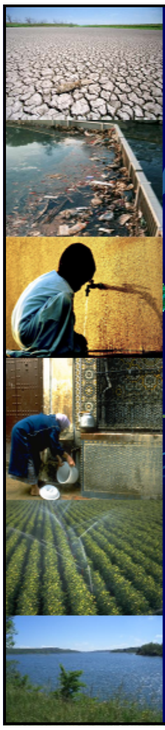

INNOVA-MED CONFERENCE

Innovative processes and practices for wastewater treatment and re-use in the Mediterranean region

Treatment and treatability of hospital wastewaters

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Girona, October 8-9 2009

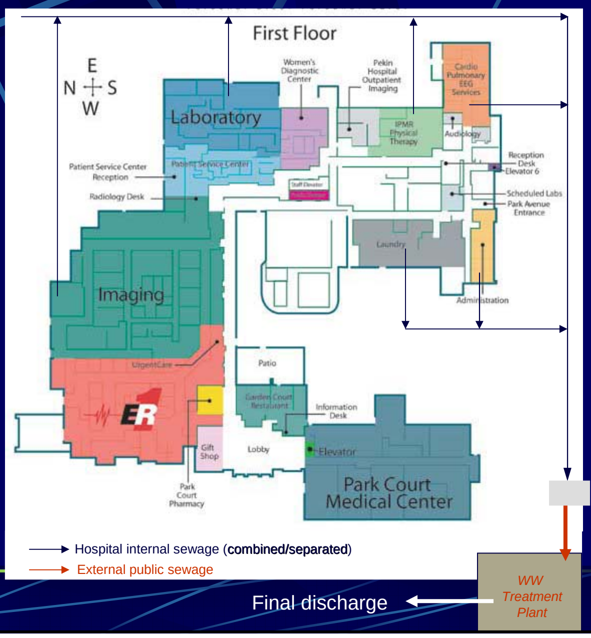
1

Hospital: its structure

General services
(kitchen, laundry, conditioning)

Diagnosis services
(laboratories, outpatients' departments, radiological departments, transfusion centres...)

Wards
(general medecine, surgery, specialities, haemodialysis, infectious diseases...)



WW = wastewater

Hospital WWs management in Italy (not only)

- Considered of the same pollutant load of domestic WWs.
- Discharged in a public sewage, according to the current law disposal, conveyed and treated at a municipal WWTP.
- (Possible) required treatment before immission in public sewage: mild disinfection.

In Switzerland, HWWs are considered of the same pollutant load of Industrial WWs

What is the best strategies in managing HWWs?

3

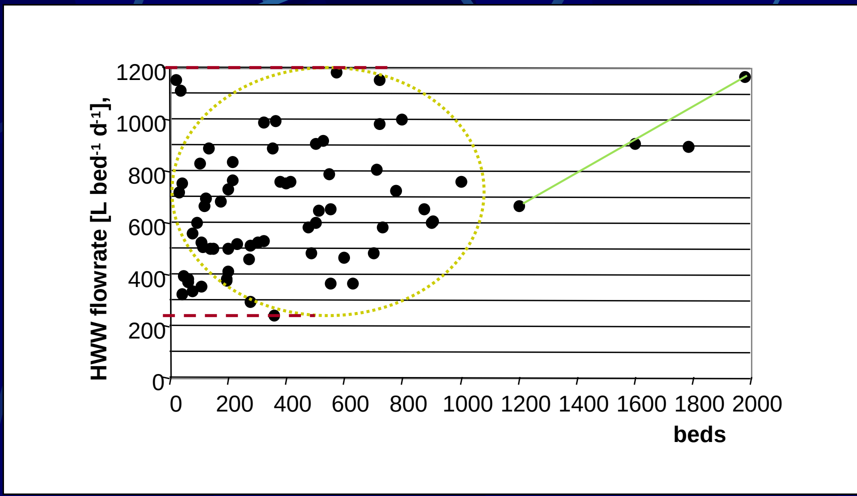
HWWs: Chemical-physical characterization

Services	Origin	Comparable to: DWWs	Comparable to: IWWs
General services	Kitchen	X	
	Laundry (???)	X	
	Air conditioning		X
	Dry treatment of polluted air		X
Diagnosis services	Laboratories		X
	Sanitary departments		X
	Radiological departments		X
	Transfusion centres	?	?
Wards	General medecine	?	?
	Surgery	?	?
	Specialities	?	?
	Haemodialysis	?	?

Legend: + = SIMILAR quality; ? = questionable

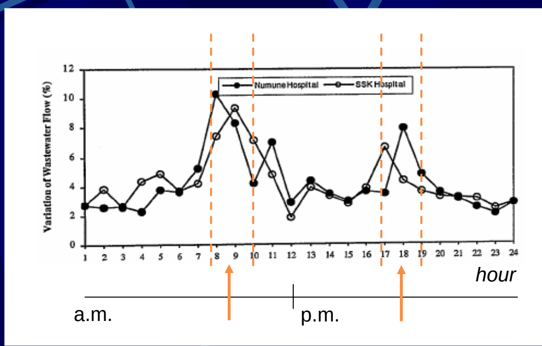
4

Hospital water consumption



Hospital wastewaters: Flow rate

Water consumption distribution along the day



Data refer to two Hospitals in Turkey

Trend similar to that of small WWTPs (< 10 000 inhabitants)

HWWs and DWWs: specific consumption

- Usual design parameter for *domestic water consumption*: **150-300 L/*person*/d**

- Usual design parameter for *hospital water consumption*: **600-1200 L/*bed*/d**

including

Bed
1000 L/(d *patient*)

Personnel
90 L/(d *pro capite*)

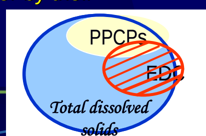
Professors and students
90 L/(d *pro capite*)

Canteen
330 L/(d *seat*)

Pollutants

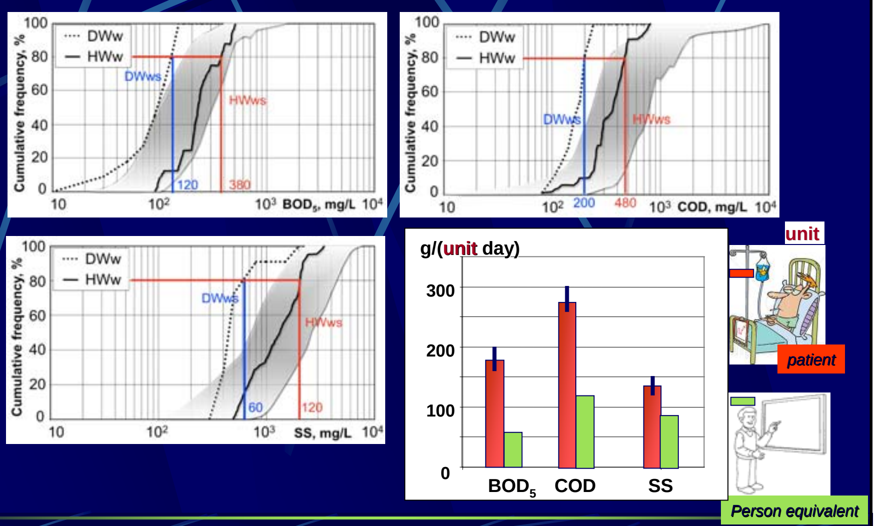
Conventional pollutants	SS, BOD, COD, COT, ammonia, nitrates, nitrites, total N, TKN, organic N, phosphorus, bacteria, viruses
Non conventional pollutants	recalcitrant organic substances, VOCs, surfactants, heavy metals, total dissolved solids
Emerging contaminants (Ecs)	Pharmaceuticals and Personal Care Products (PPCPs) antibiotics for humans and animals Endocrine Disrupter Compounds (EDCs)

