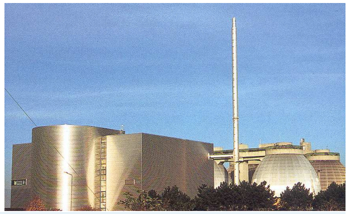
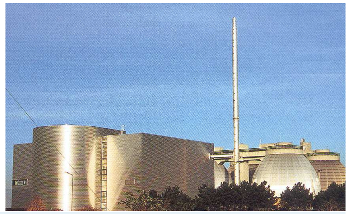


4th NORMAN Workshop
"Integrated chemical and bio-monitoring strategies for risk assessment of emerging substances"
17-18 March 2008, Lyon, France

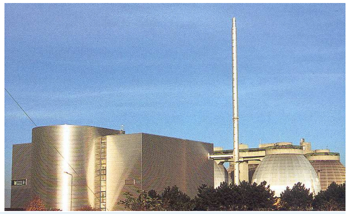
Combined chemical analyses and biomonitoring at Avedoere WWTP

by Bo N. Jacobsen,
Head, Planning and Development
Avedoere Wastewater Services

The general situation in Denmark for wastewater management

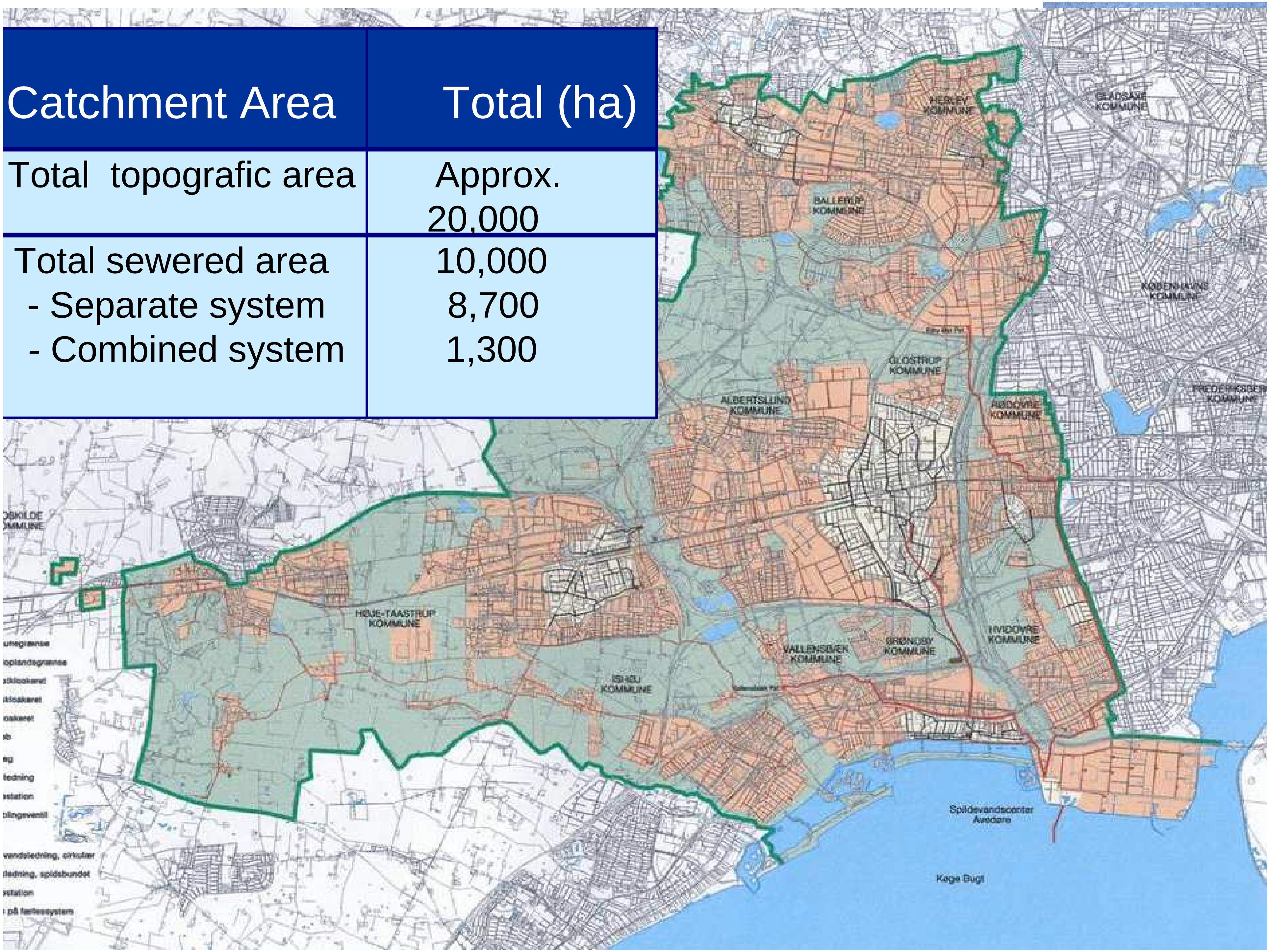


- All plants owned by the public sector
- A few operated by private contractors
- Financing by traditional utility model (i.e. consumer pays)
- Non profit organisation
- Average fees - wastewater: 15 DKK/m3 – about 2 €/m3

