.11 11:25	River 1 Deir Chemra	River
9	2	2_3	R2	33.956567	35.72195	572	21.3.11 11:35	River 2 Deir Chemra	River
10	2	2_4	R3	33.9434	35.714317	546	21.3.11 11:57	Abou Mizane	River
11	2	2_5	WWBC	33.923783	35.673267	673	21.3.11 13:10	Beit Chabeb	Wastewater
12	2	2_6	WWJ	33.9493	35.649283	310	21.3.11 15:05	Jeita	Wastewater
13	2	2_7	La1	33.994732	35.828338	1643	21.3.11 15:20	Laban	Spring
14	2	2_8	A1	34.009523	35.838656	1538	21.3.11 15:30	Assal	Spring
15	2	2_9	J700	33.946794	35.650422	96	21.3.11 10:00	Jeita	Spring (700 m from entrance)
16	2	2_10	WWL	33.995799	35.827815	1634	21.3.11 15:15	Labane Creek	Wastewater
17	2	2_11	HWWD	34.010908	35.794056	1202	21.3.11 14:55	River Downw to WW	River
18	2	2_12	HWWU	34.014021	35.792951	1205	21.3.11 14:45	River Upw. To WW	River
19	2	2_13	DB1	33.94234	35.591838	13	21.3.11 10:10	Dbayeh treated water	Tap_Raw
20	2	2_14	JM	33.945203	35.622981	37	21.3.11 11:30	Mokhada Dam_jeita	Spring_river
21	2	2_15	RD	33.946663	35.689083	344	21.3.11 13:40	Daraya River	River
22	2	2_16	RH1	34.010874	35.794075	1202	21.3.11 14:00	Nahr El Salib	River
23	2	2_17	DB1	33.94234	35.591838	13	24.3.11 11:00	Dbayeh_acidified	Tap
24	2	2_18	Ch1	34.026046	35.834777	1565	23.3.11 9:05	Chabrouh dam	dam water
25	2	2_19	D1	33.951381	35.690958	141	23.3.11 7:05	Daraya Tunnel_Jeita	Spring
26	2	2_20	A2	34.009523	35.838656	1538	23.3.11 7:45	Assal	Spring
27	2	2_21	La2	33.994732	35.828338	1643	23.3.11 8:00	Laban	Spring
28	2	2_22	J01	33.943878	35.643877	90	6.3.11 22:24	Jeita	spring (entrance)
29	2	2_23	J02	33.943878	35.643877	90	7.3.11 19:25	Jeita	spring (entrance)
30	2	2_24	J03	33.943878	35.643877	90	7.3.11 23:40	Jeita	spring (entrance)
31	2	2_25	J04	33.943878	35.643877	90	8.3.11 5:25	Jeita	spring (entrance)
32	2	2_26	J05	33.943878	35.643877	90	8.3.11 9:35	Jeita	spring (entrance)
33	2	2_27	J06	33.943878	35.643877	90	8.3.11 13:45	Jeita	spring (entrance)

Campai			Elevation_					
Sample gn	Coding	Name	Longitude	Latitude	m	Sampling_date	Source	Type_of_water
34	2 2_28	J07	33.943878	35.643877	90	8.3.11 19:05	Jeita	spring (entrance)
35	2 2_29	J08	33.943878	35.643877	90	8.3.11 22:55	Jeita	spring (entrance)
36	2 2_30	J09	33.943878	35.643877	90	9.3.11 4:25	Jeita	spring (entrance)
37	2 2_31	J10	33.943878	35.643877	90	9.3.11 9:25	Jeita	spring (entrance)
38	2 2_32	J11	33.943878	35.643877	90	9.3.11 13:45	Jeita	spring (entrance)
39	2 2_33	J12	33.943878	35.643877	90	9.3.11 19:10	Jeita	spring (entrance)
40	2 2_34	J13	33.943878	35.643877	90	9.3.11 23:05	Jeita	spring (entrance)
41	2 2_35	J14	33.943878	35.643877	90	10.3.11 4:35	Jeita	spring (entrance)
42	2 2_36	J15	33.943878	35.643877	90	10.3.11 9:48	Jeita	spring (entrance)
43	2 2_37	J16	33.943878	35.643877	90	10.3.11 13:50	Jeita	spring (entrance)
44	2 2_38	J17	33.943878	35.643877	90	10.3.11 19:20	Jeita	spring (entrance)
45	2 2_39	J18	33.943878	35.643877	90	10.3.11 23:55	Jeita	spring (entrance)