- ECs are in general *unregulated* compounds, which may be candidate for future regulation depending on research on their potential health effects and monitoring data regarding their occurrence.
- Ecs do not need to be persistent in the environment to cause negative effects since their high transformation/removal rate can be compensated for by their continuous introduction into the environment
- They include: PPCPs, EDCs, illicit drugs, gasoline additive…



Comparison between pollutant load in hospital and domestic WWs

Conventional macro-pollutants

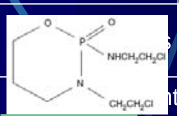


Macro-pollutants: typical range of concentration

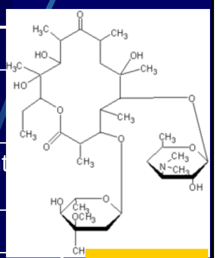
Parameter	HWws	DWws	HWws ? DWws
SS, mg/L	10-900	30-300	>
BOD_5 , mg/L	100-1600	10-130	>
COD, mg/L	280-9000	90-500	>
COD/BOD_5	1.4-6.6	1.7-2.4	>
Total P, mg/L	3-8	8	~
NH_3, mg/L	10-55	30-40	~
Chorides, mg/L	80-188	50	>
Hg, µg/L	0.04-0.28	< 0.5	>
Total surfactants, mg/L	3-7.2	4-8	~
TC, MPN/100 mL	$10^6 – 10^9$	$10^7 – 10^8$	~
FC, MPN/100 mL	$10^3 – 10^7$	$10^6 – 10^7$	~
E. coli, MPN/100 mL	$10^3 – 10^6$	$10^6 – 10^7$	~

Anomalous content in a *hospital* effluent compared to a *domestic* one

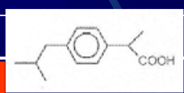
Chemical	Physical	Biological
Drugs and their metabolites	Radiactive markers	
Chemical reactives	Temperature	
Heavy metals		Pathogens
Disinfectants		
Sterilizants		



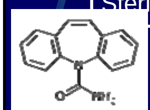
ifosfamide (***cytostatic***)



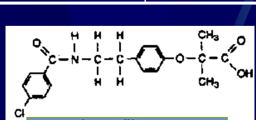
erythromycin (***antibiotic***)



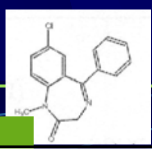
Ibuprofen (***analgesic***)



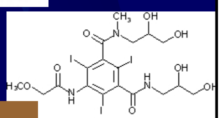
carbamazepine (***antiepileptic***)



bezafibrate (***lipid regolator***)



Diazepam



Iopromide (***contrast media***)

Micro-pollutants in HWWs

How to identify target pharmaceutical compounds?

Choice CRITERIA

- mostly administrated
- with the highest percentages of excretion
- mostly persistent in the environment and scarcely removed by conventional WWTP

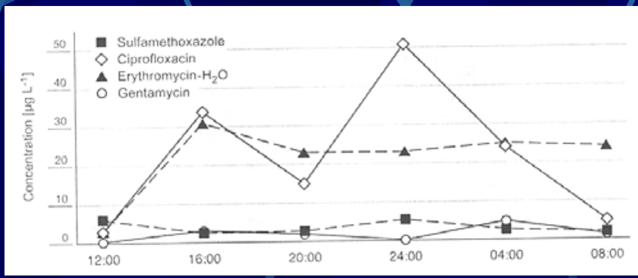
Antibiotics are the most representative micro-pollutants for hospital structures.

Their concentration range in HWWs and DWWs

	Micro-pollutant	HWWs µg/L	DWWs µg/L
Cytostatic	Ifosfamide	0.4-8	0.010-0.030
Antibiotic	Single antibiotic	2-150	< detection limit - 50
	Ofloxacin	5-40	0.1-1
	Ciprofloxacin	17-125	0.2
	Norfloxacin	2.6-7.0	
	Erythromycin	27	1.2
	Sulfamethoxazole	4	< detection limit - 0.58
Antiepileptic	Carbamazepine	0.5-2	1.2
Analgesic	Paracetamol	5-1388	1.7 – 43
	Diclofenac	0.3 - 15	0.1 – 4
Hormones	Estriol	0.18 - 0.79	0.054 – 0.24
	Estrone	0.007 – 0.047	0.017 – 0.030
	Estrogens	1 - 8	0.01 – 0.062
Contrast media	Adsorbable Organic Iodine	10 000	130

From literature data

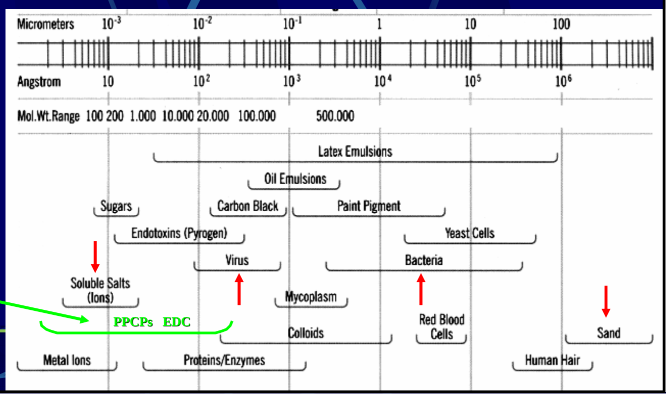
Daily Variation of drug concentration in HWWs



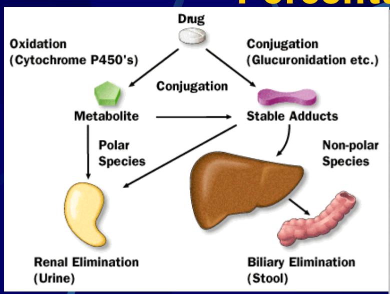
24 h composite wastewater samples are
more representative than instantaneous samples
to evaluate an average daily concentration for hospital WWs

