

WATER FUTURE

International conference
THE FUTURE OF WATER SERVICES

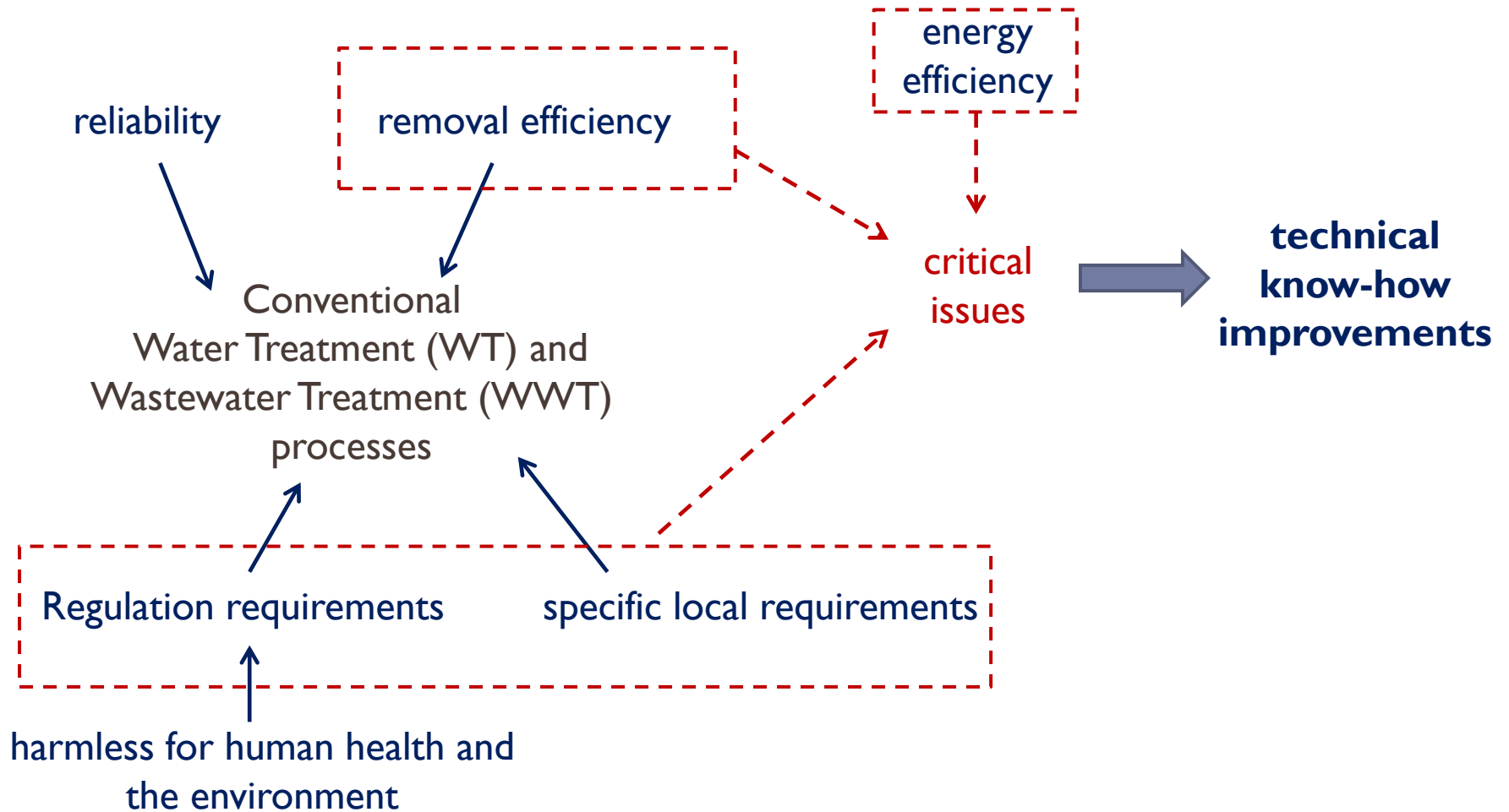


THURSDAY 7TH | FRIDAY 8TH
NOVEMBER 2013

Technological advances in Sanitation and Drinking Water Treatment

Prof. Mariachiara Zanetti
DIATI, Politecnico di Torino

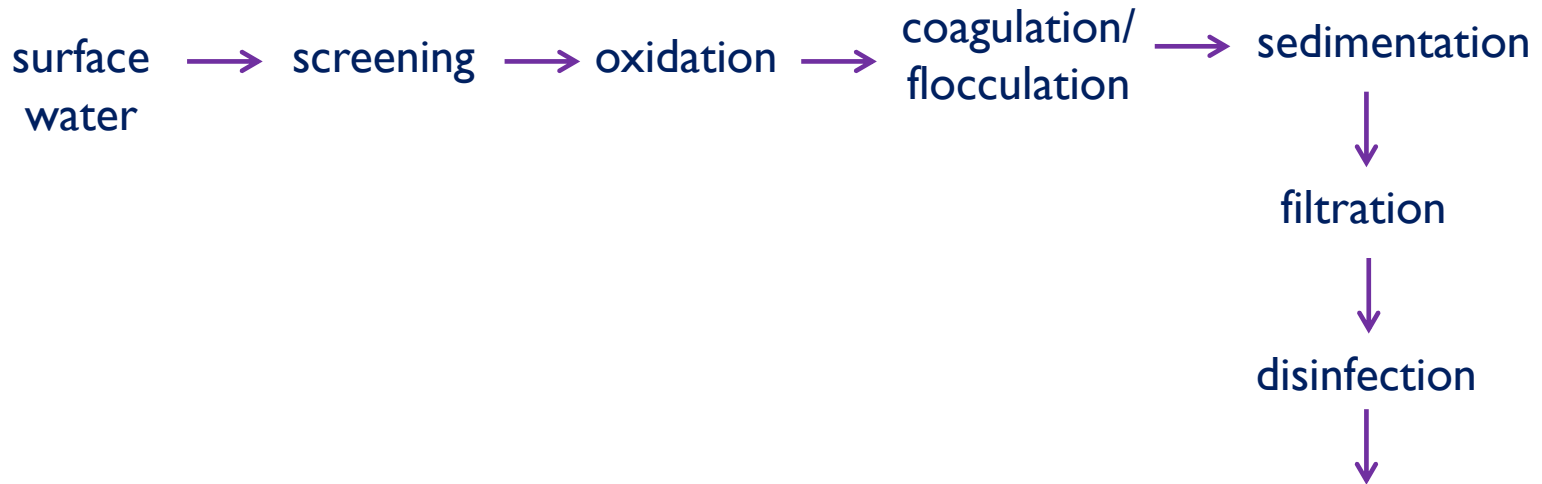
Overview



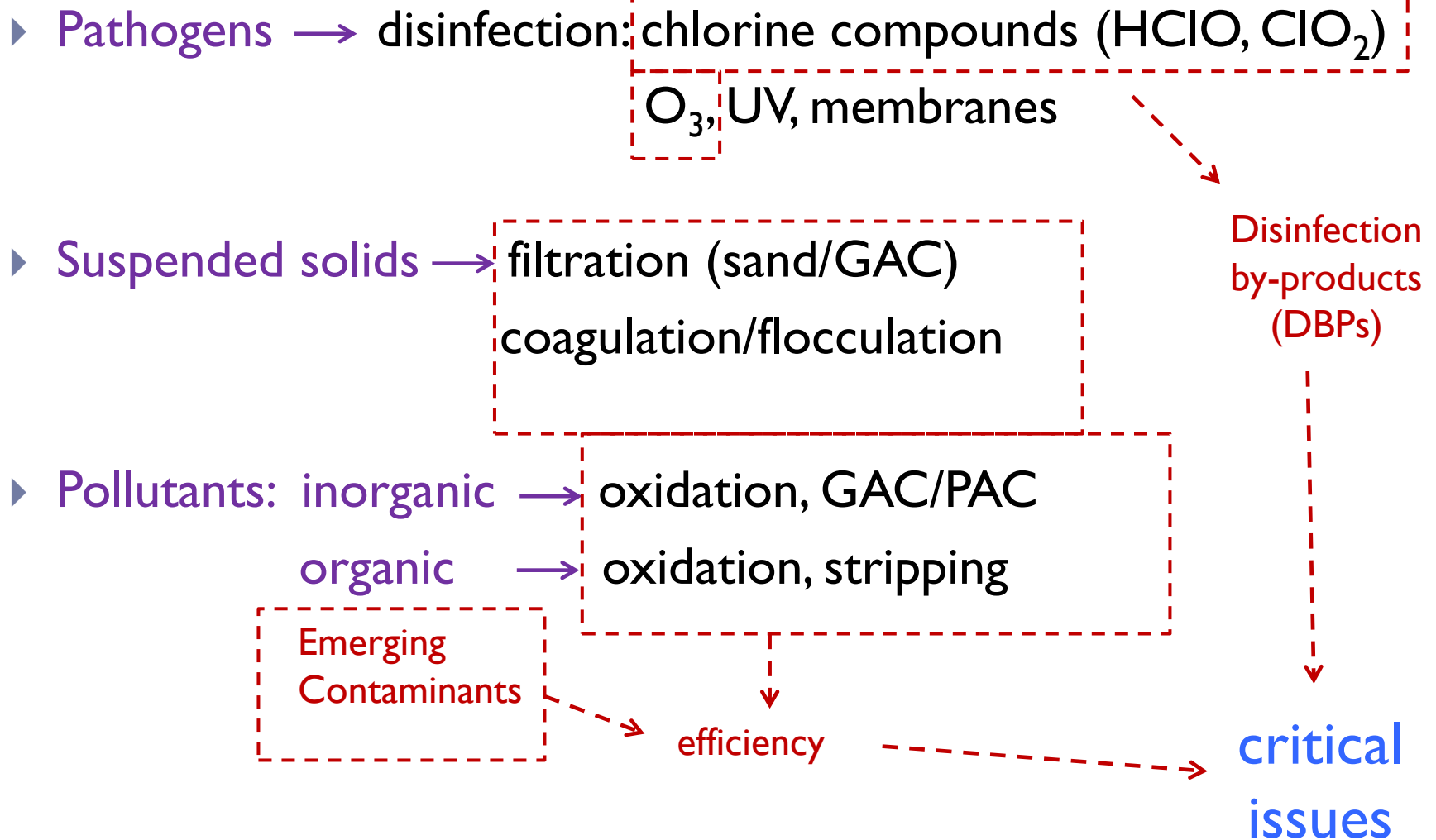
WT processes: framework



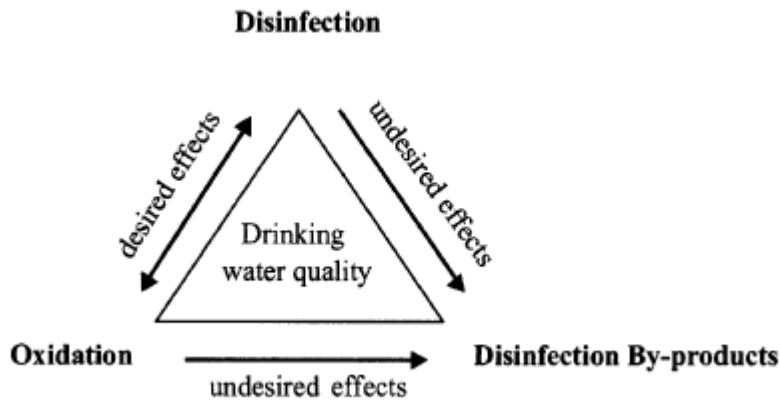
- *Fe/Mn: oxidation
- *VOC, NH₃: stripping, oxidation
- *non volatile organic compounds:
GAC



WT processes: critical issues

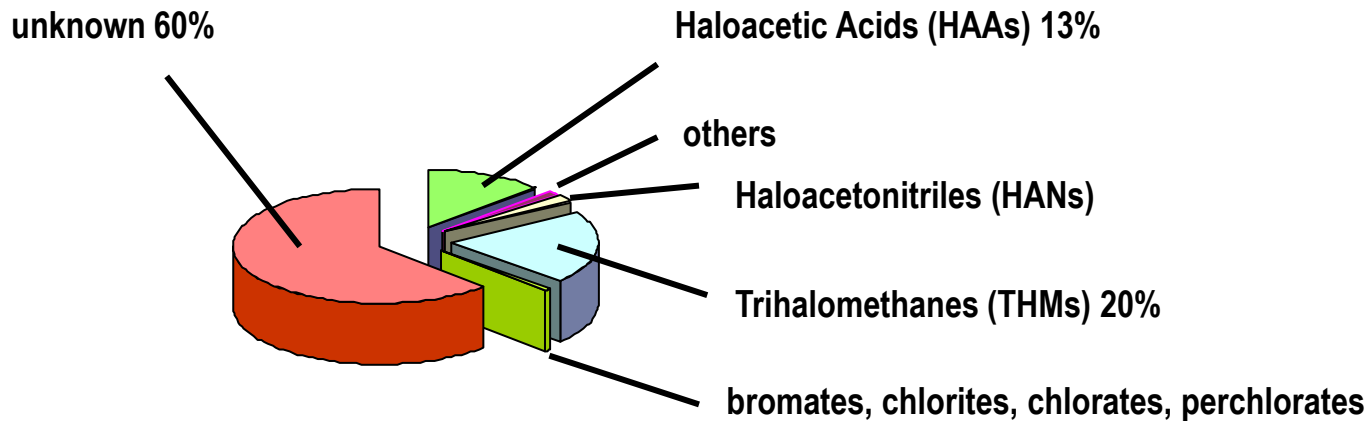


WT processes critical issues: DBPs



Disinfection by-products (DBPs):
inorganic, organic
volatile, hydrophobic
non volatile, hydrophylic
