

Deliverable D6.1

Environmental and health impact of an unplanned indirect reuse scheme

Study of impact of Les Herbiers urban wastewater treatment plant on the water quality of La Bultière reservoir used for drinking water production



The project "Innovation Demonstration for a Competitive and Innovative European Water Reuse Sector" (DEMOWARE) has received funding from the European Union's 7th Framework Programme for research, technological development and demonstration, theme ENV.2013.WATER INNO&DEMO-1 (Water innovation demonstration projects) under grant agreement no 619040

Deliverable Title	D6.1 Environmental & Health impact of an unplanned indirect reuse scheme
	Study of impact of Les Herbiers urban wastewater treatment plant on the water quality of La Bultière reservoir used for drinking water production
Related Work Package:	WP6: Demonstration of the project outcomes in an integrated case study: the Vendée Greenfield site
Deliverable lead:	Vendée Eau
Author(s):	Jérôme BORTOLI (Vendée Eau), Isabelle SAUDRAIS (VeRI), Solenne GRELIER (VeRI), Emmanuel SOYEUX (VeRI), Marie-Pierre DENIEUL (VeRI), with the support of Pascal BERMOND-GONNET (Veolia Eau)
Contact for queries	Marie-Pierre Denieul VeRI, Chemin de la Digue, F-78603 Maisons-Laffite Cedex T +33 1 34 93 81 22, E marie-pierre.denieul@veolia.com
Dissemination level:	Public
Due submission date:	2/29/2015
Actual submission:	
Grant Agreement Number:	619040
Instrument:	FP7-ENV-2013-WATER-INNO-DEMO
Start date of the project:	01.01.2014
Duration of the project:	36 months
Website:	www.demoware.eu
Abstract	This report presents the results of the task 6.1 "Environmental & Health impact of an unplanned indirect reuse scheme; Study of impact of Les Herbiers urban wastewater treatment plant (WWTP) on the water quality of La Bultière reservoir used for drinking water production" undertaken during the DEMOWARE project. This study of pollutant's fate in the aquatic environment relies on a two-year analytical campaign based on main nutrients, microbiological and biological indexes, metals and mi- cropollutants. It shows a real impact of the WWTP on the river water qual- ity at the discharge point, but the water reservoir does not show higher pollution than the water upstream of the WWTP. The methodology and conclusions of the study will be used, in the tasks 6.3 and 6.4 to assess the possible environmental and health impacts of a planned indirect re- use scheme (the system of Les Sables d'Olonne WWTP and Le Jaunay res- ervoir), not linked so far.

Versioning and Contribution History

Version	Date	Modified by	Modification reason
v.01	7/1/2015	Solenne Grellier, Emmanuel Soyeux, Marie- Pierre Denieul	Initial draft
v.02	19.01.2016	Emmanuel soyeux, Marie- Pierre Denieul	1st revision
v.03	03.02.2016	Marie-Pierre Denieul	2 nd revision: comments J. Bortoli
v.04	13.02.2016	Xavier Martinez	Initial review
V0.5		Solenne Grellier, Emmanuel Soyeux, Marie- Pierre Denieul	Modifications to address reviewer comments
v.06	01.06.2016	Rita Hochstrat	2 nd review and check of how reviewer 1 com- ments were addressed
v.07	09.09.2016	Emmanuel Soyeux, Marie- Pierre Denieul	3 rd revision
v.08	14.09.2016	Xavier Martinez	Second review
v.09	11.10.2016	Emmanuel Soyeux, Marie- Pierre Denieul	4 th revision
	17.10.2016	Xavier Martinez	Final editing

Table of contents

Ve	ersioning	and Contribution History	iii
Та	ble of co	ntents	iv
Lis	st of figur	es	v
Lis	st of table	S	vii
Ac	ronyms		ix
Ex	ecutive S	ummary	1
1	Introduc	tion	2
2	Study ar	ea main features	3
	2.1	La Bultière reservoir catchment area	3
	2.2	Hydrology	4
3	Method	ology	6
	3.1	Water Quality monitoring	6
	3.2	Aquatic environment quality assessment	11
4	Results.		15
	4.1	Water quality monitoring	15
	4.2	Water quality monitoring - Chemical fingerprints	26
	4.3	Aquatic environment quality assessment	31
	4.4	Self-purification in La Bultière reservoir	33
5	Conclusi	on	36
	5.1	Main results for La Bultière unplanned indirect reuse scheme;	36
	5.2	The advantages and limitations of the methodology used in this study;	36
	5.3	Lessons learned and recommendation for the planned indirect reuse scheme	37
6	Referen	ces	38
7	Appendi	xes	39
	7.1	Appendix 1 Measurement points and field survey	39
	7.2	Appendix 2 French water regulation applicable to wastewater and raw water	47
	7.3	Appendix 3 River flows	54
	7.4	Appendix 4 Families of compounds measured	64
	7.5	Appendix 5 Water quality results	66
	7.6	Appendix 6 Biological index results	73
	7.7	Appendix 7 61 marker compounds of Les Herbiers WWTP discharge	79

List of figures

Figure 1	La Bultière unplanned indirected reuse and Le Jaunay planned indirect reuse 2
Figure 2	La Grande Maine river, a tributary of Sèvre Nantaise river
Figure 3	Location of the WWTPs upstream La Bultière reservoir 4
Figure 4	Hydrology of La Grande Maine 5
Figure 5	Rain in Les Herbiers, flows in La Grande Maine and share of Les Herbiers WWTP discharge in the river (2014-2015)
Figure 6	Positioning of sampling points on La Grande Maine River7
Figure 7	Localization of sampling points along La Grande Maine River and tributaries
Figure 8	Concentration and loads of Nitrates16
Figure 9	Concentration and Loads of Orthophosphates 16
Figure 10	Concentration and load of TOC 17
Figure 11	Concentration and loads of <i>E. coli</i>
Figure 12	Concentration and loads of Enterococci 18
Figure 13	Concentration and flux of Cryptosporidium 18
Figure 14	Concentration and flux of Gardia 19
Figure 15	Concentration and flux RNA specific bacteriophage 19
Figure 16	Concentration and flux of sulphate reducing bacteria 20
Figure 17	Concentration and load of Diuron 21
Figure 18	Concentration and load of AMPA 21
Figure 19	Concentration and load of Glyphosate 21
Figure 20	Concentration and load of Caffeine 22
Figure 21	Concentration and load of Iomeprol 23
Figure 22	Concentration and load of lopromide 23
Figure 23	Concentration and load of Diclofenac 24
Figure 24	Concentration and load of Paracetamol 24
Figure 25	Concentration and load of Carbamazepine 24
Figure 26	Concentration and load of Metoprolol 25
Figure 27	Concentration and load and Propanolol25
Figure 28	Concentration and load of Oxazepam 26
Figure 29	Concentration (µg/l) and flux (µg/s) of Estrone
Figure 30	Distribution of the 327 compounds identified during 6 campaigns analysis 27
Figure 31	Evolution of the number of molecules identified by sampling point per family between 6 analytical campaigns (Levels 2 and 3) 27
Figure 32	Evolution of the intensity of the response molecules identified by sampling point per family between 6 analytical campaigns (Levels 2 and 3)
Figure 33	Evolution of the response stream of molecules identified by sampling point per family between 6 analytical campaigns (Levels 2 and 3)
Figure 34	Repartition by families of compounds markers at Les Herbiers WWTP (Levels 2 and 3)
Figure 35	Theoretical and monitored concentration in La Bultière reservoir – Example of Caffeine

Figure 36	Location Map of measurement points upstream Les herbiers WWTP 40
Figure 37	Location Map of measurement point Grande Maine river at la Favrie
Figure 38	Location Map of measurement point on the stream "Le Grand Ry" 42
Figure 39	Location Map of measurement point on the stream "Le Longuenais" 43
Figure 40	Location Map of measurement point on the stream "La Tricherie"
Figure 41	Location Map of measurement point on "La Grande Maine" donwsntream "La Tricherie" and on the stream "La Poisetière"
Figure 42	Location Map of measurement point on "La Grande Maine" at le Plessis des Landes45
Figure 43	Location Map of measurement points on la Bultière reservoir 46
Figure 44	French legislation on raw water quality requirements for the production of drinking water (continued)
Figure 45	French legislation on raw water quality requirements for the production of drinking water (continued)

List of tables

Table 1	Key features of La Bultière catchment area	2
Table 2	Main characteristics of the 6 WWTPs in La Bultière catchment area	4
Table 3	Water quality monitoring measurement points	7
Table 4	List of analyses undertaken in 2014 and 2015	9
Table 5	Main features of the water quality monitoring program	10
Table 6	Ecological classes of the IBD	12
Table 7	Ecological classes of the IBG	13
Table 8	Ecological classes of the IBMR	13
Table 9	Interpretation grid of sensitive species (according Lafond, 2007)	14
Table 10	Ecological status classes based on the IOBL	14
Table 11	Average concentration and load of metals	22
Table 12	List of the 22 recurrents compounds of La Grande Maine River	29
Table 13	Evolution of the ecological status of La Grande Maine (upstream to downstream)	32
Table 14	Ecological status of La Bultière reservoir	32
Table 15	Abatement in La Bultière reservoir	34
Table 16	Measurement points and purpose	39
Table 17	Industrial effluents incomings in Les Herbiers WWTP	41
Table 18	Minimum purifying requirements for Les Herbiers WWTP, according to Decree of J 22, 2007	une 47
Table 19	List of priority substances in the field of water policy	48
Table 20	List of priority substances in the field of water policy	50
Table 21	Flows on April 24, 2014	54
Table 22	Flows on May 21, 2014	55
Table 23	Flows on June 30, 2014	55
Table 24	Flows on July 31, 2014	56
Table 25	Flows on September 3, 2014	56
Table 26	Flows on September 26, 2014	57
Table 27	Flows on October 28, 2014	57
Table 28	Flows on November 25, 2014	58
Table 29	Flows on December 29, 2014	58
Table 30	Flows on January 28, 2015	59
Table 31	Flows on March 4, 2015	60
Table 32	Flows on March 23, 2015	60
Table 33	Flows on April 8, 2015	61
Table 34	Flows on April 8, 2015	61
Table 35	Flows on May 26, 2015	62
Table 36	Flows on June 29, 2015	62
Table 37	Flows on July 27, 2015	63
Table 38	Flows on August 31, 2015	63
Table 39	IBD ecological status of La Grande Maine at Les Herbiers (2015)	73

Table 40	IBD ecological status of La Grande Maine at upstream La Bultière reservoir (2015) 74
Table 41	IBG ecological status of La Grande Maine at Les Herbiers (2015)75
Table 42	IBG ecological status of La Grande Maine at upstream La Bultière reservoir (2015) 75
Table 43	IBMR ecological status of La Grande Maine at Les Herbiers (2015)77
Table 44	IBMR ecological status of La Grande Maine at upstream La Bultière reservoir (2015)
Table 45	Markers of La Bultière WWTP discharge

Acronyms

2,4 D	2,4-Dichlorophenoxyacetic acid
2,4 MCPA	4-chloro-2-methylphenoxyacetic acid
AMPA	Aminomethylphosphonic acid
AOX	Adsorbable Organic Halogen
ARS	Agence Régionale de Santé (French Regional Health Agency)
BOD ₅	Biological Oxygen Demand at 5 days
BTEX	Benzene, toluene, ethylbenzene, and xylene-volatile aromatic compounds
ССО	Communité de Commune des Olonnes (Conurbation of Sables d'Olonne)
COD	Chemical Oxygen Demand
DEHP	Di(2-EthylHexyl) Phthalate
DDD	DichloroDiphenylDichloroethane
DDE	DichloroDiphenyldichloroEthylene
DDT	DichloroDiphenylTrichloroethane
DWTP	Drinking Water Treatment Plant
HAP	Polycyclic aromatic hydrocarbons
IBD	Biological Index of Diatom Species
IBGN	Biotic Index
IBMR	Biological Index of Macrophytes in River
IOBL	Oligochaetes Index of Bioindication Lacustre
LD50	Lethal Dose, 50%
LQ	Limit of quantification
NGF	Nivellement Général de la France used to indicate the height above sea level
NGL	Global nitrogen
NTK	Total nitrogen kjeldhal
PAH	Polycyclyc Aromatic Hydrocarbons
PCB	Polychlorophenols
PE	Population Equivalent
PFOS	PerFluoroOctaneSulfonate
RSDE	Réduction des rejets de Substances Dangereuses dans les Eaux (Reduction of hazardous substances discharges in water)
TDS	Total dissolved salts
ТОС	Total organic carbon
TSS	Total suspended solids
WFD	Water Framework Directive
WWTP	Waste Water Treatment Plant

Executive Summary

This report of DEMOWARE project Work Package 6 presents the results of the impact study of Les Herbiers urban wastewater treatment plant on the water quality of La Bultière reservoir used for drinking water production.

The methodology for studying La Grande Maine River catchment area where Les Herbiers urban WWTP discharges in the upper catchment of the river which then flows to La Bultière reservoir. The results obtained during the two-year measurement campaigns (with six analytical campaigns) are presented and discussed in order to identify the different issues that are/can be encountered for an indirect reuse scheme used to feed a reservoir used for production of drinking water.

The results will be compared (in deliverable D6.3) to water quality analyses from another urban wastewater treatment plant (Les Sables d'Olonne WWTP) and a reservoir close by (Le Jaunay reservoir), not linked so far, but that could be foreseen as a planned reuse scheme.

During these campaigns, numerous parameters were studied: typical physico-chemical parameters, metals, micropollutants (quantitative analyses and chemical fingerprints), microbiological parameters and biological indices.

This two-year study shows:

- For main nutrients (nitrogen, phosphorus and total organic carbon), the pollution load from runoff or non-treated wastewater is higher than the load from Les Herbiers WWTP;
- The same trend is observed for metals;
- The monitoring of the microbiological indexes shows a self-purification in the aquatic environment (along the Grande Maine river);
- For the organic micropollutants, even if les Herbiers WWTP discharged them during every monitoring campaign, self-purification occurs as their concentration at la Bultière DWTP intake are similar to the concentrations observed upstream of the WWTP;

The self-purification in La Grande Maine River is difficult to assess as several inputs occur along the river. But a self-purification in the Bultière reservoir seems to happen. Analytical measurements on sediments could help to confirm the results and the mass balance for several parameters, as metals, carbon. The selfpurification results in this report are just an estimate of the real self-purification occurring in the studied systems.

1 Introduction

The department of Vendée (85), France, **regularly faces risks of water scarcity** from May to October along its coastline, due to the influx of tourists and crop irrigation. Hence, indirect reuse of treated wastewater treatment plants is envisaged as an additional water resource.

Within the European project DEMOWARE, **VENDEE EAU** wants to study if the indirect reuse of treated wastewater discharged upstream of a water reservoir, used for the production of drinking water, is possible, on basis on the existing reservoir of La Bultière, which is located in the same area but more in the countryside (similar climatic and hydrologic conditions).

The existing case of La Bultière is a typical example of an unplanned indirect reuse of treated wastewater: the drinking water treatment plant of La Bultière is supplied by water from an artificial dam in which the urban WWTP Les Herbiers discharges its treated effluents 21 km upstream through La Grande Maine river.

VENDEE EAU intends to use the assessment of pollutant's fate of the **unplanned** indirect wastewater reuse scheme of La Bultière to study the feasibility conditions of a **planned** indirect reuse of wastewater from a coastal urban WWTP (CCO) upstream of Le Jaunay reservoir used for drinking water production. As hown in Figure 1, the distance between those two reservoir is 50 km and their volume are similar.



Figure 1 La Bultière unplanned indirected reuse and Le Jaunay planned indirect reuse

In this context, **this report** presents the assessment of the fate of pollutants from Les Herbiers WWTP discharge down to La Bultière DWTP intake. Its findings will raise the different issues to address to design an indirect reuse scheme used to feed a similar neighbour reservoir used for production of drinking water.

Catchment area	154 km²	
Stored volume	5.0 Mm ³	
DW production	5.0 Mm³/y - 22,000 m³/d	
River flow	Mean: 1,600 L/s From June to September: 63 - 241 l/s	
WWTPs	5 WWTPs (6,000 PE)	
	Les Herbiers (28,000 PE - 5,000 m ³ /d) Average: 3,000 m ³ /d	

Table 1 Key features of La Bultière catchment area

2 Study area main features

2.1 La Bultière reservoir catchment area

La Bultière reservoir was commissioned in 1994 in order to supply in drinking water the north-eastern part of the department of Vendée (85), in the west of France. The dam was built over La Grande Maine river which is a tributary of La Sèvre-Nantaise (Figure 2).The catchement area upstream the reservoir covers 154 km². La Grande Maine originates 3 km north of Les Herbiers. Its main tributary are "Le Longuenais", "Le Grand Ry", "La Poisetière" and "La Tricherie".

The main land uses according to Corine Land Cover are: arable lands (50%), heterogeneous agricultural areas (26%), pastures (13%) and urban zones (5%). In this rural areas, the main city is Les Herbiers (16,500 inhabitants) followed by la Gaubretière (3,100 inhabitants), Beaurepaire (2,400 inhabitants), Mesnard La Barotière (1,400 inhabitants) and Bazoges-en-Paillers (1,300 inhabitants).



Figure 2 La Grande Maine river, a tributary of Sèvre Nantaise river

The urban wastewater treatment plants (WWTP) corresponds to the cities listed above, the one with the largest capacity being Les Herbiers (Table 2) which also treats industrial effluents. Their locations are shown on the map below (Figure 3)

	Table 2	Main characteristics of the 6 WWTPs in La Bultière catchment area
--	---------	---

WWTP	P.E.		Average flow in 20	013	Treatment
			m³/h	m³/day	Process
Les Herbiers		28,000	120	2,910	Activated sludge
Mesnard-la Barotière	900		4	90	Lagooning
La Tricherie	150		0.1	3	Reed bed filter
La Gaubretière	1,800	6,000	9	207	Lagooning
Beaurepaire	1,800	-	11	263	Lagooning
Bazoges-en-Paillers	1,500		7	165	Lagooning





2.2 Hydrology

In the catchment area of La Bultière, as the main rocks present are mainly volcanic and metamorphic, there is no important aquifer. Thus, without aquifer drainage towards the rivers, La Grande Maine and its tributaries flows are strongly related to rain. Hence, the base flows are low during dry period in summer (Figure 4) and the flows decreases quickly after a rain event (Figure 5).

With an average flow of 3,000 m³/d, Les Herbiers WWTP discharge can represent more than a third of the flow feeding La Bultière reservoir in July and August. Its share was assessed thanks to the monthly flow measurement campaigns undertook from April 2014 to August 2015. According to 18 measurements, the share is below 10% during high flows and above 10% during low flows with a maximum of 55% in september 2014 (Figure 5).







Figure 5 Rain in Les Herbiers, flows in La Grande Maine and share of Les Herbiers WWTP discharge in the river (2014-2015)

3 Methodology

The methodology was designed in order to:

- assess the pollutant's fate from the Les Herbiers WWTP discharge into La Grande Maine river down to the La Bultière reservoir with a particular emphasis on studying the self-purification that can occur either in the river or in the reservoir as well as highlighting other source of contamination (e.g. other WWTP or tributaries);
- assess the quality of the aquatic environment under the influence of Les Herbiers WWTP discharge: la Grande Maine river and La Bultière reservoir.