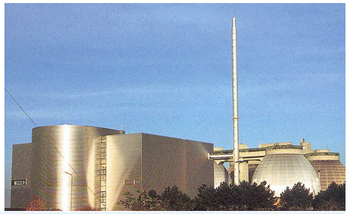


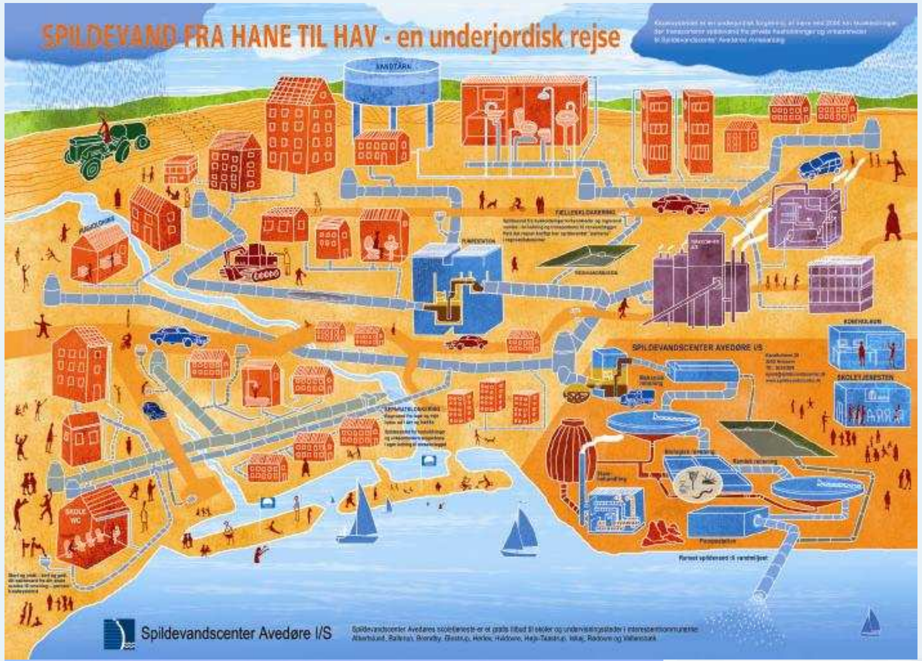
Avedøre Wastewater Services

Catchment Area	Total (ha)
Total topografic area	Approx. 20,000
Total sewered area - Separate system - Combined system	10,000 8,700 1,300



Avedoere Wastewater Services
Information Centre (Visitors 2006: 5.800)

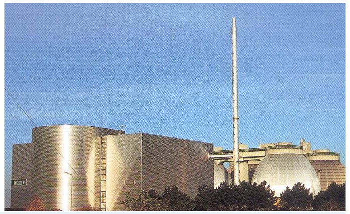


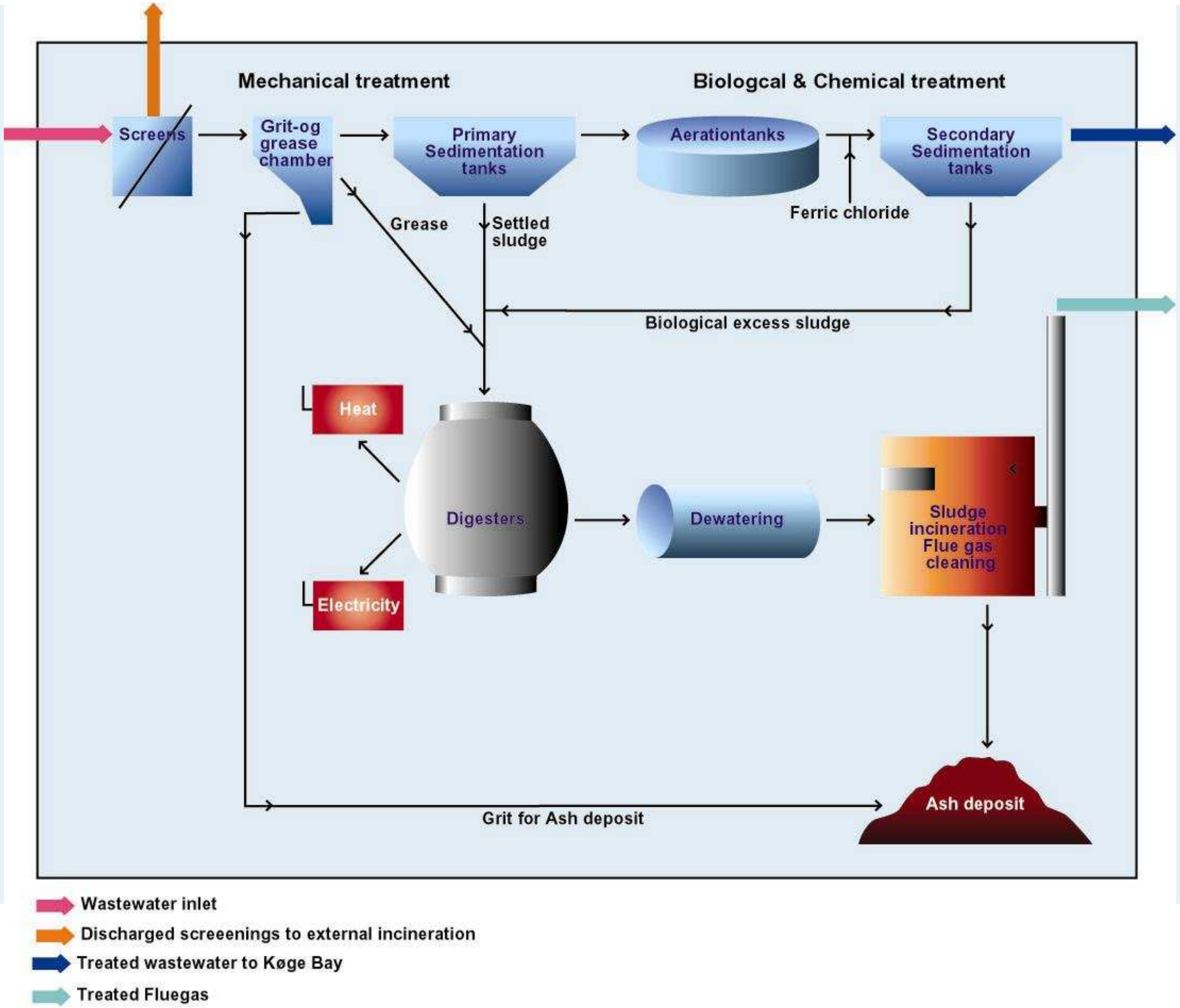


Public Awareness
- Citizens from the 10 municipalities
- School services/ education
- Exhibition
- Networking

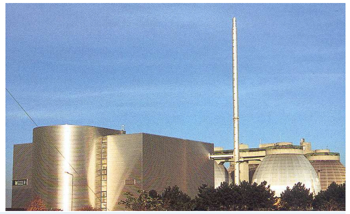
Public Information
- Green account
- Annual report
- website

