

Case study: chemical substitution of PFC

Prato, July 2016

Detox commitment of 27 mills of Prato textile district

In February 2016, for the first time in the world, **20 manufacturing companies of the Prato district and members of Confindustria Toscana Nord**, endorsed the Detox commitments and acknowledged how important it is to eliminate dangerous substances from the textile production cycle. In this group, in March, we have **added other 7 companies**, thereby significantly increasing the volumes of the products concerned by the commitment Detox.

Supported and led by the association, the companies have started their improvement process through the elimination of such substances according to the transparency, prevention and precaution principles of the Detox campaign and have accepted the media challenge of the Greenpeace campaign which has rapidly changed the attention and the contents of the great fashion brands' terms of contracts.

In this roadmap, the mills are committed to eliminate Polyfluorinated compounds (PFCs) away from their supply-chain.

Companies of the textile district which follow the Detox commitment represent different parts of the textile supply chain: factories producing yarn, fabric and raw materials, dyeing plants, yarn or fabric finishing companies, producers of chemicals for the textile industry.

Within this group, only seven mills performed processing techniques in which PFCs can be involved. So, these companies worked together as integrated supply-chain to avoid and eliminate PFC from productions:

Mills involved in PFCs use	Type of company
Daykem srl	Chemical producer
Achimo srl	Chemical producer
F.lli ciampolini & c. Spa	fabric finishing
Finissaggio t.r.t. srl	fabric finishing
Jersey mode spa	fabric finishing
Lanificio bellucci spa	Fabric producer
Emmetex	Fabric producer

Introduction

Polyfluorinated compounds (PFC) are molecules in which all carbon-hydrogen bonds are replaced by carbon-fluorine bonds.

These molecules are widely used in last 50 years due to their unique physical and chemical characteristic.

PFCs are composed of long carbon chains (at least 6 carbon atoms except the most recently substances) with a polar end-side.

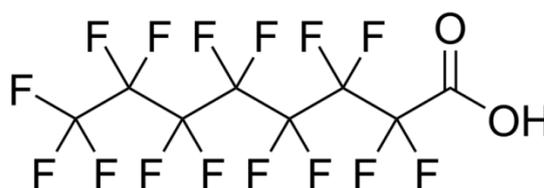
This chemical structure, on a side, give to PFCs a high thermal resistance and chemical passiveness and, on other side, give an high water and oil repellency.

These features allow PFCs to have many different uses in manufacturing (e.g. repellency) and domestic use (plastic polymers, paper, textile fibers, furs, fire estinguish foams, cosmetics, home products and so on).

At the end, there are more than 20 chemical classes of PFCs but the two molecules we have to point out are Perfluorooctan sulfonic acid (PFOS – the most important for perfluorosulfonate class) and Perfluorooctanoic acid (PFOA – the most important for perfluorocarboxylate class)



PFOS



PFOA

Unfortunately, today these molecules are known not for their uses but for their enviromental pollution.

Due to their high thermal and chemical passiveness, PFCs are not feasible to natural break down (even for photolytic, hydrolytic, areobic or anaerobic degradations)

PFOS and PFOA can gathering in living organisms, and their concentration is gained across the food chain; moreover PFCs are suspected to be toxic for plants and animals.

Anyway, many epidemiological studies have insufficient data because involving only a small group of PFC-plants employes but, in all cases, researchers point out that there are many factors involved in diseases, also non-occupational exposure.

Most significantly studies were made in the DuPont neighbouring plant in Virginia (USA): researchers noted a significantly increment of prostatic and reproductive organs cancer ratio when referred to other American states. Furthermore, comparing medical records of employees, researcher discovered another significantly increment of tumors like lymphoma, leukemia and multiple myeloma.

Another study, made directly from DuPont for evaluate the health conditions of own employees, reveal no increase ratio of tumors but only an increment of serum amount of cholesterol and triglycerides in people with high level of PFOA in blood.

Analysis method

Water analysis

Water sample are added of internal standard and extract with SPE technique.

PFC determination is made by UPLC-MSMS and confirmation by LC-Q-TOF

Textiles/chemicals analysis

Analysis is made in compliance to UNI CEN TS 15968:2010. PFC determination is made by UPLC-MSMS and confirmation by LC-Q-TOF

Case study CTN

1) WATER ANALYSIS AND MONITORING

A Detox committed company who has a water discharge has to analyze own wastewater.