3.1 Water Quality monitoring

3.1.1 Water quality monitoring program

The water quality monitoring relies on 13 sampling points enabling to study what happens in different river stretches under the influence of either Les Herbiers WWTP or La Grande Maine river tributaries. They are located upstream and downstream of Les Herbiers WWTP on the main stream "La Grande Maine" as well as its tributaries (see Figure 7). The description of the sampling points is given in Table 3 and detailed in Appendix 1.

Table 3 Water quality monitoring measurement points

Point	Measurements	Characteristics	Kilometer point in km (*)
P1	Flow	La Grande Maine upstream at Le Bignon	- 0.8
P1'	Water quality	La Grande Maine downstream industrial area stormwater network discharge	- 0.5
P1"	Flow	Discharge of industrial area stormwater network	-
P2	Flow Water quality	Discharge of Les Herbiers WWTP (28,000 PE)	0
P3	Flow Water quality	La Grande Maine at "La Favrie" where the mixing of les Herbiers WWTP discharge and the river is supposed to be completed	+ 1.5
P4	Flow	Stream "Le Grand Ry", first major tributary of La Grande Maine, with no WWTP in its catchment area	+ 6
P5	Flow	Stream "Le Longuenais" with the Mesnard la Barotière WWTP (900 PE) in its catchment	+ 8
P6	Flow	Stream "La Tricherie" with la Tricherie WWTP (150 PE) in its catch- ment area	+ 9
P7	Flow Water quality	La Grande Maine	+ 11.8
P8	Flow	Stream "La Poisetière", the largest tributary of La Grande Maine with 2 WWTP in its catchment: Beaurepaire (1,800 PE) and Gau- bretière (1,800 PE)	+ 12
Р9	Flow Water quality	La Grande Maine at Le Plessis des Landes, official measurement of the stream flow, where the flows and the water quality entering the reservoir can be assessed	+ 15
P10	Water quality	La Bultière reservoir: Preuilly Bridge over the reservoir	
P11	Water quality	La Bultière reservoir: water intake of the Drinking Water Treat- ment Plant	

(*) distance between measurement points and discharge point of Les Herbiers WWTP



Figure 6 Positioning of sampling points on La Grande Maine River



Figure 7 Localization of sampling points along La Grande Maine River and tributaries

The compounds to be monitored were taken from the list of prioritary substances mentioned in the Decree of June 22, 2007 related to wastewater discharge, RSDE list (French regulation list of Dangerous Substances Discharged in the Environment) and raw water used for drinking production French regulation:

- Physico-chemical parameters such as TSS, COD, nitrogen and phosphorus;
- Quantitative analysis of micropollutants¹: 109 micropollutants were analysed once in June 2014 and then the 19 substances found were monitored 5 times in 2015. These micropollutants were metalic and organic such as contrast agents, pharmaceuticals, hormones, PCB, Pesticides (see Appendix 4 for more details about these families)
- Qualitative analysis of micropollutants: were also undertaken using the method detailed in the Work Package 2 "Process monitoring and performance control, Task 2.2 "Monitoring and control of chemical contaminants", Subtask "22.1 Establishing and improving chemical fingerprinting to better characterise chemical contamination". These fingerprints enable a real mapping of present micropollutants in samples, on basis of screening analyses types realized in liquid chromatography (LC) and gas chromatography (GC) to cover the widest possible range of compounds. The molecules identified by these technologies belong to the following families: pesticides, pharmaceuticals, HAP, PCB and biocides.
- **Microbiology**: Bacteria indicating faecal contamination, associated parasites and indicators, viruses and indicators of viral contamination. These parameters are used in the regulation for raw water supply: they are either index of fecal contamination (E.Coli and Enterococci), or index of

¹ The properties of these micropollutants can be found in Appendix 4

wastewater treatment efficiency (sulphate reducing bacteria, parasites). In the absence of regulations on the microbiological quality of treated wastewater, it was decided to use raw water supply regulation. The measured pathogens are index of human and animal contamination. They can be classified according their resistance and their average concentration in water (from the less to the more resistant and from the more to the less concentrated in the environment): E. coli, Enterococci, Anaerobic sulphur-reducing bacteria, Cryptosporidium and Giarda.

Daily average sample were taken during 6 monitoring campaigns:

- One on June 2014, during low water where the highest concentrations were anticipated to screen the list of micropollutants and to include in the next monitoring campaign the micropollutants detected;
- 5 in 2015, in March and May during high water and in June, July and August during low water.

The Table 4 details the water analysis undertaken during the monitoring campaign of 2014 and 2015.

During the monitoring campaign, flow measurements were also performed in order to assess the loads (see Appendix 3).

Table 4List of analyses undertaken in 2014 and 2015

Compound	2014*	2015**
Physico-chemical		
Ammonium, Nitrates, Kjeldahl Nitrogen, Orthophosphates, Total Organic Carbon	х	х
Microbiology		
Cryptosporidium, Giardia, E. coli, Enterococci, Sulphate reducing bacteria, somatic coliphages, RNA		Х
specific bacteriophages, Enterovirus		
Radiocontrast Agents		
Diatrozoic acid, Iothalamic acid, Ioxithalamic acid, Iohexol	Х	
Iomeprol, Iopamidol, Iopromide	Х	Х
Pharmaceuticals		
2-hydroxy-ibuprofen, Ibuprofen, Phenazone, Fluoxetine, Primidone, Gemfibrozil, Triclocarban, Triclo- san, Sulfachloropyridazine, Sulfamerazine	Х	
Diclofenac, Paracetamol, Carbamazepine, Carbamazepine Epoxyde, Bezafibrate, Metoprolol, Pro- panolol, Oxazepam	Х	Х
Antibiotics		
Trimethoprime, Clarithromycine, Erythromycine, Roxithromycine	Х	
Sulfamethoxazole	Х	Х
Alkylphenol		
nonylphenol monoethoxylate (NP1EO), nonylphenol diethoxylate (NP2EO), Octylphenol monoethox-	Х	
ylate (OP1EO), Octylphenol diethoxylate (OP2EO),		
Nonylphenol (4-n)	Х	Х
BTEX		
Benzene, Toluene, Ethylbenzene, and Xylenes	Х	
Aromatic organochlorine		
1,2,3 trichlorobenzene, 1,2,4 trichlorobenzene, 1,3,5 trichlorobenzene, Hexachlorobenzene,	Х	
Pentachlorobenzene, Pentachlorophenol		
Volatil organohalogenated		
1,2 dichloroethane, Chloroform, Vinyle chloryde, Dichloromethane, Hexachlorobutadiene, Tetrachlo-	Х	
roethylene, Carbon Tetrachloride, Trichloroethylene		
Polycyclic Aromatic Hydrocarbons. (PAH)		
Anthracene, Benzo (a) pyrene, Benzo (b) fluoranthene, Benzo (g,h,i) perylene, Benzo (k) fluoranthene,	Х	
Fluoranthene, Indeno (1,2,3-cd) pyrene, Naphtalene		
Metals		
Cadmium, Chromium, Cobalt, Tin, Mercury, Lead	Х	
Antimony, Aluminum, Arsenic, Copper, Iron, Manganese, Nickel, Titanium, Zinc	Х	Х

Compound	2014*	2015**
Organotins		
Monobutyltin, Dibutyltin, Tributyltin, Triphenyltin	Х	
Hormones		
Estradiol alpha, Ethynyl Estradiol		
Estradiol beta, Estrone	Х	Х
PCB		
PCB 101, PCB 118, PCB 138, PCB 153, PCB 180, PCB 28, PCB 52	Х	
Pesticides		
Alachlore, Atrazine, Chlorfenvinphos, Chlorpyrifos ethyl, Alpha endosulfan, Beta endosulfan, Endosul- fan, Endrine, HCH, Alpha HCH, Beta HCH, Delta HCH, Lindane, Isoproturon, Simazine, Trifluraline, 2,4 MCPA, Aldrine, Chlordane alpha, Chlordane gamma, Chlordecone, Chlortoluron, DDD24', DDD44', DDE24', DDE44', DDT24', DDT44', Dieldrine, Hexabromodiphenyl, Heptachlor, Hydrazine, Isodrine, Linuron, Mirex, Oxadiazon, PFOS, Toxaphene, DEHP	X	
Diuron, Glyphosate, AMPA, 2,4 D	Х	Х
Metolachlore, Fipronil, Metaldehyde		Х
Others		
Aniline, Phenol Index, Methanol, Bisphenol A, Chloroalkanes C10-13, Volatil hydrocarbons index, Adsorbable organohalogenated compounds	Х	
Caffeine	Х	Х

* 2014: 1 monitoring campaign in June on 7 sampling points (P1, P2, P3, P7, P9, P10 and P11)

** 2015: 5 monitoring campaign in March, May, June, July and August on 5 sampling points (P1, P2, P3, , P9 and P11)

The water quality monitoring program can be summarised as follows.

Table 5 Main features of the water quality monitoring program

Date	June 2014	March 2015	May 2015	June 2015	July 2015	August 2015
Water regime	Low	High	High	Low	low	Low
Sampling points	All	All except P7 & P10				
Flows	Х	x	Х	Х	х	x
Physico-chemical	Х	X	Х	Х	Х	x
Microbiology	-	8	8	8	8	8
Metals	16	9	9	9	9	9
Micropollutants	109	19	19	19	19	19

3.1.2 Self-purification in rivers and reservoirs: objective and method

In rivers and lakes, numerous processes of self-purification occur (Wetzel, 2001). Combined with dilution, it lowers the concentration of anthropogenic pollutants. The main factors and processes are (Doklady, 2004):

- Physical and physicochemical (Lemmin, 1995):
 - o Dissolution and dilution,
 - o Sorption onto suspended particles followed by sedimentation
 - o Sorption onto sediments
 - o Evaporation
- Chemical (Gaillard, 1995):
 - o Hydrolysis
 - o Photochemical transformations
 - o Redox catalytic transformations

- o Free-radical transformations
- o Decrease in CP (chemical pollutant) toxicity due to their binding with DOCs (dissolved organic compound)
- o Chemical oxidation of CPs involving oxygen
- Biotic (Capblancq, 1995; Servais et al., 1995)
 - o The sorption and accumulation of CPs and biogenic substances by hydrobionts
 - o Biotransformation: redox reactions, decomposition, and conjugation
 - Regulation of the numbers and activity of organisms involved in water purification as a result of interactions between organisms

The self-purification in the La Grande Maine river can be assessed using the monitoring of pollutant concentrations and fluxes undertook in 2014 and 2015 along the river as detailed in the sections below. For the self-purification in La Bultière reservoir, we use the concentrations monitored during 2015 at the inlet of the reservoir (P9: Le Plessis des Landes stream-gauging station) and at La Bultière Drinking Water Treatment Plant intake (P11). The aim is to assess the theoretical concentration in the reservoir considering dilution only.

Then, comparing the mean theoretical concentration with only dilution in the reservoir with the mean monitored concentration, we can deduce the mean abatement due to self-purification for the considered pollutant.

Using the river flow monitored daily and the pollutant concentration sampled 5 times from March to August 2015, we assess the pollutant fluxes entering La Bultière reservoir, with the hypothesis that the concentrations vary linearly with time from a sampling period to the next one. We consider that the initial concentration in the reservoir is equal to the initial concentration monitored at the La Bultière Drinking Water Treatment Plant intake (P11). The pollutants flowing into the reservoir are supposed to be entirely mixed. As the reservoir volume is monitored each day as well as the flow discharge from the reservoir downstream the dam, we can compute the stock of pollutants in the reservoir and deduce the theoretical concentration using the 2 following equations:

$$Stock(d) = Stock(d-1) + Q_{in}(d) \times C_{in}(d) - Q_{out}(d) \times C_{theoretical}(d-1) \text{ and } C_{theoretical}(d) = \frac{Stock(d)}{Volume(d)}$$

With:

Stock(d):	Stock of pollutant in the reservoir on day d
Q _{in} (d):	Flow into the reservoir on day d
Q _{out} (d):	Flow discharged from the reservoir on day d
C _{in} :	initial concentration in the reservoir, equal to the initial concentration monitored at the La Bultière Drinking Water Treatment Plant intake (P11)
Ctheoretical (d):	Theoretical concentration considering only dilution on day d
Volume(d):	Volume of water in the reservoir on day d

3.2 Aquatic environment quality assessment

As aquatic environment assessment is independent from flow regime, the monitoring campaign was undertaken once during summer 2015, using the following biological indices:

- Biotic Index (IBGN in French), according to French standard NF XP T 90-333
- Biological Index of Diatom species (IBD in French), according to French standard NF T 90-354
- Biological Index of Macrophytes in River (IBMR in French), according to French standard NF T 90-395

- Oligochaetes Index of Bioindication Lacustre (IOBL in French), according to French standard NF T 90-391.
- The IBGN and the IBD together with the IBMR allow characterizing the ecological state of this sector of La Grande Maine River, but as well the biological capacity of the environment to absorb pollution and the possible incidence of the hydromorphology on this capacity.
- The IBMR gives a particular angle on the eutrophication due to contributions of nutrients (nitrogen and phosphorus) on the river biology and then of the reservoir one.
- The IOBL is used to characterize the sediments quality in the reservoir, thus indicating the reaction to anthropological pressures over a rather long period (6 months to 1 year).

The IBGN, IBD and IBMR are measured on 5 different locations along the Grande Maine River (P1, P1', P3, P7 and P9 as describe in Table 3), including upstream and downstream of Les Herbiers WWTP while the IOBL is measured in 4 different locations in La Bultière reservoir:

- Preuilly Bridge over the reservoir (P10)
- La Maurosière
- La Basse Permoulène
- Water intake of the Drinking Water Treatment Plant (P11)

These points are described in Appendix 1.

3.2.1 IBD

Diatoms are brown microscopic algae (Diatomophycees) with a siliceous exoskeleton. They constitute a major component of algal assemblage of rivers and lakes.

Diatoms are considered very sensitive to environmental conditions. They are known to react with organic pollution, nutrients (nitrogen, phosphorus), salt...

The samples are taken from the natural environment and laboratory analyses (microscopic observation) are carried out according to the NF T 90-354 protocol (December 2007).

The definition of ecological status according to the French Decree of 25/01/2010 (Ministère de l'écologie, 2015) uses a grid where there are five classes of ecological status. The limit values for each class evolve with IBD, hydro-ecoregion (HER) and the rank of the water body of the river.

La Grande Maine belongs to the Armorican Massif hydro-ecoregion (number 58). Classes of limit values for IBD are indicated below (Table 6):

HER 2	Ecological status	Very good	Good	Medium	Poor	Bad
58	IBD note	20 – 16.5	< 16.5 - 14	< 14 – 10.5	< 10.5 - 6	< 6

Table 6Ecological classes of the IBD

3.2.2 IBG

The biological quality determination of rivers is based in particular on the study of benthic invertebrates: invertebrates colonizing the surface and the first centimeters of submerged sediments of the river and whose size is greater than or equal to 500 microns (macro-invertebrates).

The definition of ecological status using invertebrates according to the Decree of 25/01/2010 uses a grid where there are five classes of ecological status. The boundaries of each class change according to the IBG, hydro-ecoregion and the rank of the mass of water of the river.

Classes of limit values for the IBG are indicated below:

Table 7	Ecological of	classes	of the	IBG

HER 2	Ecological status	Very good	Good	Medium	Poor	Bad
58	IBG note	20 – 15	14 - 13	12 – 9	8 - 6	5 -1

3.2.3 IBMR

The macrophytic Biological Index in River (IBMR) is based on the examination of aquatic plants to assess the trophic status of rivers. It applys to the continental parts of natural or artificial surfaces water. The IBMR therefore reflects mainly the degree of trophy of rivers related to their ammonium levels (reduced form of nitrates) and orthophosphate, as well as major organic pollution. The IBMR may also vary, but to a lesser extent, according to certain physical characteristics of the environment like the light intensity and / or the flow dynamics.

The index score of IBMR ranges from 0 to 20. It thus highlights the trophic level of the river and does not express exactly a "quality" of water. Thus, under "natural" conditions a river IBMR index will be close to 20 in its upstream part because its waters are oligotrophic. Conversely, the same river will have a IBMR index close to 0 in its downstream part because its waters are "naturally fortified" with nutrients and are not necessarily "bad" quality.

In addition to the index IBMR, the score robustness is calculated to highlight the balance of macrophytic stock in the river (information homogeneity or score influenced by a dominant taxon).

The following Table 8 summarizes the thresholds for assessing the trophy streams:

Table 8 Ecological classes of the IBMR

Trophic level of water	Very low	Low	Medium	High	Very high
IBMR Index	>14 à 20	12 <ibmr≤ 14<="" td=""><td>10 <ibmr≤ 12<="" td=""><td>8 <ibmr≤ 10<="" td=""><td>IBMR≤ 8</td></ibmr≤></td></ibmr≤></td></ibmr≤>	10 <ibmr≤ 12<="" td=""><td>8 <ibmr≤ 10<="" td=""><td>IBMR≤ 8</td></ibmr≤></td></ibmr≤>	8 <ibmr≤ 10<="" td=""><td>IBMR≤ 8</td></ibmr≤>	IBMR≤ 8

Note: At present, macrophytes are not yet part of the biological elements to assess the ecological status according to the Decree of 25/01/2010.

3.2.4 Global ecological status

The global ecological status of the station is assessed from the classes of ecological status obtained for the IBG and IBD. The quality of the station is given by the worse result from the two indices.

3.2.5 IOBL

This protocol derived from the NF T 90-391 of March 2005, applies to natural freshwater lakes and reservoirs whose depth is at least 5 meters.

The purpose of this sampling protocol of oligochaetes in lake ecosystem is to sample the sediment where the percentage of sensitive species (*Oligochaeta sensitive* to pollution in lake sediments from 5 meters deep) is estimated from the numbers of these species in the 100 oligochaete specimens examined by sample.

Table 9 Interpretation grid of sensitive species (according Lafond, 2007)

% Of susceptible species	Class	Diagnosis
> 50%	5	Very good sediment quality
21 to 50%	4	Good sediments quality
11 to 20%	3	Medium quality of sediments
6 to 10%	2	Poor quality of sediments and/or trophic dead end
< 5%	1	Bad quality of sediments and/or trophic dead end

The definition of ecological status using oligochaetes according to Decree of 25/01/2010 uses a grid where there are five classes of ecological status. The boundaries of each class change according to the IOBL and type of water.

Table 10 Ecological status classes based on the IOBL

	Natural water bodies							
IOBL	>15	[15 -10[[10 -6[[6 -3[≤3			
Ecological status	Very good	Good	Medium	Poor	Bad			

4 Results

4.1 Water quality monitoring

6 water quality monitoring campaigns were undertaken:

- 2 campaigns at "high water" level in March and May 2015 where the share of Les Herbiers WWTP discharge flow in la Grande Maine river was 4% and 11 % respectively (see Figure 4);
- 4 campaigns at "low water" level in June 2014, then June, July and August 2015 where the shayre of Les Herbiers in la Grande Maine river was 10%, 25%, 27 % and 20% respectively (see Figure 4).

The monitoring campaign in June, July and August took place during a period of dry weather, the impact of les Herbiers WWTP discharge being at its maximum.