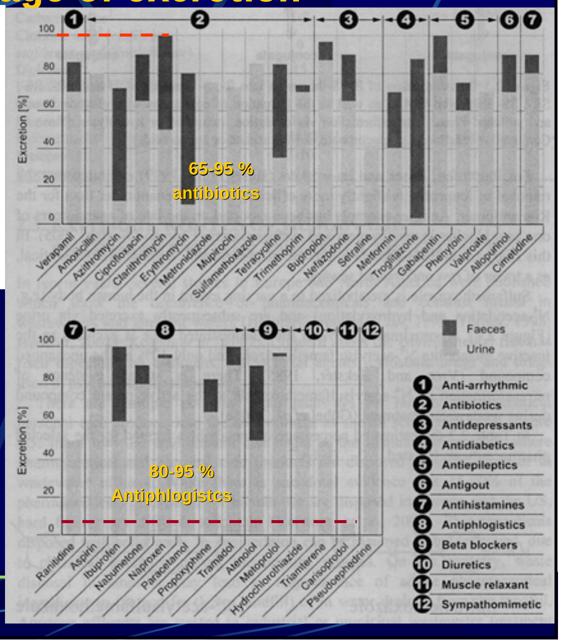
Pharmaceutical compounds differ for....

- Dimension and molecular weight
- Percentage of excretion
- Persistence in the environment, stability
- Biodegradability
- Volatility
- Tendency to adsorb onto a solid phase



Percentage of excretion



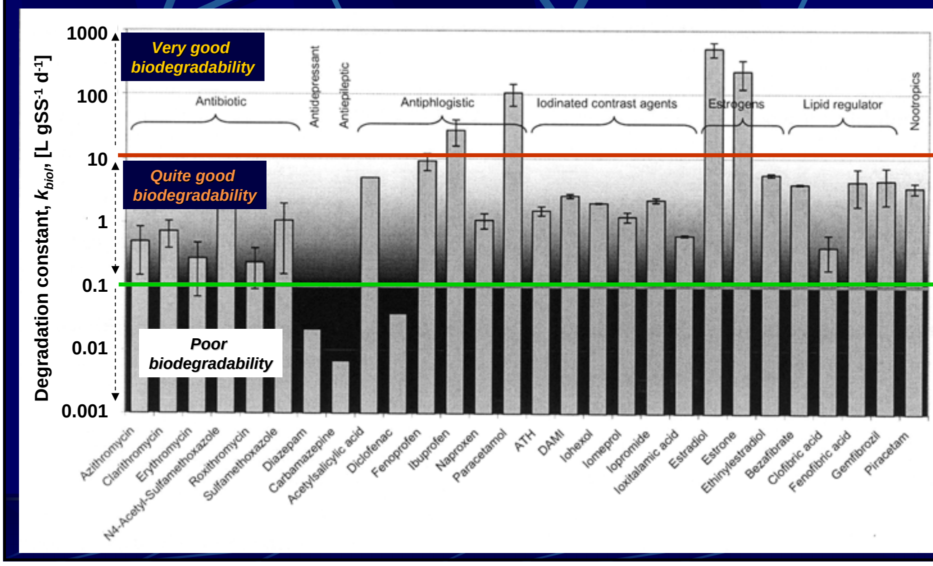


% excretion:
2-95%

Biodegradability

$$\frac{dc_A}{dt} = -k_{biol}\, c_A^n$$

c_A = concentration of compound A, t = time, k_{biol} = degradation constant, n = reaction order



Sorption onto a solid phase (sludge, active carbons…)

K_{OW}= water octanol partition, k_d sorption coefficient

$$\text{Log } k_d = 1.14 + 0.58 \text{ Log } K_{ow}$$

Analytes	Use	MW (g/mol)	Log K_{ow}
Gemfibrozil	Anti-cholesterol	250.2	4.77
Triclosan	Antibiotic	289.6	4.76
Estradiol	Steroid	272.2	4.01
Ibuprofen	Pain reliever	206.1	3.97
Progesterone	Steroid	314.2	3.87
Oxybenzone	Sunscreen	228.1	3.79
Ethynylestradiol	Birth control	296.2	3.67
Testosterone	Steroid	288.2	3.32
Naproxen	Analgesic	230.1	3.18
Estrone	Steroid	270.4	3.13
Erythromycin-H_2O	Antibiotic	733.9	3.06
Diazepam	Anti-anxiety	284.8	2.82
Androstenedione	Steroid	286.2	2.75
Atrazine	Herbicide	215.1	2.61
Dilantin	Anti-convulsant	252.3	2.47
Carbamazepine	Analgesic	236.3	2.45
Estriol	Steroid	288.4	2.45
DEET	Insect repellent	191.3	2.18
TCEP	Fire retardant	285.5	1.44
Trimethoprim	Antibiotic	290.1	0.91
Sulfamethoxazole	Antibiotic	253.1	0.89
Diclofenac	Arthritis	318.1	0.70
Meprobamate	Anti-anxiety	218.3	0.70
Acetaminophen	Analgesic	151.2	0.46
Pentoxifylline	Blood viscosity control	278.1	0.29
Caffeine	Stimulant	194.2	−0.07
Iopromide	X-ray contrast media	790.9	−2.1