46	2 2_40	J19	33.943878	35.643877	90	11.3.11 6:25	Jeita	spring (entrance)
47	2 2_41	J20	33.943878	35.643877	90	11.3.11 12:20	Jeita	spring (entrance)
48	2 2_42	J21	33.943878	35.643877	90	11.3.11 21:35	Jeita	spring (entrance)
49	2 2_43	J22	33.943878	35.643877	90	12.3.11 9:15	Jeita	spring (entrance)
50	2 2_44	J23	33.943878	35.643877	90	12.3.11 23:45	Jeita	spring (entrance)
51	2 2_45	J24	33.943878	35.643877	90	13.3.11 17:50	Jeita	spring (entrance)
52	2 2_46	J25	33.943878	35.643877	90	14.3.11 17:35	Jeita	spring (entrance)
53	2 2_47	J26	33.943878	35.643877	90	15.3.11 19:00	Jeita	spring (entrance)
54	2 2_48	J27	33.943878	35.643877	90	16.3.11 14:15	Jeita	spring (entrance)
55	2 2_49	J28	33.943878	35.643877	90	19.3.11 11:20	Jeita	spring (entrance)
56	2 2_50	J29	33.943878	35.643877	90	21.3.11 16:00	Jeita	spring (entrance)
57	2 2_51	J30	33.943878	35.643877	90	22.3.11 9:15	Jeita	spring (entrance)
58	3 3_1	J01	33.943878	35.643877	104	13.9.11 12:00	Jeita	Spring (3800m from Daraya)
59	3 3_2	J02	33.942776	35.646835	99	13.9.11 13:12	Jeita	Spring (4300m from Daraya)
60	3 3_3	J03	33.943215	35.645537	98	13.9.11 13:25	Jeita	Spring (4400m from Daraya)
61	3 3_4	J04	33.946794	35.650422	96	13.9.11 13:27	Jeita	Spring (4600m from Daraya)
62	3 3_5	J05	33.943878	35.643877	90	13.9.11 13:40	Jeita	Spring (entrance; 0 m from Daraya)
63	3 3_6	D02	33.951381	35.690958	141	14.9.11 9:00	Jeita	Spring
64	3 3_7	Q02	33.943974	35.637827	55	14.9.11 17:15	Qachqouch	Spring
65	3 3_8	JTr	33.94234	35.591838	13	14.9.11 22:10	Jeita	Spring
66	3 3_9	JM	33.945203	35.622981	37	14.9.11 14:30	Kalb River	River

Campai			Elevation_					
Sample gn	Coding	Name	Longitude	Latitude	m	Sampling_date	Source	Type_of_water
67	3_3_10	J06	33.943878	35.643877		90 7.9.11 14:30	Jeita	spring (entrance)
68	3_3_11	J07	33.946794	35.650422		96 7.9.11 14:00	Jeita	spring (entrance)
69	3_3_12	Qan1	34.04211	35.808996		1595 14.9.11 15:00	Qana	Spring
70	3_3_13	La3	33.994732	35.828338		1643 14.9.11 15:44	Laban	Spring
71	3_3_14	A3	34.009523	35.838656		1538 11.9.11 14:30	Assal	Spring
72	3_3_15	A4	34.009523	35.838656		1538 14.9.11 15:34	Assal	Spring
73	3_3_16	Af1	34.066575	35.892335		1186 14.9.11 13:55	Afqa	Spring
74	4_4_1	A1	34.009523	35.838656		1538 28.12.11 11:55	Assal	Spring (entrance)
75	4_4_2	Chr	34.026046	35.834777		1565 28.12.11 12:10	Chabrouh Branch	After Chabrouh
76	4_4_3	Af	34.066575	35.892335		1186 28.12.11 14:50	Afqa	Spring (entrance)
77	4_4_4	L1	33.994732	35.828338		1643 28.12.11 11:44	Laban	Spring (entrance)
78	4_4_5	Assb	34.01042	35.836274		1507 28.12.11 12:05	Assal Branch	After Assal
79	4_4_6	Hup	34.010908	35.794056		1202 28.12.11 12:55	Nahr El Salib	Before WW Hrajel
80	4_4_7	Hdow	34.014021	35.792951		1205 28.12.11 12:30	Nahr El Salib	After WW Hrajel
81	4_4_8	Kfr	33.999978	35.762861		1129 28.12.11 22:40	Nahr el Salib	KfarZebiane Bridge
82	4_4_9	HWW10	34.010874	35.794075		1202 28.12.11 12:40	Hrajel	WW Hrajel