Micropollutants monitored during the 5 monitoring campaign in 2015 are those detected according the results of the june 2014 campaign (see Table 4).

On the graphs (only) presented in this report, the P1 sampling point has to be considered as the P1' sampling point (just downstream the industrial area).

5 sampling points were monitored: P1, P2, P3, P9 and P11 (see Table 3).

Mar

Jun 14

The results will be presented by families of compounds and all the analytical results are presented in Appendix 5.

4.1.1 N, P and TOC

4.1.1.1 Nitrogen

2.000 1.000

P1

P2 P3 pg



Figure 8, its load from the WWTP discharge is quite low and other inputs between P3 and P9, contribute to the load entering La Bultière reservoir. These inputs seems to occur mainly during spring, during high water, from non point-source pollution due to fertilizers used in agriculture.

Thus, Les Herbiers WWTP, which complies with its discharge regulation, isn't a major source of Nitrogen in La Bultière catchment area and the concentration at the DWTP intake is bellow the maximum concentration required for raw water used for drinking water.



Figure 8 Concentration and loads of Nitrates

4.1.1.2 Phosphorus and total organic carbon (TOC)

• The WWTP complies with the discharge requirements in Phosphorus. Its load from the WWTP is quite low. As for Nitrates, other inputs, between P3 and P9, contribute to the load entering La Bultière reservoir. The flux increase during spring may come from runoff on naked agricultural. During the other monitoring campaigns the increase in Phosphorus load downstream probably come from the 5 WWTP between Les Herbiers and La Bultière reservoir which aren't efficient for phosphorus treatment.



Figure 9 Concentration and Loads of Orthophosphates

The tise of the TOC load between P3 and P9 could be due to runoff, especially in March 2015 with high rainfall during the 2 previous weeks (see Figure 4).



Figure 10 Concentration and load of TOC

4.1.2 Microbiology

4.1.2.1 *E. coli* and Enterococci

The biological quality criterias of raw water intended for human consumption are set only for bacteria: *E. coli* (< 20,000 n/100 ml) and Enterococci (< 10,000 n/100 ml). Both are not fulfilled at the discharge of the WWTP, particularly in summer, but their concentrations decrease along the river to reach concentrations near or bellow limit of quantification.

If concentrations decrease between the discharge of WWTP and the downstream sampling points, loads remain high except in summer (from June to August), where these bacteria are partially removed either by the effect of UV or by heat.

Moreover, Enterococci are known to survive longer in the aquatic environment than *E. coli*. This behavior is observed with a higher decrease along the river for *E. coli* than for Enterococci (see Figure 11 and Figure 12).









4.1.2.2 Cryptosporidium, Giardia, Bacteriophage pathogens and sulphate reducing bacteria

In the discharge of the WWTP, concentration and flux of <u>Cryptosporidium</u> are low (see Figure 13). There is a significant increase between P3 and P9, which could be related to the 5 others WWTP as well as livestock farming or feces of wild animals.

The analysis protocol measures all the parasitic protozoa pathogens (dead and alive). These pathogens are very resistant, and can survive several months in the environment. This could explain the load increase along the river as the analysis detects even the dead parasites. It is common to have higher concentrations in winter due to livestock farming (as shown in Figure 13 for concentrations). In summer UV may have a positive effect on cryptosporidium degradation also (as shown in Figure 13 for loads).



Figure 13 Concentration and flux of Cryptosporidium

<u>Giardia</u> is a good microbiological index as it is more frequently detected in water but less resistant than other pathogens. Moreover, its infectious dose is higher than the one of Cryptosportidium. Giardia concentrations and loads show (see *¡Error! No se encuentra el origen de la referencia.*):

- Input between P3 and P9, probably linked to livestock farming, other WWTP or wild animals feces;
- Higher concentrations in winter than in warmer months, due to a more efficient UV degradation along the river in summer



Figure 14 Concentration and flux of Gardia

<u>RNA specific bacteriophage</u> is a good index for human or animal activities. The load of bacteriophages show a higher contamination level downstream of the WWTP than the WWTP input (Figure 15). The trends along the river show a load increase for colder months, but a decrease after P3 for warmer months (June to August).





Sulphate reducing bacteria are a good index for old feacal pollution. Their load trends are the similar to bacteriophage: their increase along the river (especially during the colder months) could be explained by inputs from runoff and/or other WWTP and by a low UV degradation during these colder months.



Figure 16 Concentration and flux of sulphate reducing bacteria

4.1.2.3 Conclusions

Les Herbiers WWTP discharge (P2) is globally the main source of microbial pollution in the river for Giardia, *E. coli* and Enterococci. For Cryptosporidium, bacteriophages and sulphate reducing bacteria the main load input comes from upstream of the WWTP and from an input source before P9. Runoff, livestock farming, the 5 small WWTP may have a significant contribution to the microbiological load in the river.

Moreover, significant loads of all the microbiological parameters are observed upstream Les Herbiers WWTP during all monitoring campaign. This means that some household aren't connected correctly to the sewage system and that loads are discharged to La Grande Maine river through the stormwater system.

4.1.3 Pesticides

The load of **Diuron** from the WWTP is quite low whereas significan loads come from upstream the WWTP in June 2014 and Marc 2015 with no visible degradation along the river, down to P9 (Figure 17).

The concentration and loads of **AMPA** are significant in the WWTP discharge, and the load further increases between P3 and P9 due to loads from streams (Figure 18).

Nevertheless, **Glyphosate** is found at low concentrations in the WWTP discharge and the loads are increasing downstream (Figure 19).

As AMPA is a by-product of glyphosate, its load increase could also be due to the glyphosate degradation.

The load increase of AMPA and Glyphosate can be explained by contribution of the 5 small WWTP and runoff from farm fields.







Figure 18 Concentration and load of AMPA



Figure 19 Concentration and load of Glyphosate

Other analyzed pesticides as 2,4-D, Metolachlor, Fipronil and Metaldhedyde are either not detected or detected at trace levels, below the LQ.

4.1.4 Metals

Table 11 includes the concentration and loads for metals, averaged from the 6 values between June 2014 and August 2015.

Only Zinc is part of the raw water quality criteria for human consumption with a limit at 5 mg/l. All measured values (at the WWTP discharge or for the other points) are well below this value. On average, the main Zinc

load brought to the river doesn't comes from the WWTP: the load from P2 represents 25 % of the load in P9 and is lower than the load coming from upstream the WWTP. For the other metals, the contribution of the WWTP to the loads downstream is less than 10%.

Metal		Cond	centration (µg/I)		Load (µg/s)				% Load
	P1	P2	Р3	P9	P11	P1	P2	P3	Р9	P2/max(Pi)
Aluminum	226	24	462	180	147	22,100	665	70,700	78,500	1%
Arsenic	2.7	< 5.0	2.5	7.0	3	174	111	277	1,524	7%
Iron	390	175	743	350	233	44,400	4,400	97,300	154,600	3%
Manganese	39	54	86	71	63	430	1,300	9,200	16,200	8%
Titane	13	< 10	30	7	6	710	125	1,900	1,300	7%
Zinc	11	19	19	< 10	13	850	570	2,000	2,300	25%
Antimony	< 0.5	< 5	< 0.5	< 0.5	< 0.5	< 35	< 85	< 35	< 35	-
Nickel	< 5	< 10	< 5	< 5	< 5	< 270	< 154	< 379	< 942	-
Copper	< 5	< 5	< 5	< 5	7,8	< 270	< 77	< 379	< 942	-

Table 11 Average concentration and load of metals

There is also a significant input upstream of the WWTP (P1) of Aluminum and of Titanium to a lesser extent, probably related to the industrial area (boat manufacturing for example). The load of Arsenic observed in P9 could either come from small WWTP or from run off.

4.1.5 Caffeine

Caffeine is well removed in the WWTP and most loads comes from the river upstream of its outlet (Figure 20). As for the microbial parameters, this suggest once more that some household aren't connected correctly to the sewage system and that loads are discharged to La Grande Maine river through the stormwater system.

There are few traces of this element in the dam at the intake of the DWTP (0.07 μ g/l on average in P11).

Caffeine flux is independent of the season since we found it at all points regardless of the period of the year.





4.1.6 Radio contrast media

Among the 3 contrast agents, Iohexol, Iomeprol and Iopromide iohexol wasn't not detected.

Iomeprol and Iopromide do not come mainly from the WWTP, but loads are brought in P9 as shown on Figure 21 and Figure 22. Nevertheless the high concentration of Iopromide in P9, in June 2015, seems suspicious. This punctual sampling is very different from all the other concentration values.

These two molecules were found at the water intake of the DWTP, either as traces (for lopromide) or as an average concentration of 0.11 μ g/l for lomeprol (see data in Appendix 5).



Figure 21 Concentration and load of lomeprol





4.1.7 Pharmaceuticals

Out of the 9 pharmaceutical compounds monitored, only **Carbamazepine epoxide** is not detected in the samples and **Bezafibrate** remains at very low concentrations. (See all the results in Appendix 5).

All the other molecules are detected on one or more measurement points.

We notice that **Paracetamol** is particularly well eliminated by WWTP, which is not the case of **Diclofenac**, **Carbamazepine**, **Oxazepam** and **Sulfametoxazole** and the 2 beta-blockers **Metoprolol** and **Propranolol**.

This is consistent with Luo et al. (2014) who report WWTP removal of 98 to 100% for Paracetamol; 0 to 81% for Diclofenac; 0 to 62% for Carbamazepine; 4 to 89% for Sulfametoxazole; 3 to 56% for Metoprolol.







Figure 24 Concentration and load of Paracetamol





These molecules, as well as Oxazepam, are found exclusively at Les Herbiers WWTP discharge, but not upstream. There may be used as **"tracers**", due to their low degradability at the WWTP and also in the natural environment.

No significant input seems to occur (except in P3 in March 2015 for Propanolol) along La Grande Maine River.

The calculation of theoretical dilution (see *section 4.5*) shows a reduction in the reservoir of La Bultière from about 25 % for these two molecules.



Figure 26 Concentration and load of Metoprolol

(Note: The points obtained on flow graphs for Metoprolol and Propranolol in P9 may not reflect reality because they are derived from calculations between the recalculated concentrations due values $< LQ^2$ and a flow water at La Grande Maine very high. These points are specified in clear color on the two graphs.)



Figure 27 Concentration and load and Propanolol

(Note: The points obtained on flow graphs for Metoprolol and Propranolol in P9 may not reflect reality because they are derived from calculations between the recalculated concentrations due values $< LQ^3$ and a flow water at La Grande Maine very high. These points are specified in clear color on the two graphs.)

² Nevertheless, these molecules are detected with the chemical fingerprint analyses.

³ Nevertheless, these molecules are detected with the chemical fingerprint analyses.



Figure 28 Concentration and load of Oxazepam

4.1.8 Hormones

Out of the two hormones Estradial beta and Estrone, only the latest is detected in very small amounts (ng/l and ng/s).

The WWTP do not fully degrade this molecule, but most flux comes from other sources as high flux values show in P3 and P9 (probably from other small WWTP).



Figure 29 Concentration (µg/l) and flux (µg/s) of Estrone

(Note: The point obtained on this flow graph in P9 in March 2015 do not reflect reality because it's derived from calculation between the recalculated concentration due value < LQ and a flow water at La Grande Maine high. This point is specified in clear color on the graph.)

4.2 Water quality monitoring - Chemical fingerprints

The first 3 campaigns conducted in June 2014, March 2015 and May 2015 have established a list of 572 compounds (compounds detected at least once during the campaigns). This list was used to target screening for campaigns of June 2015, July 2015 and August 2015.

Overall, the 6 analyzes campaigns are similar: no clear seasonal effect is observed, despite some notable differences.

The analysis of the 6 campaigns shows a total of **327 molecules identified** with a high degree of certainty, 43% of pharmaceuticals and to lesser extent industrial contaminants (20%), pesticides (18%), synthetic everyday products (10%), natural compounds (8%) and some illicit substances (1%).


Figure 30 Distribution of the 327 compounds identified during 6 campaigns analysis

• The **6** analyses campaigns are broadly similar in terms of number of molecules, compounds of response intensity and family repartition. The flows are a little bit different (because the rates have varied according to the campaigns).



Figure 31 Evolution of the number of molecules identified by sampling point per family between 6 analytical campaigns (Levels 2 and 3)



Figure 32 Evolution of the intensity of the response molecules identified by sampling point per family between 6 analytical campaigns (Levels 2 and 3)



Figure 33 Evolution of the response stream of molecules identified by sampling point per family between 6 analytical campaigns (Levels 2 and 3)

Overall, among the 327 molecules identified, **22 were found in four samples of the river** (point P1', P3, P9 and P11) for at least 5 of the 6 campaigns (either with a frequency rate \geq 83%). The list of these 22 molecules recurring in La Grande Maine River is presented in Table 12. The distribution by families is: pharmaceutical products (11 molecules), pesticides (5 molecules), synthetic products of common use (3 molecules), natural compounds (2 molecules) and 1 molecule of industrial contaminant.

Compound name	CAS number	Class	Sub class
N-Desmethyl-cis-tra-	147762-57-0	Pharmaceuticals	Antalgics and Anti inflammato-
Tramadol	27203-92-5	Pharmaceuticals	Antalgics and Anti inflammato-
Acebutolol	37517-30-9	Pharmaceuticals	Cardiology - Angiology

Table 12 List of the 22 recurrents compounds of La Grande Maine River

Compound name	CAS number	Class	Sub class
Diacetolol	28197-69-5	Pharmaceuticals	Cardiology - Angiology
Flecainide	54143-55-4	Pharmaceuticals	Cardiology - Angiology
Irbesartan	138402-11-6	Pharmaceuticals	Cardiology - Angiology
Telmisartan	144701-48-4	Pharmaceuticals	Cardiology - Angiology
N_Desmethylvenlafaxine	149289-30-5	Pharmaceuticals	Psychiatry
Oxazepam	604-75-1	Pharmaceuticals	Psychiatry
Varenicline	249296-44-4	Pharmaceuticals	Psychiatry
Venlafaxine	93413-69-5	Pharmaceuticals	Psychiatry
5-Methyl-1H-benzotria-	136-85-6	Industrial contaminants	Anticorrosives
PFOS	1763-23-1	Synthetic products for common	Surfactants
AHTN_Tonalid	21145-77-7	Synthetic products for common	Synthetic fragrances
Ethylstearate	111-61-5	Synthetic products for common	Synthetic fragrances
Hydroxyatrazine	2163-68-0	Pesticides	Herbicides
Hydroxyterbuthylazine	66753-07-9	Pesticides	Herbicides
Metolachlor_ESA	171118-09-5	Pesticides	Herbicides
Propazine	139-40-2	Pesticides	Herbicides
Terbutryn	886-50-0	Pesticides	Herbicides
Cafeine	58-08-2	Natural compounds	Consumers products
Cotinine	486-56-6	Natural compounds	Consumers products

61 compounds were identified as markers of Les Herbiers WWTP. Figure 34 present the repartition by family of markers identified.

The list of the 61 compounds is presented in Appendix 0.





- The effluent from Les Herbiers WWTP (P2) has a significant impact on La Grande Maine River (increase of molecules and the response intensity) for the majority of micro-pollutant families (except for natural compounds that have an origin different from the WWTP).
- Then along the river, the number and intensity of the response of the compounds decreases progressively to the dam of La Bultière (between P3 and P11), where the micro-pollutant composition is substantially similar to the one upstream WWTP (P1').

The impact of Les Herbiers WWTP, for micropollutants, is always present in time but geographically limited, with no significant influence on La Bultière reservoir.

4.3 Aquatic environment quality assessment

The WWTP impacts (between downstream and upstream of the WWTP) are not really noticeable (see Table 13). This can be explained:

- by an upstream sample too far from the discharge point, and thus a dilution of the potential pollution,
- but also by other discharge points along the Grand Maine River, especially the industrial area upstream P2, the WWTP discharge. The water quality in P1' shows high metals concentration (Al, Ti, Fe, Zn...) (see *Table 11*) which could be due to a discharge from this industrial zone.
- The loads in P3 and P9, for almost all analysed parameters (i.e. N, P, TOC, metals, pesticides, some pharmaceutical compounds, hormones) show new inputs in the Grand Maine River which prevent an improvement of the river ecological status (that could be expected from dilution, self purification...).

The IBD and IBMR indices are sensitive to nutrients, pH, organic matter and water oxygenation, and the IBD level along the river shows poor to medium ecological status. This may suggest that the river pollution is mostly due to nutrients and organic matter (high loads of nitrates, phosphorus and TOC are no-



ticed downstream of the WWTP discharge, see

Figure 8 to Figure 10)

The IBG index shows a good ecological status (in P1 and P9). This may suggest that the pollution in the river (at least between P1' and P7) is not new.

The comparison with the SEQ-Eau status⁴ for zinc and copper concentrations in the analyzed water samples shows a similar capability class than the ecological status (medium status). Thus the water chemical composition (in terms of N, P, C, metals) leads to similar conclusions than the study of the biological indices. Further downstream (from P3 to P9), the environmental quality of the river is slighly improving, but without an improvement of the ecological status.

	IBD	IBG	IBMR*	Ecological status
La Grande Maine at Le Bignon (P1)	9.5	13	8.35	Poor
La Grande Maine, Upstream WWTP (P1')	13.5	10	12	Medium
La Grande Maine at La Favrie (P3)	11.5	9	7.82	Medium
La Grande Maine at St Fulgent (P7)	13.8	12	8.33	Medium
La Grande Maine at Le Plessis des Landes (P9)	13.3	14	9.39	Medium

Table 13 Evolution of the ecological status of La Grande Maine (upstream to downstream)

* No color is associated to the IBMR index as it does not enter in the calculation of the ecological status.

Concerning La Bultière reservoir, which is an A6b artificial reservoir type according to the circular DCE 2005/11, on national typology of surface water (rivers, lakes, transitional waters and coastal waters), the ecological status for this type of reservoir can not be currently assessed using the IOBL index

Table 14 Ecological status of La Bultière reservoir

	La Bultière reserv	oir		
	Upstream Preuilly Bridge	La Maurosière	La Basse Permoulière	Upstream Dam
Global IOBL	4.2	4.3	2.3	3.2
Metabolic potential	Medium	Low	Low	Low
% Total of sensitive species	0	0	0	0
Sediments quality	Poor	Poor	Poor	Poor
Total density for 0.1 m ²	5	13.3	1.7	2.3
Total taxonomic richness	4	1	1	3
Ecological status class	Not qualify	Not qualify	Not qualify	Not qualify

* color is only an indication because currently withholding anthropogenic origins can not be qualified

Nevertheless, the results show that the metabolic potential of La Bultière reservoir (its ability to assimilate and recycle mineral and organic substances) **is low to very low**. The overall IOBL, assessed on each sampling area varies between 2.3 and 4.3.

The percentage of sensitive species is zero on all stations. **Sediment quality is classified as poor**. These results have to be linked to the low taxonomic richness and very low densities of oligochaete observed on each sampling point.

⁴ http://www.observatoire-eau-bretagne.fr/Ressources-et-documentation/Documents-de-planification/Systeme-d-evaluation-de-la-qualite-de-leau-des-cours-d-eau-SEQ-Eau Even if the wealth and density of oligochaetes is lower for natural water bodies with the crystal geology under La Bultière reservoir), the hypolimnion (deep layer) of the water bodies appears to be deoxygenated or very weakly oxygenated. The environment becomes hostile to most of the aquatic fauna, including oligochaetes, which are resistant to low oxygen species.