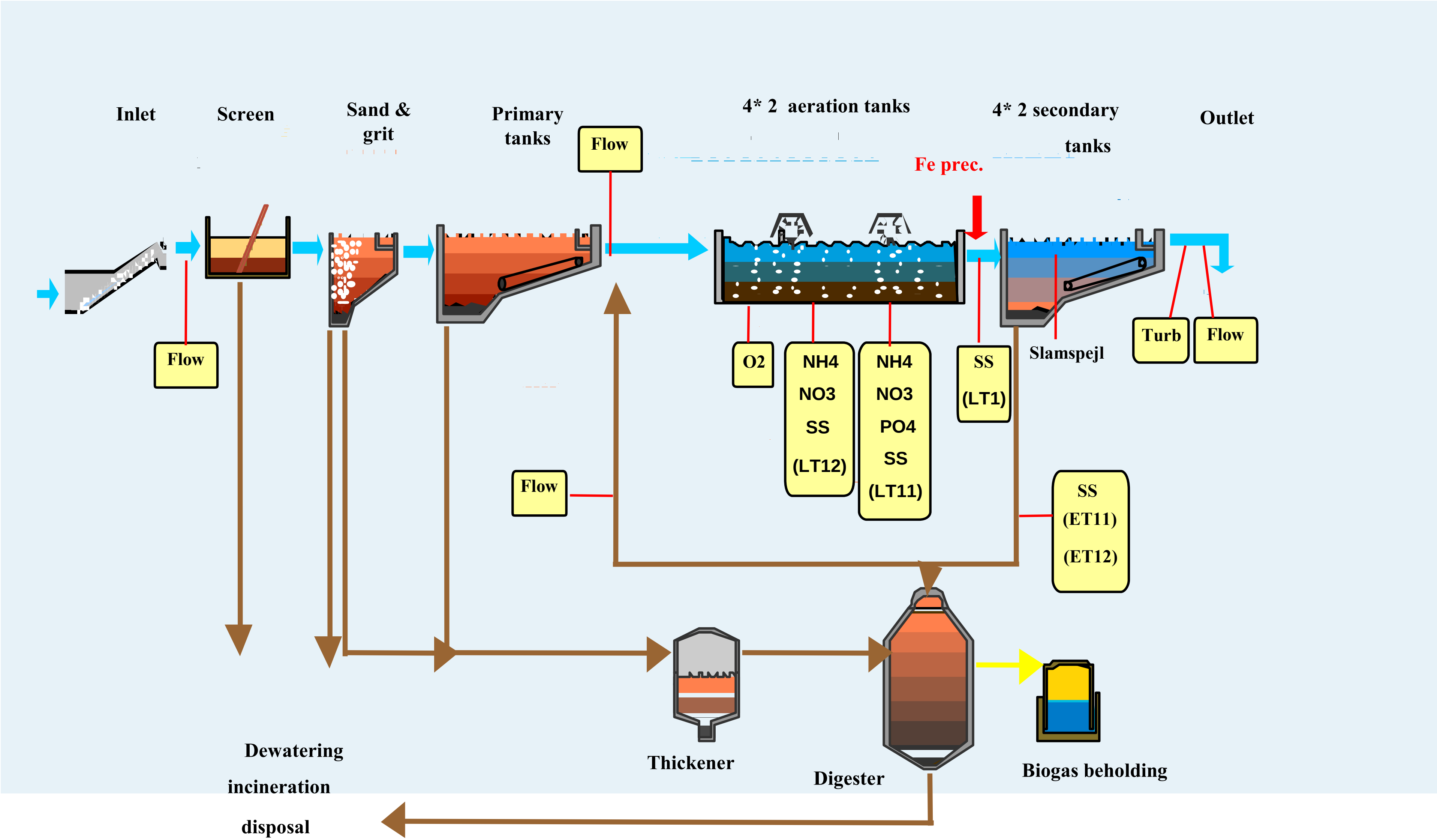
Flow

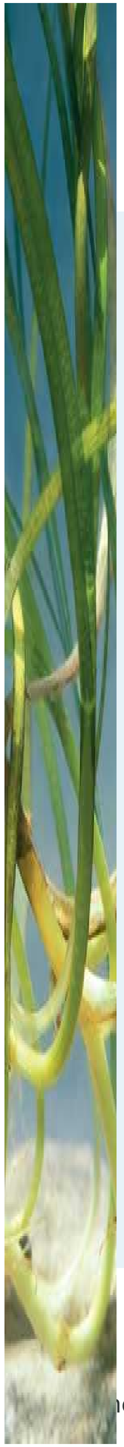



Mechanical treatment
Biologcal & Chemical treatment
Screens
Grit-og grease chamber
Primary Sedimentation tanks
Aerationtanks
Secondary Sedimentation tanks
Grease
Settled sludge
Ferric chloride
Biological excess sludge
Heat
Digesters
Electricity
Dewatering
Sludge incineration Flue gas cleaning
Ash deposit
Grit for Ash deposit
Wastewater inlet
Discharged screeenings to external incineration
Treated wastewater to Køge Bay
Treated Fluegas