chlorinated, non chlorinated
aliphatic, aromatic

Generated by chlorine disinfectants (HClO , ClO_2) and O_3



WT processes critical issues: DBPs

DBPs precursors:

Natural Organic Matter (NOM)

Turbidity, Fe

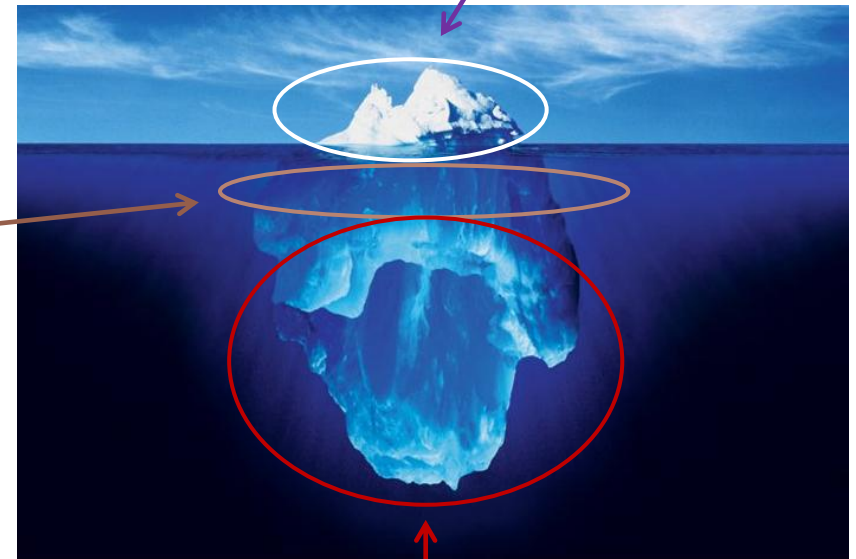
Temperature, pH

Disinfectant dose

$\text{NH}_3/\text{NH}_4^+$

known DBPs
UNlimited by
regulations

known DBPs
limited by
regulations



UNknown DBPs



WT processes critical issues: DBPs

DBPs features:

probable carcinogenic

probable endocrine disruptor

	WHO 2011	EPA 2008	EU DIR 1998	I DL 2001
THMs	Cloroformio: 300 Bromoformio: 100 Dibromoclorometano: 100 Bromodichlorometano: 60	80	100 (150*)	30
CHLORITE	700	1000	700	700 (200*)
CHLORATE	700	-	-	-
BROMATE	10	10	10 (25*)	10 (25*)
PERCHLORATE	-	15	-	-