Detox committed companies in Prato district performed analysis on their wastewater at the sign of commitment, and then started to monitor the PFCs parameters.

In this context, on February 2016, CTN and GIDA (company who manage the wastewater treatment plant) signed an agreement for a long-period monitoring analysis planning for recycled water for the 11 group of MRSL of Prato District.



As starting point, in April and May 2016 were performed the first analysis on recycled water (the work was achieved by the students of class 5 chemical graduates – section F- of Institute BUZZI in Prato) with these results

	Sampling of Monday 18/04/2016		Sampling of Thursday 28/04/2016		Sampling of Monday 09/05/2016	
	M1 line	M2 line	M1 line	M2 line	M1 line	M2 line
PFC	ND (<1 ng/L)	ND (<1 ng/L)	21 ng/L PFHpA 112 ng/L PFOA 21 ng/L PFNA 25 ng/L PFDA 3 ng/L PFUnA	6 ng/L PFHpA 27 ng/L PFOA 5 ng/L PFNA 5 ng/L PFDA 1 ng/L PFUnA	4 ng/L PFHpA 220 ng/L PFOA 54 ng/L PFNA 63 ng/L PFDA 5 ng/L PFUnA	11 ng/L PFHpA 64 ng/L PFOA 14 ng/L PFNA 16 ng/L PFDA 1.2 ng/L PFUnA

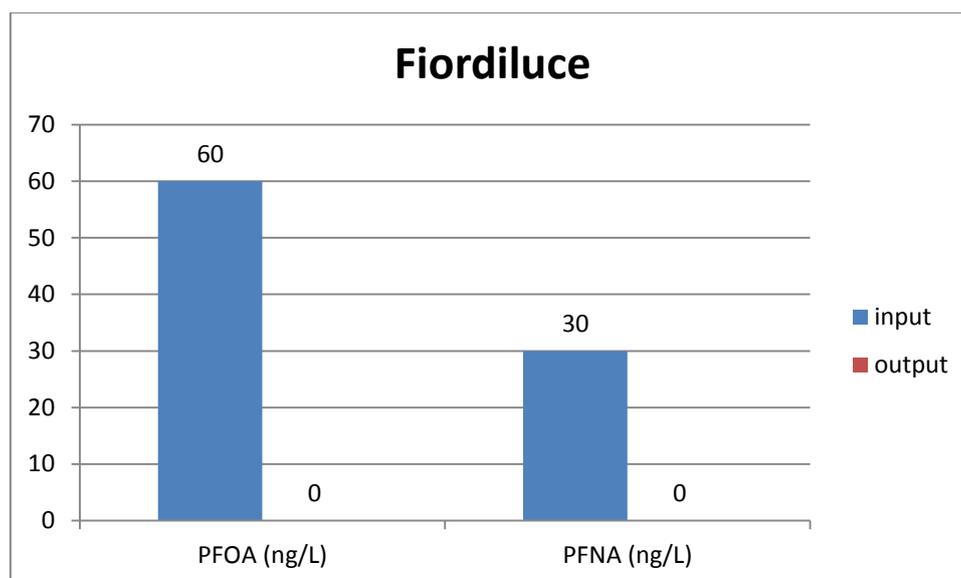
M1: purification system line by active charcoal