Excellent adsorption

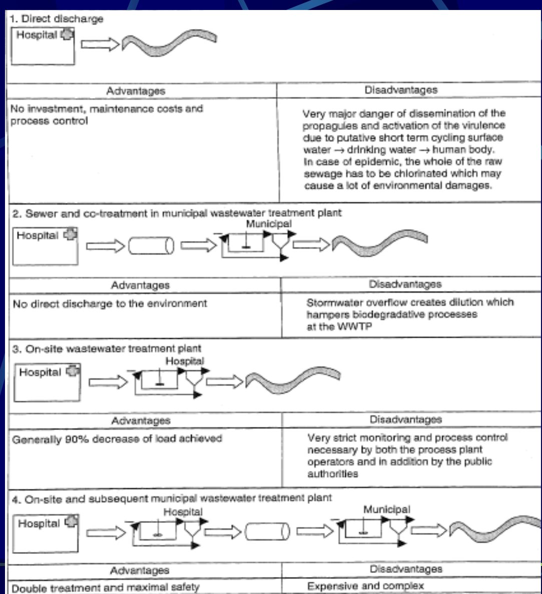
Log K_{ow} = 4

Good adsorption

Log K_{ow} = 2.5

Low adsorption

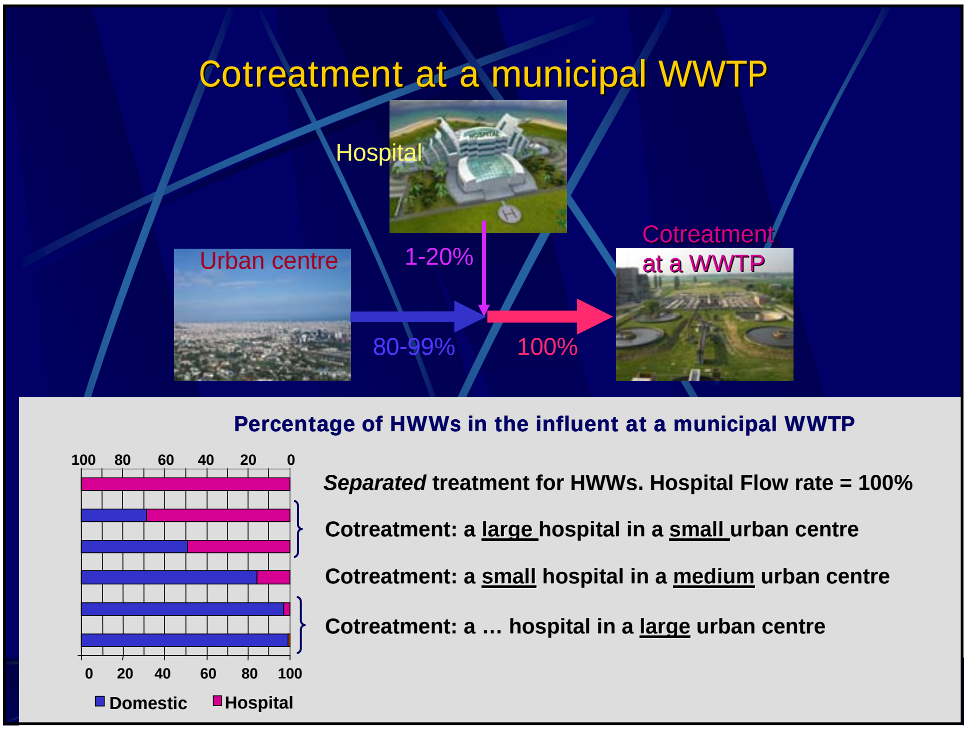
How to manage hospital WWs?

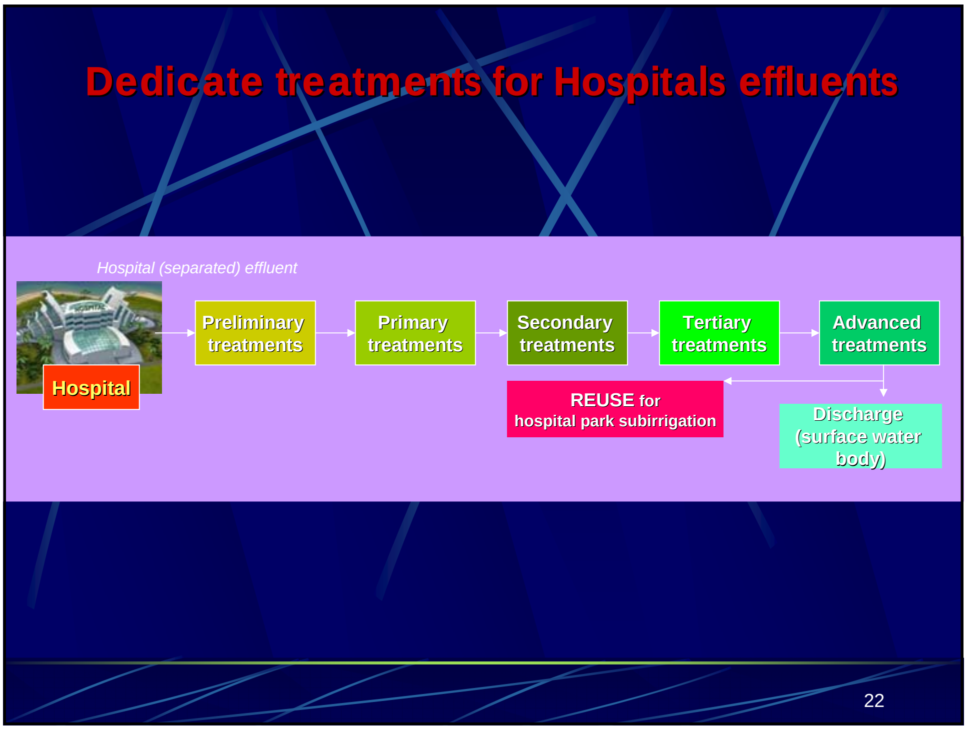


Unfortunately in some countries!

The commonest practice

Possible? Necessary? BAT?


Cotreatment at a municipal WWTP
Hospital
Urban centre
1-20%
Cotreatment
at a WWTP
80-99%
100%
Percentage of HWWs in the influent at a municipal WWTP
100 80 60 40 20 0
0 20 40 60 80 100
Domestic
Hospital
Separated treatment for HWWs. Hospital Flow rate = 100%
Cotreatment: a large hospital in a small urban centre
Cotreatment: a small hospital in a medium urban centre
Cotreatment: a … hospital in a large urban centre


Dedicate treatments for Hospitals effluents
Hospital (separated) effluent
Hospital
Preliminary treatments
Primary treatments
Secondary treatments
Tertiary treatments
Advanced treatments
REUSE for hospital park subirrigation
Discharge (surface water body)
22

Preliminary disinfection (on site treatment)

- In raw hospital effluents, like in raw DWWs, a **high content of organic substances** is present and they can react with the disinfectant.
- This must be carefully considered in defining the **right dose** of the chemical used in this step, in order to achieve a significant (expected) microrganisms removal rate.
- In the following table **guidelines for the dosages**

Kind of wastewaters	Chlorine demand
Raw fresh domestic wastewaters	12-15 mg/L ←
Raw septic domestic wastewaters	15-40 mg/L ←
Primary effluent	12-16 mg/L
Septic tank effluent	30-45 mg/L
Nitrified filtered effluent	2-10 mg/L

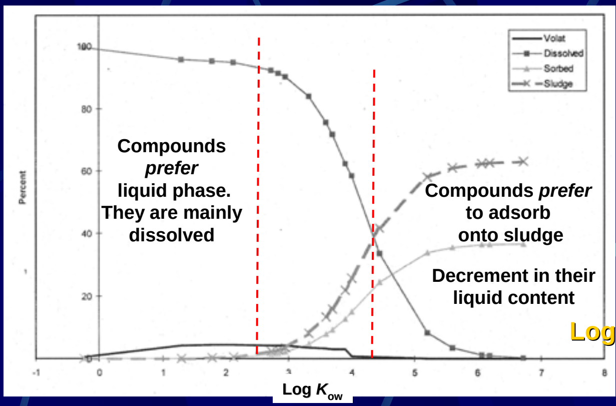
Preliminary disinfection (on site treatment)

- effluent from an infectious disease ward of a hospital in Milan, Italy
- 10-15 mg ClO_2/L, t_{con} = 20 min

able to guarantee a high removal of bacteria and viruses (poliovirus 1) (Nardi et al., 1995)