Some existing species, like Limnodrilus hoffmeisteri and Lumbriculus variegatus are pollution-resistant.

All these indices show an alteration of the biological quality of sediments of La Bultière reservoir, due to a likely degradation of the water quality of the reservoir and La Grande Maine River.

4.4 Self-purification in La Bultière reservoir

The figure below illustrate the approach detailed in section 3.1.2 (p. 10) for Caffeine.

This approach was validated using results on ions where no abatement is supposed to happen (Chlorides, Fluorides and Sulfates)



Figure 35 Theoretical and monitored concentration in La Bultière reservoir – Example of Caffeine

For Caffeine, from March 2015 to August 2016, if there is only dilution, the theoretical concentration remains between 0.08 and 0.10 μ g/L. As the monitored concentration of Caffeine at the outlet of the reservoir decreases to near 0.04 μ g/L, there is abatement of this compound within the reservoir.

To assess the abatement in La Bultière reservoir, the mean monitored concentration during the monitoring campaign is compared to the theoretical concentration. In this example, they are respectively 0.067 and 0.089. Thus the abatement is 25 %: 0.089 x (1 - 25%) = 0.067.

All the abatements computed are summarized in the following table.

Table 15 Abatement in La Bultière reservoir

Parameter	Units	Mean Monitored Concentration	 Mean Theoretical concentration	Abatement
Contrast agents				
lomeprol	μg/l	0,106	0,121	12%
lopromide	μg/l	0,039	0,069	43%
Pharmaceutical compounds				
Diclofenac	μg/l	0,126	0,036	-255%
Paracetamol	μg/l	0,007	0,009	25%
Carbamazepine	μg/l	0,027	0,036	24%
Carbamazepine Epoxyde	μg/l	0,007	0,015	55%
Bezafibrate	μg/l	0,007	0,009	25%
Metoprolol	μg/l	0,007	0,009	25%
Propanolol	μg/l	0,007	0,009	25%
Oxazepam	μg/l	0,045	0,050	10%
Antibiotics				
Sulfamethoxazole	μg/l	0,009	0,012	28%
Metals				
Antimony	μg/l	0,380	0,476	20%
Aluminium	μg/l	196,600	370,218	47%
Arsenic	μg/l	3,580	4,319	17%
Copper	μg/l	7,216	4,721	-53%
Iron	μg/l	291	558	48%
Manganese	μg/l	76	66	-16%
Nickel	μg/l	0,000	0,000	-
Titanium	μg/l	6,740	12,812	47%
Zinc	μg/l	14	10	-46%
Hormones				
Oestrone	ng/L	0,140	0,783	82%
Pesticides				
Diuron	μg/l	0,014	0,031	55%
Glyphosate	μg/l	0,046	0,094	51%
Aminomethylphosphonique acid	μg/l	0,177	0,395	55%
2,4D	μg/l	0,014	0,019	25%
Metaldehyde	μg/l	0,014	0,019	25%
Nitrogen and Phosphorus				
Ammonium (NH4)	mg N/L	0,21	0,26	19%
Nitrate (NO ₃)	mg N/L	3,33	6,44	48%
Orthophosphate (PO ₄)	mg P/L	0,05	0,14	65%
Kjeldhal Nitrogen	mg N/L	1,40	1,61	13%

Parameter	Units	Mean Monitored Concentration	Mean Theoretical concentration	Abatement
Other parameters				
СОТ	mg C/L	8,27	9,25	11%
Caffeine	μg/l	0,067	0,089	25%
Microbiology				
E. coli	n/100 mL	10	483	98%
Enterococci	n/100 mL	10	117	92%
Sulphate reducing anaerobic bacteria	n/100 mL	110	2 274	95%
Cryptosporidium	n/10 L	2	58	96%
Giardia	n/10 L	3	57	94%
F-specific RNA bacteriophage	PFP/ml	1	2	67%

The main lesson learned is that there is significant self-purification in La Bultière reservoir as the mean monitored concentration are lower than the theoretical concentration with only dilution for the vast majority of pollutants.

For the organic compounds, except for Diclofenac where the results aren't consistent, the abatement range from 10 to more than 80%. Here, the main mechanism should be degradation by microorganisms or UV.

For Metals, except for Copper, Manganese and Zinc where the results aren't consistent, the abatement range from 15 to near 50% mainly due to adsorption on settling suspended solids.

Except F-specific RNA bacteriophage with an abatement of near 70%, the abatement of the others microorganisms are greater than 90% due to mortality.

Nevertheless, even if this self-purification occurs, the aquatic environment quality assessment shows a strong alteration of the biological quality of sediments of La Bultière reservoir.

5 Conclusion

In order to design a planned indirect reuse scheme involving a waste water treatment plant supplying a reservoir (CCO WWTP-Le Jaunay reservoir), a similar system located 50 km away was studied: Les Herbiers WWTP-La Bultière reservoir. A large analytical campaign took place to study this unplanned indirect reuse scheme. On one hand, 6 analytical campaigns were undertaken to highlight the fate of pollutants coming from a WWTP in a river and in reservoir. On the other hand, the quality of the aquatic environment was assessed with one analytical campaign in order to know what could be the impact of a WWTP.

The main findings of this study concerns:

- The results for La Bultière unplanned indirect reuse scheme;
- The advantages and limitations of the methodology used in this study;
- The lessons learned and the recommendation for the planned indirect reuse scheme

5.1 Main results for La Bultière unplanned indirect reuse scheme;

For **nitrogen**, **phosphorus and total organic carbon**, the WWTP of les Herbiers isn't the main origin of the loads monitored at the entrance of La Bultière reservoir.

The same trend is observed for **metals** which loads from the WWTP discharge are much lower than the loads coming either from upstream or from the tributaries downstream. The abatement assessed in the reservoir ranged from 15 to near 50%.

For the **microbiological parameters** (virus, bacteria and protozoa), the WWTP is generally the main the main source for Giardia, E. coli and Enterococci whereas this is not the case for Cryptosporidium, bacteriophages and sulphate reducing bacteria. A self purification was observed along the river and in the reservoir as well.

Concerning the **organic micropollutants**, 8 compounds were always present in Les Herbiers WWTP discharge during the 6 monitoring campaign (Diclofenac, Carbamazepine, Metoprolol, Propanolol, Oxazepam, Sulfametoxazole, Glyphosate and AMPA). Among them, only 5 can be considered as tracers because they do not appear upstream of the WWTP: Carbamazepine, Metoprolol, Propanolol, Oxazepam and Sulfametoxazole. Finally, for these 5 molecules identified as tracers of the WWTP, 3 of them are found in measurable values at La Bultière DWTP intake: **Carbamazepine, Oxazepam and Sulfametoxazole**.

Chemical fingerprints, whose identification spectrum is much wider, allow the identification of **61 marker compounds**, including the 5 identified previously (see Appendix 7).

The self-purification phenomenon in the reservoir leads to pollutants degradation by micro-organisms, absorption, sedimentation and UV radiation. This should'nt hide that, on the other hand, the assessment of the aquatic environement showed degraded sediments in the reservoir.

5.2 The advantages and limitations of the methodology used in this study;

The assessment of pollutant loads from the WWTP, upstream and downstream its discharge was mandatory to understand the system. On such catchment area, it requires performing flow measurement together with water quality sampling.

The use of chemical fingerprints enables to detect a large range of pollutants and contributes to definine the key parameters coming from the WWTP.

This study underlined that, apart from the WWTP, other significant sources of contaminants are present on the catchment area: households not connected to the WWTP, runoff on agricultural land, livestock farming. These sources of contamination, located upstream and dowstream made difficult the assessment of self-purification in the river. Concerning the self-purification in the reservoir, it was assessed using a good knowledge of the reservoir (water levels and volume, flow in and out) and the monitoring campaign. Nevertheless, the hypotheses are strong and analytical measurements on sediments could confirm the presence of pollutants and the consequence on the aquatic environment quality.

5.3 Lessons learned and recommendation for the planned indirect reuse scheme

3 organic compounds, coming from les Herbiers WWTP were found in measurable value in La Bultière DWTP intake: **Carbamazepine**, **Oxazepam and Sulfametoxazole**. This means that no self-purification occurred for them neither along la Grande Maine river nor in La Bultière reservoir. Thus, on a similar system, the **level of treatment of these 3 compounds should be optimized and their concentration monitored** at the DWTP intake.

The aquatic environment in la Grande Maine river and in La Bultière reservoir seems to be degraded according to the assessement of aquatic environment quality. Thus, before implementing the reuse scheme, assessing the initial state of the reservoir is recommended.

It we also be necessary to assess the pollutants loads to the reservoir, their origin and their fate, as part of this initial state.

6 References

- Bruce Petrie, Ruth Barden, Barbara Kasprzyk-Hordern, A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring. Water Research 1-25, 2014
- Caupos E., Mazellier P., Croue J.-P.. *Photodegradation de l'estrone induite par la matière organique naturelle dissoute sous lumière solaire*. GRUTEE, Nancy, France. hal-00822554, 2009.
- Coquery M., Choubert J.-M., Miège C., Synthèse des travaux du projet AMPERES. 24 p., 2009. (http://www.onema.fr/IMG/pdf/2009_B011.pdf)
- Doklady Biological Sciences, Vol. 396, pp. 206–211, 2004. Translated from Doklady Akademii Nauk, Vol. 396, No. 1, pp. 136–141, 2004.
- Feng X., Ding S., Tu J., Wu F., Deng N., *Degradation of estrone in aqueous solution by photo-Fenton system*. Sci Total Environ. 345(1-3):229-37, 2005.
- Lemmin U., *Limnologie physique.*, in *Limnologie Générale*, Pourriot R., Meybeck M. (ed.), Collection d'Ecologie, Masson, Paris, Chap. 2, pp. 60-114, 1995
- Gaillard J.--F., *Limnologie physique : principes et processus*, in *Limnologie Générale*, Pourriot R., Meybeck M. (ed.), Collection d'Ecologie, Masson, Paris, Chap. 3., pp 115-156, 1995
- Capblancq J., *Production primaire autotrophe*, in *Limnologie Générale*, Pourriot R., Meybeck M. (ed.), Collection d'Ecologie, Masson, Paris, Chap. Chap. 6, pp. 229-252, 1995
- Servais P., Dufour Ph., Caumette P., Hirschler A., Matheron R. *L'activité bactérienne*, in *Limnologie Générale*, Pourriot R., Meybeck M. (ed.), Collection d'Ecologie, Masson, Paris, Chap. 7, pp. 253-295, 1995
- Ministère de l'écologie, Arrêté du 25 janvier 2010 relatif aux méthodes et critères d'évaluation de l'état écologique, de l'état chimique et du potentiel écologique des eaux de surface pris en application des articles R. 212-10, R. 212-11 et R. 212-18 du code de l'environnemen, DEVO1001032A, 2015.
- Verbovšek T., A comparison of parameters below the limit of detection in geochemical analyses by substitution methods, RMZ Materials and Geoenvironment, Vol. 58, No. 4, pp. 393–404, 2011.
- Wetzel R.G., *Limnology: Lake and river ecosystems*. Third Edition. Academic Press, San Diego, CA, USA, 1006 p, 2001.
- Yunlong Luo, Wenshan Guo, Huu Hao Ngo, Long Duc Nghiem, Faisal Ibney Hai, Jian Zhang, Shuang Liang,
 Xiaochang C. Wang, A review on the occurrence of micropollutants in the aquatic environment and
 their fate and removal during wastewater treatment. Science of the Total Environment, 473–474,
 619–641, 2014.

7 Appendixes

7.1 Appendix 1 Measurement points and field survey

The measurements points are described downstream, from the most upstream point located in Les Herbiers down to La Bultière reservoir. They are located either on la Grande Maine, its tributaries or La Bultiere reservoir. The table bellow lists all points and its purpose: flow, water sampling for chemical analysis, sampling of aquatic fauna and flora or sampling of sediments

Point	Characteristics
P1	La Grande Maine upstream at Le Bignon
P1'	La Grande Maine downstream industrial area
P1"	Discharge of industrial area stormwater network
P2	Discharge of Les Herbiers WWTP
P3	La Grande Maine at "La Favrie
P4	Stream "Le Grand Ry"
Р5	Stream "Le Longuenais"
P6	Stream "La Tricherie"
Р7	La Grande Maine, downstream La Tricherie
P8	Stream "La Poisetière"
P9	La Grande Maine
P10	La Bultière reservoir: Upstream Preuilly Bridge over
	La Bultière reservoir. La Maurosière
	La Bultière reservoir. La Basse Permoulène
P11	La Bultière reservoir : water intake of the DWTP

Table 16Measurement points and purpose

7.1.1 Measurement points located upstream Les Herbiers WWTP

As shown on Figure 36, 3 measurements points are located upstream les Herbiers WWTP:

 In P1 (La Grande Maine upstream at Le Bignon), la Grande Maine flow is measured under the bridge where road D11 crosses the river. The fauna and flora were sampled few meters downstream this bridge. This point is located upstream Les Herbiers WWTP and upstream Le Bignon industrial area discharge.



• In P1', downstream Le Bignon industrial area stormwater discharge, water, fauna and flora were sampled. This point is considered as the reference point where les Herbiers WWTP has no influence.



Water, fauna and flora sampling in P1'

• In P1", the flow coming from the stormwater storage pond of Le Bignon industrial area was measured in ordre to check, during the water quality monitoring campaign if water sampled in P1' could be influenced by this industrial area.



Figure 36 Location Map of measurement points upstream Les herbiers WWTP

Le Bignon industrial zone stormwater storage pond collects runoff on 80 ha impervious area which are mainly

- Chantiers Jeanneau (35 ha): boat building
- EtablissementsTexier (2 ha): General and precision mechanics (mechanical welding and metal surface treatment)
- K-line (9 ha): manufacturer of windows and doors system in aluminum
- Scabev (1 ha): beef slaughterhouse

7.1.2 P2: Les Herbiers WWTP

Les Herbiers WWTP (28 000 P.E.) discharges 2,500 to 3,000 m³/d in the Grande Maine river downstream Les Herbiers. With an activated sludge treatment line, it treats both urban (15,000 inhabitants) and industrial waste waters. The main industries are listed in **jError! No se encuentra el origen de la referencia**..



Les Herbiers WWTP

In P2, flows of the WWTP discharge was measured and water samples taken.

Table 17 Industrial effluents incomings in Les Herbiers WWTP

Name	Zone	Туре	Activity
Euralis Gastronomie	ZI du Bois Joly	Agribusiness	Slaughterhouse and cutting fat duck. Foie gras production
Achille Bertrand	ZI du Bois Joly	Agribusiness	Cutting and processing meat
Chantiers Jeanneau	Avenue des Sables	Mechanical	Boat building
General Transmissions	ZI du Bois Joly	Mechanical	Design and manufacturing of trans- mission components for gardening gear
K-line	Avenue des Sables	Mechanical	Manufacturer of windows and doors system in aluminum
La Boulangère	Zl La Buzenière	Agribusiness	Industrial bakery
SCABEV	Rue de l'abattoir	Agribusiness	Beef slaughterhouse

Whereas the WWTP includes a specific pretratment of SCABEV slaughterhouse waste water, the 2 other slaughterhouses connected to the WWTP leads to difficulties in the daily management of the plant.

The other management is due to significant rain events where, even if the urban sewers are supposed to be separative, stormwater in these sewers leads to untreated waste water overflows despite a buffer basin.

7.1.3 P3: La Grande Maine at La Favrie

Flows are measured 1,500 m downstream Les Herbiers WWTP where the mixing of its discharge with the river is supposed to be completed. Water, fauna and flora samples where also taken at this location.





Figure 37 Location Map of measurement point Grande Maine river at la Favrie

7.1.4 P4: Stream "Le Grand Ry"

The confluence of Le Grand Ry with la Grande Maine is 6 km downstream les Herbiers WWTP discharge. Flow measurements were performed at a ford near the Hamlet "La Guignaudière".

As there is no WWTP in the catchment area of this stream, on-site sanitation can be a source of diffuse anthropogenic pollutants.



View of the ford





7.1.5 P5: Stream "Le Longuenais"

The confluence of "Le Longuenais" with "La Grande Maine" is located 8 km downstream the WWTP Les Herbiers discharge. In order to assess the load coming from Mesnard-la-Barotière WWTP (900 PE)P5, flow were measured and water samples taken at the hamlet "La Haute Millière".



Figure 39 Location Map of measurement point on the stream "Le Longuenais"

7.1.6 P6: Stream "La Tricherie"

The confluence of "La Tricherie" with "La Grande Maine" is located 9 km downstream Les Herbiers WWTP discharge into La Grande Maine. A small WWTP (150 PE) discharges in this stream.

For this stream, there is no suitable location to use of flow meter. Moreover, from May to October, the stream bed is dry. Thus, the flows for this stream will be assessed visually in the hamlet of "La Dalle".





7.1.7 P7: La Grande Maine downstream La Tricherie

In P7, in order to assess the additional pollutant's loads coming from the streams "Le Longuenais", "Le Grand Ry" and la Tricherie", flows were measured and water sample taken few meters upstream the confluence between "La Grande Maine" and the stream of "La Poisetière". Samples for fauna and flora were taken at the same location.



P7 is located 11.8 km downstream Les Herbiers WWTP discharge into "La Grande Maine".

Confluence of "La Poisetière" with "La Grande Maine"



Figure 41 Location Map of measurement point on "La Grande Maine" donwsntream "La Tricherie" and on the stream "La Poisetière"

7.1.8 P8: Stream la Poisetière

As shown on the previous map, the flow of the stream "La Poisetière" can be measured at the confluence with La Grande Maine at a ford used by vehicles. There are 2 WWTP in the catchment area of la Poisetière: La Gaubretière (1 800 PE) and Beaurepaire (1,800 PE). The confluence between la Poisetière stream and la Grande Maine" is 12 km downstream Les Herbiers WWTP discharge into la Grande Maine.



View of the ford

7.1.9 P9: La Grande Maine at "Le Plessis des Landes"

The Plessis des Landes stream-gauging station continuously measure the flow passing through La Grande Maine and feeding the Bultière reservoir. Samples for water analysis were taken at this stream-gauging station to assess the pollutant's loads. Samples of fauna and flora were taken few hectometers upstream. Between P7 (12 km) and P9 (15 km) downstream Les Herbiers WWTP discharge, "La Grande Maine" collects the discharge of Bazoges-en-Paillers WWTP (1,500 PE).