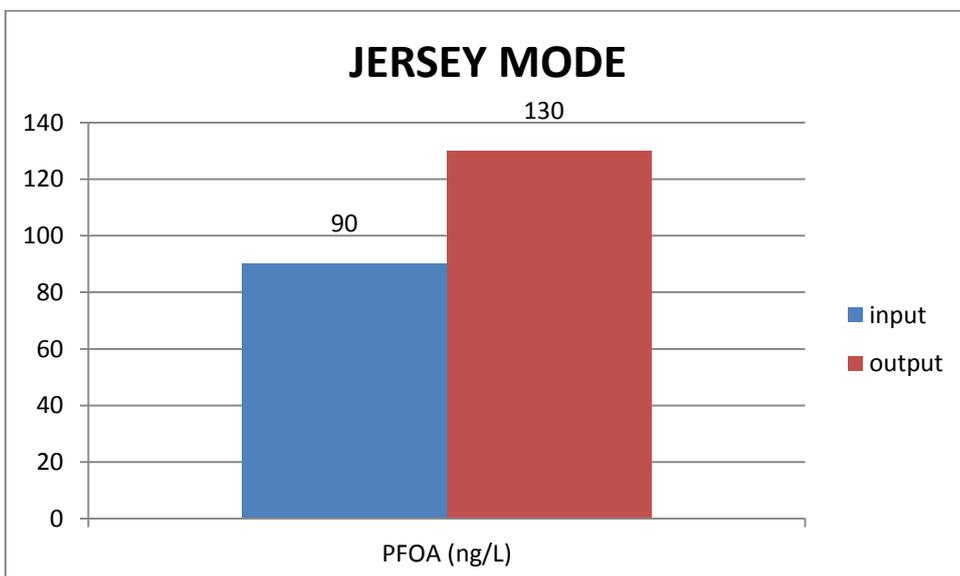
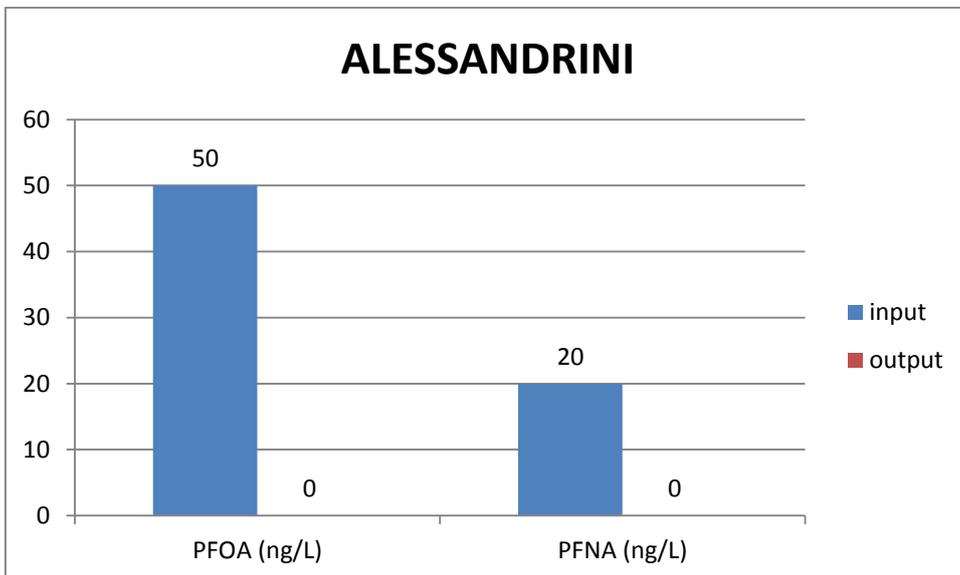
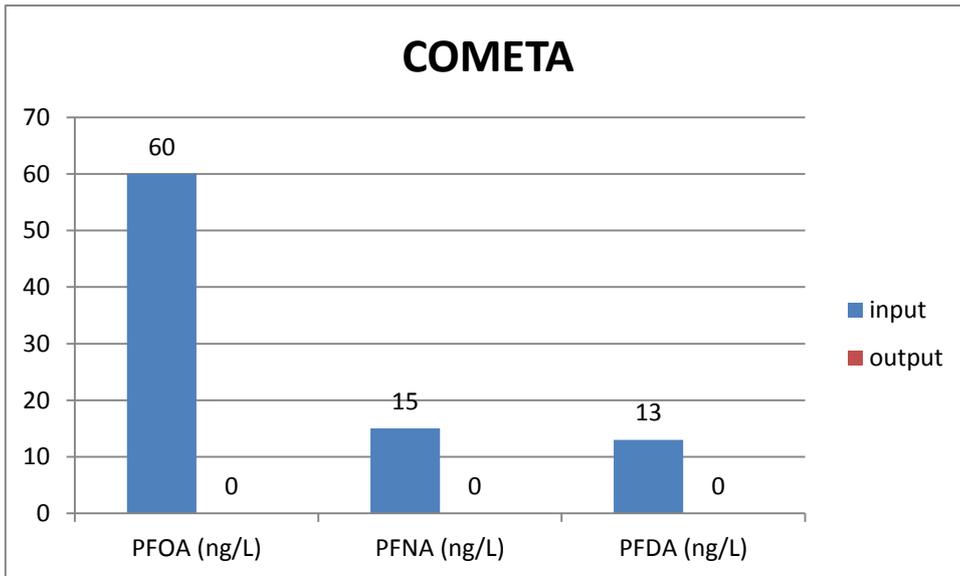
M2: purification system line by ozone and further dilution