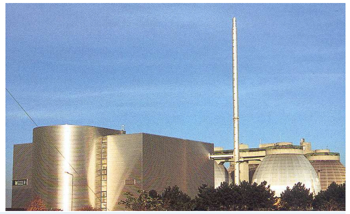
Position of on-line sensors, Avedøre







Effluent standards 2007

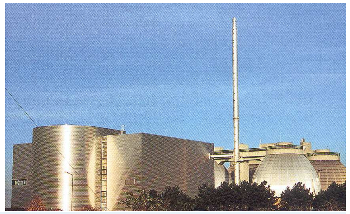


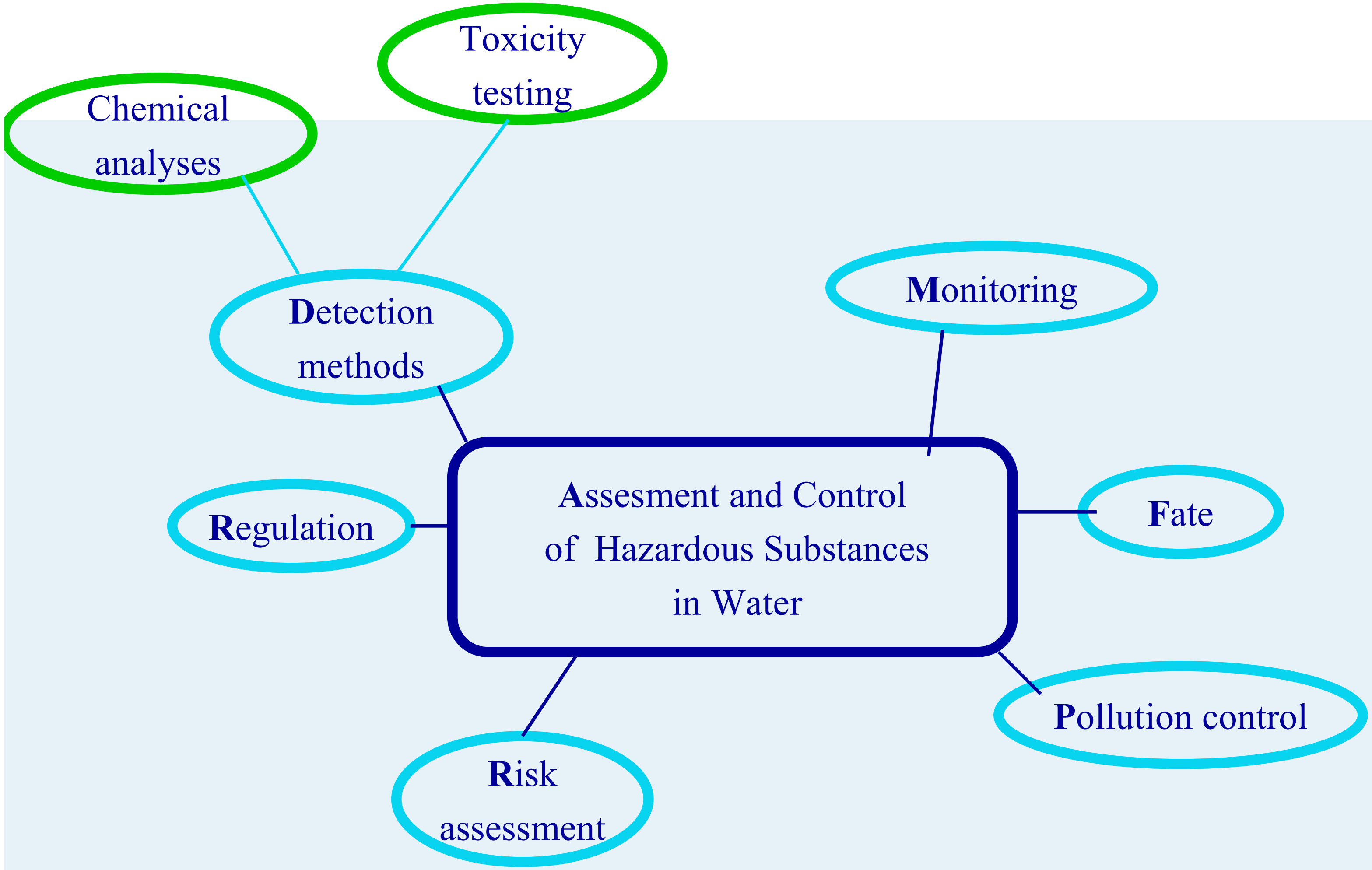
Effluent standards

Parameter	Criteria[1)] (mg/l)	Compliance assessment[1)] (mg/l)	Flow-weighted average 2007 (mg/l)
Organic matter (COD)	< 75	30	31
Organic matter (BOD_5)	< 15	3,1	3,8
Total nitrogen (N)	< 8	4,6	5,9
Total phosphorous (P)	< 1,5	0,65	0,7
Suspended solid (SS)	< 20	12	15

Environmental authority: Region Roskilde

[1)] Yearly average evaluated on a statistical basis




Chemical analyses
Toxicity testing
Detection methods
Monitoring
Regulation
Assesment and Control of Hazardous Substances in Water
Fate
Pollution control
Risk assessment

Specific organic compounds (example, Paris)

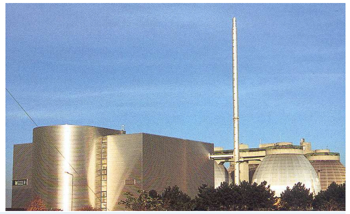
Table 1 Selected compounds identified in plant 1 (µg/L)

Compound	Raw water	Raw water+ recycled waters	Treated water	Seine river upstram of WWTP	Seine river after WWTP
2-Butoxyethanol (butylglycol)	110.2	140.6	< 0.1	< 0.1	< 0.1
Butoxyethanol phosphate	15.7	7.8	0.7	1.3	0.3
2-Méthoxyethyl éther	1.5	< 0.1	0.5	< 0.1	< 0.1
Dipropylene glycol méthyl éther	10.1	24.8	0.6	< 0.1	< 0.1
2-Butoxyethoxyéthanol	317.0	1270.0	< 0.1	< 0.1	< 0.1
1,1-Methyl-2-(2-propenyloxy)ethoxy-2-propanol	3.9	< 0.1	< 0.1	< 0.1	< 0.1
Nonylphénols	< 0.1	5.9	< 0.1	< 0.1	< 0.1
Diethyl phtalate	12.5	26.9	< 0.1	< 0.1	< 0.1
Butyl isobutyl phtalate	0.8	82.1	11.1	3.2	4.4
Benzylbutyl phtalate	< 0.1	21.3	< 0.1	< 0.1	< 0.1
Diisooctyl phtalate	46.4	102.2	16.3	9.1	14.3
Nicotine	Traces~ 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Caffeine	34.1	70.1	0.3	0.1	0.1
Camphor	3.5	4.7	< 0.1	0.1	< 0.1
β-Sitosterol	13.6	19.3	<0.1	<0.1	1.2
Stigmastanol	1.8	3.3	<0.1	<0.1	<0.1
17-β-estradiol *	0.010	NA	0.003	NA	NA
Estriol*	0.015	NA	0.004	NA	NA
Estrone*	0.020	NA	0.008	NA	NA
Ethinyl-estradiol*	0.0025	NA	0.00014	NA	NA
Sunscreen UV 15	1.6	0.9	<0.1	<0.1	<0.1

*specific quantitative method

Bruchet et al., 2001

Effluent Concentrations Avedoere WWTP in relation to Water Quality Standards, WQS (DK Statutory Order 921)

