
MARIO NEGRI
ISTITUTO DI RICERCHE FARMACOLOGICHE
Sara Castiglioni
Mario Negri Institute
Department of Environmental Health Sciences
Laboratory of Nutrition's Toxicology
Occurrence and Fate of the Main Classes of Emerging Pollutants in the Aquatic Ecosystem of a Highly Urbanized Area
NORMAN Worshop – Amsterdam 29 November 2012
DEPARTMENT Environmental Health Sciences

Emerging pollutants

(Richardson and Ternes, *Anal. Chem.* 2011, 83, 4614)

Anthropic Source

Personal Care Products
Musks
Sunscreens/UV filters
Disinfectants

Therapeutic drugs
Pharmaceuticals
Hormones
Transformation products

Illicit drugs

Microorganisms

Industrial Source

Perfluorinated compounds (PFCs)
Brominated Flame Retardants
Benzotriazole, Dioxane, Siloxane
Perchlorate
Nanomaterials

Food or Water Production
Artificial sweeteners (Sucralose)
Antimony from plastics or petroleum refineries
Water disinfection by-products

Agricolture
Pesticides transformation products
Algal toxins

Which kind of contaminants?

- ✓ Used in **high quantities**
- ✓ **Heterogeneous group**
- ✓ Continuos **discharge**
- ✓ **Polar compounds** (generally small)
- ✓ Biologically **active substances**
- ✓ Complex **mixtures** – potential **toxic effects**

Aim of the project

Evaluate pollution of urban aquatic environment in a highly urbanized area in Italy

- Selection of **environmental pollutants**
- Set up of **analytical methods**
- **Monitoring occurrence** and **fate** in:
  - ✓ wastewater (raw and treated)
  - ✓ surface water
  - ✓ groundwater
- **Mass balance of pollutants** through the Milan area

Selection of contaminants

Pharmaceuticals

Antibiotics
Anti-inflammatory
Anti-cancer drugs
Anti-hypertensive
Bronchodilators
Cardiovascular
CNS drugs
Diuretics
Estrogens-Hormones
Gastrointestinal
Lipid regulator

Personal care products

Sunscreen Chemicals: Benzophenone-3 (**BP-3**); Benzophenone-4 (**BP-4**); 2-phenylbenzimidazole-5-sulfonic acid-(**PBSA**); 4-Methylbenzylidene camphor (**4-MBC**)
Disinfectants: triclosan, triclocarban

Perfluorinated compounds

PFOS
PFOA

Alkylphenols

Bisphenol A, octylphenol, 4-ter-octylphenol, nonylphenol

Illicit drugs and metabolites

Amphetamines
Cannabis
Cocaine
Opioids (heroin)
Other synthetic drugs

Markers of anthropic pollution

Caffeine and metabolites
Nicotine and cotinine

Analytical methods

Therapeutic drugs: 36 compounds + 6 deuterated standards

(Castiglioni et al., *J Chrom A.* 2005; Castiglioni et al., *ES&T* 2006)

Illicit drugs: 29 compounds + 20 deuterated standards

(Castiglioni *et al.*, *Anal. Chem.* 2006; Castiglioni et al., *Mass Spectrom Rev.* 2008; Zuccato et al., *Water Res.* 2008, Castiglioni et al., Water Res. 2011)

Personal care products: 4 compounds + 1 deuterated standard

(Rodil et al., *Anal. Chem.* 2008)

Household biocides: 2 compounds + 1 deuterated standard

(González-Mariño et al., *Rapid Comm. Mass Spectrom.* 2009)

Perfluorinated compounds: 2 compounds + 2 deuterated standards

(Loos et al., *Chemosphere*, 2008)

Alkylphenols: 4 compounds + 1 deuterated standard

(Maggioni et al., *Environ Sci Pollut Res Int*, 2012)

Antrophic markers: 5 compounds + 3 deuterated standard

(Huerta-Fontela et al., *Anal. Chem.* 2007; Bueno et al., *Water Res*, 2011)