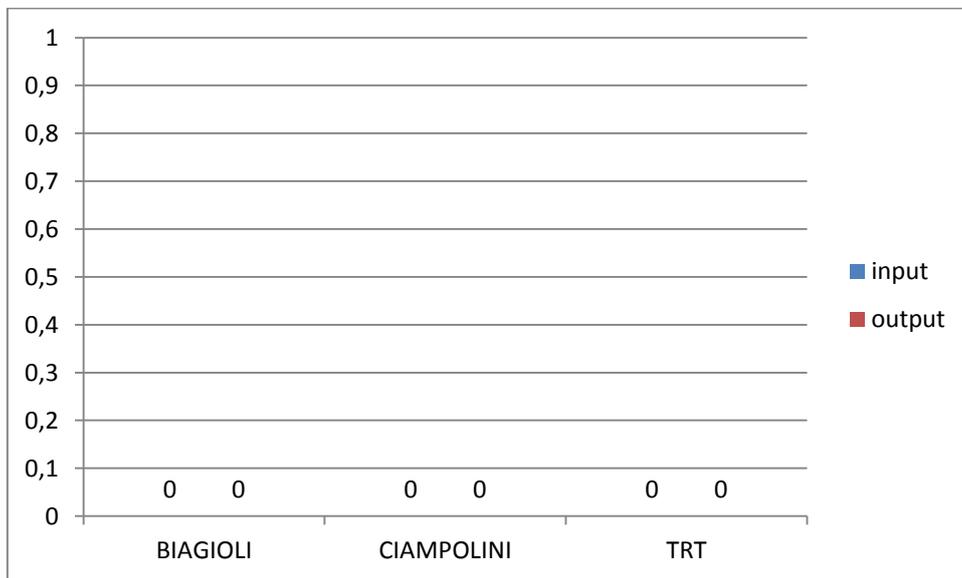
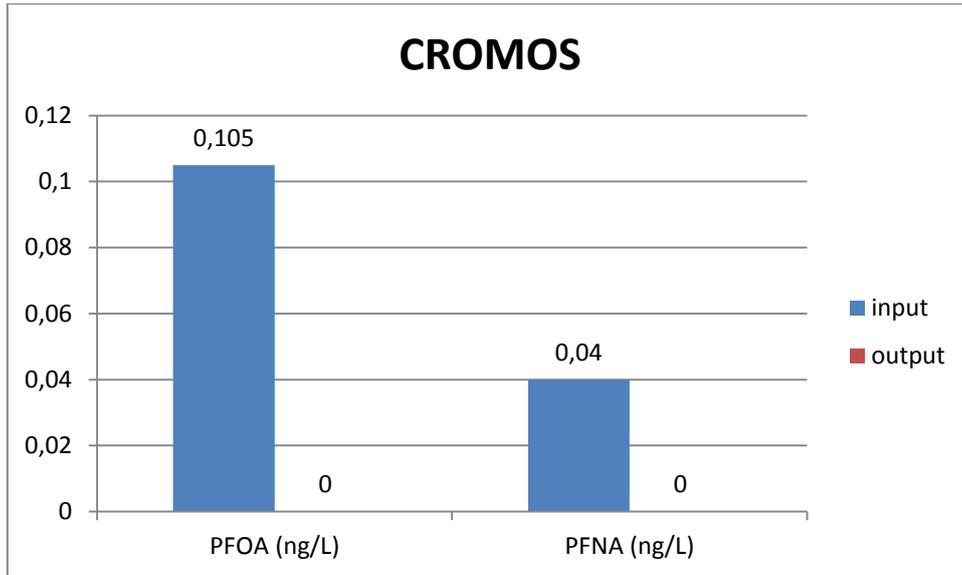
ND: not detectable (< MRSL limit)

Chemical analysis of Input and output water of Prato District Company at the sign of Detox commitment

Company	60 ng/L PFOA 30 ng/L PFNA	PFC output water
FIORDILUCE	60 ng/L PFOA 15 ng/L PFNA 13 ng/L PFDA	ND
COMETA	50 ng/L PFOA 20 ng/L PFNA	ND
ALESSANDRINI	90 ng/L PFOA	ND
JERSEY-MODE	105 ng/L PFOA 40 ng/L PFNA	130 ng/L PFOA
CROMOS	60 ng/L PFOA 30 ng/L PFNA	ND
BIAGIOLI	ND	ND
CIAMPOLINI	ND	ND
TRT	ND	ND