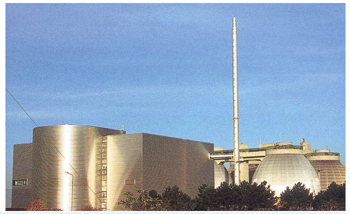


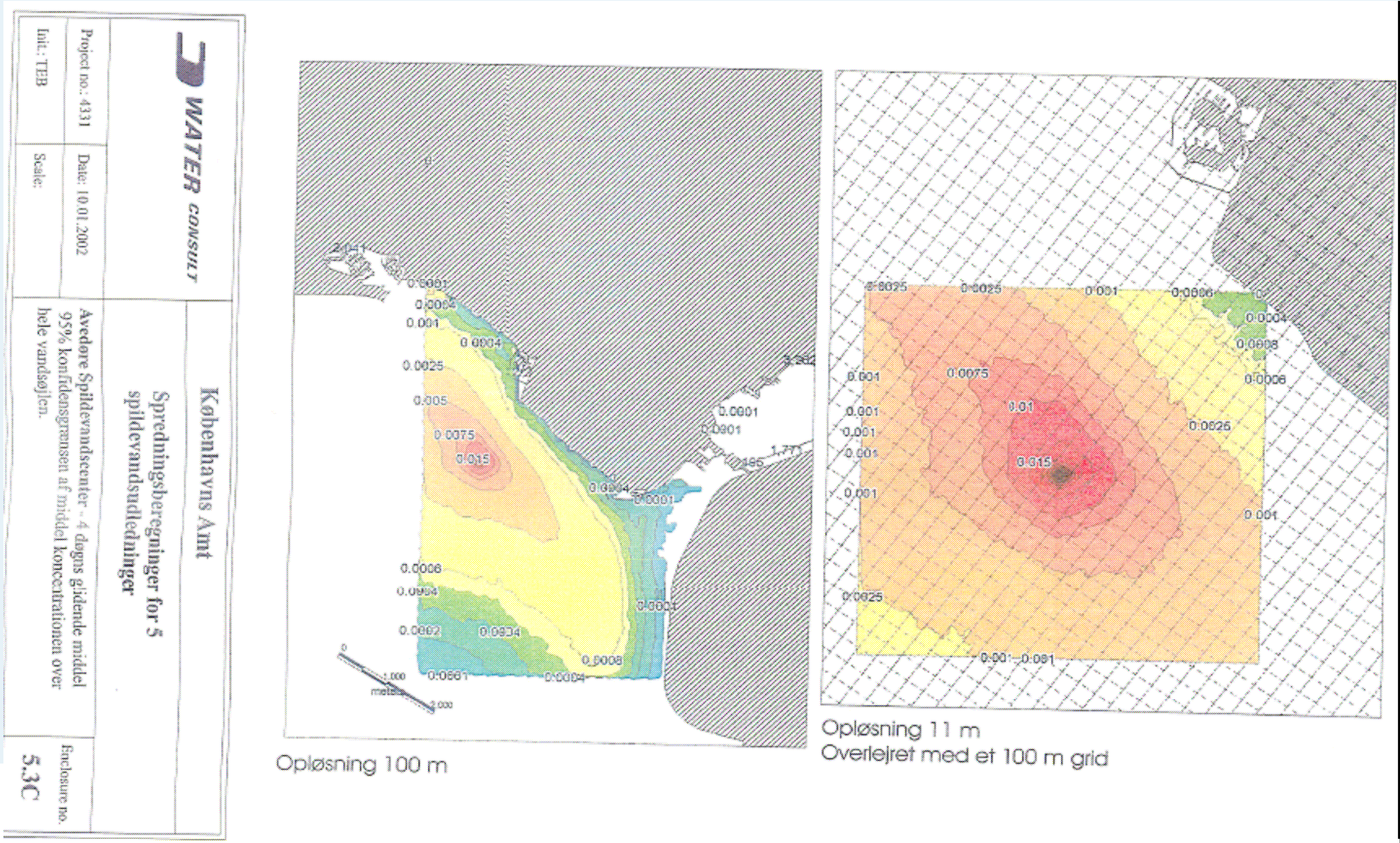
Stofnavn	VKK, g/l	Indløb/VKK >1	Indløb/VKK >5	Indløb/VKK >20	Udløb/VKK [1] >1	Udløb/VKK [1] >5	Udløb/VKK [1] >20	Rensnings-grad [2], %
Nonylphenoler (NP+NPE)	0,03			x		x		90
PAH'er								
Phenanthren	0,001			x			x	85
Benz(a)anthracen	0,001			x				>95
Fluoranthen	0,001			x				>90
Benzo(e)pyren	0,0005			x				>45
Benzfluranthen b+j+k	0,001			x				>97
2-methylphenanthren	0,00003			x				85
Fluoren	0,001			x				>80
Anthracen	0,01		x					>65
Pyren	0,001			x				>90
Benz(a)pyren	0,001			x				>35
Arsen	4	x						45
Bly	5,6	x						80
Chrom	1,0			x		x		65
Kobber	2,9			x	x			90
Kviksølv	0,3	x						>85
Nikkel	8,8	x			x			30
Benzylbutylphthalat	0,8		x					>98
Dibutylphthalat	1,0	x						>55
Triphenylphosphat	0,001			x			x	95
Stoffer kun målt i udløb								
Cyanid, total	5				x			
Barium	15						x	

[1]) Udløb/VVK < 1, hvis der ikke er anført et "x"

[2]) Beregnet som: 100%*(gns.indløb-gns.udløb)/gns.indløb, og afrundet til nærmeste 5%