83	4_4_10	HWW20	34.010874	35.794075		1202 28.12.11 12:40	Hrajel	WW Hrajel
84	4_4_11	J1	33.943878	35.643877		90 28.12.11 14:00	Jeita	Spring (entrance)
85	4_4_12	J2	33.942145	35.648887		94 28.12.11 12:00	Jeita	Spring (500 m from entrance)
86	4_4_13	Q1	33.943974	35.637827		55 28.12.11 12:00	Qachqouch	Spring
87	4_4_14	R3	33.9434	35.714317		521 28.12.11 12:00	Nahr El Kalb River	Abu Mizane
88	4_4_15	R2	33.95439	35.72134		571 28.12.11 12:00	Nahr El Kalb River	southern branch
89	4_4_16	R1	33.95466	35.72128		572 28.12.11 12:00	Nahr El Kalb River	northern Branch
90	4_4_17	RQ	33.944344	35.637434		54 28.12.11 12:00	Nahr El Kalb River	After Qachqouch
91	4_4_18	DR	33.946663	35.689083		344 28.12.11 12:00	Nahr El Kalb River	Daraya
92	4_4_19	M-1	33.945203	35.622981		37 28.12.11 12:00	Mokhada canal	Spring/ River Station LWA
93	4_4_20	WQ	33.943974	35.637827		55 28.12.11 12:00	Well Qachqouch	Well next to spring
94	4_4_21	D1	33.951381	35.690958		141 3.1.12 16:07	Jeita spring	Daraya main tunnel
95	4_4_22	D2	33.951381	35.690958		141 3.1.12 16:10	Jeita spring	Daraya main tunnel
96	4_4_23	J3	33.946386	35.651023		98 3.1.12 13:30	Jeita spring	Spring (4500m from Daraya)
97	4_4_24	J4	33.946794	35.650422		96 3.1.12 13:45	Jeita spring	Spring (4600m from Daraya)
98	4_4_25	J5	33.946437	35.648185		94 3.1.12 13:47	Jeita spring	Spring (4800m from Daraya)
99	4_4_26	J6	33.945355	35.646237		93 3.1.12 13:49	Jeita spring	Spring (5000m from Daraya)
100	4_4_27	J7	33.943878	35.643877		90 3.1.12 13:55	Jeita spring	Spring (entrance)
101	4_4_28	L2	33.994732	35.828338		1643 28.12.11 11:44	Laban	Spring (entrance)

Application			Antibiotics					Lipid regulators			Antihistamines			Anticonvulsants and sedatives			SSRI			Pesticides and pesticide metabolites						Corrosion inhibitors				
Compound			Clarithromycin	Erythromycin	Roxithromycin	Sulfamethoxazole	Trimethoprim	Bezafibrate	Clofibric acid	Gemfibrozil	Cetirizine	Loratadine	Carbamazepine	Diazepam	Primidone	Tetrazepam	Citalopram	Fluoxetine	Sertraline	Atrazine	Desethylatrazine	Desisopropylatrazine	Diuron	Isoproturon	Mecoprop	Metazachlor	1H-Benzotriazole	Tolyltriazole	Benzoyllecgonine	Pantoprazole
[ng/l]			7.5	4.3	9.5	2.6	2.5	3.5	3.4	2.0	2.2	2.7	2.2	1.4	2.7	2.5	3.2	16	16	1.4	1.7	5.6	3.3	3.0	1.2	1.8	4.70	4.9	2.3	4.8
Coding	Code	Sampling_date	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1_1	Ch0	22.9.11 0:00	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1_2	J01	22.9.11 0:00	-	-	-	4.39	-	-	-	-	-	29.61	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.99	-	3.46	-
1_3	J02	22.9.11 0:00	-	-	-	3.762	-	-	-	-	-	30.66	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.23	-	2.89	-
1_4	Q0	22.9.11 0:00	-	-	-	14.33	-	2.988	-	-	-	59.35	3.424	-	-	-	-	-	-	-	-	-	-	-	-	-	12.29	6.79	4.54	-