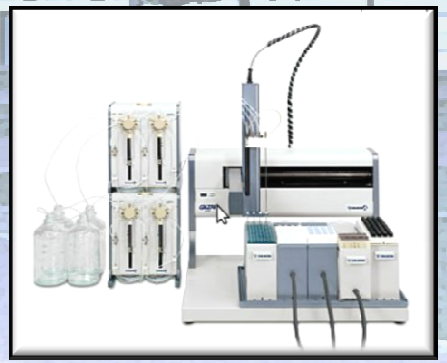
Analytical methods

Sampling mode

- **Wastewater**: 24h composite samples (1 week sampling)
- **Surface water**: 2h composite samples
- **Groundwater**: grab samples

Sample preparation

- Filtration (1.6 and 0.45 µm)
- Solid Phase Extraction (SPE)
  Oasis HLB and MCX (60 mg and 150mg)



Analytical methods

HPLC-MS/MS analysis

HPLC Column : C18 and HILIC phases
Mass Spectrometer:
AB-SCIEX API 3000
triple quadrupole, turbo ion spray source

HPLC-MS/MS analysis

HPLC Column : Atlantis C18
Mass Spectrometer:
Agilent 6410 Triple Quad LC/MS
triple quadrupole, ESI source

Analysis and Quantification

- Use of both **positive and negative** ionisation mode
- **SRM analysis**
- **Two most abundant** precursor/product ion transition
- **Isotope dilution** using the corresponding deuterated internal standards

Analytical methods - Results

Method Recoveries > 80% **SD** < 10%

Limits of quantification:

IQL= tens-hundreds pg/injected

LOQ= wastewater 0.5-30 ng/L ; surface water 0.2-5 ng/L; ground water 0.1-1 ng/L

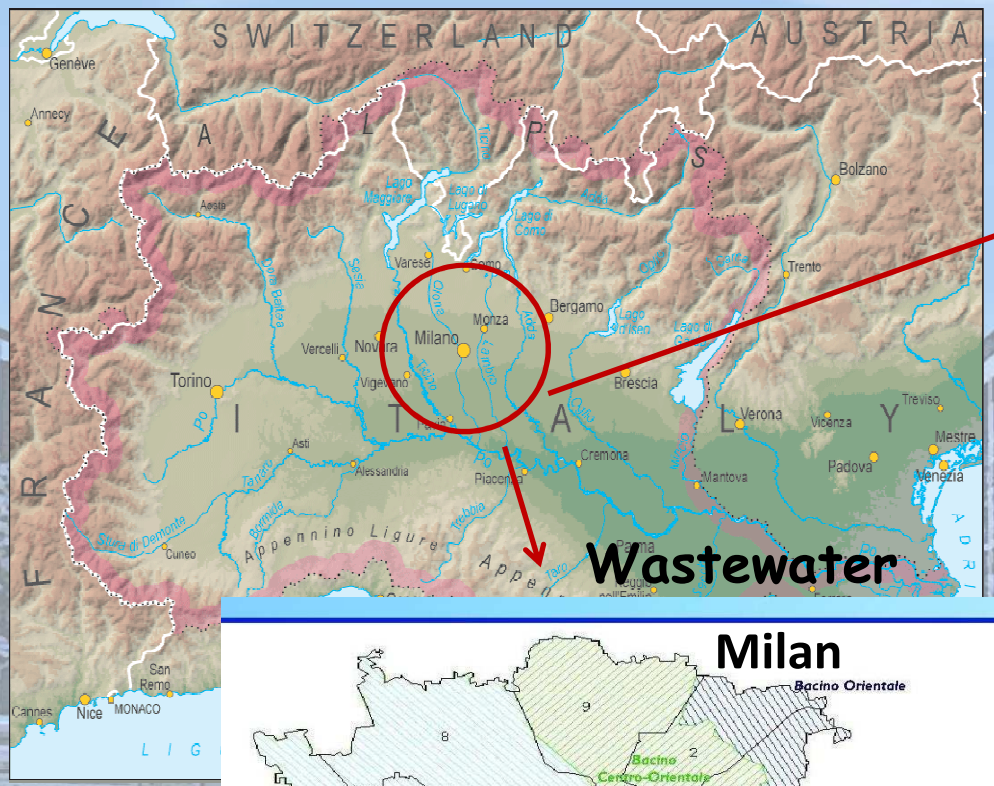
r^2 > 0.9995 ± SD < 0.004

Interday RSD% standard < 10%

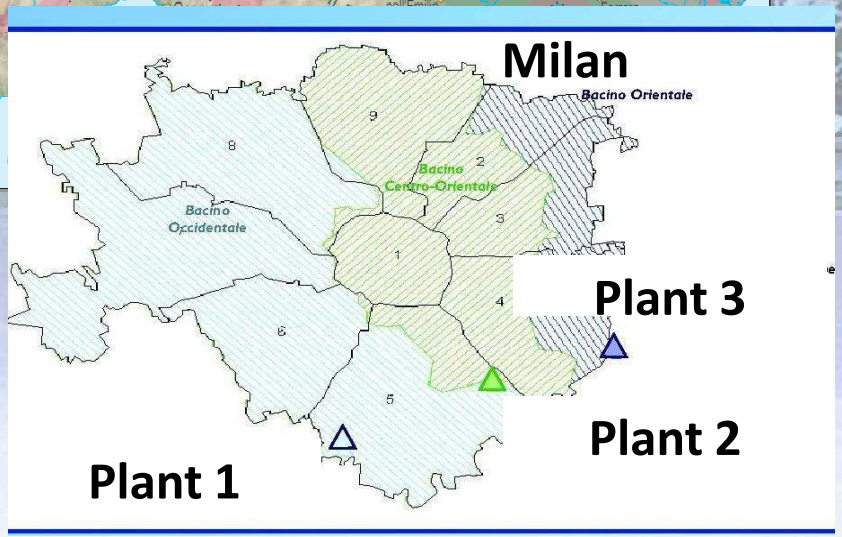
Intraday RSD% in wastewater < 10-15%

Sampling sites

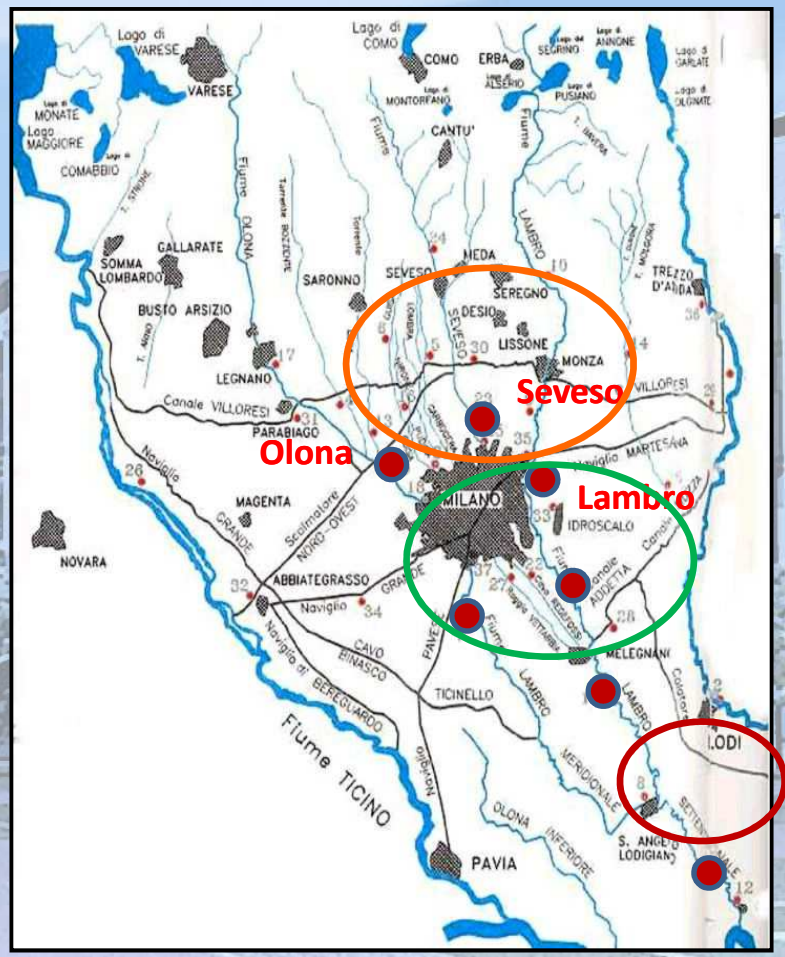
North of Italy, Milan Area



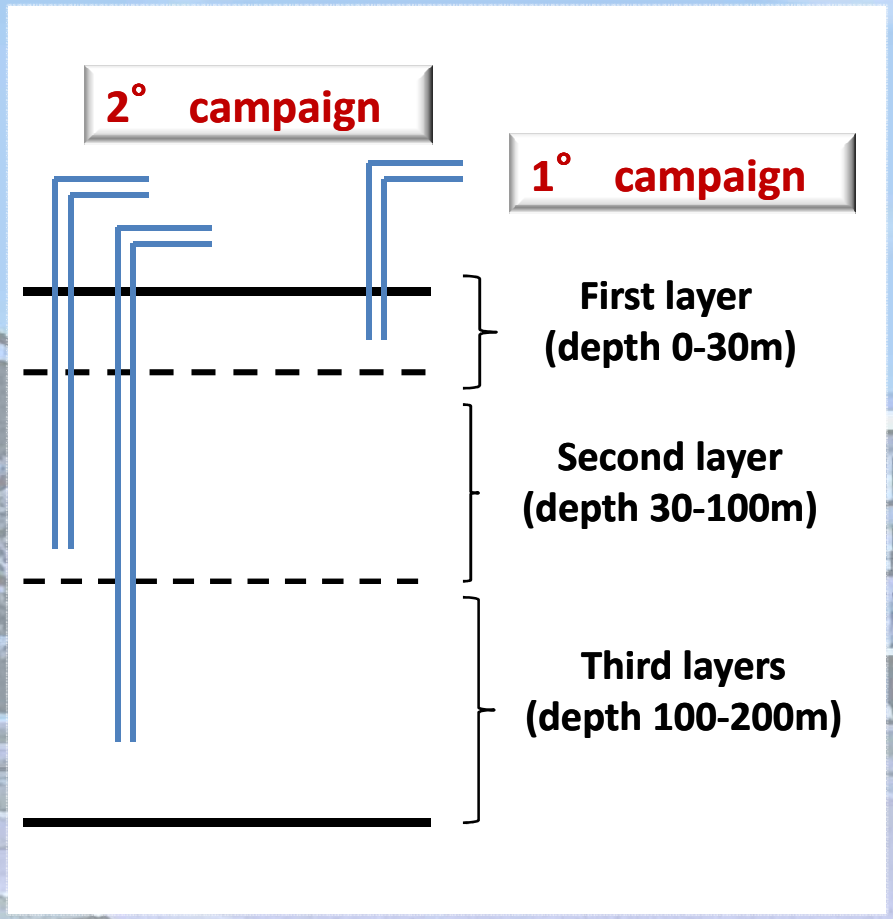
Wastewater



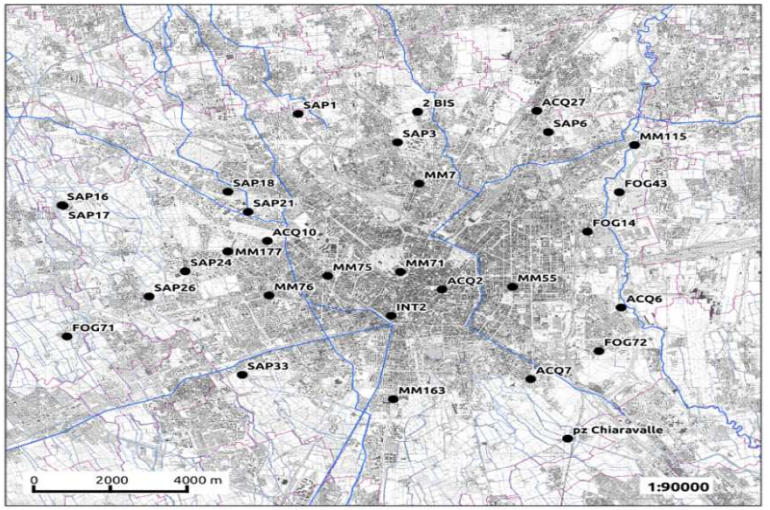
Surface water