Spredningsberegninger – Kbh. amt

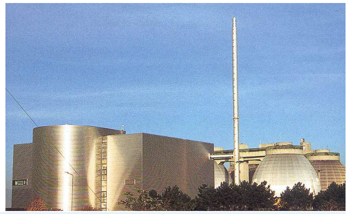




Opløsning 100 m

Opløsning 11 m
Overlejret med et 100 m grid

Toxicity testing / "explainability" - example



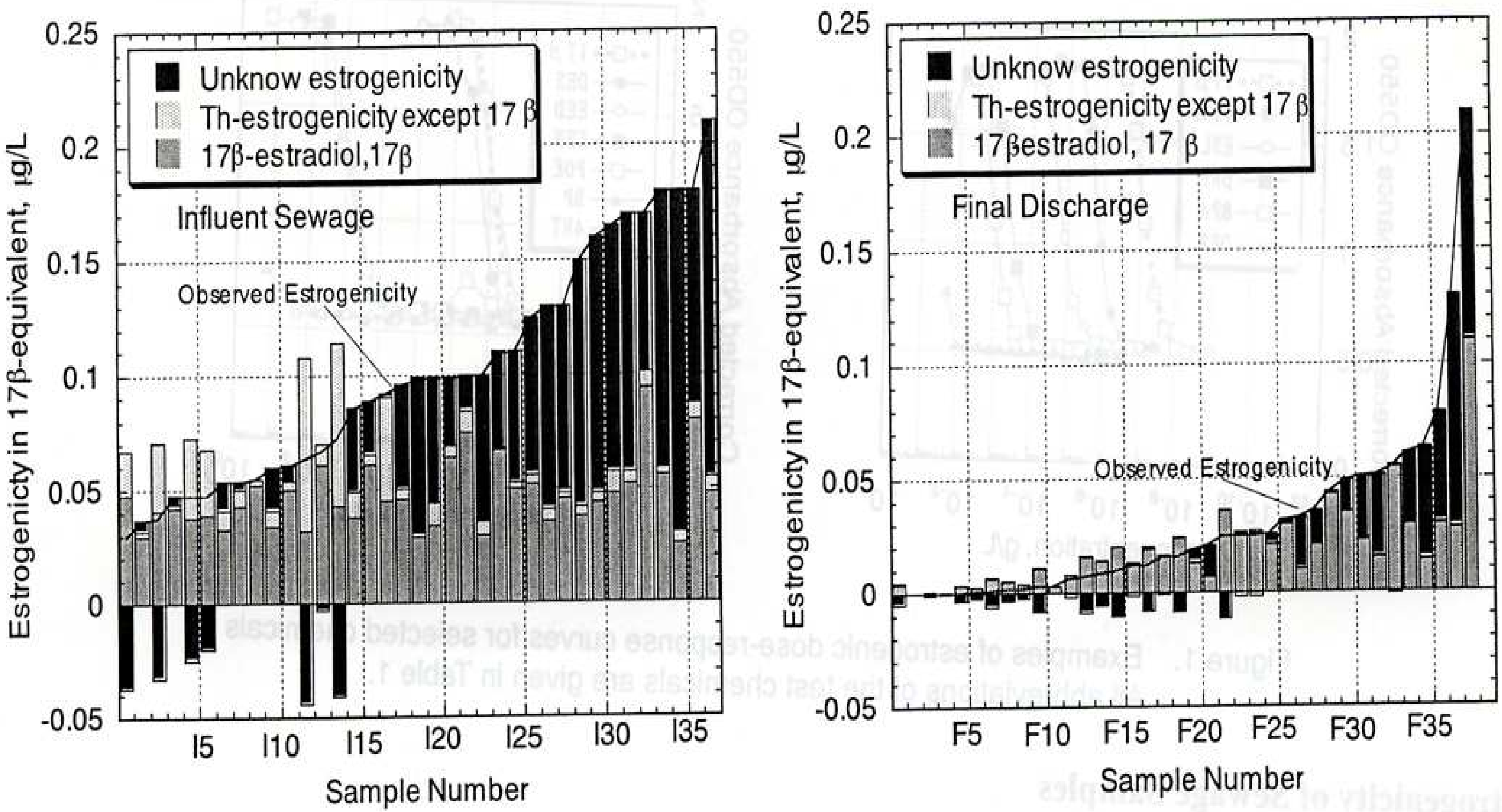
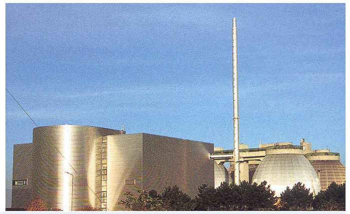


Figure 4. Estrogenicity, 17β–estradiol and theoretical estrogenicity observed in influent sewage and final discharge in all the sewage treatment plants in this study

(Tanaka et al, 2000)

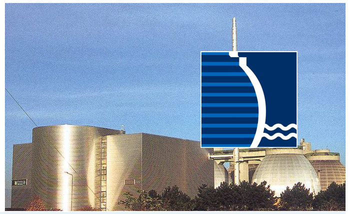
Selected results from 4 influent and effluent 1-week flow proportional samples

Data provided by County of Copenhagen; WQS and EC50 compiled by DHI (2003)



Parameter	Average concentrations influent	Average concentrations effluent	Load reduction	WQC	EC50
Heavy metals	µg/l		%	µg/l	
Lead, Pb	13	2.8	80	0.65	2655
Chromium, Cr	24	9.4	62	1	153
Copper, Cu	85	8.0	91	2.9	31
Nikkel, Ni	19	13.5	32	8.3	180
Zink, Zn	220	70	68	86	196
Phenols					
nonylphenol	4.0	0.32	92	0.03	410
bisphenol A	1.7	0.28	85	1	2600
Halogenated aliphatic hydrocarbons					
Dichlormetane	27	-	-	10	660000
Vinylchlorid	0.66	-	-	0.2	942
Polyaromatic hydrocarbons					
Pyrene	0.10	0.01	93	0.001	256
Phosphorous-tri-esters					
Triphenylphosphate	1.4	0.09	93	0.001	230
Plastic softeners					
DEHP	34	1.28	96	0.1	960
Diethylphthalate	10	-	-	3	69500
Anionic detergents					
LAS (C10-C14)	1700	10	99	10	53700
Other List I dangerous substances					
Barium, Ba		319		10	
Cobolt, Co		15		1	180
Selenium, Se		1.8		0.5	99000

Algae toxicity



Toxic Units for EC10,$_{72h}$

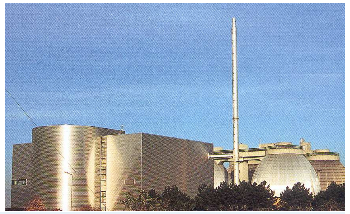
(DHI, 2006;)