Figure 42 Location Map of measurement point on "La Grande Maine" at le Plessis des Landes

7.1.10 Measurement points located on La Bultière reservoir

La Bultière dam was commissioned in March 1995. Its catchment area is 154 km², its maximum volume is 5,000,000 m³ with an area of 72 hectares surface. The height of the dam is 21 m. The dam management strategy is as follows:

- In spring, the reservoir is filled up until its target level of 60 m NGF and this level is mainained until May as la Grande Maine flows are higher than the withdrawal for drinking water production;
- In summer, due to lower flows of la Grande Maine, the water level can fall down to its minimum at the end of September or beginning of October. During this period, the water levels ranges bebetween 53 m and 56 m NGF and the flow discharged downstream the dam must be 160 L/s;
- In autumn, the water level rises thanks to higher flows from la Grande Maine due to the autumn rains, until the so-called "winter level" (58 m NGF) which is reached between November and January
- In winter, the water level is maintained around 58 m NGF until March in order to keep available storage volume to control floods

The 4 measurement points on the reservoir are the following:

In P10 (Preuilly bridge), 18 km downstream Les herbiers WWTP, water was sampled as well as sediments. A dam under the bridge is equipped with a 100 m long weir which capacity is 270 m³/s in case of floods. Upstream this weir, water level is maintained at 1.25 m during low flows and sedimentation occurs in order to protect the main part of La Bultière reservoir. The volume strored in the pre-reservoir representents 200,000 m³ out of 5,000,000 m³ in the main reservoir of La Bultière.



The pre-reservoir from the bridge and view of the weir bellow the bridge

- As shown the map bellow, sediments were sampling the reservoir and in 2 points located downstream P10: La Maurosière and La Basse Permoulène
- P11 Intake of the drinking water treatment plant where water and sediments samples were taken.



La Bultière dam



Figure 43 Location Map of measurement points on la Bultière reservoir

7.2 Appendix 2 French water regulation applicable to wastewater and raw water

The following paragraphs present the French regulations to which the different water bodies of the study are subject and then the purification requirements and the parameters that have to be monitored according to the corresponding regulations:

- Les Herbiers WWTP discharge \rightarrow Decree of June 22, 2007 related to wastewaters and RSDE;
- La Bultière reservoir, which is used raw water for drinking water production → Public Health Code, Order of January 11, 2007.

7.2.1 Decree of June 22, 2007 (wastewater)

Regulation distinguishes several cases:

- Discharges of urban wastewater, that is to say the water from treatment plants or lagoons. Discharge standards of urban wastewater are described in the order of June 22, 2007 for individual sewerage systems receiving a gross load of organic pollution than 1.2 kg/day of BOD₅.
- Discharges from non-collective installations receiving a gross load of organic pollution less than 1.2 kg/day of BOD₅ (similar to domestic water). The arrested of May 6, 1996 fixing the technical requirements, inspection procedures and discharge standards in device output knowing that rejection to the surface water environment can only be done in exceptional cases where the conditions of infiltration or effluent characteristics do not ensure their distribution in soil.

The urban WWTP of Les Herbiers is subject to this regulation of June 22, 2007. However, the quality requirements are for COD, BOD_5 , nitrogen (in all forms), Total Suspended Solid (TSS) and phosphorus, but do not take into account other micropollutants. The WWTP Les Herbiers comes under the category > 10,000 inhab. and receiving more than 600 kg BOD_5 /day of organic pollution. An extract of the requirements for treatment performance and maximum concentrations in the discharge to the river is presented below.

MINIMUM PURIFYING REQUIREMENTS for WWTP receiving organic pollution load > 120 kg /d of BOD ₅ (> 2 000 PE)			
Gross load of organic pollution	> 600 kg/d of BDO5 > 10 000 inhab.		
	Maximum concentration	Minimum performance	
PARAMETERS	mg/l	%	
BDO ₅	25	80	
COD	125	75	
TSS	35	90	
Areas sensitive to nitrogen and	phosphorus		
PARAMETERS	mg/l %		
NGL	15	70	
Pt	2	80	

Table 18 Minimum purifying requirements for Les Herbiers WWTP, according to Decree of June 22, 2007⁵

⁵ <u>http://www.legifrance.gouv.fr/affichTexte.do?cidTexte=JORFTEXT000000276647&categorieLien=id</u>

7.2.2 Reduction of Discharges of Hazardous Substances in Water (RSDE)

The European regulation aims since the mid-70s (Directive 2006/11/EC) to reduce pollution of the aquatic environment by dangerous substances, because of their toxic, persistent or bioaccumulative. Subsequently, the European Directive 2000/60/EC, known as the "Water Framework Directive" (WFD) of October 23, 2000 reinforced the environmental protection objectives by fixing deadlines. It aims to achieve good water status by 2015 and the reduction or elimination of emissions of a list of hazardous substances. It defines a list of 33 priority hazardous substances.

These objectives were included in French legislation through the legislation on classified installations (Decree of February 2, 1998) and the national program of action against pollution of aquatic environments (Decree of June 25, 2005 modified).

The RSDE action is notably declined (Ministerial Circular of September 29, 2010) for municipal wastewater treatment plants over 10 000 PE (> 600 kg/d BOD₅) submitted first to an initial monitoring (conducted before end of 2012), and depending on the results, to regular monitoring.

Priority substances and some other pollutants according to Appendix I of Directive 2008/105/EC are presented hereafter more in details.

• Priority substances

45 substances or groups of substances are on the list of priority substances for which environmental quality standards were set from 2008 to 2015, including selected existing chemicals, plant protection products, biocides, metals and other groups like Polyaromatic Hydrocarbons (PAH) that are mainly incineration by-products and Polybrominated Biphenylethers (PBDE) that are used as flame retardants. The complete list is given below.

No	CAS number (i)	Name of prioirty substance (ii)
(1)	15972-60-8	Alachlore
(2)	120-12-7	Anthracène
(3)	1912-24-9	Atrazine
(4)	71-43-2	Benzene
(5)	7440-43-9	Brominated diphenylethers
(6 bis)	56-23-5	Carbon tetrachloride (iii)
(7)	85535-84-8	C10-13 Chloroalkanes
(8)	470-90-6	Chlorfenvinphos
(9)	2921-88-2	Chlorpyrifos (ethylchlorpyri- fos)
(9 bis)	309-00-2 60-57-1 72-20-8 465- 73-6	Cyclodiene pesticides: Aldrine (iii), Dieldrine (iii), Endrine (iii) and Isodrine (iii)
(9 ter)	not applicable	DDT total (vi). (iv)
	50-29-3	para-para-DDT (iii)
(10)	107-06-2	1.2-dichloroethane
(11)	75-09-2	Dichloromethane
(12)	117-81-7	Di(2-ethyl-hexyle)-phthalate (DEHP)
(13)	330-54-1	Diuron

Table 19 List of priority substances in the field of water policy

No	CAS number (i)	Name of prioirty substance (ii)
(14)	115-29-7	Endosulfan
(15)	206-44-0	Fluoranthene
(16)	118-74-1	Hexachlorobenzene
(17)	87-68-3	Hexachlorobutadiene
(18)	608-73-1	Hexachlorocyclohexane
(19)	34123-59-6	Isoproturon
(20)	7439-92-1	Lead and its compounds
(21)	7439-97-6	Mercury and its compounds
(22)	91-20-3	Naphtalene
(23)	7440-02-0	Nickel and its compound
(24)	84852-15-3	Nonylphenols (4-nonylphenol)
(25)	140-66-9	Octylphenols (4-(1.1'.3.3'- tetramethyl-butyl)-phenol)
(26)	608-93-5	Pentachlorobenzene
(27)	87-86-5	Pentachlorophenol
(28)	not applicable	Polyaromatic hydrocarbons (HAP)
	50-32-8	Benzo(a)pyrene
	205-99-2	Benzo(b)fluoranthene
	207-08-9	Benzo(k)fluoranthene
	191-24-2	Benzo(g.h.i)pe-rylene
	193-39-5	Indeno(1.2.3- cd)-pyrene
(29)	122-34-9	Simazine
(29 bis)	127-18-4	Tetrachloroethylene (iii)
(29 ter)	79-01-6	Trichloroethylene (iii)
(30)	36643-28-4	Tributyltin compounds (tributyltin- cation)
(31)	12002-48-1	Trichlorobenzenes
(32)	67-66-3	Trichloromethane
(33)	1582-09-8	Trifluralin
(34)	115-32-2	Dicofol
(35)	45298-90-6	Perfluorooctane sulfonic acid and its derivatives (PFOS)
(36)	124495-18-7	Quinoxyfene
(37)		Dioxins and dioxine-like compounds
(38)	74070-46-5	Aclonifen
(39)	42576-02-3	Bifenox
(40)	28159-98-0	Cybutryne
(41)	52315-07-8	Cypermethrine
(42)	62-73-7	Dichlorvos
(43)		Hexabromocyclododecane (HBCDD)
(44)	76-44-8/ 1024-57-3	Heptachlor and heptachlor epoxide
(45)	886-50-0	Terbutryn

i. CAS: Chemical Abstracts Service.

- ii. Where groups of substances have been selected, typical individual representatives are listed as indicative parameters (in brackets and without number). For these groups of substances, the indicative parameter must be defined through the analytical method.
- iii. This substance is not a priority substance but one of the other pollutants for which the EQS are identical to those laid down in the legislation that applied prior to 13 January 2009.
- DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2(o-chlorophenyl)-2-(p-chlorophenyl) ethane (CAS number 789-02-6; EU number 212-332-5); 1,1-dichloro-2,2 bis (p-chlorophenyl) ethylene (CAS number 72-55-9; EU number 200-784-6); and 1,1-dichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 72-54-8; EU number 200-783-0).
- v. Refers to α -hexabromocyclododecane (CAS nr. 134237-50-6), β -Hexabromocyclododecane (CAS nr. 134237-51-7) and γ hexabromocyclododecane (CAS nr. 134237-52-8).
 - Some other pollutants

These eight pollutants, which fall under the scope of Directive 86/280/EEC(1) and which are included in List I of the Appendix to Directive 76/464/EEC, are not in the priority substances list. However, environmental quality standards for these substances are included in the Environmental Quality Standards Directive 2008/105/EC.

(1) Amended by Directive 88/347/EEC and 90/415/EEC

	CAS number	Name of other pollutants	
(6a)	56-23-5	Carbon-tetrachloride(1)	
(9b)	not applicable	DDT total (1)(2)	
	50-29-3	para-para-DDT (1)	
(9a)		Cyclodiene pesticides	
	309-00-2	Aldrin (1)	
	60-57-1	Dieldrin (1)	
	72-20-8	Endrin (1)	
	465-73-6	Isodrin (1)	
(29a)	127-18-4	Tetrachloro-ethylene (1)	
(29b)	79-01-6	Trichloro-ethylene (1)	

Table 20List of priority substances in the field of water policy

(1) This substance is not a priority substance but one of the other pollutants for which the EQS are identical to those laid down in the legislation that applied prior to 13 January 2009

(2) DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2 (o-chlorophenyl)-2-(p-chlorophenyl) ethane (CAS number 789-02-6; EU Number 212-332-5); 1,1-dichloro-2,2 bis (p-chlorophenyl) ethylene (CAS number 72-55-9; EU Number 200-784-6); and 1,1-di-chloro-2,2 bis (p-chlorophenyl) ethane (CAS number 72-54-8; EU Number 200-783-0).

7.2.3 French Public Health Code (raw water used for drinking water)

The French Public Health Code defines quality criteria for raw water and water intended for human consumption (with the exception of natural mineral waters) in the Order of January 11, 2007. It takes into account the acceptable limits for metals, pesticides, Polycyclic Aromatic Hydrocarbons (PAH), Trihalomethane (THM). These criteria are particularly important and require specific attention in the monitoring of La Grande Maine and La Bultière reservoirs.

An extract of the order of January 11, 2007 which defines quality of raw water and water intended for human consumption is given bellow.



Figure 44 French legislation on raw water quality requirements for the production of drinking water (continued)

			NUL	DUCES	FIGH I	INBO		EAU BRUTE		EAU DISTRIBUEL	
		*		*	-	A3		1	1000		
PARAMETRES	UNITE	0	-	0	-	0	-	UMITIS	LIMITES	RURINCIS	UEU DE MESURE
Chlorures	ngn.	802		200		807	3	200	ta	250	3
Chrome	1/8rl		8.		05		8.	20	95	and the second	02
Conductivity à 10°C	plater	1000		1000	•	1000	4		×	180 à 1000	60+64
Conductivity à 15°C	moi24	1100		1100		1100				200 4 1100	10+4
Couleur (PT/Co)	mg/L	2	2	8	8	8,	200	oot		12 O	10+G
Cuinte	T/Bm	0'03	5010	5010		-	•		1		6
Cyanures fotaux	1/8rt		8	•	9,		8	20	\$	2	æ
DBO5 4 10°C	mg/L	6.9		<5>		44	a.	-		4	-
000	mert	+	à	×	3	2	×	×	×		
1.2-dichloroethane	1/8d	•	4	*			٠	•	3		2
Epichlorhydrine	1/8/1			•	•			141	O,I CBM	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	P2+D2
Equilibre calcocarbonique		5	1	1	•	4	•		×.	A l'hquiller op	5
Fer dissous (sur echantion fibre 2 aug pm)	1/Bu	9	50	•	*			ä			
fer total	1/81	8	2	8	-	43		4		902	P2 + D1 [N utilise comme agen de feculation] + D2
Fluorures	mg/L	o 7h	57	Cryto.		Curlo .	ł		2		52
Hydrocarbures aromutiques polycycliques	1/8/1	1	(m) 210	8	1		1	s subs. (ii)	4 subs. (ke)	4	8
Hydrocarburns dissous	mg/L		20.05	•	3	0.5	-		and a second	20	
Mungantse	1/8m	5010	¥4	8		1	+		•	Sala	(is traitement de demangareration) + P.
Matteres En Suspension	ngu	52	ġ.	8		-	•		•		
Mercure	1/8rt	50	-	58	-	50	*		H.		æ
Total microcytines	NgH	10	-25	•	•75		13	•	•	•2	P1 entrick profection again
Nickel	ngu		4		•	4	8	-	8		02
Nitrates	1/Jun	52	8	(e)	я.	R	8	0 05	8.	2	P+D*
(Nitrates/yo) + (Nitrites/3)	mg/t	2		•		×	÷		+		
Nitrites	WBU	•	4	30	:e:	4.1	E.	e.	02 010		84
Odeun-Saveur à 25°C	fact.dil.	*	1	2	+	2	ł.	ġ.	8	96	P1+D1
Orydabilité au permanganate	mg/L 02	1	2	20	10	г.	5	12	2	5	£
Oxygène dissous (taux de saturation)	% O2	04.4	÷	\$. ^		of c	-	of c	•	2	4

	La règlement ou à d'autres	tation est usages d	applic to the second	lable à	toutes	les eau	x qui so	ant des	tines à la hoè	sson, à la cuisson, à	la préparation d'alim	ents
(jarati)	Les eaux de ne pas cont constituant étre confor satisfaire à	stinées à benir un n t un dang mes aux l des référ	la consu combre per potte limites ences d	omma ou un entiel y de qui fe qui	tion hi e conce pour la alité dé Iné.	maine intratio sants, finies,	doivent n de m	00.00	gantmes, de p	arasites ou de tout	es autres substances	
Surfly	Les limites et suuf mention	t néférenc	tes doiv	rent ét	re resp	ottesa	uix robi	nets n	ormalement u	diises pour la cons	ommation humaine	
Set principal	Les limites Les limites Les limites et de distri	de qualita de qualita de qualita bution, ar	é des el é des el é l'anne nnexe l	aux de aux br bree H (h	utes de et les n	perfici toute i effenno festinée	olles (ar origine es de qu	(janne) jalité (onsom	II) e II) paramètres ins mation huma	dicateurs du fonctis ine	nnement des install	ations de production
NB-Les comm	tentaints des r	notes du l	Lableau	-	ent au	who do	docum	tuy				
				EAU D	S DUCI S	UP6874	I		EAU BRUTE		EAU DISTRIBUTE	
			At	(1)	2	17	Ag	2		NULLY,		
PARAMETS	SES	UNITE	Glub	1(3)	0	-	0	-	IMMITS	CIIMIN	KEPTREPACES	THEN DE WERNING
						PARAA	NETRE!	VH4 S	SICO-CHIMI	QUES		
Acrylamide		1/84		•	÷	•		•		C,1 CRM		P2 (7) + D2 (9)
Agents de su	urface .	mg/L	0,2	•	0,2	ł	0.5	ä	0.5			
Aluminium	total	1/8/1		1	4	ÿ.	4	ŧ.			007	P2 + D1 (8) (s) utilist comme
Ammonium		mart	100	1	1	X			4		01	agent de flooulation) Pr 0] + Dr
						2					030	
Antimoine		P\$4			+	÷	4			5		50
Arsenic		1/8rt	1	8		8	2	001	100	0		52
Abote Kjeld	7	mg/L			*	1	-		10 Mar			
Baryum		mg/L	•	0,3	÷	1			0	0.7		53
Benziène		1/8/1			1		4	•		A CONTRACTOR OF A CONTRACTOR O		4
Benzo(a)pyn	the	1/84	-	,		,	•	•	1.1	0,01		D2
Bore		1/Bui	-	1		,	-	÷	4	1		æ
Bromates		1/8/1	2	1	8	8	27	1	*	9	•	N connection ou chicketion
Cadmium		1/8/1	-	5	-	5	-	5	5	5		Da
Carbone On	ganique Total	mg/LC	•		•	•	-		10		36	£
Chlore libre	et total		T.	,	+	ŧ	1	÷	+	*	0	9+0
Chiorites		1/8/	8	3	-	e,	i.	£.,			r'o	Dig fill tradit thismuch die chilome
Chlorum de	vinde	1/en	1	'	•	,			4	A. C.		Pr a Dr

Eaux destinées à la consommation humaine

Figure 45 French legislation on raw water quality requirements for the production of drinking water (continued)

7.3 Appendix 3 River flows

The flow of la grande Maine is measured on-line in the framework of the French hydrologic monitoring program (Banque Hydro) since 1990. The gauging station is located at Plessis des Landes (P9), 15 km down-stream Les Herbiers WWTP discharge.

Whereas the mean flow is 1.340 m³/s, the mean monthly flow ranges from 0.102 m³/s in August to 3.810 m³/s in January (Figure 4).

Upstream the gauging station, neither the flows of La grande Maine tributaries nor the discharges of les Herbiers WWTP are well known. Thus their were monitored during the water sampling to assess the pollutant loads but also on a monthly basis from April 2014 to August 2015 to study their contribution to the flow downstream and to assess the dilution factor of les Herbiers WWTP discharge. This dilution factor is assessed comparing Les Herbiers WWTP discharge flow with the flow measured in P9 (La Grande Maine at Le Plessis des Landes) where a gauging station measures the flow on-line.

7.3.1 Flows on April 24, 2014

As the rainfall in the previous week (2.8 mm the day before) and the stable flows in P9, the flows can be considered as **dry weather flows**. The flow in P9 is about a quarter of its mean value in April (1,090 L/s).

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	21	9%
P1": Discharge of industrial area stormwater network	-	-
P2: Discharge of Les Herbiers WWTP	30	12%
P3: La Grande Maine at La Favrie	57	24%
P4: Stream "Le Grand Ry"	56	23%
P5: Stream "Le Longuenais"	32	13%
P6: Stream "La Tricherie"	4	2%
P7: La Grande Maine downstream Tricherie	160	66%
P8: Stream "La Poisetière"	42	17%
P9: La Grande Maine at Le Plessis des Landes	242	100%

Table 21Flows on April 24, 2014

As all the discharges and streams between P1 and P9 couldn't be measured and because of uncertainties in the measurements, there are some inconsistencies between the flows measured and the official measurement in P9. These inconsistencies can also be noticed during the other flow monitoring campaigns.