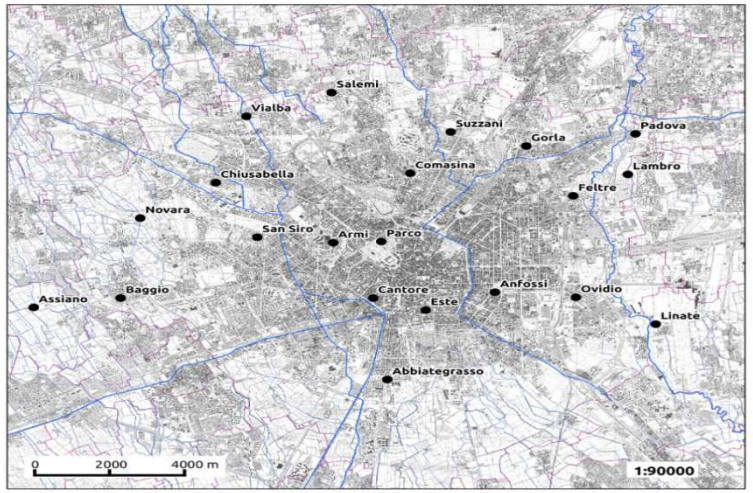
Sampling sites - Groundwater



1° campaign: 30 piezometers, water not for drinking use



2° campaign: 21 wells for drinking water supply. Collection before treatment



Removal of emerging contaminants in STPs

Water concentrations (ng/L) were **multipled** by the sewage treatments plants **flow rates** to obtain the **total loads (g/d)** entering the plant

Classes of compounds	Raw wastewater (mean values of 7 days, 3 plants)	Treated wastewater (mean values of 7 days, 3 plants)	Removal rates