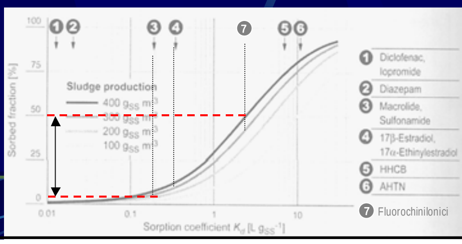
Sample	Chlorine demand	ClO_2 mg/L	AOX mg Cl/L	Total coliform MPN/100 mL	Fecal coliform MPN/100 mL	Fecal strept. MPN/100 mL	Salmonelle	Coliphagi Col/100 mL
A	11,7	-	2,4	$2,4 \cdot 10^6$	400	$4,3 \cdot 10^5$	assenti	<5
		5	2,6	$1,1 \cdot 10^4$	40	$2,4 \cdot 10^3$	assenti	<5
		10	2,7	$1,1 \cdot 10^4$	<3	460	assenti	<5
		15	2,8	$1,1 \cdot 10^3$	<3	4	assenti	<5
B	23,2	-	3,1	$9,3 \cdot 10^6$	$4,4 \cdot 10^4$	$1,1 \cdot 10^7$	assenti	100280
		5	3,4	$1,1 \cdot 10^6$	$9,3 \cdot 10^3$	$1,5 \cdot 10^4$	assenti	8717
		10	3,5	$4,3 \cdot 10^3$	$4,3 \cdot 10^3$	$1,1 \cdot 10^4$	assenti	1334
		15	3,5	9	<3	460	assenti	69
C	11,1	-	0,2	$2,3 \cdot 10^6$	$4,0 \cdot 10^5$	$2,4 \cdot 10^7$	assenti	322000
		5	0,3	$4,6 \cdot 10^4$	$4,6 \cdot 10^4$	$2,4 \cdot 10^7$	assenti	4370
		10	0,3	$9,3 \cdot 10^3$	$4,6 \cdot 10^3$	$4,6 \cdot 10^4$	assenti	23
		15	0,4	240	93	$1,1 \cdot 10^4$	assenti	<5
D	22,0	-	1,2	$4,3 \cdot 10^6$	$4,0 \cdot 10^5$	$1,5 \cdot 10^6$	assenti	3450
		5	1,2	$4,6 \cdot 10^5$	$9,3 \cdot 10^4$	$1,5 \cdot 10^5$	assenti	46
		10	1,3	$2,4 \cdot 10^4$	400	$2,4 \cdot 10^4$	assenti	<5
		15	1,3	$1,1 \cdot 10^3$	9	$1,1 \cdot 10^3$	assenti	<5

Primary treatment: sedimentation



Mechanisms which occur in primary sedimentation

$$\text{Log } k_d = 1.14 + 0.58 \text{ Log } K_{ow}$$



Sorption fraction vs sorption coefficient K_d

fragrances

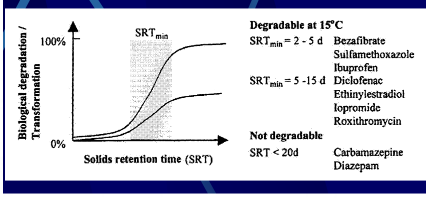
Some antibiotics

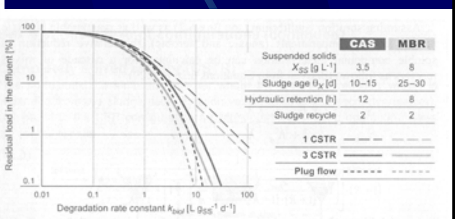
Biological treatment

micropollutant In the influent → degradation → volatilized / still in liquid phase (effluent) / Sorbed onto sludge