* temporary value



WT processes critical issues: DBPs

DBPs + precursors removal:

conventional processes: chemical oxidation (ClO_2 , O_3 , H_2O_2)
adsorption on activated carbon (GAC or PAC)

Novel processes: **ADVANCED OXIDATION PROCESSES (AOPs)**

Oxidant: hydroxyl radical $\cdot\text{OH}$

- $\text{H}_2\text{O}_2 / \text{Fe}^{2+}$ (Fenton)
- $\text{H}_2\text{O}_2 / \text{Fe}^{3+}$ (Fenton - like)
- $\text{H}_2\text{O}_2 / \text{Fe}^{2+} (\text{Fe}^{3+}) / \text{UV}$ (Photo assisted Fenton)
- $\text{H}_2\text{O}_2 / \text{Fe}^{3+}$ - Oxalate
- Mn^{2+} /Oxalic acid/Ozone
- $\text{TiO}_2 / \text{hv} / \text{O}_2$ (Photocatalysis)
- $\text{O}_3 / \text{H}_2\text{O}_2$
- O_3 / UV
- $\text{H}_2\text{O}_2 / \text{UV}$

Advanced Oxidation Processes (AOPs):

Agente ossidante	Potenziale di ossidazione elettrochimica (E), Volts	Valori di E relativi al Cloro
Fluoro (F ₂)	3.06	2.25
Radicale ossidrile (OH•)	2.80	2.05
Ossigeno (atomico) (O•)	2.42	1.78
Ozono (O ₃)	2.08	1.52
Perossido di Idrogeno (H ₂ O ₂)	1.78	1.39
Radicale Idroperossido (HO ₂ •)	1.70	1.30
Ipoclorito (HOCl)	1.49	1.10
Cloro (Cl ₂)	1.36	1.00
Biossido di Cloro (ClO ₂)	1.27	0.93
Ossigeno (molecolare) (O ₂)	1.23	0.90

WT processes critical issues: inorganic pollutants

conventional treatments

Mn (II), Fe (II)
H₂S/S²⁻



chemical oxidation

NH₃/NH₄⁺



stripping, chemical oxidation

As (H₂AsO₃⁻)
CN⁻, Br⁻
ClO₄⁻
NO₃⁻



coagulation/flocculation
adsorption
ion exchange

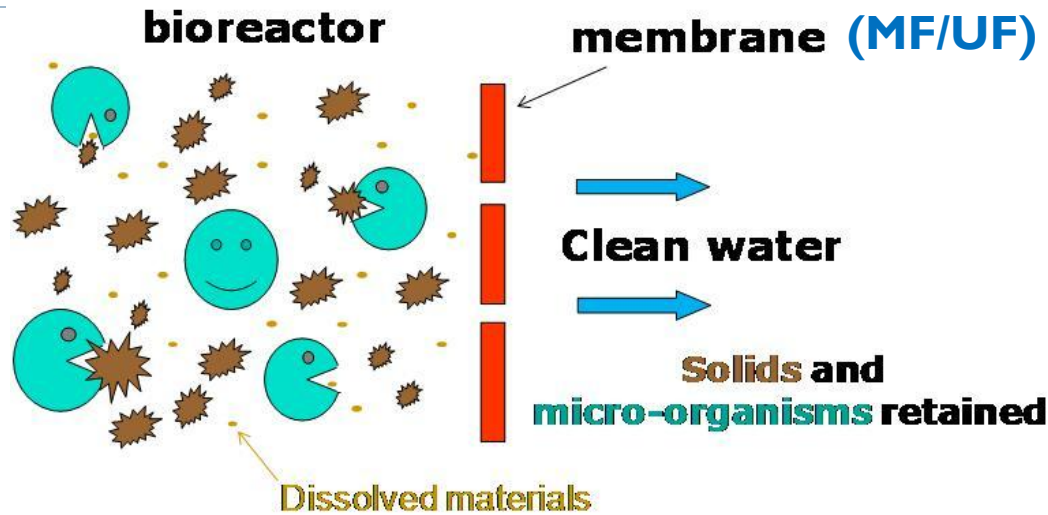
novel treatments

biological oxidation: Membrane Biofilm Reactor (MBR)

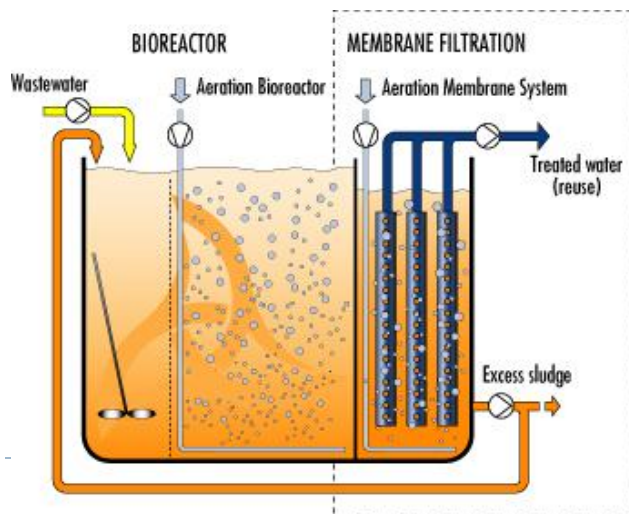
membrane processes: microfiltration + reverse osmosis (RO)
nanofiltration + ultralow pressure RO



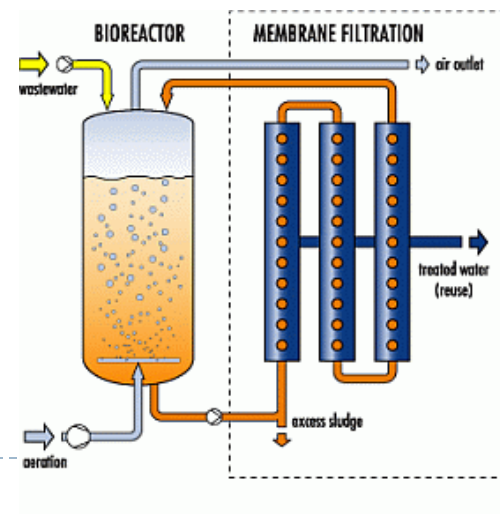
Biological oxidation + membrane processes



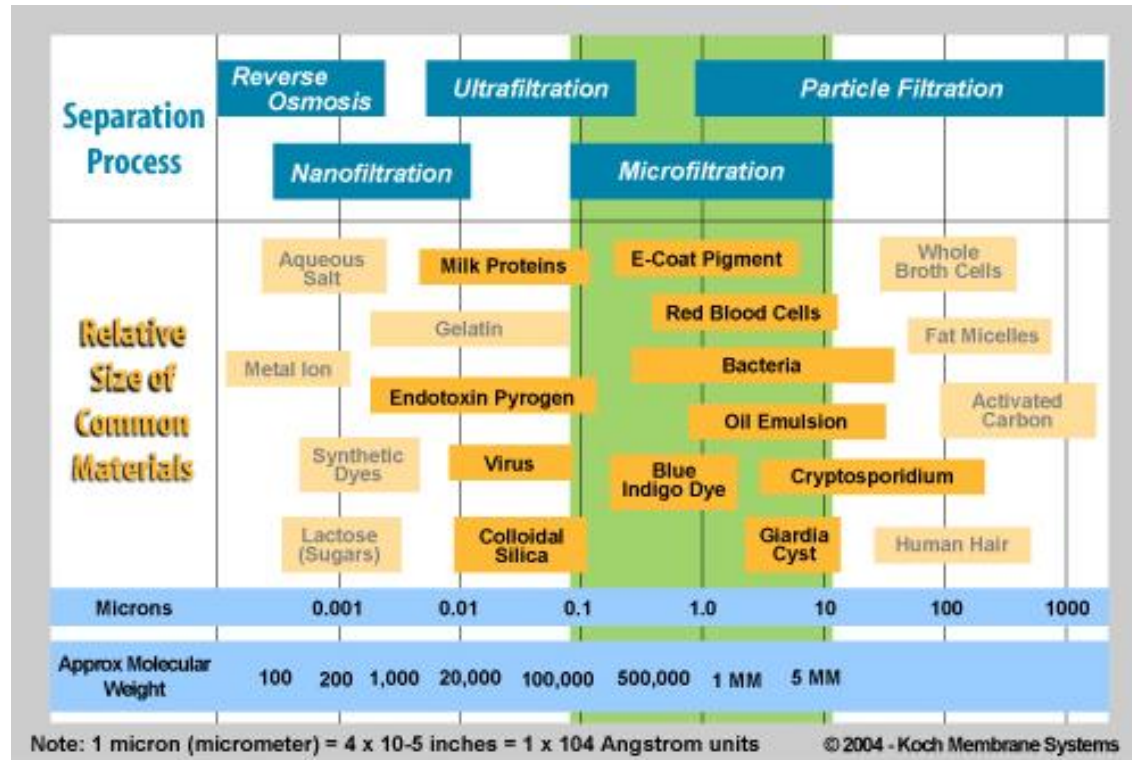
Integrated MBR



Recirculated MBR



Membrane processes



WT processes critical issues: organic pollutants

pesticides, solvents, phenols, PAH
fuel additives (BTEX, MTBE)
DBPs, pharmaceuticals