Year	n	Influent *	Effluent
1999	4	21	< 3,3
2002	4	28	< 2
2005	4 / 2 **	21	< 2

Arithmetic average of flowproportionale week composite samples

Algae: *Pseudokirchneriella subcapitata* ; ISO Standard 8692

* *incl. Reject water* ** *4 influent- og 2 effluent samples*

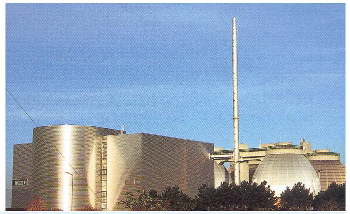


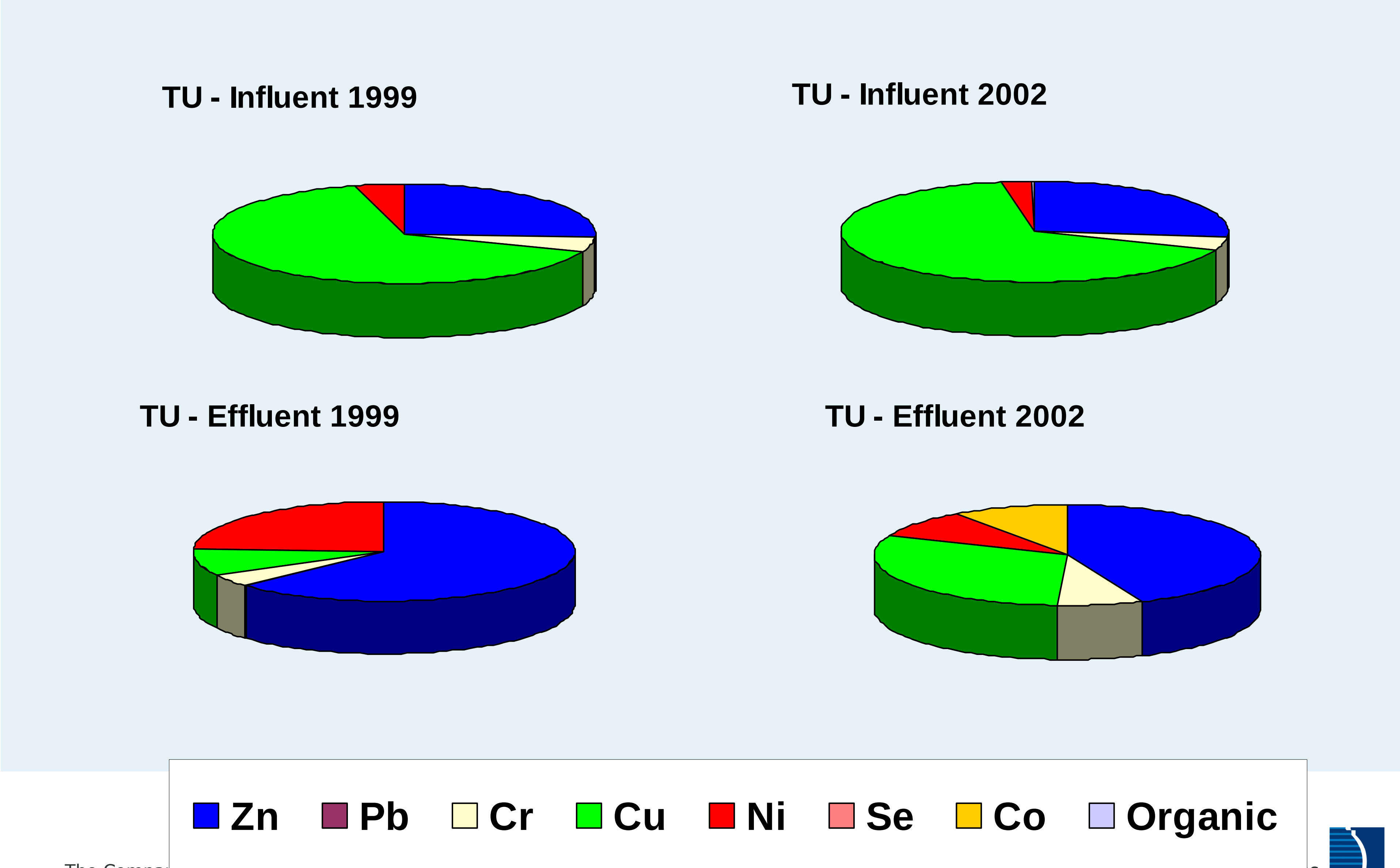
Measured and calculated toxic units (TU) for Avedoere WWTP influent and effluent samples 1996, 1999, og 2002 (DHI, 2003):

$\sum TU_i$ values are based on EC50-values for freshwater algae.

Sample	Sample No.	**1996**		**1999**		**2002**	
		Measured TU_b	Calculated $\sum TU_i$	Measured TU_b	Calculated $\sum TU_1$	Measured TU_b	Calculated $\sum TU_1$
Influent	1	<4	6	<5	4,3	5,8	5,2
	2	<4	5	<5	4,4	<5	3,8
	3	<4	7	3,7	5,2	2,7	3,4
	4			5,3	5,5	11	5,3
Effluent	1			<3,3	0,5	<2	1,0
	2			<3,3	0,5	<2	0,6
	3			<3,3	0,6	<2	0,8
	4			<3,3	0,3	<2	1,0

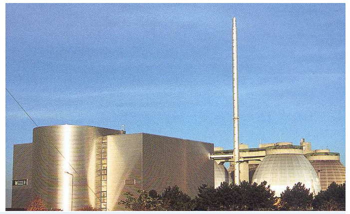
Contributions to calculated Toxic Units for algae EC50 Avedoere WWTP





Comparisons of EC50 and LC50 for different test methods

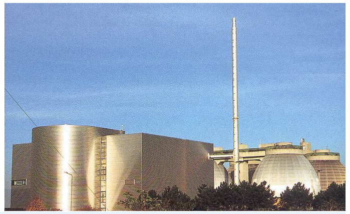
Toxkit data provided by Persoone (2003)