	Loads (g/day)	Loads (g/day)	(%)
Therapeutic Drugs	10043	2694	73
Illicit Drugs	1413	106	92
Disinfectants	706	40	94
Sunscreens/UV Filters	556	377	32
PFOS/PFOA	12	12	0
Anthropic markers	101393	328	100
Alkylphenols	1527	98	94

Removal of emerging contaminants in STPs

Removals depends on compounds and treatment

Plant 1 and 2: Activated sludge secondary treatment followed by disinfection

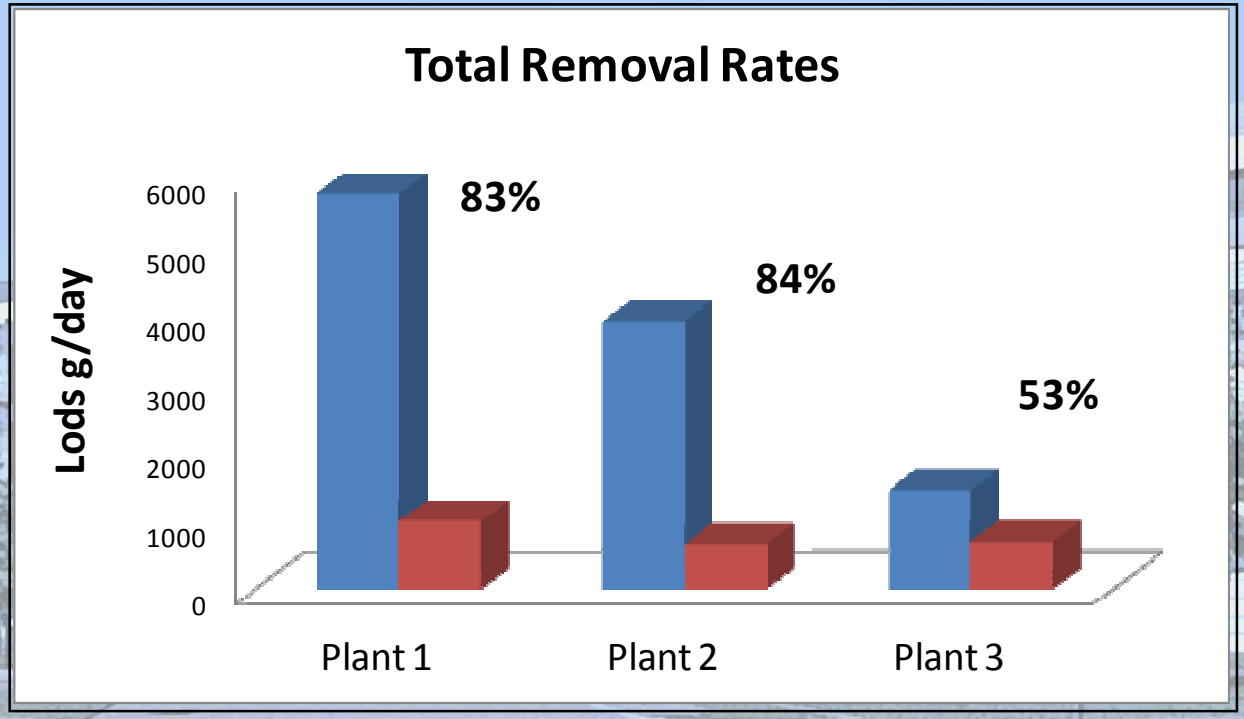
Plant 3: Biofilters secondary treatment and UV disinfection