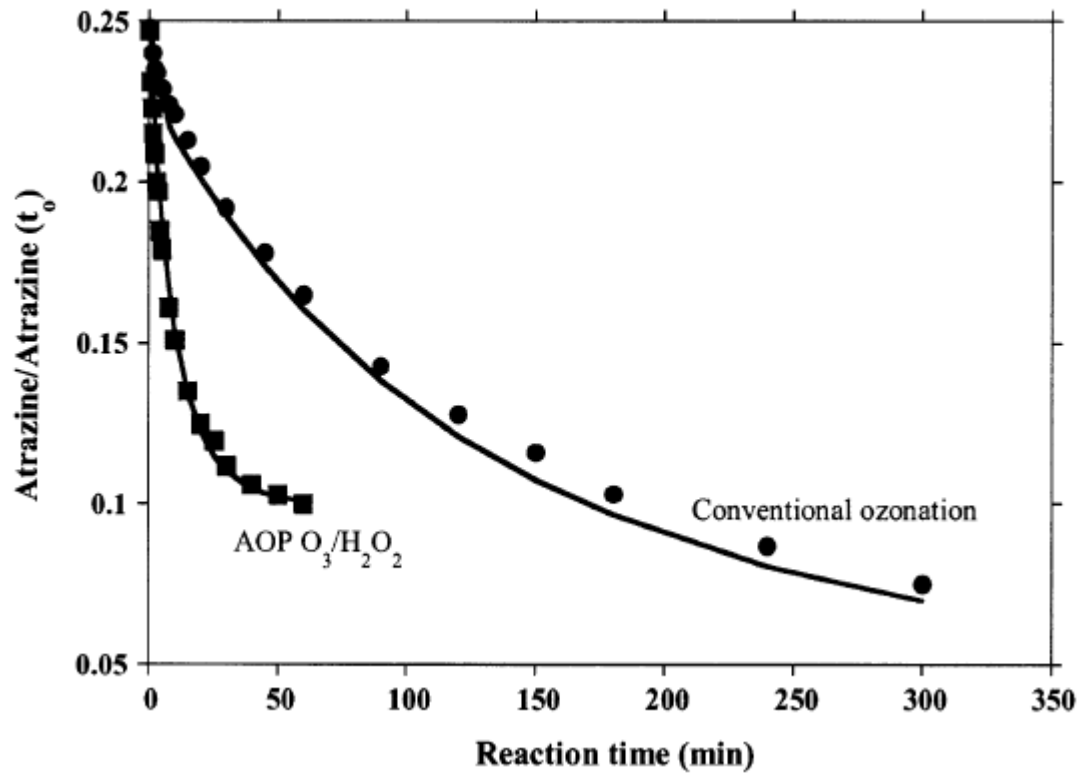
Conventional treatments: adsorption on activated carbon (GAC or PAC)
chemical oxidation (ClO_2 , O_3 , H_2O_2)

Novel treatments: biological oxidation
Advanced Oxidation Processes (AOPs)



WT processes critical issues: organic pollutants

ADVANCED OXIDATION PROCESSES (AOPs)



U. von Gunten / Water Research 37 (2003) 1443–1467



WT processes critical issues: bio-pollutants

Warm temperature + high nutrient load → blooming of **ALGAL PRODUCTS** and **cyanobacteria** (blue-green algae)

Toxin growth, depletion of water organoleptic features

Conventional treatments: coagulation/flocculation

Novel treatments:

membrane processes

acidification (CO_2 or HCl) + coagulation/flocculation



Coagulation/flocculation critical issues

Removal of turbidity

algal products

NOM

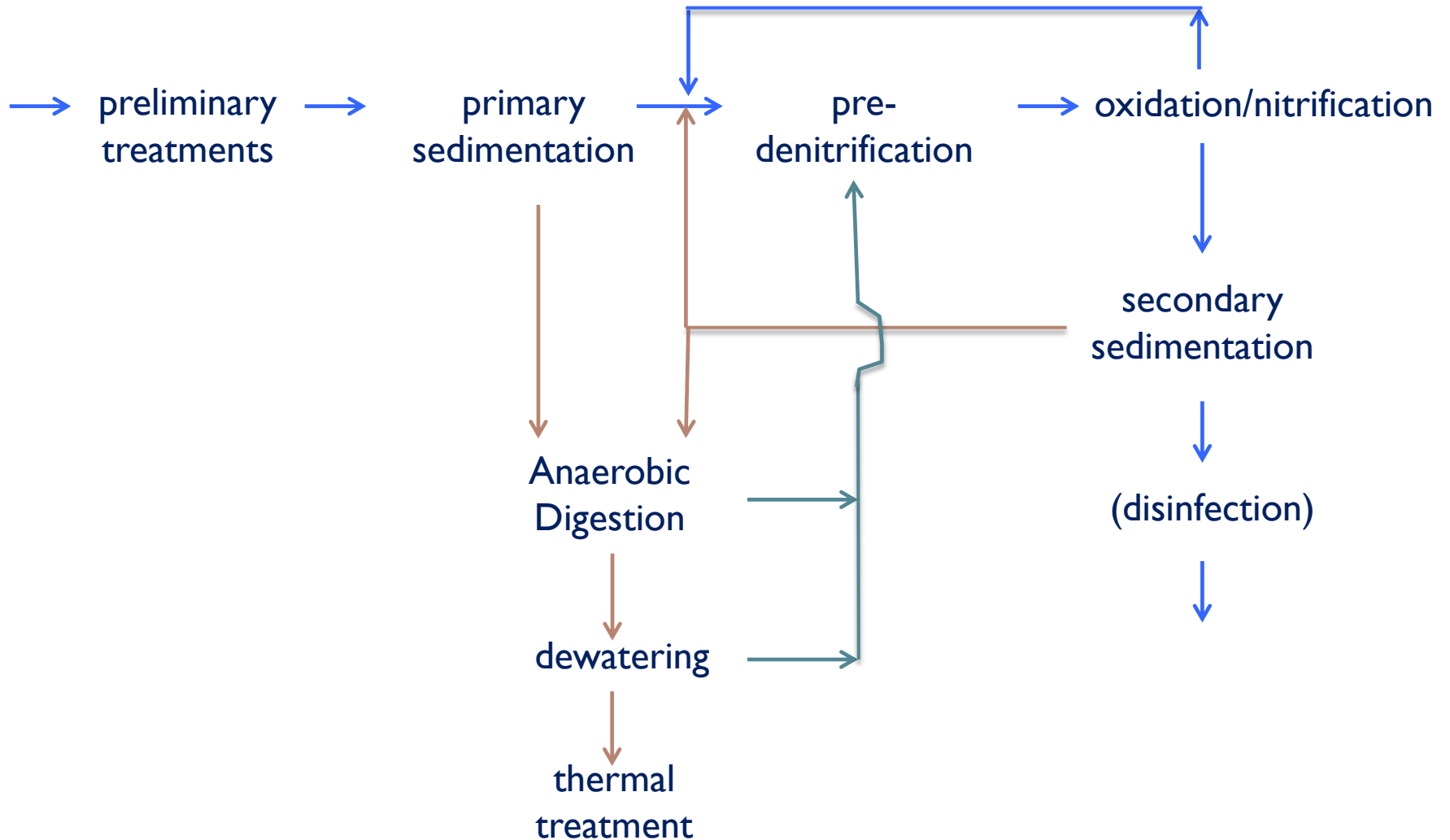
dissolved salts

Technical improvements:

- 1) **new coagulants:** new poly aluminium chloride (PAC) reagents, Fe +Al salts, pre-hydrolyzed reagents with cationic polymers, organic polymers;
 - 2) **coagulation/flocculation + other unit processes:**
 - ferric sulfate + ion exchange
 - nano activated carbon + alum
 - coagulation + membrane processes
-



WWT processes: framework



WT processes: critical issues

- ▶ **Improvement of Removal efficiency:**

- Nitrogen removal
- specific local requirements about N, P
- Emerging Contaminants

- ▶ **Enhancement of sludge valorization**

- ⇒ energy efficiency

- ⇒ environmental sustainability



WT processes critical issues: N removal

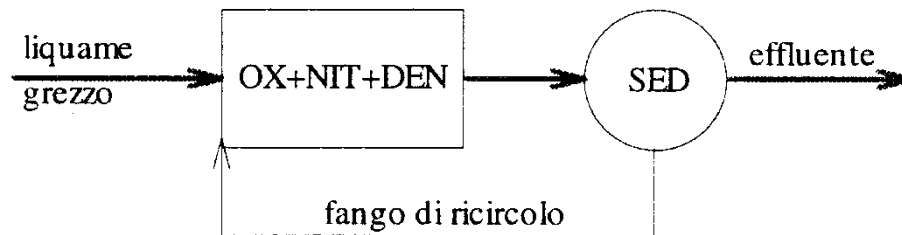
- ▶ Conventional processes: pre-denitrification/nitrification
Sequencing Batch Reactor (SBR)
- ▶ Critical issues: **sidestreams with low C/N (<1)**
(++ sludge water from Anaerobic Digestion)

- 15-20% of influent N load
- TKN = 600 – 1000 mg/L
- Alkalinity: ~50% of the necessary amount to obtain a complete nitrification

Parameter	Value / Range	References
pH	7.18 - 8.42	Marsalek et al. (2004)
BOD ₅ (mg/l)	230	Helliga et al, (1999)
	109 ± 44	Vandaele et al., (2000)
COD (mg/l)	1400 - 2000	Gali Serra A., (2006)
	650	Köz Utku, (2007)
BOD ₅ / COD	700 - 1000	Wett et al., (1998)
COD _{sol} / NH ₄ ⁺ -N	0.14 - 0.2	Vymazal (2010)
NH ₄ ⁺ -N (mg/l)	0.29 - 1.19	Marsalek et al. (2004)
	943 - 1513	Marsalek et al. (2004)
	1180 ± 140	Van Dongen et al., (2001)
	800 - 900	Dosta et al., (2007)
TKN (mg/l)	450 - 750	Vymazal (2010)
	1053	Helliga et al, (1999)
NO ₂ ⁻ -N, NO ₃ ⁻ -N (mg/l)	859	Vymazal (2010)
	0-3	Vymazal (2010)

N removal: innovative processes

Continuous flow nitrification/denitrification in an alternated single phase



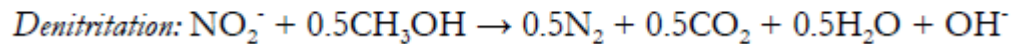
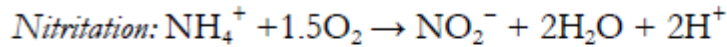
- CSTR with on/off temporized aeration
- on-line monitoring of process parameters (DO, ORP, pH, NH_4^+ , NO_3^-)
- tailored length of biological process phases \Rightarrow removal efficiency improvement
- no mixed liquor recirculation + aeration optimization \Rightarrow energy efficiency improvement
- several full scale applications in Italy



N removal: innovative processes

Autotrophic processes:

Nitrification/Denitrification

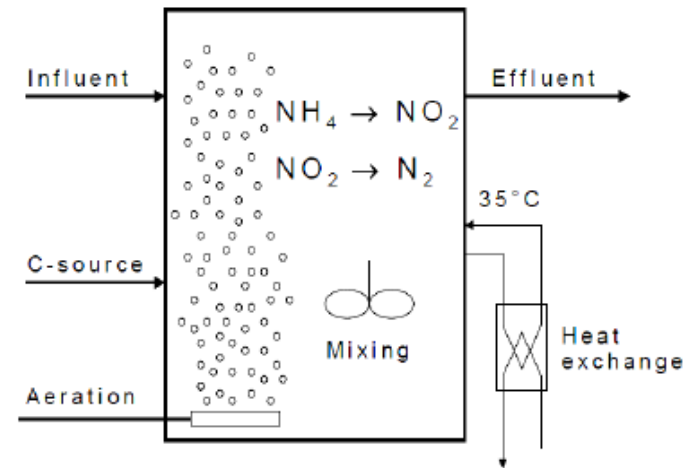
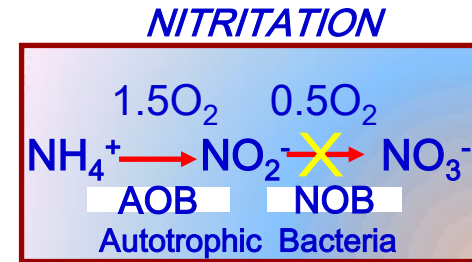


AOB (ammonia oxidant bacteria) growth is promoted against NOB (nitrate oxidant bacteria):

- $T > 25^\circ\text{C}$
- $\text{DO} < 2 \text{ mg/L}$
- NH_4^+ ($\text{pH} > 7.5\text{-}8$)
- low HRT

SHARON[®] (Single Reactor High Activity Ammonia Removal over Nitrite) (1990, Delft University)

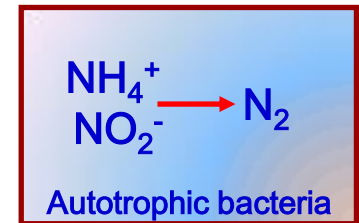
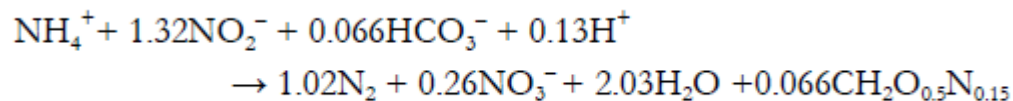
- 25% Oxygen demand
- 40% C demand
- sludge generation lower than active sludge processes
- several full scale applications worldwide



WT processes critical issues: N removal

Autotrophic processes:

ANAMMOX[®] (Anaerobic Ammonium Oxidation) (1999, Delft)



NH_4^+ is directly oxidized to N_2 using NO_2^- as the e- acceptor under anoxic conditions

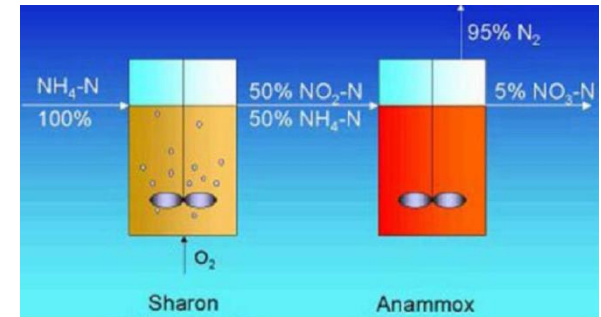
- no need of Oxygen
 - no need of Carbon (CO_2 is employed to produce biomass)
 - depletion of 60/90% energy demand
 - reduction of CO_2 emissions (up to 90%)
 - sludge generation lower than active sludge processes
-



N removal, autotrophic processes:

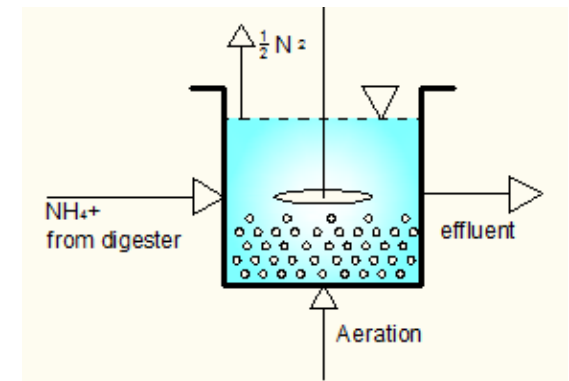
- several full scale applications worldwide:

SHARON + ANAMMOX in 2 separate reactors



CANON® (Completely Autotrophic N Removal over Nitrite) or SNAP® (Single stage Nitrogen removal using Anammox and Partial Nitritation)
(SHARON + ANAMMOX in a single reactor)

DEANNAMMOX® or DEMON® (denitrification + ANAMMOX)



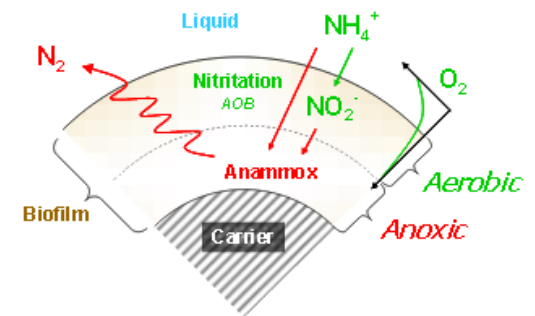
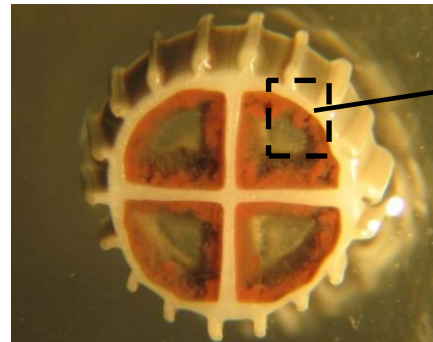
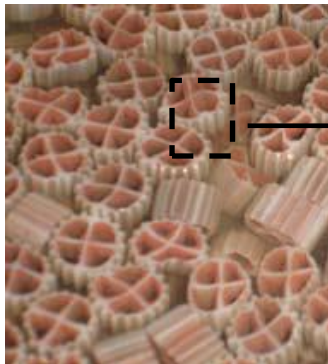
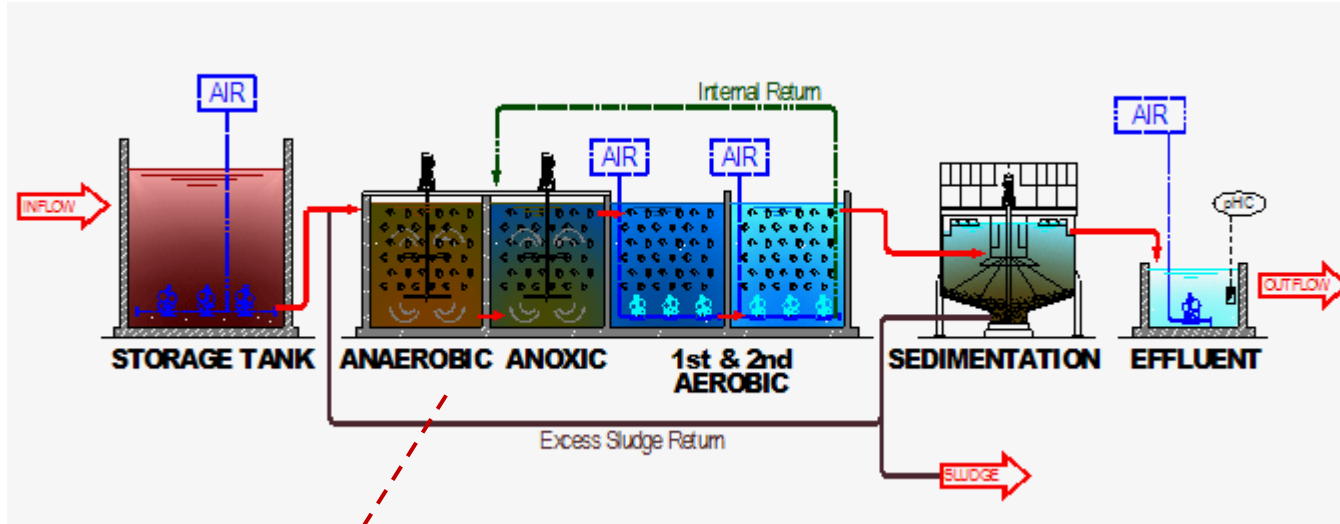
Industrial/full scale applications:

Processo	Configurazione impiantistica	Alimentazione	T (°C)	DO (mg/l)	ANR* (kgN/m ³ d)	Fattori di controllo	Rif.
CANON - Completely Autotrophic nitrogen removal over nitrite	SBR		30	<0,1	0,06	DO, ammonia, AOB population	Sliekers et al. (2002)
	Air pulsing SBR	Sludge liquor	21	0,5	0,36		Padin et al. (2009)
	Airlift	Syntetic	-	0,5	1,5		Sliekers et al. (2003)
	UASB	Sludge liquor	30	External aeration 0,6	0,06		Ahn & Choi (2006)
	MBBR	Sludge liquor	30	1,8	0,36		Cema et al. (2006)
	MABR	Syntetic	35	0,5	0,77		Gong et al. (2007)
DEMON - DEamMONification	SBR	Sludge liquor	28	0,3	0,70	Time, pH, DO	Wett (2007)
OLAND - Oxygen – limited autotrophic nitrification and denitrification	RBC	Sludge liquor	14	1,0	0,42	-	Pynaert et al. (2004)
	SBR	Syntetic	33	low	0,05	Time, pH,	Kuai et al. (1998)
	SBR, high rate		-	-	1,058	Time, pH	Pynaert et al. (2003)
Aerobic Deammonification	RBC	Leachate	-	-	0,6	-	Hippen et al (1997)
SNAP Single Stage Nitrogen Removal	+ biomass carrier	Leachate	35	0,5 – 2,5	0,31-0,45	HRT, aeration rate, T, pH	Lieu et al. (2005)

* ANR = Nitrogen Removal rate by Anammox bacteria



i.e. Phosphorous removal and Demon Moving Bed Biofilm Reactor (Demon MBBR)



WT processes critical issues: Emerging Contaminants (EC)

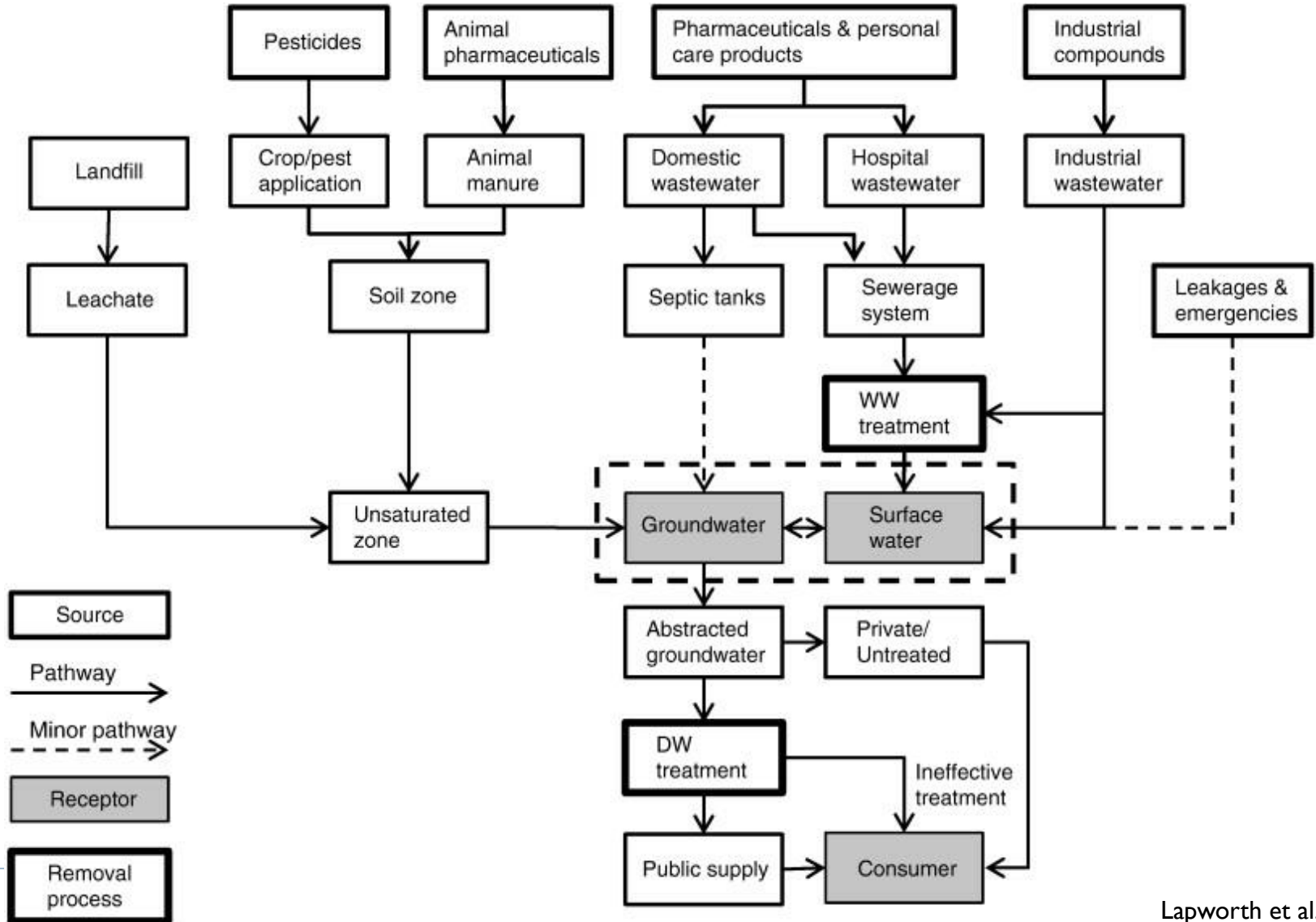
- ▶ Xenobiotic compounds
- ▶ Endocrine disruptor compounds
- ▶ Organic micropollutants
- ▶ Pharmaceuticals and Personal Care Products (PPCPs)
- ▶