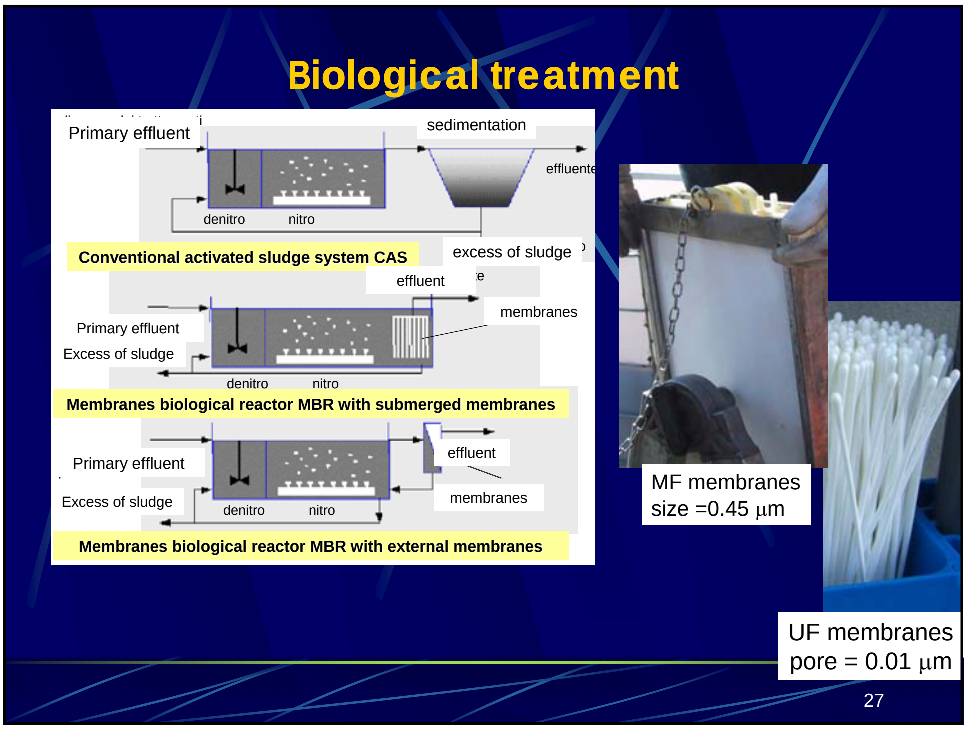
SRT

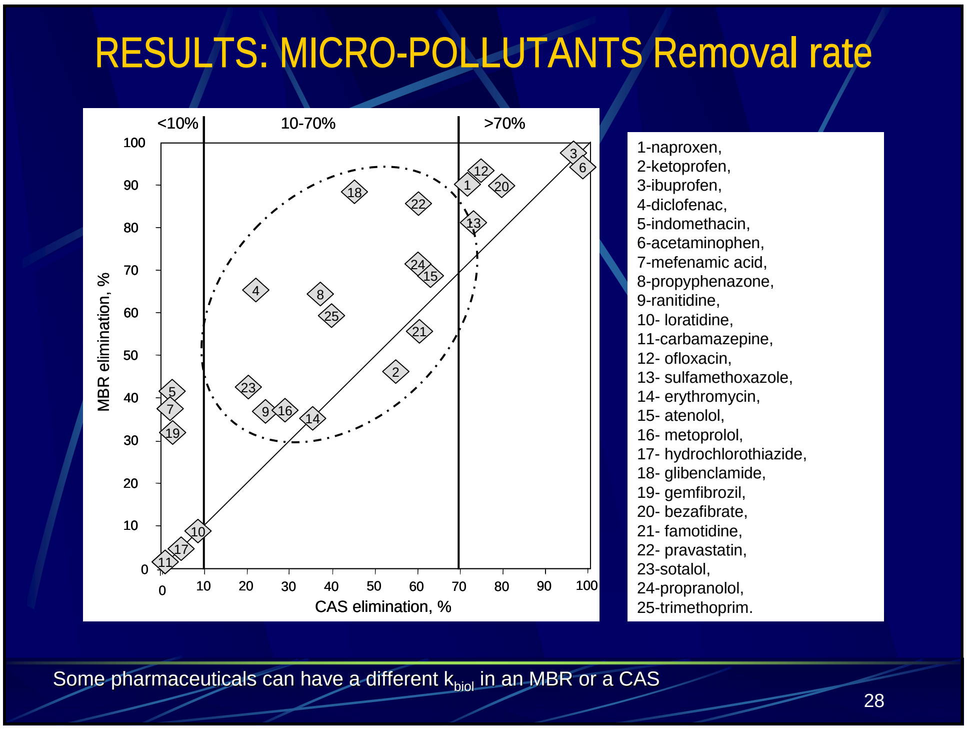
Compound	Sludge age [d]	Biologic transformation	Sorption onto sludge	Effluent
Antibiotics				
Azithromycin[1]	10 – 30	<40%	<10%	>90%
Ciprofloxacin[4]	10 – 12	<10%	70% - 80%	≤30%
Clarithromycin[1]	<20	<10%	<5%	75% - 90%
	>50	~90%	<5%	~10%
Anhydro-erythromycin[1]	<20	<10%	≤10%	>90%
	>50	~90%	≤10%	~90%
N[4]-Acetyl-Sulfamet.[1]	10 – 30	≥90%	<5%	≤15%
Norfloxacin[4]	10 – 12	<10%	80% - 90%	≤20%
Roxithromycin[1]	4 – 30	<60%	<5%	>35%
Sulfamethoxazole (incl. N[4]-Ac-SMX)[1]	4 – 12	50-90%	<5%	10% - 50%
Sulfapyridine[1]	10 – 30	≤70%	<10%	≥30%
Trimethoprim[1]	<20	<10%	≤5%	>90%
	>50	~90%	≤5%	~10%
Hormones				
Estradiol[2]	10 – 30	85% - 99%	<5%	<15%
Estrone[2]	10 – 30	35% - 97%	≤5%	5% - 60%
Ethinylestradiol[2]	10 – 30	45% - 95%%	≤5%	5% - 50%
Drugs				
Carbamazepine[3]	4 – 60	<40%	<5%	>60%
Diclofenac[3]	4 – 60	5% - 45%	<5%	55%- 95%
Ibuprofen[3]	4 – 60	90% - 100%	<5%	0% - 10%
Iopromide[3]	10 – 30	20% - 95%	<5%	5% - 80%
Naproxen[3]	10 – 30	55% - 85%	<5%	15% - 45%
Fragrance				
AHTN[3]	4 – 60	<55%	>20%	>30%
HHCB[3]	10 – 30	<55%	>10%	>30%



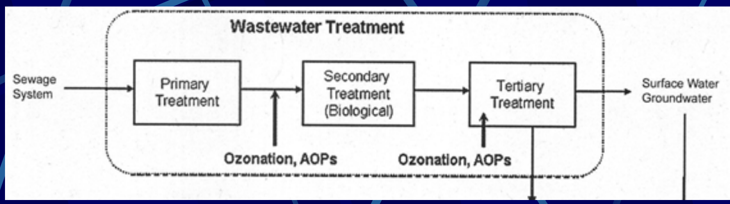


CAS = Conventional Activated Sludges
MBR = Membrane Biological Reactors


Biological treatment
Primary effluent
sedimentation
effluente
denitro
nitro
Conventional activated sludge system CAS
excess of sludge
effluent
membranes
Primary effluent
Excess of sludge
denitro
nitro
Membranes biological reactor MBR with submerged membranes
Primary effluent
effluent
Excess of sludge
membranes
denitro
nitro
Membranes biological reactor MBR with external membranes
MF membranes
size =0.45 µm
UF membranes
pore = 0.01 µm
27

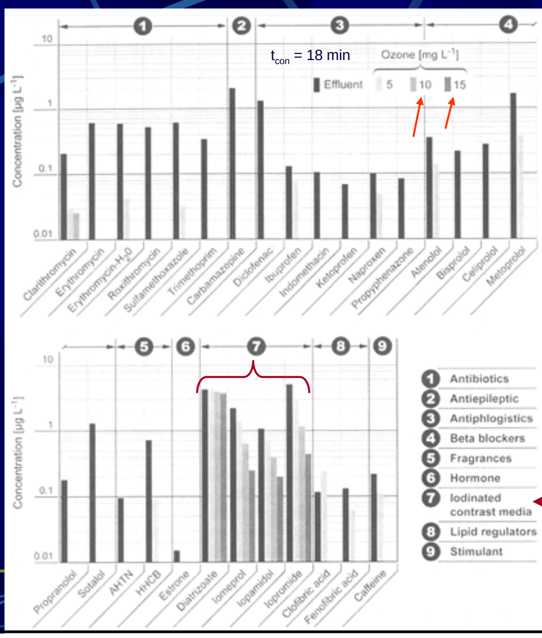

RESULTS: MICRO-POLLUTANTS Removal rate
<10%
10-70%
>70%
MBR elimination, %
CAS elimination, %
1-naproxen,
2-ketoprofen,
3-ibuprofen,
4-diclofenac,
5-indomethacin,
6-acetaminophen,
7-mefenamic acid,
8-propyphenazone,
9-ranitidine,
10- loratidine,
11-carbamazepine,
12- ofloxacin,
13- sulfamethoxazole,
14- erythromycin,
15- atenolol,
16- metoprolol,
17- hydrochlorothiazide,
18- glibenclamide,
19- gemfibrozil,
20- bezafibrate,
21- famotidine,
22- pravastatin,
23-sotalol,
24-propranolol,
25-trimethoprim.
Some pharmaceuticals can have a different k_biol in an MBR or a CAS
28

Advanced chemical treatments: ozonation



Ozone is
a highly reactive and unstable compound,
able to break bonds in stable molecules
resulting
in an increment of the biodegradable molecules in the treated wastewater