Selected Pharmaceuticals	Influent PLANT 1 (7 samples) (g/d)	Effluent PLANT 1 (7 samples) (g/d)	Influent PLANT 2 (7 samples) (g/d)	Effluent PLANT 2 (7 samples) (g/d)	Influent PLANT 3 (7 samples) (g/d)	Effluent PLANT 3 (7 samples) (g/d)	Removal rate (%) PLANT 1	PLANT 2	PLANT3
Atenolol	731±189	100±15	593±53	161±45	132±18	108±105	86	73	18
Bezafibrate	66±42	5±2	36±8	50±22	226±208	132±105	92	0	42
Carbamazepine	138±40	73±12	104±13	88±8	133±143	23±3	47	15	83
Ciprofloxacin	172±47	35±9	229±35	51±16	53±34	30±8	80	78	43
Clarithromycin	445±90	73±14	152±29	92±11	89±16	81±10	84	39	9
Furosemide	326±148	117±32	115±49	528±57	55±22	49±3	64	0	11
Ibuprofen	668±192	1.2±0.1	485±106	7±5.2	87±18	17±6	100	99	80
Hydrochlorothiazide	323±127	417±403	139±19	289±28	38±7	13±9	0	0	66
Ketoprofene	621±296	76.4±26	265±17	152±61	86±21	17±10	88	42	80
Naproxene	612±224	23±5	286±140	55±69	57±9	51±6	96	81	11
Ofloxacin	106±28	50±8	191±28	78±6	47±29	39±11	53	59	17
Ranitidine	36±11	1.3±0.3	45±13	31±3	11±3	15±3	96	31	0

Selected SunScreens/ UVFilters	Influent PLANT 1 (7 samples) (g/d)	Effluent PLANT 1 (7 samples) (g/d)	Influent PLANT 2 (7 samples) (g/d)	Effluent PLANT 2 (7 samples) (g/d)	Influent PLANT 3 (7 samples) (g/d)	Effluent PLANT 3 (7 samples) (g/d)	Removal rate (%) PLANT 1	PLANT 2	PLANT3
PBSA	99.2±11.3	65±7.8	149.3±16.2	94±10.3	31.3±9.6	18.4±2.6	35	37	41
BP-4	212.0±17.3	61.7±8.3	215.9±23.1	123.2±17.3	18.9±5.9	13.4±2.1	71	43	29
BP-3	24.8±4.2	-	14±3.5	-	3.5±2.2	0.3±0.1	100	100	92

Removal of emerging contaminants in STPs

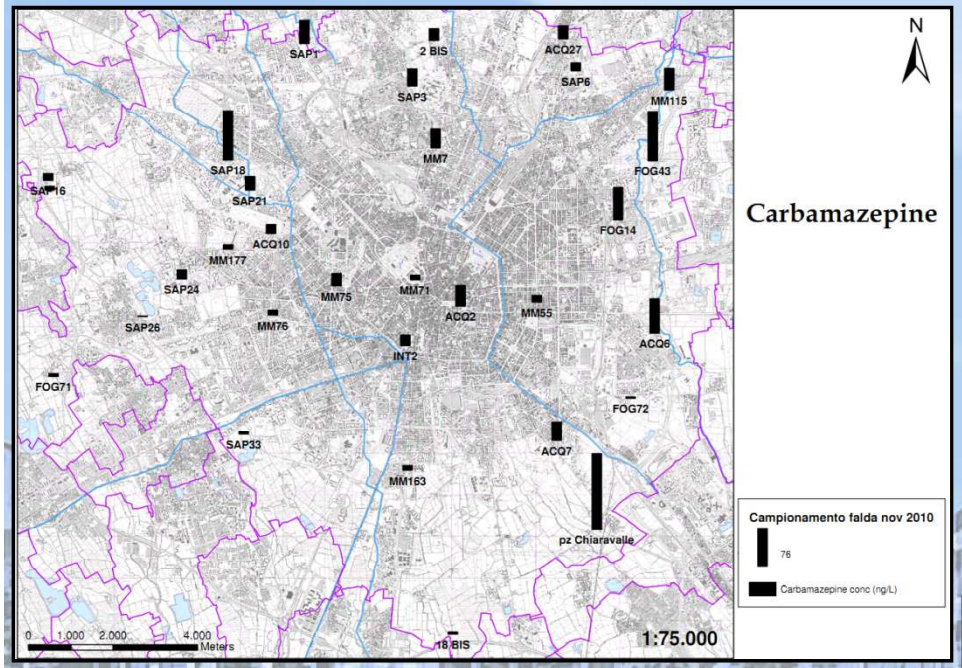
Therapeutic drugs: different removals among STPs