↓
antiseptics/disinfectants, fragrances, pesticides, insects repellents,
sun protection lotions, alkylphenols
External use, NO METABOLIC PROCESSES involved

↓
Persistant Organic Pollutants



Emerging Contaminants (EC): origin and diffusion



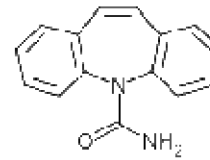
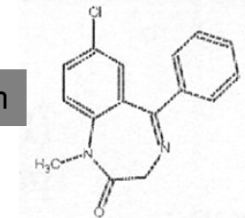
Pharmaceuticals

- Antiflogistici (**ibuprofene**)
- Regolatori di lipidi (acido clofibrico)
- Antiepilettici (**carbamazepina**)
- Psicoattivi, tranquillanti (**diazepam**)
- Betabloccanti (sotalol)
- Antistaminici
- Citostatici
- Mezzi di contrasto (**iopromide**)
- Antibiotici (**eritromicina**)
- Ormoni (17α -etinilestradiolo)

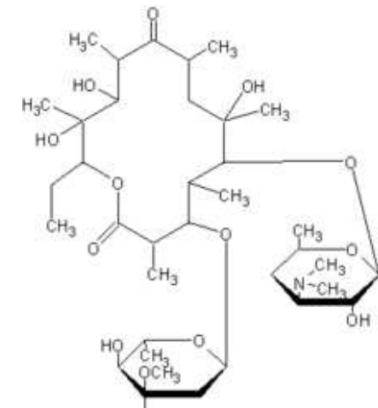
ibuprofene



diazepam

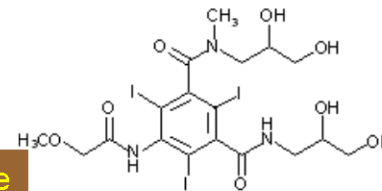


carbamazepina



eritromicina

iopromide



Pharmaceuticals: diffusion

Table 1
Occurrence level of several EDCs detected in municipal wastewaters, surface waters and drinking waters

Type of water	Location	Compounds detected	Conc., (ng/L)
Municipal wastewaters	UK [7]	Nonylphenol	1.2–2.7
		Estrone (E1)	15–220
		Estradiol (E2)	7–88
	Germany [8]	Nonylphenol	199
		Estrone (E1)	3.4
		Estradiol (E2)	0.9
		Ethinylestradiol (EE2)	1.4
	Japan [9]	Nonylphenol	80–1240
		Estradiol (E2)	2.7–48
Surface waters	Germany [8]	Nonylphenol	34
		Estrone (E1)	0.7
		Estradiol (E2)	0.6
	Japan [10]	Nonylphenol	250
		Estradiol (E2)	2.1
Drinking water	Germany [8]	Nonylphenol	8
		Estrone (E1)	0.4
		Estradiol (E2)	0.3

Conventional treatments:

Adsorption on activated carbon

Coagulation/flocculation

Chemical oxidation

Biological processes

low-medium biodegradability

Removal efficiency

40-90%

<20%

60-90%

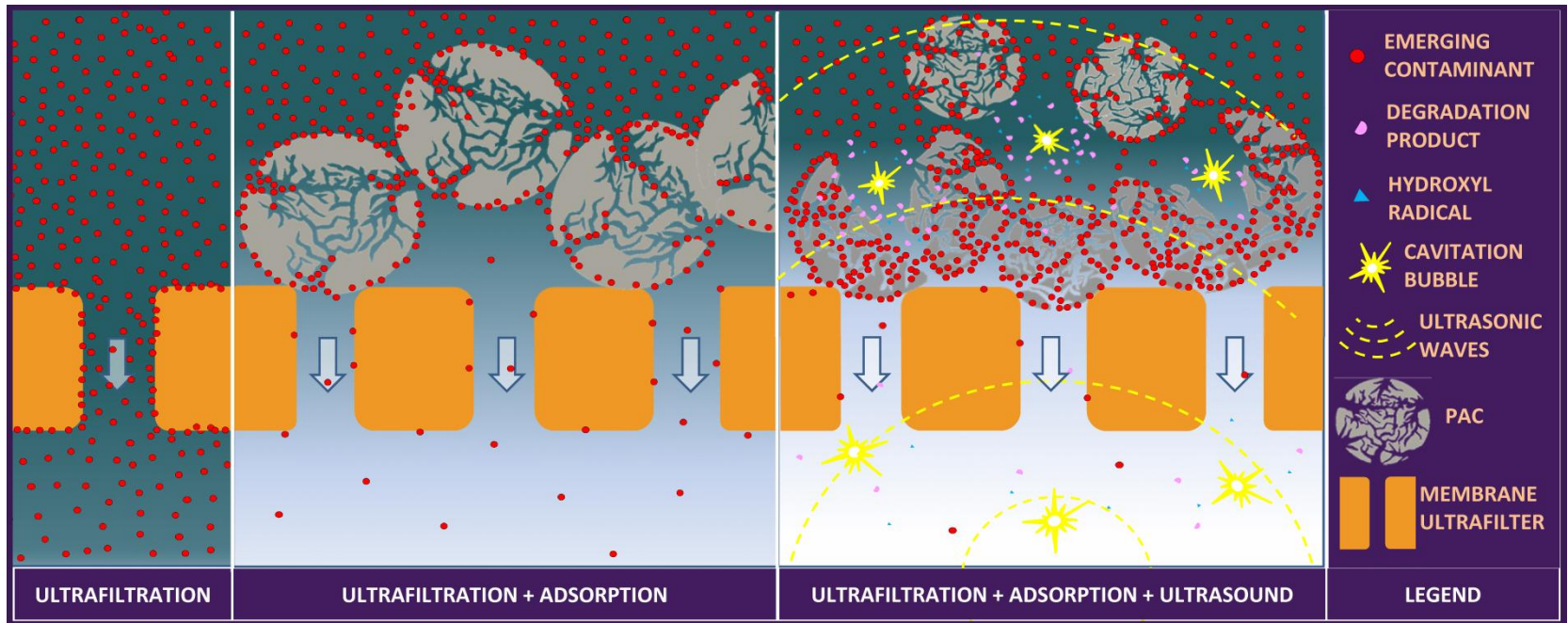
40-80%



Pharmaceuticals: novel treatments

many patented Advanced Oxidation Processes (AOPs) tested on laboratory/pilot scale:

i.e. **USAMe[®]** (SEED, UniSA)