Advanced chemical treatments: ozonation

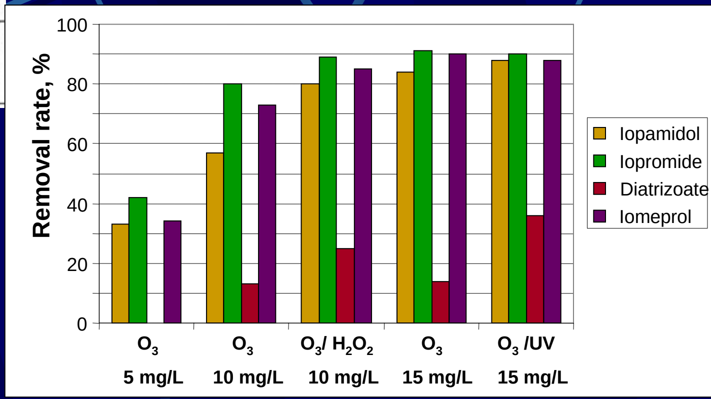


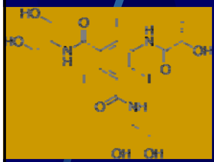
Advanced oxidation processes

(O_3/H_2O_2, O_3/UV)

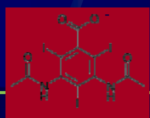
Too much stable compounds!
Ozone-proof substances!!

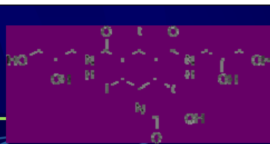
	Mean STP effluent ($n = 6$) ($\mu g\ l^{-1}$)
Iopamidol	1.1±0.1
Iopromide	5.2±0.8
Diatrizoate	5.7±1.4
Iomeprol	2.3±0.1




iopamidol


iopromide


diatrizoate


iomeprol

31

Advanced treatments: active carbons

Compound	Limit of quantification (LOQ) ($\mu g\ L^{-1}$)	Elimination of pharmaceuticals from spiked MBR wastewater (%)		
		Without PAC dosage	PAC dosage ≤50 mg L^{-1}	PAC dosage >50 <200 mg L^{-1}
Fluoroquinolonic acid (FQ)	0.5	27	77	94
Flufenamic acid (FF)	10	n.d. (< LOQ)	n.d. (< LOQ)	n.d. (< LOQ)
Ciprofloxacin	2.5	73	96	>99
Enrofloxacin	2.5	56	96	>99
Moxifloxacin	2.5	78	97	>99

PAC = powder active carbons

32

Disinfection during

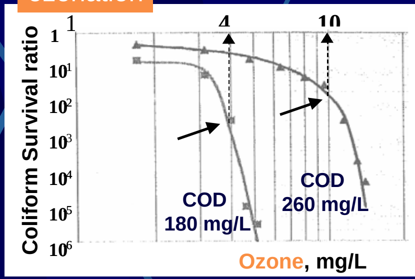
Biological treatment

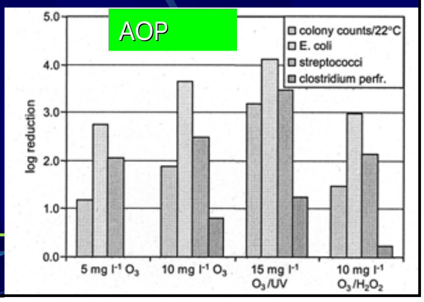
Bacteria	Raw HWws	CAS effluent	MBR effluent
TC	6.1	5.0	2.9
FC	5.3	3.9	1.7
Enterococchi	4.2	2.8	1.1

Retained by UF membranes (pore =10 nm)

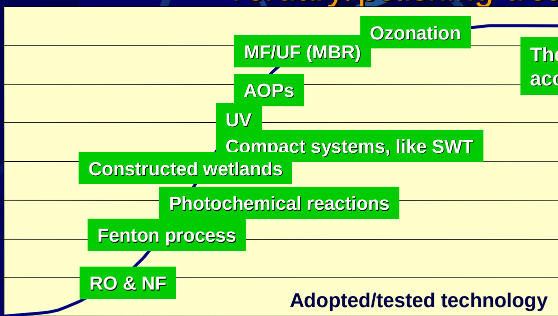
Virus	Size, nm
Enterovirus	20-30
Adenovirus	70-80
Rotavirus	60-80
Parvovirus	20
Reovirus	60-80
Norwalk	27-40
Astrovirus	27-32
Calicivirus	30-40
Coronavirus	80-160