For this dry weather flow measurement campaign, the flow of Les Herbiers WWTP represents 12% of la Grande Maine flow in P9. In other words, **12% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP**.

7.3.2 Flows on May 21, 2014:

With heavy rains two days before (16 mm) and during the monitoring campaign (21 mm), the hydrogram in P9 reached a peak during the measurements and the flows can be considered as wet weather flows. Nevertheless, the flow in P9 is near its mean value in May.

Table 22 Flows on May 21, 2014

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	60	10%
P1'': Discharge of industrial area stormwater network	-	-
P2: Discharge of Les Herbiers WWTP	41	7%
P3: La Grande Maine at La Favrie	128	21%
P4: Stream "Le Grand Ry"	90	15%
P5: Stream "Le Longuenais"	145	24%
P6: Stream "La Tricherie"	8	1%
P7: La Grande Maine downstream Tricherie	409	68%
P8: Stream "La Poisetière"	60	10%
P9: La Grande Maine at Le Plessis des Landes	600	100%

For this wet weather flow measurement campaign, 7% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.3 Flows on June 30, 2014

With heavy rains two days before (15 mm) and the day before the monitoring campaign (8 mm), the hydrogram in P9 reached a peak the day before the measurements. Moreover, the flow in P9 is near its mean value in June. Thus the flows can be considered as dry weather flows.

Water samples were taken the same day.

Table 23 Flows on June 30, 2014

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	53	18%
P1": Discharge of industrial area stormwater network	5	2%
P2: Discharge of Les Herbiers WWTP	31	10%
P3: La Grande Maine at La Favrie	97	32%
P4: Stream "Le Grand Ry"	36	12%
P5: Stream "Le Longuenais"	87	29%
P6: Stream "La Tricherie"	3	1%
P7: La Grande Maine downstream Tricherie	250	83%
P8: Stream "La Poisetière"	58	19%
P9: La Grande Maine at Le Plessis des Landes	300	100%

For this dry weather flow measurement campaign, 10% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.4 Flows on July 31, 2014:

With small rains 4 days (4 mm) and 3 days before (2 mm), the flows in P9 are stable and reached half of their mean value in July. Thus the flows can be considered as dry weather flows.

Table 24Flows on July 31, 2014

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	25	42%
P1": Discharge of industrial area stormwater network	3	5%
P2: Discharge of Les Herbiers WWTP	25	42%
P3: La Grande Maine at La Favrie	56	93%
P4: Stream "Le Grand Ry"	8	13%
P5: Stream "Le Longuenais"	6	10%
P6: Stream "La Tricherie"	3	5%
P7: La Grande Maine downstream Tricherie	64	107%
P8: Stream "La Poisetière"	1	2%
P9: La Grande Maine at Le Plessis des Landes	60	100%

During this monitoring campaign, the flows measured in P3 and P7 (107% of P9) can be considered as overestimated. For this dry weather flow measurement campaign, 42% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.5 Flows on September 3, 2014:

Despite heavy storms in August, there was 6 days without rain before the measurements, the flows in P9 are slightly decreasing and are in the range of their mean value in september. Thus the flows can be considered as dry weather flows.

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	28	28%
P1'': Discharge of industrial area stormwater network	2	2%
P2: Discharge of Les Herbiers WWTP	29	29%
P3: La Grande Maine at La Favrie	62	62%
P4: Stream "Le Grand Ry"	6	6%
P5: Stream "Le Longuenais"	21	21%
P6: Stream "La Tricherie"	< 1.5	0%
P7: La Grande Maine downstream Tricherie	98	98%
P8: Stream "La Poisetière"	6	6%

Table 25 Flows on September 3, 2014

Point	Flow L/s	% of flow in P9
P9: La Grande Maine at Le Plessis des Landes	100	100%

During this monitoring campaign, the flows measured in P7 (98% of P9) can be considered as overestimated. For this dry weather flow measurement campaign, 29% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.6 Flows on September 26, 2014:

With no rains during 4 weeks, the flow in P9 is stable at about a quarter of its mean value in September (172 L/s. Thus the flows can be considered as dry weather flows.

Table 26	Flows on	September	26.2014
	110113 011	ooptombol	20,2011

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	17	45%
P1": Discharge of industrial area stormwater network	1	3%
P2: Discharge of Les Herbiers WWTP	21	55%
P3: La Grande Maine at La Favrie	37	97%
P4: Stream "Le Grand Ry"	0	0%
P5: Stream "Le Longuenais"	<3	0%
P6: Stream "La Tricherie"	<1	0%
P7: La Grande Maine downstream Tricherie	44	116%
P8: Stream "La Poisetière"	0	0%
P9: La Grande Maine at Le Plessis des Landes	38	100%

During this monitoring campaign, the flows measured in P3 and P7 (116% of P9) can be considered as overestimated. For this dry weather flow measurement campaign, 55% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.7 Flows on October 28, 2014

With no significant rain during 10 days, the flow in P9 is stable at about 40 % of its mean value in October (172 L/s). Thus the flows can be considered as dry weather flows.

Table 27	Flows on	October 28,	2014
----------	----------	-------------	------

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	24	34%
P1": Discharge of industrial area stormwater network	2	3%
P2: Discharge of Les Herbiers WWTP	19	27%
P3: La Grande Maine at La Favrie	48	69%
P4: Stream "Le Grand Ry"	8	11%

Point	Flow L/s	% of flow in P9
P5: Stream "Le Longuenais"	14	20%
P6: Stream "La Tricherie"	3	4%
P7: La Grande Maine downstream Tricherie	65	93%
P8: Stream "La Poisetière"	11	16%
P9: La Grande Maine at Le Plessis des Landes	70	100%

For this dry weather flow measurement campaign, 27% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.8 Flows on November 25, 2014

With a significant rain the day before (4 mm) and 3 heavy rains during the first half of November, the flow in P9 is stabilising at about 70 % of its mean value in November (1,660 L/s). Thus the flows can be considered as wet weather flows.

Table 28 Flows on November 25, 2014

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	107	9%
P1": Discharge of industrial area stormwater network	0	0%
P2: Discharge of Les Herbiers WWTP	36	3%
P3: La Grande Maine at La Favrie	182	15%
P4: Stream "Le Grand Ry"	193	16%
P5: Stream "Le Longuenais"	333	28%
P6: Stream "La Tricherie"	19	2%
P7: La Grande Maine downstream Tricherie	960	80%
P8: Stream "La Poisetière"	181	15%
P9: La Grande Maine at Le Plessis des Landes	1,200	100%

For this wet weather flow measurement campaign, 3% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.9 Flows on December 29, 2014:

With small rain almost everyday in December, the flow in P9 is decreasing at about 40 % of its mean value in December (2,760 L/s). Nevertheless, the flows can be considered as wet weather flows.

Table 29 Flows on December 29, 2014

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	224	22%

Point	Flow L/s	% of flow in P9
P1": Discharge of industrial area stormwater network	4	0%
P2: Discharge of Les Herbiers WWTP	31	3%
P3: La Grande Maine at La Favrie	266	27%
P4: Stream "Le Grand Ry"	178	18%
P5: Stream "Le Longuenais"	292	29%
P6: Stream "La Tricherie"	19	2%
P7: La Grande Maine downstream Tricherie	891	89%
P8: Stream "La Poisetière"	96	10%
P9: La Grande Maine at Le Plessis des Landes	1,000	100%

For this wet weather flow measurement campaign, 3% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.10 Flows on January 28, 2015

With small rain almost everyday in January, the flow in P9 is decreasing at about 50 % of its mean value in January (3,810 L/s). Nevertheless, the flows can be considered as wet weather flows.

Table 30 Flows on January 28, 2015

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	196	11%
P1": Discharge of industrial area stormwater network	1	0%
P2: Discharge of Les Herbiers WWTP	38	2%
P3: La Grande Maine at La Favrie	280	16%
P4: Stream "Le Grand Ry"	351	20%
P5: Stream "Le Longuenais"	360	20%
P6: Stream "La Tricherie"	19	1%
P7: La Grande Maine downstream Tricherie	1,368	78%
P8: Stream "La Poisetière"	356	20%
P9: La Grande Maine at Le Plessis des Landes	1,760	100%

For this wet weather flow measurement campaign, 2% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.11 Flows on March 4, 2015:

With small rain almost everyday in second part of February, the flow in P9 is decreasing but stay about 40 % above its mean value in March (1,880 L/s). Thus, the flows can be considered as wet weather flows.

Table 31 Flows on March 4, 2015

–	– Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	381	15%
P1": Discharge of industrial area stormwater network	3	0%
P2: Discharge of Les Herbiers WWTP	39	2%
P3: La Grande Maine at La Favrie	448	17%
P4: Stream "Le Grand Ry"	484	19%
P5: Stream "Le Longuenais"	670	26%
P6: Stream "La Tricherie"	28	1%
P7: La Grande Maine downstream Tricherie	1,755	68%
P8: Stream "La Poisetière"	442	17%
P9: La Grande Maine at Le Plessis des Landes	2,570	100%

For this wet weather flow measurement campaign, 2% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.12 Flows on March 23, 2015

With no rain in March except a heavy rain 3 days before, the flow in P9 is decreasing to 50 % of its mean value in March (1,880 L/s). Thus, the flows can be considered as dry weather flows.

Water samples were taken the same day.

Table 32Flows on March 23, 2015

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	245	28%
P1": Discharge of industrial area stormwater network	3	0%
P2: Discharge of Les Herbiers WWTP	36	4%
P3: La Grande Maine at La Favrie	300	34%
P4: Stream "Le Grand Ry"	194	22%
P5: Stream "Le Longuenais"	236	27%
P6: Stream "La Tricherie"	14	2%
P7: La Grande Maine downstream Tricherie	749	86%
P8: Stream "La Poisetière"	228	26%
P9: La Grande Maine at Le Plessis des Landes	870	100%

For this dry weather flow measurement campaign, 4% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.13 Flows on April 8, 2015

With no significant rain during one week, the flow in P9 is decreasing to 50 % of its mean value in April (1,090 L/s). Thus, the flows can be considered as dry weather flows.

Table 33 Flows on April 8, 2015

– – Point –	– Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	154	27%
P1'': Discharge of industrial area stormwater network	2	0%
P2: Discharge of Les Herbiers WWTP	31	5%
P3: La Grande Maine at La Favrie	183	32%
P4: Stream "Le Grand Ry"	108	19%
P5: Stream "Le Longuenais"	120	21%
P6: Stream "La Tricherie"	14	2%
P7: La Grande Maine downstream Tricherie	367	64%
P8: Stream "La Poisetière"	167	29%
P9: La Grande Maine at Le Plessis des Landes	570	100%

For this dry weather flow measurement campaign, 5% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.14 Flows on April 29, 2015

With one significant rain in 3 weeks, the flow in P9 is decreasing to 25% of its mean value in April (1,090 L/s). Thus, the flows can be considered as dry weather flows.

Table 34Flows on April 8, 2015

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	82	33%
P1": Discharge of industrial area stormwater network	1	0%
P2: Discharge of Les Herbiers WWTP	26	10%
P3: La Grande Maine at La Favrie	112	45%
P4: Stream "Le Grand Ry"	48	19%
P5: Stream "Le Longuenais"	36	14%
P6: Stream "La Tricherie"	14	6%
P7: La Grande Maine downstream Tricherie	218	87%
P8: Stream "La Poisetière"	60	24%
P9: La Grande Maine at Le Plessis des Landes	250	100%

For this dry weather flow measurement campaign, 10% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.15 Flows on May 26, 2015

Since the last significant rain event in early May, the flow in P9 is decreasing to 50 % of its mean value in May (0,620 L/s). Thus, the flows can be considered as dry weather flows.

Water samples were taken the same day.

Table 35Flows on May 26, 2015

– – Point	– Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	93	27%
P1'': Discharge of industrial area stormwater network	1	0%
P2: Discharge of Les Herbiers WWTP	39	11%
P3: La Grande Maine at La Favrie	133	39%
P4: Stream "Le Grand Ry"	76	22%
P5: Stream "Le Longuenais"	46	14%
P6: Stream "La Tricherie"	11	3%
P7: La Grande Maine downstream Tricherie	259	76%
P8: Stream "La Poisetière"	83	24%
P9: La Grande Maine at Le Plessis des Landes	340	100%

For this dry weather flow measurement campaign, 11% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.16 Flows on June 29, 2015

Since the last significant rain event in mi-June, the flow in P9 is decreasing to 50 % of its mean value in June (0,240 L/s). Thus, the flows can be considered as dry weather flows.

Water samples were taken the same day.

Table 36Flows on June 29, 2015

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	29	29%
P2: Discharge of Les Herbiers WWTP	25	25%
P3: La Grande Maine at La Favrie	61	61%
P9: La Grande Maine at Le Plessis des Landes	100	100%

For this dry weather flow measurement campaign, 25% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.17 Flows on July 27, 2015

Since the last significant rain event in mi-June, the flow in P9 stays stable around its mean value in July (0,129 L/s). Thus, the flows can be considered as dry weather flows.

Water samples were taken the same day.
Table 37 Flows on July 27, 2015

–	– Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	14	16%
P2: Discharge of Les Herbiers WWTP	24	27%
P3: La Grande Maine at La Favrie	42	47%
P9: La Grande Maine at Le Plessis des Landes	90	100%

For this dry weather flow measurement campaign, 27% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.3.18 Flows on August 31, 2015

Even with heavy rains during the las ten days, their impact on the flow in P9 was transient and it came back to its mean value in August (0,102 L/s). Thus, the flows can be considered as dry weather flows.

Water samples were taken the same day.

Table 38Flows on August 31, 2015

Point	Flow L/s	% of flow in P9
P1: La Grande Maine upstream at Le Bignon	37	37%
P2: Discharge of Les Herbiers WWTP	20	20%
P3: La Grande Maine at La Favrie	58	58%
P9: La Grande Maine at Le Plessis des Landes	100	100%

For this dry weather flow measurement campaign, 20% of the flow feeding La Bultière reservoir comes from Les Herbiers WWTP.

7.4 Appendix 4 Families of compounds measured

Iodinated contrast agents: They are used in medical imaging (IRM), radiology practices (X-ray radiography) and in hospitals and clinics. They are used to artificially increase the contrast to better visualize anatomical or pathological structure typically little or no contrast. These products are injected in patients and excreted in the urine.

Pharmaceutical compounds:

- *Analgesics:* They are used in medicine in the treatment against pain. Analgesics, reducing pain, are like paracetamol or ibuprofen, as analgesics, eliminating sensitivity to pain, are morphine derivatives.
- *Antidepressants:* They are psychotropic drugs including depression. The target molecule is present, fluoxetine, which is found in the drug "Prozac" for example.
- *Antiepileptic drugs:* They belong to the group of drugs used for prevention of epilepsy.
- Lipo-regulating pharmaceuticals: They treat cases of hypercholesterolemia and hyperlipidemia.
- *Pharmaceutical compounds beta-blockers:* This type of molecule is used especially for the treatment of coronary heart disease or hypertension.
- *Anti-bacterial pharmaceuticals:* These are molecules acting as an antiseptic, bactericidal and/or fungicidal (eg solubacter).
- *Psychotropes:* The desired molecule, oxazepam, is an antidepressant and anxiolytic. It is used in the treatment of anxiety, anxiety attacks, delirium tremens and alcohol withdrawal.
- Antibiotics (sulfonamides, diaminopyrimidines, macrolides, tetracyclines): These are natural or synthetic molecules that destroy or inhibit the growth at low concentrations of pathogenic bacteria and have selective toxicity. Some products are used to fight against livestock diseases (breeding cattle, pigs and poultry) as sulfachloropyridazine (bactericidal agent) or trimethoprim (bacteriostatic agent).

Alkylphenol: The alkylphenols are used massively for producing detergents, as fuel additives and lubricants, polymers, components and phenolic resins. They are also used to produce perfumes, thermoplastic elastomers, antioxidants, etc. and are also found in tires, adhesives, coatings, carbon paper and high-performance rubbers. These xenobiotic compounds are endocrine disruptors.

Aniline: the most important use of aniline relates to the manufacture of 4,4'-MDI (monomer manufacturing polyurethane). This production accounts for about 85% of produced aniline. Among other uses, the chemical manufacturing is rubber (9%), herbicides (2%) and pigments or coloring agents (2%).

Bisphenol A: Bisphenol A is mainly used as epoxy monomer (lining the inner boxes of canned and cans) and polycarbonates (sunglasses, CD- DVD). As indicative of the coloration printing, bisphenol A is present in free form in many receipts, credit card receipts (thermal paper) and banknotes. It is an endocrine disruptor.

Alkyl benzenes (benzene, toluene, ethylbenzene, xylene): they are benzene derivatives, which are components of many chemicals, solvents, detergents... They are very volatile.

Aromatic organochlorines (chlorobenzenes, chlorophenols): These molecules used in the manufacture of pesticides and herbicides. They are harmful molecules to humans.

Volatile and semi-volatile organic compounds (VOC): VOC are one of the causes of "indoor pollution"; that mean the air pollution inside buildings, dwelling places, public places and workplaces. The sources include paints, glues and wood treatment products. Some VOC, such as formaldehyde, can lead to irritation of eyes, nose and throat; others are carcinogenic.

Polycyclic aromatic hydrocarbons (PAH): These compounds are generated by the combustion of fossil fuels (in particular diesel engines) in gaseous or particulate form. The most studied is benzo (a) pyrene.

In addition to their carcinogenic properties, PAH have mutagenic character depending on the chemical structure of the metabolites formed. They can also cause a decrease in the immune system, increasing the risk of infection.

Trace elements and minerals micro pollutants (metals): metallic salts are in the composition of many compounds and are found in solution in the water. They are more or less toxic according to their characteristics (radioactivity, heavy metal, chemical toxicity, bioavailability...).

Some metals (iron, copper and zinc in particular) are essential. They are toxic beyond a certain dose, but a deficiency causes severe metabolic disorders.

Organotins: organotin compounds (or organotins) as TBT (tributyltin, highly toxic to many marine organisms, for algae and various marine organisms including molluscs) were widely used in antifouling paints for ship hulls. The TBT and its degradation products are the cause of widespread marine pollution of the French coast and much of the coastal industrialized countries.

They are often toxic and eco-toxic in the environment, even at very low doses. In addition, they have a long lifetime.

Hormones: Hormones are involved in many processes of living beings (animals and plants), whose reproduction, cell differentiation, homeostasis, or growth... Natural hormones (including phytoestrogens) have a short lifespan. They do not accumulate in fatty tissue and are rapidly destroyed in the body, including certain liver enzymes. Unlike synthetic molecules (ethinyl estradiol) are less rapidly degraded, have a higher persistence in the environment and in the body, typically up to several years, and can be accumulated in the fatty tissues and muscles animals and humans. They are endocrine disruptors.

PCB (Polychlorinated Biphenyls): PCB are otherwise called pyralenes. They were produced in France until 1987 for a majority use in electrical transformers and capacitors through their quasi-flammable electrical insulating properties.

PCB are toxic, ecotoxic and toxic for reproduction (including low dose as endocrine disruptors). They are ubiquitous and persistent pollutants (half-life 94 days to 2,700 years). Very soluble, they are part of bioaccumulative contaminants commonly found in fatty tissue in humans (including breast milk). They are classified as "probable carcinogens".