WT processes critical issues: **sludge treatment**

Pre-treatments aimed to increase biogas production in AD:

- **mechanical**: ultrasonic, lysis centrifuge, liquid shear, grinding
- **chemical**: oxidation (O_3 , H_2O_2 , Fenton) – alkali treatments ($NaOH > KOH > Mg(OH)_2$ and $Ca(OH)_2$)
- **thermal** : low ($< 100^\circ C$) and high ($> 100^\circ C$) temperatures

Pretreatment method	Treatment conditions	Feed concentration	VS destruction	Electrical consumed (kWh kg ⁻¹ VS fed)	Thermal consumed (kWh kg ⁻¹ VS fed)	Max biogas (kWh kg ⁻¹ TS fed)
None-mesophilic		6%	40%	0.04	0.5	1.9
None-thermophilic		6%	50%	0.03	1.0	2.4
Biological (thermal)	70°C 9–48 h	6%	50%	0.03	1.0	2.4
Thermal hydrolysis	170°C 15–30 min	9%	60%	0.04	2.0	2.9
Sonication	100 W, 16 s, 30 kW m ⁻³	6%	50%	0.37	0.5	2.4
Ball milling		6%	50%	1.04	0.5	2.4
High pressure	200 bar	6%	50%	0.33	1.0	2.6

WT processes critical issues: **sludge disposal**

Conventional management strategies:

- **landfilling**: traditional strategy
not allowed by current Regulations;
- **agricultural use**: material recovery
limits defined by Regulations
persistent organic pollutants
- **thermal treatments**



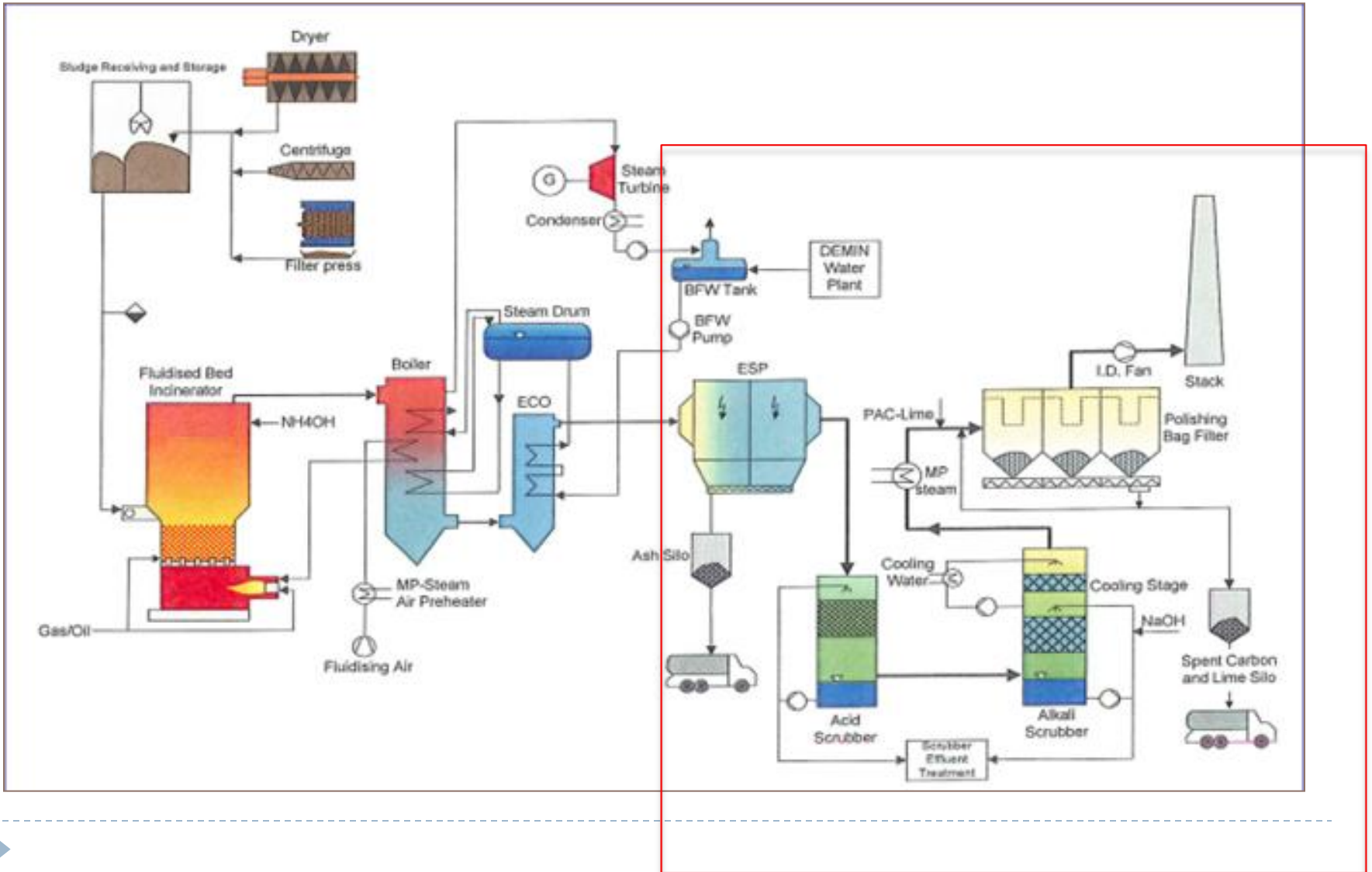
WT processes critical issues: sludges

Thermal treatment:

- Co-incineration with MSW
- Co-incineration in high energy demand plants
- incineration: large WWT plants
 - costs evaluation
 - environmental impact

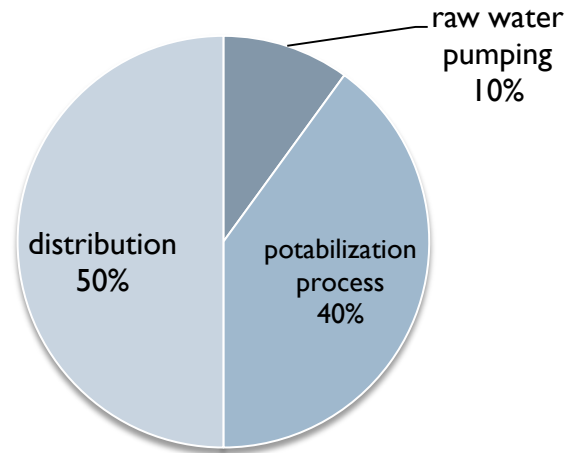


Sludge Incineration: fluid bed reactor, atmospheric pressure

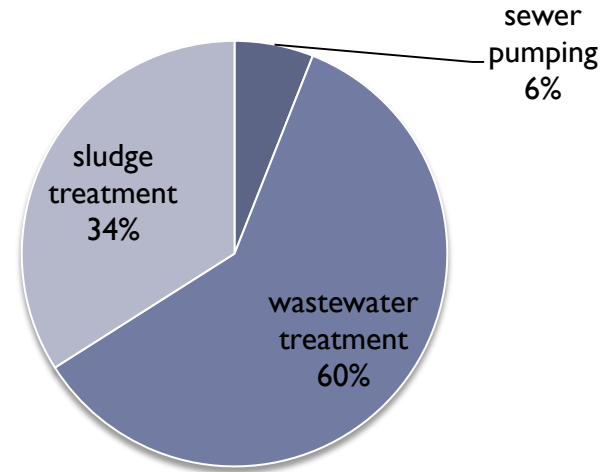


WT and WWT processes: energy demand

Water Treatment



Wastewater treatment



WT and WWT processes: energy efficiency

	max Energy savings:
General intervents: maintenance optimization	5-10%
optimization of buildings cooling/heating/lighting	10%
WT plants: inverters on pumps	15-33%
optimization of coagulant dose	5-35%
WWTPs: inverters on pumps	<30%
enhanced SS, COD, BOD removal in primary settling (+ coagulants)	25%
high efficiency aeration devices	25%
optimization of oxygen demand	15%
control of process parameters (D.O., NH4+, NO3-)	20-30%
optimization of mixed liquor recirculating flow rate	16%