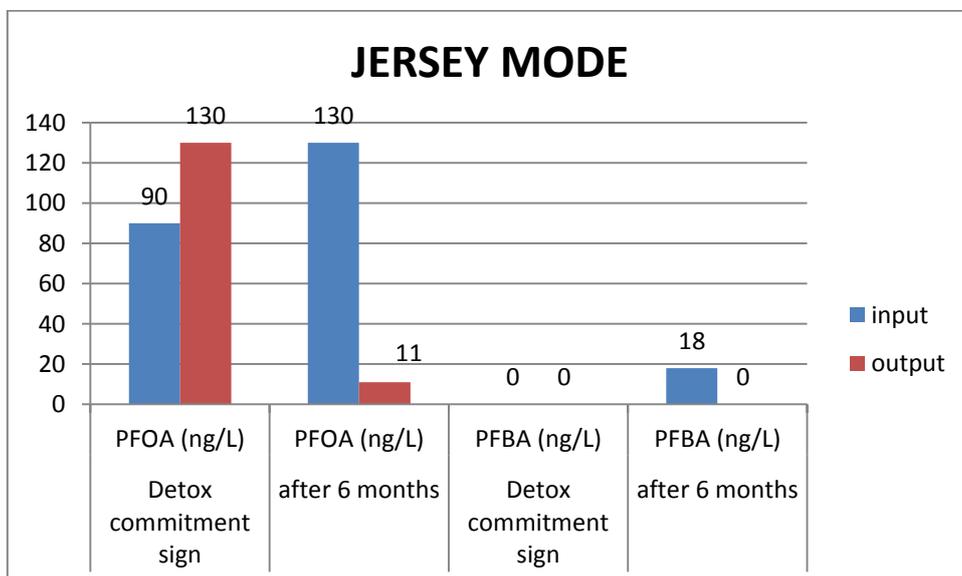
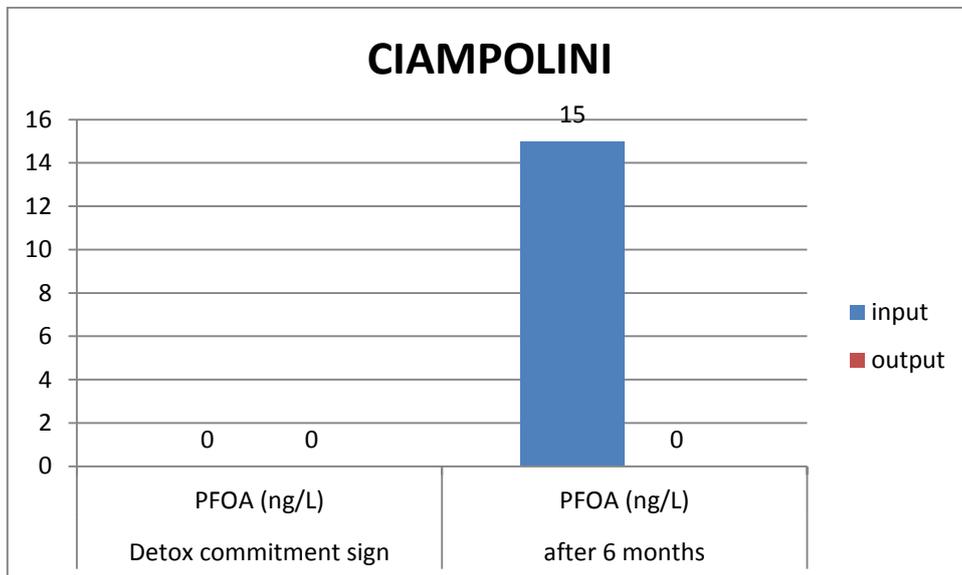
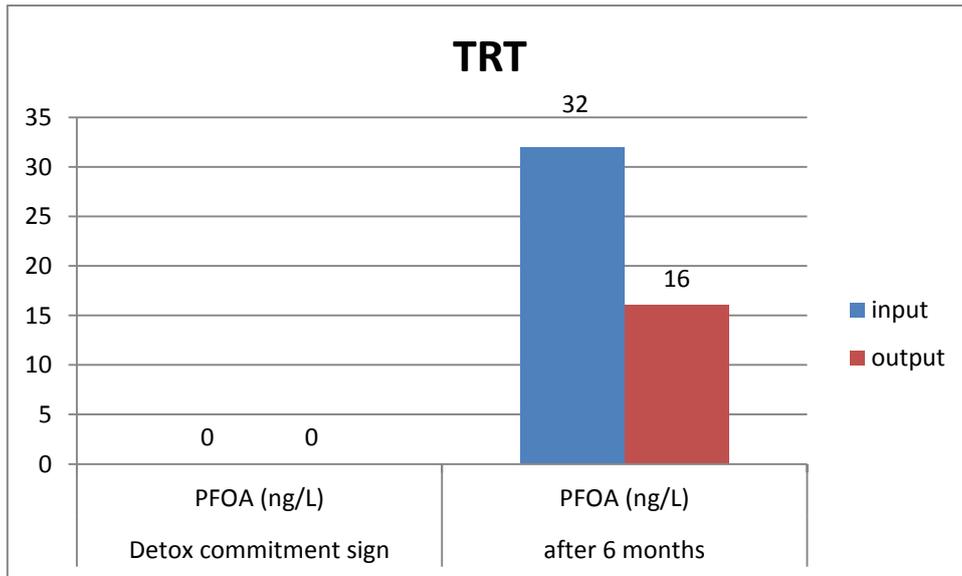