1_5	A0	22.9.11 0:00	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1_6	L0	22.9.11 0:00	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_1	Q1	21.3.11 10:20	-	-	-	-	-	-	-	-	-	12.55	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_2	R1	21.3.11 11:25	-	-	-	-	-	10.87	-	-	-	5.192	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	16.5	-
2_3	R2	21.3.11 11:35	-	-	-	-	-	4.72	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_4	R3	21.3.11 11:57	-	-	-	-	-	63.2	-	-	-	7.63	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.09	-
2_5	WWBC	21.3.11 13:10	-	-	-	-	-	1424	28.28	-	227.2	-	-	-	-	-	-	-	-	-	-	-	-	6.1	-	-	-	-	104	-
2_6	WWJ	21.3.11 15:05	-	-	-	-	-	299.5	153.7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1346.10	451	-	-
2_7	La1	21.3.11 15:20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_8	A1	21.3.11 15:30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_9	J700	21.3.11 10:00	-	-	-	-	-	-	-	-	-	6.56	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_10	WWL	21.3.11 15:15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	19	-	-	12.43	26.1	-	-
2_11	HWWDD	21.3.11 14:55	-	-	-	-	-	28.26	-	-	104.8	-	-	-	-	-	-	-	-	-	-	-	-	2.8	-	-	-	-	217	-
2_12	HWWU	21.3.11 14:45	-	-	-	-	-	42.21	25.19	-	91.19	-	-	-	-	-	-	-	-	-	-	-	-	2.8	-	-	-	-	252	-
2_13	DB1	21.3.11 10:10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_14	JM	21.3.11 11:30	-	-	-	-	-	-	-	-	-	9.244	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_15	RD	21.3.11 13:40	-	-	-	-	-	25.25	-	-	3.674	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.07	-
2_16	RH1	21.3.11 14:00	-	-	-	-	-	2.102	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_17	DB1	24.3.11 11:00	-	-	-	-	-	-	-	-	7.938	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2_18	Ch1	23.3.11 9:05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Application			Antibiotics					Lipid regulators			Antihistamines			Anticonvulsants and sedatives			SSRI			Pesticides and pesticide metabolites						Corrosion inhibitors				
Compound			Clarithromycin	Erythromycin	Roxithromycin	Sulfamethoxazole	Trimethoprim	Bezafibrate	Clofibric acid	Gemfibrozil	Cetirizine	Loratadine	Carbamazepine	Diazepam	Primidone	Tetrazepam	Citalopram	Fluoxetine	Sertraline	Atrazine	Desethylatrazine	Desisopropylatrazine	Diuron	Isoproturon	Mecoprop	Metazachlor	1H-Benzotriazole	Tolytriazole	Benzoyllegonine	Pantoprazole
[ng/l]			7.5	4.3	9.5	2.6	2.5	3.5	3.4	2.0	2.2	2.7	2.2	1.4	2.7	2.5	3.2	16	16	1.4	1.7	5.6	3.3	3.0	1.2	1.8	4.70	4.9	2.3	4.8
4_2	Chr	28.12.11 12:10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4_3	Af	28.12.11 14:50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4_4	L1	28.12.11 11:44	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.64	-	-	-
4_5	Assb	28.12.11 12:05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.4	-	-
4_6	Hup	28.12.11 12:55	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.09	-	-	-	-