ozonation



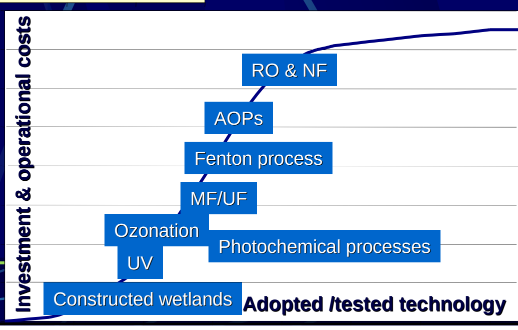


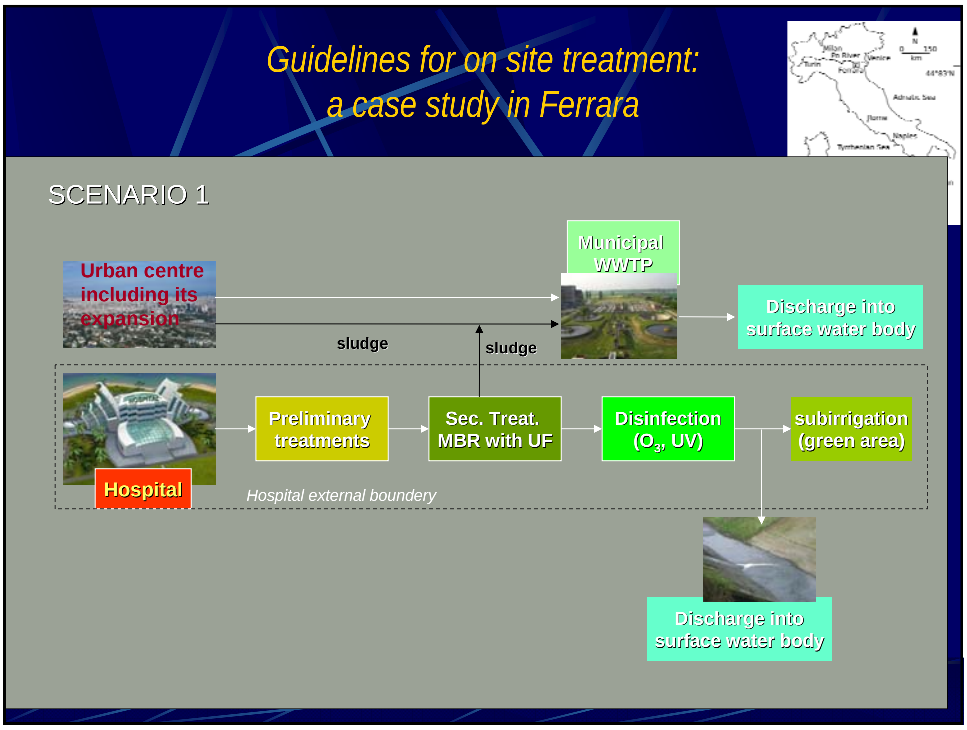
Tertiary/polishing treatments

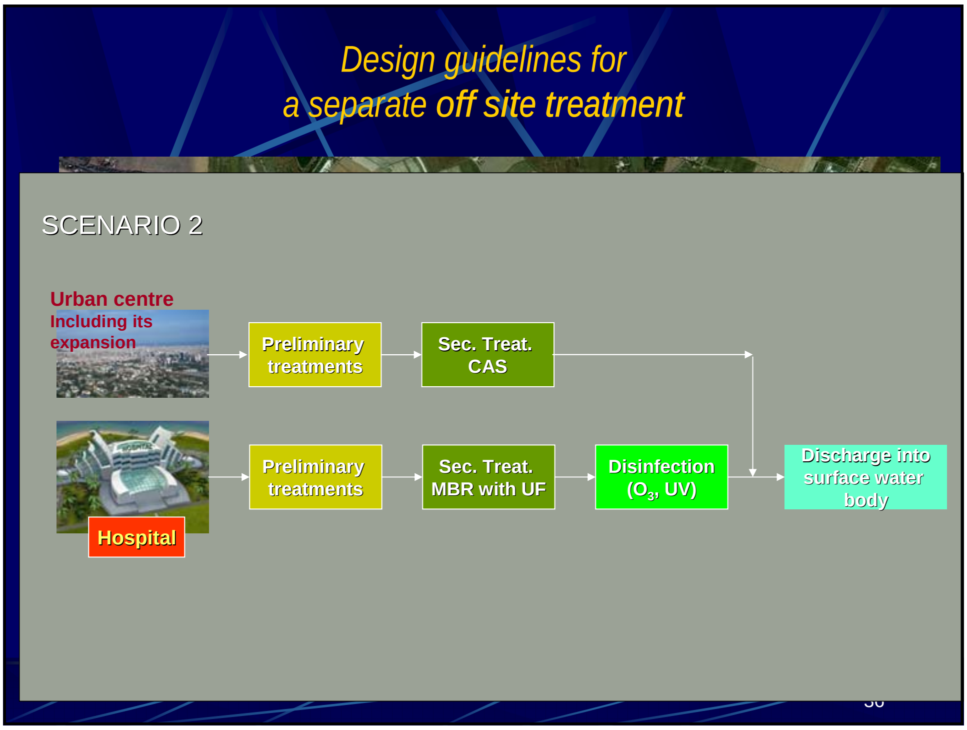


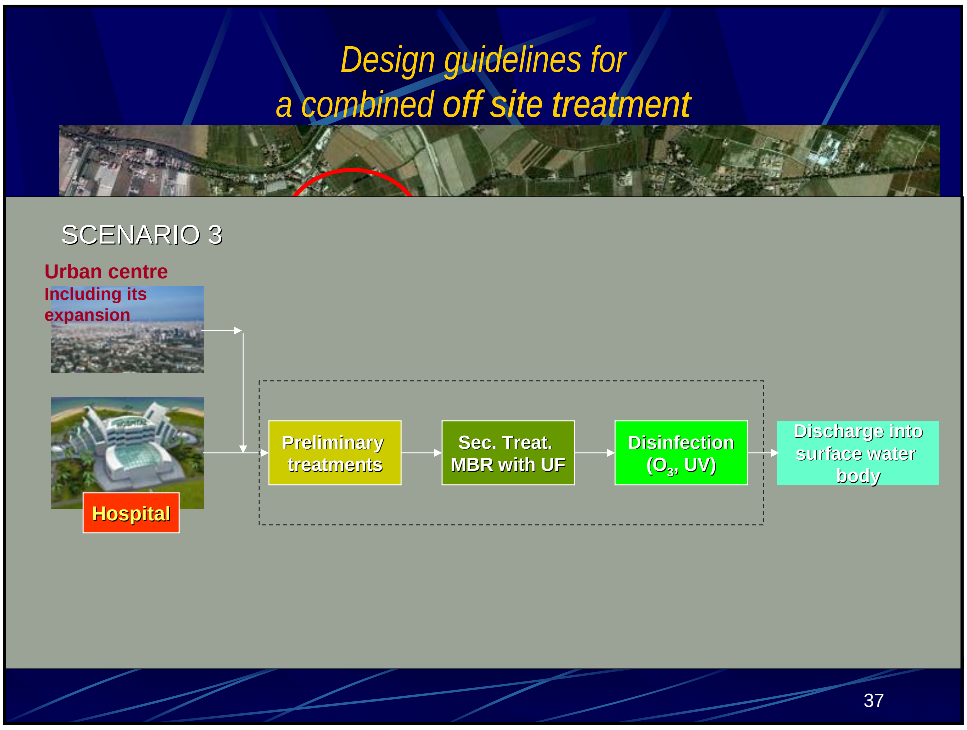
The most promising technologies according to the most recent studies

Qualitative comparison about investment and operational costs




Guidelines for on site treatment:
a case study in Ferrara
SCENARIO 1
Urban centre including its expansion
Municipal WWTP
Discharge into surface water body
sludge
sludge
Preliminary treatments
Sec. Treat. MBR with UF
Disinfection (O_3, UV)
subirrigation (green area)
Hospital
Hospital external boundery
Discharge into surface water body


Design guidelines for
a separate off site treatment
SCENARIO 2
Urban centre Including its expansion
Preliminary treatments
Sec. Treat. CAS
Preliminary treatments
Sec. Treat. MBR with UF
Disinfection (O_3, UV)
Discharge into surface water body
Hospital



Conclusions

- It is not correct to consider hospital effluent as if they were domestic effluent
- Further researches are necessary to deepen HWWs chemical characterization, in particular their micropollutant load
- Important to evaluate case by case: HWWS flow rate contribution to the WWTP influent, other local possible PPCPs sources, characteristics of the receiving surface water body.
- Removal of PPCPs requires advanced biological treatments with a high sludge retention age.

38

Conclusioni (2)

- An MBR treatment is to prefer to a CASP as an MBR is able to guarantee a constant chemical and microbiological quality, a really high retention of SS and of those compounds which are adsorbed onto sludge (including PPCPs).
- UF is better than MF, expected an efficient retention of viruses
- Ozonation treatments are considered the best advanced available technology (BAT) in the removing of pharmaceutical micropollutants.
- Advanced oxidation processes are under study, technical and economical consideration must be taken in greater consideration

39

Thank You for
Your attention…

40