Pesticides (insecticides, fungicides, herbicides, parasiticides): Commonly used for domestic purposes, pesticides are a large family of over 900 molecules. Pesticides are ecotoxic, slash (eg DDT), and some are considered as endocrine disruptors.

7.5 Appendix 5 Water quality results

Compound	Date	P1' Upstream WWTP	P2 Les Herbiers WWTP	P3 Downstream WWTP "La Favrie"	P9 Plessis-des- Landes	P11 DWTP intake
		N, P &	ТОС			
Ammonium	30-Jun-14	< 0.78	< 0.78	< 0.78	< 0.78	< 0.78
(mg NH ₄ /L)	23-Mar-15	< 0,01	0.55	0.06	0.55	0.07
	26-May-15	0.09	< 1.00	0.06	0.30	0.05
	29-Jun-15	0.25	3.82	1.50	0.14	0.11
	27-Jul-15	0.16	< 1.00	0.07	0.03	0.39
	31-Aug-15	0.40	< 1.00	0.09	0.04	0.59
Nitrates	30-Jun-16	19	27	19	6	7
(mg NO3/L)	23-Mar-15	31	19	28	19	26
	26-May-15	25	22	22	19	20
	29-Jun-15	22	< 2	15	22	15
	27-Jul-15	19	< 2	8	2	10
	31-Aug-15	20	< 2	11	8	3
Kjeldhal Nitrogen	30-Jun-14	1.00	< 2.00	0.86	1.23	1.61
(mg N/L)	23-Mar-15	0.80	2.10	0.92	1.33	1.17
	26-May-15	0.70	2.20	1.22	1.17	1.16
	29-Jun-15	0.69	2.97	2.32	0.98	1.34
	27-Jul-15	5.01	1.58	1.07	2.68	1.45
	31-Aug-15	0.84	1.50	0.89	1.08	1.87
Orthophosphates	30-Jun-14	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6
(mg PO4/L)	23-Mar-15	0.07	0.24	0.05	0.25	0.16
	26-May-15	0.20	0.26	0.23	0.44	0.19
	29-Jun-15	0.40	0.56	0.68	1.00	0.06
	27-Jul-15	0.54	0.40	0.68	0.67	0.12
	31-Aug-15	0.53	1.10	0.78	0.67	0.24
ТОС	30-Jun-14	5.20	7.60	6.10	8.20	7.20
(mg C/L)	23-Mar-15	4.25	8.21	5.13	7.31	7.47
	26-May-15	4.29	7.27	5.09	6.10	8.77
	29-Jun-15	3.90	9.01	6.48	7.06	8.35
	27-Jul-15	5.89	8.11	7.89	7.41	8.01
	31-Aug-15	4.57	7.21	5.61	7.97	8.76
		Microbi	ology			
E. Coli	30-Jun-14	-	-	-	-	-
(n/100 mL)	23-Mar-15	5,035	20,850	2,601	1,021	< 15
	26-May-15	2,130	6,880	1,794	344	< 15
	29-Jun-15	1,502	139,920	9,043	309	< 15
	27-Jul-15	6,119	62,170	5,598	438	15
	31-Aug-15	9,043	59,470	5,352	371	< 15

Compound	Date	P1' Upstream WWTP	P2 Les Herbiers WWTP	P3 Downstream WWTP "La Favrie"	P9 Plessis-des- Landes	P11 DWTP intake
Enterococci	30-Jun-14	-	-	-	-	-
(n/100 mL)	23-Mar-15	368	4.030	415	179	< 15
	26-May-15	504	2,498	442	94	< 15
	29-Jun-15	365	12,700	1,881	234	< 15
	27-Jul-15	509	6,350	332	179	< 15
	31-Aug-15	509	6,880	920	285	15
Sulphate reducing bacteria	30-Jun-14	-	-	-	-	-
(n/100 mL)	23-Mar-15	190	1300	160	2800	320
	26-May-15	170	1200	440	2700	16
	29-Jun-15	430	1500	1400	380	39
	27-Jul-15	640	3400	1100	270	36
	31-Aug-15	910	8000	1200	970	140
Cryptosporidium	30-Jun-14	-	-	-	-	-
(n/ 10 L)	23-Mar-15	55	6	45	114	12
	26-May-15	50	2	69	40	0
	29-Jun-15	1	2	3	3	None
	27-Jul-15	10	2	6	2	None
	31-Aug-15	2	11	26	11	None
Giardia	30-Jun-14	-	-	-	-	-
(n/ 10 L)	23-Mar-15	150	534	130	99	16
	26-May-15	174	107	189	43	1
	29-Jun-15	8	127	40	2	None
	27-Jul-15	32	127	31	6	None
	31-Aug-15	14	117	58	21	None
RNA specific bacteriophages	30-Jun-14	-	-	-	-	-
(n/mL)	23-Mar-15	< 1	5	7	5	< 1
	26-May-15	1	1	1	1	< 1
	29-Jun-15	77	4	8	< 1	< 1
	27-Jul-15	3	3	< 1	< 1	< 1
	31-Aug-15	60	4	7	< 1	1
Enterovirus	30-Jun-14	-	-	-	-	-
(II/ 20 L)	23-Mar-15	None	None	None	None	None
	26-May-15	None	None	None	None	None
	29-Jun-15	None	None	None	None	None
	27-Jul-15	None	None	None	None	None
	31-Aug-15	None	None	None	None	None
	1	Pestic	ides			
Diuron	30-Jun-14	0.382	0.130	0.295	0.085	0.050
(mg/ l)	23-Mar-15	0.238	0.079	0.063	0.046	Traces
	26-May-15	0.027	0.029	Traces	Traces	Traces

Compound	Date	P1' Upstream WWTP	P2 Les Herbiers WWTP	P3 Downstream WWTP "La Favrie"	P9 Plessis-des- Landes	P11 DWTP intake
	29-Jun-15	Traces	0.237	0.087	0.042	Traces
	27-Jul-15	< 0.02	< 0.02	< 0.02	Traces	Traces
	31-Aug-15	0.051	0.250	0.125	0.089	Traces
Glyphosate	30-Jun-14	0.18	< 0.5	0.43	0.53	< 0.08
(μg/L)	23-Mar-15	< 0.05	0.40	0.11	0.18	< 0.05
	26-May-15	< 0.05	0.61	0.14	< 0.05	0.09
	29-Jun-15	< 0.05	0.64	0.35	0.14	< 0,05
	27-Jul-15	< 0.05	0.33	0.20	< 0.05	< 0.05
	31-Aug-15	0.07	0.84	0.28	< 0.05	< 0.05
AMPA	30-Jun-14	0.31	2.30	0.84	0.82	< 0.08
(µg/L)	23-Mar-15	0.09	1.60	0.30	0.18	0.11
	26-May-15	0.11	2.30	0.55	0.39	< 0.05
	29-Jun-15	0.24	4.20	2.10	1.10	0.19
	27-Jul-15	0.45	2.90	2.10	1.60	0.15
	31-Aug-15	0.30	1.80	1.40	1.20	0.40
2,4 D	30-Jun-14	0.023	0.079	< 0.020	< 0.020	< 0.020
(µg/L)	23-Mar-15	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020
	26-May-15	< 0.020	0.143	Traces	< 0.020	< 0.020
	29-Jun-15	< 0.020	0.046	Traces	< 0.020	< 0.020
	27-Jul-15	< 0.020	0.151	0.139	Traces	Traces
	31-Aug-15	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020
Metolachlor (µg/L)	30-Jun-14	-	-	-	-	-
	23-Mar-15	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01
	26-May-15	< 0.01	< 0.02	< 0.01	< 0.02	Traces
	29-Jun-15	< 0.01	< 0.02	< 0.01	< 0.02	Traces
	27-Jul-15	< 0.01	< 0.02	< 0.01	< 0.01	Traces
	31-Aug-15	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01
Fipronil	30-Jun-14	-	-	-	-	-
(µg/L)	23-Mar-15	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
	26-May-15	< 0.02	Traces	< 0.02	< 0.02	< 0.02
	29-Jun-15	< 0.02	Traces	< 0.02	< 0.02	< 0.02
	27-Jul-15	< 0.02	Traces	Traces	< 0.02	< 0.02
	31-Aug-15	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Metaldehyde	30-Jun-14	-	-	-	-	-
(µg/L)	23-Mar-15	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
	26-May-15	< 0.02	Traces	< 0.02	< 0.02	Traces
	29-Jun-15	< 0.02	Traces	Traces	Traces	Traces
	27-Jul-15	< 0.02	0.039	Traces	Traces	Traces
	31-Aug-15	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02

Compound	Date	P1' Upstream WWTP	P2 Les Herbiers WWTP	P3 Downstream WWTP "La Favrie"	P9 Plessis-des- Landes	P11 DWTP intake
		Meta	als			
Antimony	30-Jun-14	< 1.0	1.3	< 1.0	< 1.0	< 1.0
(µg/L)	23-Mar-15	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5
	26-May-15	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5
	29-Jun-15	< 0.5	< 5.0	< 0.5	< 0.5	< 0.5
	27-Jul-15	0.7	< 5.0	0.9	0.5	< 0.5
	31-Aug-15	< 0.5	< 5.0	< 0.5	0.7	0.5
Aluminum	30-Jun-14	130.0	21.0	180.0	160.0	40.0
(µg/L)	23-Mar-15	213.0	23.9	621.0	290.0	347.0
	26-May-15	474.0	26.0	852.0	225.0	180.0
	29-Jun-15	202.0	22.0	471.0	142.0	124.0
	27-Jul-15	113.0	26.4	188.0	82.0	43.0
	31-Aug-15	77.0	25.3	161.0	162.0	289.0
Arsenic	30-Jun-14	4.9	5.4	4.8	9.8	5.0
(µg/L)	23-Mar-15	1.3	< 5.0	1.4	2.8	2.1
	26-May-15	2.0	< 5.0	2.1	3.9	3.0
	29-Jun-15	2.3	< 5.0	2.1	6.8	2.5
	27-Jul-15	2.9	< 5.0	2.2	11.8	3.4
	31-Aug-15	3.0	< 5.0	2.4	6.7	6.9
Copper	30-Jun-14	3.4	3.3	3.3	3.2	3.1
(µg/L)	23-Mar-15	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
	26-May-15	< 5.0	< 5.0	< 5.0	< 5.0	7.0
	29-Jun-15	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
	27-Jul-15	< 5.0	< 5.0	< 5.0	< 5.0	17.0
	31-Aug-15	< 5.0	< 5.0	< 5.0	< 5.0	5.0
Iron	30-Jun-14	660	110	380	520	91
(μg/L)	23-Mar-15	356	121	769	500	367
	26-May-15	745	142	1,260	450	277
	29-Jun-15	295	302	632	252	194
	27-Jul-15	164	135	311	197	95
	31-Aug-15	236	142	295	378	522
Manganese	30-Jun-14	29	18	32	41	91
(µg/L)	23-Mar-15	56	65	76	49	40
	26-May-15	59	35	80	54	31
	29-Jun-15	23	80	89	54	29
	27-Jul-15	19	38	99	126	152
	31-Aug-15	30	75	51	119	129
Nickel	30-Jun-14	1.7	2.2	1.8	1.8	1.6
(μg/L)	23-Mar-15	< 5.0	< 10.0	< 5.0	< 5.0	< 5.0
	26-May-15	< 5.0	< 10.0	< 5.0	< 5.0	< 5.0

Compound	Date	P1' Upstream WWTP	P2 Les Herbiers WWTP	P3 Downstream WWTP "La Favrie"	P9 Plessis-des- Landes	P11 DWTP intake
	29-Jun-15	< 5.0	< 10.0	< 5.0	< 5.0	< 5.0
	27-Jul-15	< 5.0	< 10.0	< 5.0	< 5.0	< 5.0
	31-Aug-15	< 5.0	< 10.0	< 5.0	< 5.0	< 5.0
Titanium	30-Jun-14	8.40	< 5.0	10.00	8.40	< 5.0
(µg/L)	23-Mar-15	10.50	< 10.0	39.30	7.60	10.90
	26-May-15	30.60	< 10.0	52.70	10.30	6.30
	29-Jun-15	7.30	< 10.0	22.30	6.30	5.10
	27-Jul-15	4.50	< 10.0	7.20	2.50	1.40
	31-Aug-15	2.70	< 10.0	5.90	3.90	10.00
Zinc	30-Jun-14	13.0	22.0	13.0	7.1	< 5.0
(μg/L)	23-Mar-15	< 10.0	27.5	14.0	< 10.0	< 10.0
	26-May-15	14.0	24.2	19.0	< 10.0	< 10.0
	29-Jun-15	13.0	17.5	19.0	< 10.0	12.0
	27-Jul-15	12.0	< 10	23.0	< 10.0	38.0
	31-Aug-15	16.0	43.6	21.0	21.0	< 10.0
		Other para	ameters			
Caffeine (μg/L)	30-Jun-14	0.162	< 0.040	< 0.020	0.037	0.038
	23-Mar-15	0.113	Traces	0.061	0.047	0.096
	26-May-15	0.200	< 0.040	0.075	0.052	0.067
	29-Jun-15	0.327	Traces	0.088	0.042	0.060
	27-Jul-15	0.145	< 0.040	0.062	< 0.040	0.065
	31-Aug-15	0.511	0.044	0.190	0.067	0.046
		Radiocontra	ist agents			
Iohexol	30-Jun-14	0.043	< 0.010	0.033	0.123	0.039
(µg/L)	23-Mar-15	< 0.050	Traces	< 0.050	< 0.050	< 0.050
	26-May-15	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
	29-Jun-15	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
	27-Jul-15	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
	31-Aug-15	< 0.050	< 0.050	< 0.050	< 0.050	< 0.050
lomeprol	30-Jun-14	<0.010	<0.010	0.01	0.025	0.015
(µg/L)	23-Mar-15	< 0,050	0.078	Traces	0.168	0.063
	26-May-15	< 0,050	< 0,050	< 0,050	0.056	0.108
	29-Jun-15	Traces	0.545	0.278	0.085	0.111
	27-Jul-15	< 0,050	< 0,050	< 0,050	0.229	0.119
	31-Aug-15	< 0,050	< 0,050	< 0,050	0.423	0.130
lopromide	30-Jun-14	<0.010	<0.010	<0.010	0.015	0.039
(µg/L)	23-Mar-15	< 0,050	0.33	Traces	< 0,050	< 0,050
	26-May-15	< 0,050	< 0,050	< 0,050	< 0,050	< 0,050
	29-Jun-15	< 0,050	< 0,050	< 0,050	0.39	< 0,050
	27-Jul-15	< 0,050	0.106	< 0,050	0.179	0.055

Compound	Date	P1' Upstream WWTP	P2 Les Herbiers WWTP	P3 Downstream WWTP "La Favrie"	P9 Plessis-des- Landes	P11 DWTP intake
	31-Aug-15	< 0,050	< 0,050	0.059	< 0,050	< 0,050
		Pharmace	euticals			
Diclofenac	30-Jun-14	0.120	0.840	0.140	0.051	0.013
(µg/L)	23-Mar-15	0.099	0.886	0.124	< 0.010	< 0.010
	26-May-15	0.011	0.736	0.174	0.044	Traces
	29-Jun-15	< 0.010	1.570	0.625	0.134	< 0.010
	27-Jul-15	0.074	0.990	0.014	0.053	0.581
	31-Aug-15	0.013	1.190	0.396	0.040	0.029
Paracetamol	30-Jun-14	0.018	0.082	0.012	<0.010	<0.010
(µg/L)	23-Mar-15	0.313	< 0,025	0.217	<0.010	<0.010
	26-May-15	0.344	< 0,025	0.079	<0.010	<0.010
	29-Jun-15	0.320	< 0,025	0.042	<0.010	<0.010
	27-Jul-15	<0.010	< 0,025	<0.010	<0.010	<0.010
	31-Aug-15	0.988	< 0,025	0.151	<0.010	<0.010
Carbamazepine	30-Jun-14	< 0.010	0.042	0.180	0.410	0.220
(μg/L)	23-Mar-15	< 0.010	0.598	0.084	0.025	Traces
	26-May-15	< 0.010	0.564	0.103	0.034	0.014
	29-Jun-15	0.012	0.675	0.295	0.100	0.023
	27-Jul-15	0.011	0.869	0.509	0.257	0.024
	31-Aug-15	0.016	0.577	0.239	0.047	0.069
Carbamazepine Epoxyde	30-Jun-14	< 0.010	0.07	0.019	0.012	< 0.010
(µg/L)	23-Mar-15	< 0.010	< 0.025	< 0.010	< 0.010	< 0.010
	26-May-15	< 0.010	< 0.025	< 0.010	0.02	< 0.010
	29-Jun-15	< 0.010	< 0.025	< 0.010	< 0.010	< 0.010
	27-Jul-15	< 0.010	< 0.025	< 0.010	< 0.010	< 0.010
	31-Aug-15	< 0.010	< 0.025	< 0.010	< 0.010	< 0.010
Bezafibrate	30-Jun-14	0.031	< 0.025	0.016	0.014	< 0.010
(µg/L)	23-Mar-15	0.023	0.038	traces	< 0.010	< 0.010
	26-May-15	< 0.010	< 0.025	< 0,01	< 0.010	< 0.010
	29-Jun-15	< 0.010	Traces	Traces	Traces	< 0.010
	27-Jul-15	< 0.010	Traces	0.010	< 0.010	< 0.010
	31-Aug-15	< 0.010	< 0,025	Traces	< 0.010	< 0.010
Metoprolol	30-Jun-14	< 0.010	0.320	0.013	< 0.010	< 0.010
(µg/L)	23-Mar-15	< 0.010	0.039	Traces	< 0.010	< 0.010
	26-May-15	< 0.010	0.031	< 0.010	< 0.010	< 0.010
	29-Jun-15	< 0.010	0.052	0.024	Traces	< 0.010
	27-Jul-15	< 0.010	0.032	0.020	< 0.010	< 0.010
	31-Aug-15	< 0.010	0.034	0.017	< 0.010	< 0.010
Propanolol	30-Jun-14	< 0.010	0.098	0.033	< 0.010	< 0.010
(μg/L)	23-Mar-15	< 0.010	0.170	0.029	Traces	< 0.010

Compound	Date	P1' Upstream WWTP	P2 Les Herbiers WWTP	P3 Downstream WWTP "La Favrie"	P9 Plessis-des- Landes	P11 DWTP intake
	26-May-15	< 0.010	0.104	0.024	< 0.010	< 0.010
	29-Jun-15	< 0.010	0.127	0.060	Traces	< 0.010
	27-Jul-15	< 0.010	0.083	0.047	Traces	< 0.010
	31-Aug-15	Traces	0.099	0.041	Traces	< 0.010
Oxazepam	30-Jun-14	< 0.010	0.330	0.080	0.015	< 0.010
(µg/L)	23-Mar-15	< 0.010	1.470	0.207	0.060	0.023
	26-May-15	< 0.010	1.480	0.270	< 0.010	0.034
	29-Jun-15	< 0.010	1.520	0.644	0.217	0.042
	27-Jul-15	0.027	1.460	0.828	0.389	0.035
	31-Aug-15	0.047	1.610	0.483	0.090	0.090
		Hormo	ones			
Estradiol beta	30-Jun-14	< 0.2	< 0.4	< 0.2	< 0.2	< 0.2
(ng/L)	23-Mar-15	< 0.2	< 0.4	< 0.2	< 0.2	< 0.2
	26-May-15	< 0.2	< 0.4	< 0.2	< 0.2	< 0.2
	29-Jun-15	< 0.2	< 0.4	< 0.2	< 0.2	< 0.2
	27-Jul-15	< 0.2	< 0.4	< 0.2	< 0.2	< 0.2
	31-Aug-15	< 0.2	< 0.4	< 0.2	< 0.2	< 0.2
Estrone	30-Jun-14	0.3	< 0.4	1.2	0.6	< 0.2
(ng/L)	23-Mar-15	< 0,2	1.0	0.2	Traces	< 0,2
	26-May-15	1.5	1.6	1.6	1.4	< 0,2
	29-Jun-15	< 0,2	< 0,4	< 0,2	< 0,2	< 0,2
	27-Jul-15	< 0,2	< 0,4	0.3	< 0,2	< 0,2
	31-Aug-15	1.8	< 0,4	2.5	< 0,2	< 0,2
		Antibio	otics			
Sulfamethoxazole	30-Jun-14	< 0.010	0.054	0.017	< 0.010	< 0.010
(μg/L)	23-Mar-15	< 0.010	0.055	0.010	traces	< 0.010
	26-May-15	< 0.010	0.140	0.028	0.012	< 0.010
	29-Jun-15	< 0.010	0.054	0.032	0.015	0.011
	27-Jul-15	< 0.010	0.093	0.065	0.037	Traces
	31-Aug-15	< 0.010	0.042	0.025	< 0,01	0.013
	·	Alkylph	ienol			
4-n-Nonylphenol	30-Jun-14	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
(µg/L)	23-Mar-15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	26-May-15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	29-Jun-15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	27-Jul-15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	31-Aug-15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

7.6 Appendix 6 Biological index results

7.6.1 Diatomés (IBD)

7.6.1.1 La Grande Maine at Les Herbiers

With an IBD score of 9.5, the ecological status is considered poor at La Grande Maine (P1). *Nitzschia amphibia* ranks first (34.4%) and shows an altered environment. It's followed by *Gomphonema parvulum*, *Eolimna minima* and *Planothidium frequentissimum* which are indicators of a high load of organic matter, and support of eutrophic waters.