4_7	Hdow	28.12.11 12:30	-	-	-	-	-	-	5.822	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.99	-	4.58	-	-
4_8	Kfr	28.12.11 22:40	-	-	-	-	-	-	12.97	-	6.33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	11.7	-	-
4_9	HWW10	28.12.11 12:40	-	-	-	-	-	-	1571	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	548.65	-	101	-	-
4_10	HWW20	28.12.11 12:40	-	-	-	-	-	-	1571	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	548.65	-	101	-	-
4_11	J1	28.12.11 14:00	-	-	-	-	-	-	-	-	8.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4_12	J2	28.12.11 12:00	-	-	-	-	-	-	-	-	7.232	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4_13	Q1	28.12.11 12:00	-	-	-	-	-	-	2.826	-	23.02	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.68	-	-
4_14	R3	28.12.11 12:00	8.7	-	-	-	-	-	24.14	3.886	-	11.54	-	19.73	-	-	-	-	-	29	-	-	-	-	-	-	5.95	-	-	-
4_15	R2	28.12.11 12:00	-	-	-	-	-	-	9.464	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4_16	R1	28.12.11 12:00	-	-	-	-	-	-	5.43	-	4.186	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.58	-	-
4_17	RQ	28.12.11 12:00	-	-	-	-	-	-	10.81	-	6.758	-	-	-	-	-	-	-	-	5.59	-	-	-	-	-	-	-	6.8	-	-
4_18	DR	28.12.11 12:00	-	-	-	-	-	-	10.13	-	2.554	-	-	-	-	-	-	-	-	5.58	-	-	-	-	-	-	-	7.47	-	-
4_19	M-1	28.12.11 12:00	-	-	-	-	-	-	-	-	8.182	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4_20	WQ	28.12.11 12:00	-	-	-	11.07	-	-	-	-	-	20.77	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.62	-	-
4_21	D1	3.1.12 16:07	-	-	-	-	-	-	-	-	4.238	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.63	-	-
4_22	D2	3.1.12 16:10	-	-	-	-	-	-	-	-	4.248	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.76	-	-
4_23	J3	3.1.12 13:30	-	-	-	-	-	-	-	-	5.184	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.43	-	-
4_24	J4	3.1.12 13:45	-	-	-	-	-	-	-	-	6.524	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.78	-	-
4_25	J5	3.1.12 13:47	-	-	-	-	-	-	-	-	5.706	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.15	-	-

Application	Antibiotics					Lipid regulators			Antihistamines			Anticonvulsants and sedatives			SSRI			Pesticides and pesticide metabolites						Corrosion inhibitors				
Compound	Clarithromycin	Erythromycin	Roxithromycin	Sulfamethoxazole	Trimethoprim	Bezafibrate	Clofibric acid	Gemfibrozil	Cetirizine	Loratadine	Carbamazepine	Diazepam	Primidone	Tetrazepam	Citalopram	Fluoxetine	Sertraline	Atrazine	Desethylatrazine	Desisopropylatrazine	Diuron	Isoproturon	Mecoprop	Metazachlor	1H-Benzotriazole	Tolytriazole	Benzoylcegonine	Pantoprazole
[ng/l]	7.5	4.3	9.5	2.6	2.5	3.5	3.4	2.0	2.2	2.7	2.2	1.4	2.7	2.5	3.2	16	16	1.4	1.7	5.6	3.3	3.0	1.2	1.8	4.70	4.9	2.3	4.8
4_26 J6 3.1.12 13:49	-	-	-	-	-	-	-	-	-	-	6.122	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.15	-
4_27 J7 3.1.12 13:55	-	-	-	-	-	-	-	-	-	-	6.26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.07	-
4_28 L2 28.12.11 11:44	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-