Monitoring of input/output water

Here the result of PFCs analysis after 6 months for some company (at the date of publication)

PFC monitoring analysis		
Company	PFC input water	PFC output water
TRT	32 ng/L PFOA	16 ng/L PFOA
CIAMPOLINI	15 ng/L PFOA	ND
JERSEY-MODE	13 ng/L PFOA 18 ng/L PFBA	11 ng/L PFOA



Results of initial and monitoring analysis of Prato District Companies are in agreement with result obtained by GIDA recycled water analysis, and confirm that Detox committed companies in Prato don't input PFCs in their water discharge

2) CHEMICAL AUXILIARIES ANALYSIS

Chemical suppliers/vendor performed PFC analysis for their water-repellent products

Company	Number of tested chemicals	PFC presence
Daykem	6	NO
Achimo	Company declare non use of PFC products since many years. At the moment, company is working at new chemical formulation for a water repellent product not-PFC based.	

3) CHEMICAL ANALYSIS OF WATER REPELLENT FABRIC

Textile companies who produce water repellent fabric/yarn performed analysis on finished products

Company	Number of product tested	PFC presence
Bellucci	1	NO
Emmetex	2	NO
TRT	2	NO
Bemiva	18	NO

4) PERFORMANCES EVALUATIONS

One of the most challenging topic for water-repellent-fabric producers is to guarantee to customers the same performances for PFCs and Not-PFCs treated products.

Daykem (chemical producer) performed (in collaboration with other companies in Prato District) an in-depth study for evaluating water repellent performances of fabrics treated with no-PFCs products.

Performances were evaluated by water repellency test (spray test) on initial fabric and after laundering and/or dry wash cycles

Results can be found at link:

<http://www.daykem.it/wp-content/uploads/2012/11/Sostituzione-pfc-case-study-daykem.pdf>

Measure to improve quality

Measure to improve quality are:

1-continuous monitoring of articles (fabric, raw materials, chemicals) in order to avoid the presence of any PFCs

2- improve frequency of wastewater analysis for PFCs parameter.

This action can be set in the CTN-GIDA agreement in order to enhancing the evaluation of recycled water from treatment plant and so the quality of input and output water of single companies.

Conclusions

At the moment, articles produced in Detox Committed companies in Prato District are stand out for absence of PFCs; of course, control plans have to be put in all supply chain.

PFCs presence in output wastewater is essentially due to presence themselves in incoming recycled water supplied by water treatment plant.

However, It's important to point out that the use of recycled water by Detox committed companies represent an extremely sustainable behaviour, because permit a drastic reduction of water consumption, especially for ground water.

This particular situation of Prato District was well-known by all stakeholders at Detox Commitment signature and so permit to use recycled water to Detox committed companies, with awareness that an increase of number of Detox committed companies will bring an improvement of wastewater quality and so an improvement of recycled water too.

For Detox companies still remain the commitment to control the supply chain and of course the water quality.