IBD on La Grande Maine upstream Les Herbiers WWTP (P1 ') refers to an average ecological status. *Amphora pediculus* is the first taxon (35.0%). This taxon is sensitive to organic pollution and supports nutrient-rich waters. This last character is confirmed by the presence of second place *Rhoicosphenia abbreviata* (12.6%). The environment upstream WWTP appears already loaded in nutrients.

Downstream WWTP on P3, the river is loaded with organic matter. The index scores are decreasing. This station gets an average ecological status. *Amphora pediculus* and *Nitzschia amphibia* form the leading duo. The diatomic procession illustrates a eutrophic environment and impacted by organic matter, ad hoc basis or alternating.

	La Grande Maine at Le Bignon (P1)	La Grande Maine Upstream WWTP (P1')	La Grande Maine Downstream WWTP at La Favrie (P3)
Score IBD (/20)	9.5	13.5	11.5
Score IPS (/20)	7.9	11.8	10.0
Taxonomic richness	30	45	49
Shannon-Weaver (bits/ind)	3.38	3.74	4.49
Ecological status class	Poor	Medium	Medium

Table 39 IBD ecological status of La Grande Maine at Les Herbiers (2015)

IBD shows a deterioration of the diatomic population downstream of the discharge from Les Herbiers WWTP

7.6.1.2 La Grande Maine upstream La Bultière reservoir

The IBD score of La Grande Maine at P7 point refers to an average ecological status.

Amphora pediculus represents almost one third of the workforce (31.2 %), and is supported by *Rhoicosphenia abbreviata* (17.3 %). This station appears to be very rich in nutrients.

IBD score of **La Grande Maine at P9 point** refers to an average ecological status. The two first taxon *cryp-totenella Navicula* and *Amphora pediculus* show a water not really impacted by organic matter, but rich in nutrients.

	La Grande Maine at St Fulgent (P7)	La Grande Maine at Le Plessis des Landes (P9)
Score IBD (/ 20)	13.8	13.3
Score IPS (/20)	12.8	11.7
Taxonomic richness	52	56
Shannon-Weaver Index (bits/ind)	3.95	4.51
Ecological status class	Medium	Medium

Table 40 IBD ecological status of La Grande Maine at upstream La Bultière reservoir (2015)

IBD does not show significant changes in the diatomic population in this sector

7.6.2 Benthic invertebrates (IBGN)

7.6.2.1 La Grande Maine at Les Herbiers

La Grande Maine in P1 has a good hydrobiological quality, with an IBG index at 13/20. Nevertheless the faunal analysis reflects a deterioration of the aquatic environment.

The settlement is well diversified, with 40 taxons in total, but its structure is unbalanced. *Oligochaetes*, *Diptera chironomids* and pollution-tolerant molluscs (*Potamopyrgus and Physa*) predominate over the rest of the population, and represent over 75% of the total workforce.

All these indications show an alteration of the water quality. Habitat degradation as a result of ancient hydraulic works increases this disturbance.

La Grande Maine, upstream Les Herbiers WWTP, and downstream of the industrial area, has an average hydrobiological quality, with IBG Index of 10/20. The score is 3 points and a quality class less compared to downstream.

The Fauna group indicator is bad. Pollution-sensitive taxons wealth is very low, and decreases sharply compared to upstream. Upstream, 11 taxons represented by 151 individuals were collected, whereas on this station, there are only four taxons for 37 individuals. The total wealth declines also strongly (24 taxons on this site, compared to 40 upstream).

All these index show a environnement degradation sharper in this station, that in the station located upstream.

La Grande Maine downstream Les Herbiers WWTP, has an average and fragile hydrobiological quality (IBG of 9/20), at the limit of the poor level.

The Fauna group indicator is bad (*leptoceridae*, GFI 4/9). Wealth and number of pollution-sensitive taxons (PST) are very bad, and fall compared to the station upstream of the WWTP:

- Upstream discharge: 4 PST represented by 37 individuals,
- Downstream discharge: 2 PST represented by 12 individuals.

The total wealth is bad, and also decreases compared to the upstream (18 taxons on this site, compared to 24 upstream). Diversity indices are very bad and show a strong imbalance of the population. *Chironomids* and *oligochaetes* pollution-resistant taxons, represent almost 93% of the population.

	La Grande Maine at Le Bignon	La Grande Maine Uptream WWTP	La Grande Maine Downstream WWTP (La Favrie)
Equivalent IBG index (XP T 90-333)	13	10	9
Equivalent Richness IBGN	32	20	117
Total Richness (XT 90-338)	40	24	18
GFI order	5	4	4
Taxonomic richness of EPT	11	4	2
Ecological status class	Good	Medium	Medium

Table 41 IBG ecological status of La Grande Maine at Les Herbiers (2015)

All these indices show a deterioration of macrobenthic population downstream of the discharge from Les Herbiers WWTP

7.6.2.2 La Grande Maine upstream La Bultière reservoir

La Grande Maine on P7, has an average hydrobiological quality with IBG Index at 12/20. The index increases by 3 points, compared to P3 point, while maintaining its quality class.

The Fauna Group indicator is medium with Hydroptilidae (GFI 5/9). Wealth and population in pollutionsensitive taxons are low with 8 taxons and 91 individuals, they nevertheless increase compared to upstream. The total wealth is medium with 33 taxons for all samples. *Chironomids* and *oligochaetes* pollutionresistant taxons are preponderant with about 73% of the population.

All these indicators show an alteration of the water quality, which is nevertheless less important than downstream of Les Herbiers WWTP discharge.

La Grande Maine at Le Plessis des Landes, at P9 point, has good, but fragile, hydrobiological quality with IBG 14/20.

The Fauna Group Indicator is good (GFI 7/9: *Goeridae*), but the robustness test demonstrates its fragility. The following indicator group is of order 5 (*Hydroptilidae*). Wealth and population in PST progress compared to upstream:

- 14 taxons for 446 individuals collected on this site,
- 8 taxons for 91 individuals on the Maine Grande in St-Fulgent.

Diversity indices are medium, they show a slight imbalance in the population structure.

Table 42 IBG ecological status of La Grande Maine at upstream La Bultière reservoir (2015)

	La Grande Maine at St Fulgent (P7)	La Grande Maine at Le Plessis des Landes (P9)
Equivalent IBG index (XP T 90-333)	12	14
Equivalent Richness IBGN	27	28
Total Richness (XT 90-338)	33	37

GFI order	5	7
Taxonomic richness of EPT	8	14
Ecological status class	Medium	Good

All these indices demonstrate good but fragile quality of macro-benthic settlement. It improves upon La Grande Maine station in P7 point, located upstream.

7.6.3 Macrophytes (IBMR)

7.6.3.1 La Grande Maine at Les Herbiers

IBMR on La Grande Maine upstream Les Herbiers WWTP (P1) indicates a high trophic level.

Species richness of the resort is average, with 20 taxas to 13 present, contributing to the IBMR. The algae, though not very diversified, dominate this macrophytic collection. *Diatomaceous Melosira sp.* is the most abundant species (31%). The floristic consists exclusively of taxa meso-eutrophic environments medium, such as water plants *Callitriche platycarpa* or *Lemna minor*, and most important trophic level taxa (hypertrophe to eutrophic), as green filamentous alga *Cladophora sp.* or *bryophyte Leptodictyum riparium*. Note that the latter case may be indicative of organic pollution and / or high ammonia.

IBMR on La Grande Maine downstream of the industrial zone and upstream Les Herbiers WWTP (P1') indicates an average trophic level, but questionable. Because the gap between the robustness and IBMR rating is high (2,0). The index is described as non robust. Indeed, the species diversity of the resort is very low (3 taxa present only 2 contributing to the IBMR) and for almost zero abundance (0.01 %).

Artificialisation of the aquatic environment (recalibration, dyke...) and homogeneity of the hydro-morphological conditions of the river can be a cause of very weak development of macrophytes on the station. The predominance of a sandy bottom, and therefore mobile during periods of high water regimes, is also a factor to consider in this situation.

IBMR **downstream WWTP (P3)** shows a high trophic level. The index down more than 4 points and 2 classes, vis- à-vis the sample taken upstream from the discharge of the sewage plant.

The station is very vegetated (0.18 %) and floristic richness is low: 10 taxa in total and only 8 contributing to the index. The floristic is representative of a more eutrophic environment, see hyper-eutrophic with taxa such as *green filamentous alga Cladophora sp.* (Csi = 6), the hydrophyte *Potamogeton crispus* (Csi = 7) or foam *Leptodictyum riparium* (Csi = 5).

	La Grande Maine at Le Bignon	La Grande Maine Uptream WWTP	La Grande Maine Downstream WWTP (La Favrie)
IBMR Score on 20	8.35	12.00	7.82
Robustess of IBMR	9.16	10.00	8.00
Average specific rating (Csi)	9.23	11.5	8.25
Average coefficient of steno- ecie (Ei)	1.31	1.50	1.38
Total number of taxons	20	3	10
% of total vegetative area	36	0.03	0.18

Table 43 IBMR ecological status of La Grande Maine at Les Herbiers (2015)

IBMR reflects a deterioration of macrophytic stand downstream of the discharge from Les Herbiers WWTP

7.6.3.2 La Grande Maine upstream La Bultière reservoir

With a score of IBMR of 8.33, the trophic level of **La Grande Maine in St-Fulgent, on P7 point**, is high. The gap between the robustness and IBMR rating is very high (2.23). The index is seen as very robust. This is partly due to the low number of taxa present. The dominant species is the *bryophyte Fontinalis antipyretica* (total 3% recovery) with a CSI of 10. This species is characteristic of water rich in nutrients. The other two species are mainly present *bryophyte Leptodictyum riparium* (full recovery 2%) at the CSI of 5 and *red seaweed Hildenbrandia sp.* to a CSI of 15 (0.05% recovery).

The average specific dimensions is low (9.29), and confirms the character eutrophic to meso-eutrophic watercourse. The creek bed, shaded throughout the station and fort clogging substrates, do not allow for interesting species richness.

With an IBMR score of 9.39, the trophic level of **La Grande Maine at Le Plessis Landes (P9 point)** is high. The gap between the robustness and IBMR rating is relatively low (0.46); the index can be described as robust.

The recovery plant is average with 25.4% vegetation surface. The dominant species is the diatom *Melosira sp.* (9.2% total recovery), with a CSI of 10. This species is characteristic of water rich in nutrients but has strong ecological amplitude (coef. EI of 1). The other two species are present predominantly *bryophytes Fontinalis antipyretica* to Csi of 10 and *Octodiceras fontanum* to Csi of 7. These two species are respectively subservient to meso-eutrophic and eutrophic waters.

The average of specific dimensions is low (9.44). It confirms the eutrophic at meso-eutrophic character of watercourse.

	La Grande Maine at St Fulgent (P7)	La Grande Maine at Le Plessis des Landes (P9)
IBMR Score on 20	8.33	9.39
Robustess of IBMR	10.56	9.85
Average specific rating (Csi)	9.29	9.44
Average coefficient of stenoecie (Ei)	1.29	1.61
Total number of taxons	7	19
% of total vegetative area	5.09	25.37

Table 44 IBMR ecological status of La Grande Maine at upstream La Bultière reservoir (2015)

IBMR attests to a degradation of macrophytic stand above La Bultière reservoir. The illumination of the largest rivers in Le Plessis des Landes station (P9), promotes diversification of settlement, without that we observe a significant improvement in macrophytic settlement.

7.7 Appendix 7 61 marker compounds of Les Herbiers WWTP discharge

The chemical fingerprints considered as markers are those that were found specifically in Les Herbiers WWTP discharge, retrieved downstream and not retrieved in samples from the tributaries.

Compound name	CAS number	Class	Sub class
Cetirizine	83881-51-0	Pharmaceuticals	Allergology
Fexofenadine	83799-24-0	Pharmaceuticals	Allergology
Codeine	76-57-3	Pharmaceuticals	Analgics and Anti inflamma- tories
Diclofenac	15307-86-5	Pharmaceuticals	Analgics and Anti inflamma- tories
Dihydrocodeine	125-28-0	Pharmaceuticals	Analgics and Anti inflamma- tories
N-Desmethyl-cis-tramadol	147762-57-0	Pharmaceuticals	Analgics and Anti inflamma- tories
Niflumic Acid	4394-00-7	Pharmaceuticals	Analgics and Anti inflamma- tories
Tramadol	27203-92-5	Pharmaceuticals	Analgics and Anti inflamma- tories
Atenolol	29122-68-7	Pharmaceuticals	Cardiology - Angiology
Atenolol acid	56392-14-4	Pharmaceuticals	Cardiology - Angiology
Bisoprolol	66722-44-9	Pharmaceuticals	Cardiology - Angiology
Candesartan	139481-59-7	Pharmaceuticals	Cardiology - Angiology
Celiprolol	56980-93-9	Pharmaceuticals	Cardiology - Angiology
Clopidogrel_carboxylic acid	14457-28-3	Pharmaceuticals	Cardiology - Angiology
Diacetolol	28197-69-5	Pharmaceuticals	Cardiology - Angiology
Flecainide	54143-55-4	Pharmaceuticals	Cardiology - Angiology
Irbesartan	138402-11-6	Pharmaceuticals	Cardiology - Angiology
Metoprolol	37350-58-6	Pharmaceuticals	Cardiology - Angiology
Perindopril	82834-16-0	Pharmaceuticals	Cardiology - Angiology
Propafenone	54063-53-5	Pharmaceuticals	Cardiology - Angiology
Propranolol	525-66-6	Pharmaceuticals	Cardiology - Angiology
Sotalol	3930-20-9	Pharmaceuticals	Cardiology - Angiology
Telmisartan	144701-48-4	Pharmaceuticals	Cardiology - Angiology
Urapidil	34661-75-1	Pharmaceuticals	Cardiology - Angiology
Verapamil_metabolite_D617	34245-14-2	Pharmaceuticals	Cardiology - Angiology
Amantadine	768-94-5	Pharmaceuticals	Infectiology and parasitology
Darunavir	206361-99-1	Pharmaceuticals	Infectiology and parasitology
Flubendazole	31430-15-6	Pharmaceuticals	Infectiology and parasitology
Fluconazole	86386-73-4	Pharmaceuticals	Infectiology and parasitology
Sulfamethoxazole	723-46-6	Pharmaceuticals	Infectiology and parasitology

Table 45 Markers of La Bultière WWTP discharge

Compound name	CAS number	Class	Sub class
Gliclazide	21187-98-4	Pharmaceuticals	Metabolism diabetes nutri- tion
Sitagliptin	486460-32-6	Pharmaceuticals	Metabolism diabetes nutri- tion
(10.11-)Dihydro-10.11-dihy- droxycarbamazepine	58955-93-4	Pharmaceuticals	Neurology
Carbamazepine	298-46-4	Pharmaceuticals	Neurology
Carbamazepineepoxide	36507-30-9	Pharmaceuticals	Neurology
Lamotrigine	84057-84-1	Pharmaceuticals	Neurology
Lidocaine	137-58-6	Pharmaceuticals	Neurology
Oxcarbazepine	28721-07-5	Pharmaceuticals	Neurology
Primidone	125-33-7	Pharmaceuticals	Neurology
Bicalutamide	90357-06-5	Pharmaceuticals	Oncology
Amisulpride	71675-85-9	Pharmaceuticals	Psychiatry
Amitriptyline	50-48-6	Pharmaceuticals	Psychiatry
Citalopram	59729-33-8	Pharmaceuticals	Psychiatry
Desmethylcitalopram	144010-85-5	Pharmaceuticals	Psychiatry
Doxylamine	469-21-6	Pharmaceuticals	Psychiatry
Mianserine	24219-97-4	Pharmaceuticals	Psychiatry
Milnacipram	92623-85-3	Pharmaceuticals	Psychiatry
Oxazepam	604-75-1	Pharmaceuticals	Psychiatry
Ritalinic acid	19395-41-6	Pharmaceuticals	Psychiatry
Sulpiride	15676-16-1	Pharmaceuticals	Psychiatry
Tiapride	51012-32-9	Pharmaceuticals	Psychiatry
Venlafaxine	93413-69-5	Pharmaceuticals	Psychiatry
Phenylbenzimidazole sul- fonic acid	27503-81-7	Synthetic products for com- mon use	Anti UV filters
Methyl triclosan	4640-01-1	Synthetic products for com- mon use	Antibacterial agents
Sucralose	56038-13-2	Synthetic products for com- mon use	Artificial sweeteners
Bitertanol	55179-31-2	Pesticides	Fongicides
Indole-3-butyricacid	133-32-4	Pesticides	Herbicides
Lenacile	2164-08-1	Pesticides	Herbicides
N,N-Diethyl-m-toluamide	134-62-3	Pesticides	Insecticides
Methoxymethamphetamine	124206-66-2	Illicit drugs	Amphetamines, Ampheta- mines like and Hallucinogens
Ecgonine	481-37-8	Illicit drugs	Cocain and derivatives