Plant 1 and 2: Activated sludge secondary treatment followed by disinfection

Plant 3: Biofilters secondary treatment and UV disinfection

Ground Water Contamination

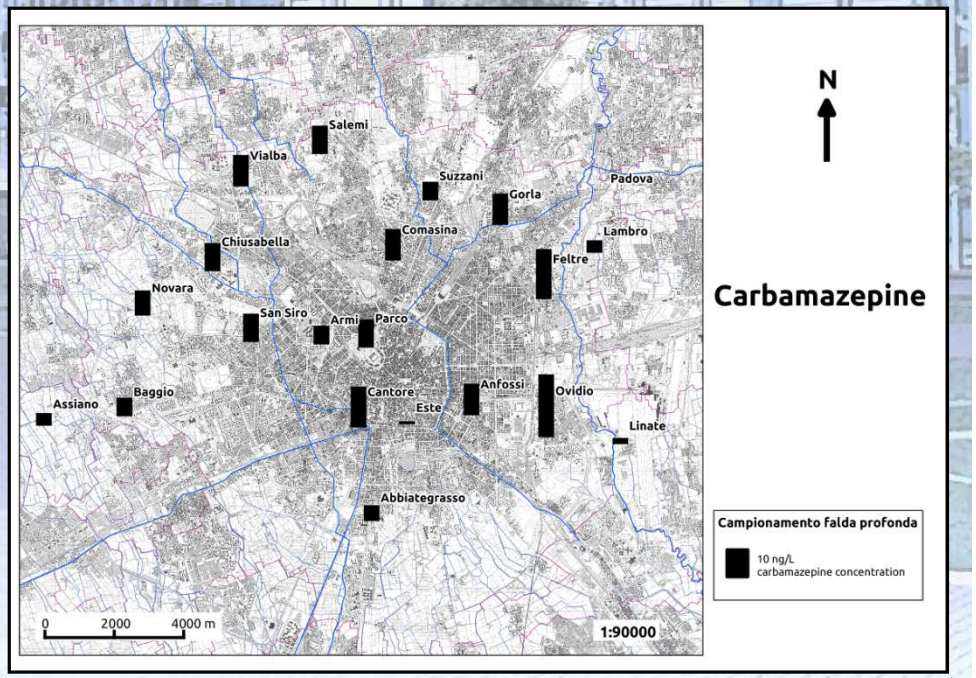


- ✓ Concentrations were generally < 10 ng/L
- ✓ Carbamazepine and PFOS-PFOA were detected in all the samples

Different pattern of contamination between the layers analyzed

First layer groundwater (depth 0-30m)
Concentrations 1.5-152 ng/L

Second and third layer groundwater (depth 40-200 m)
Concentrations 0.2-32 ng/L



Conclusions

✓Assessment of the **environmental occurrence** of different classes of **emerging pollutants**

✓ Study of **fate in STPs** depends on **chemicals structure** and **type of treatment** adopted

✓ **Mass Balance** calculation allowed the **identification of various sources** of contamination

✓ A **different pattern of contamination** among groundwater layers was observed

Thanks

Ettore Zuccato
Roberto Fanelli
Renzo Bagnati
Enrico Davoli
Manuela Melis
Paolo Camporini
Marinella Palmiotto

Metropolitana Milanese
and STPs personnel

Mario Negri Institute for
Pharmacological Research, Milan, Italy

Project supported by Fondazione Cariplo
(grant 2009-3468-2009-3513)

Thanks for your attention!

MARIO NEGRI
ISTITUTO DI RICERCHE FARMACOLOGICHE

DEPARTMENT
Environmental
Health Sciences