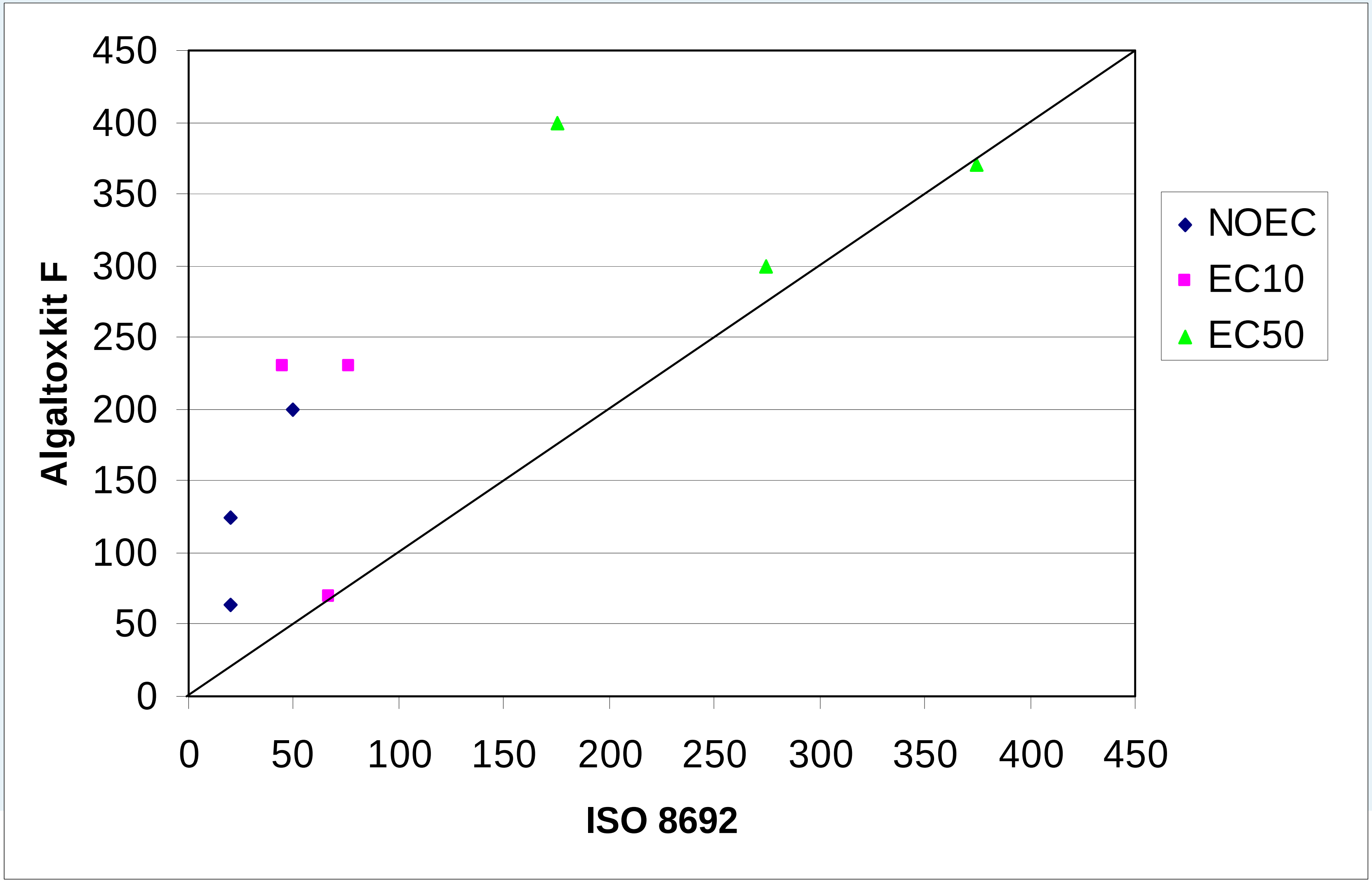


Toxic unit [-] = 1000 / L(E)C50 [ml/l]

AVEDORE WASTEWATER SERVICES	Thamno Toxkit F	Daphtoxkit F		Algaltoxkit F	ISO 8692
Year 2002	24h LC50	24h LC50	48h LC50	72h EC50	
Influent week 15	2.5	1.2	1.3	2.5	5.7
Influent week 22	2.8	1.2	1.3	3.3	3.6
Influent week 24	1.8	1.0	1.3	2.7	2.7
Influent week 36					11.1
Effluent week 15	< 1	< 1	< 1	not toxic	< 2
Effluent week 22	< 1	< 1	< 1		< 2
Effluent week 24	< 1	< 1	< 1	< 1	< 2
Effluent week 36					< 2

Comparison of mini test and ISO 8692



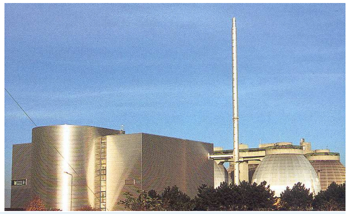


Endocrine disruptors

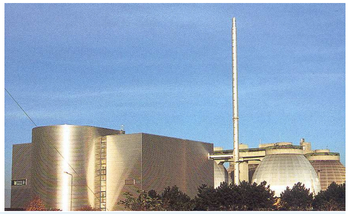
Endocrine disruptors

Fish species	Relative ww-proportion	Relative increase compared to blank
Juvenile Rainbow Trout	56%	2%
	78%	8%
	pos. Control	350%
Male Flounder	65%	84%
	82%	78%
	pos. Control	800%
Juvenile Silvereel	56 - 82 %	no increase
	pos. Control	350%

Specific hormones and EDCs, Avedoere WWTP 2002

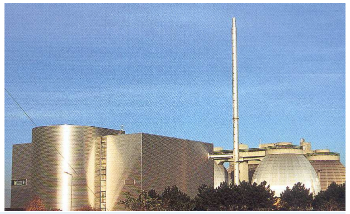


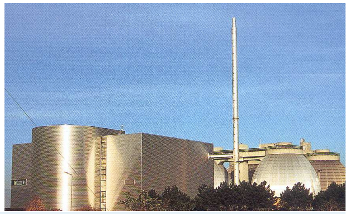
Parameter	Unit	Influent		Effluent	
		average	range	**average**	range
Specific hormones					
Estrone (E1)	ng/l	**45**	19 - 75	**7**	5 - 11
17b-estradiol (E2)	ng/l	**13**	6.1 - 27	**1.5**	< 0.1 - 4.5
17a-ethinylestradiol (EE2)	ng/l	**1.0**	< 1 - 1.7	**2.2**	< 1 - 5.2
Other endocrine disruption compounds (EDCs)					
Nonylphenol	µg/l	**3.9**	3.5 - 4.1	**0.2**	< 0.2 - 0.3
NPE, 1-2 EO	µg/l	**4.0**	2.3 - 4.9	**0.1**	< 0.1 - 0.2
Octylphenol	µg/l	**< 0.1**		**< 0.1**	
Bisphenol A	µg/l	**2.2**	1.0 - 2.7	**0.6**	0.1 - 1.4
Diethylphthalat	µg/l	**10**	10 - 11	**< 0.2**	
Di-n-butylphthalat	µg/l	**2.2**	1.5 - 2.5	**< 0.5**	
Butylbenzylphthalat	µg/l	**1.0**	0.7 - 1.5	**< 0.1**	
Diethylhexylphthalat	µg/l	**45**	43 - 46	**< 0.5**	
Di-n-octylphthalat	µg/l	**0.1**	< 0.1 - 0.2	**< 0.1**	
Di-iso-nonylphthalat	µg/l	**0.1**	< 0.1 - 0.2	**< 0.1**	



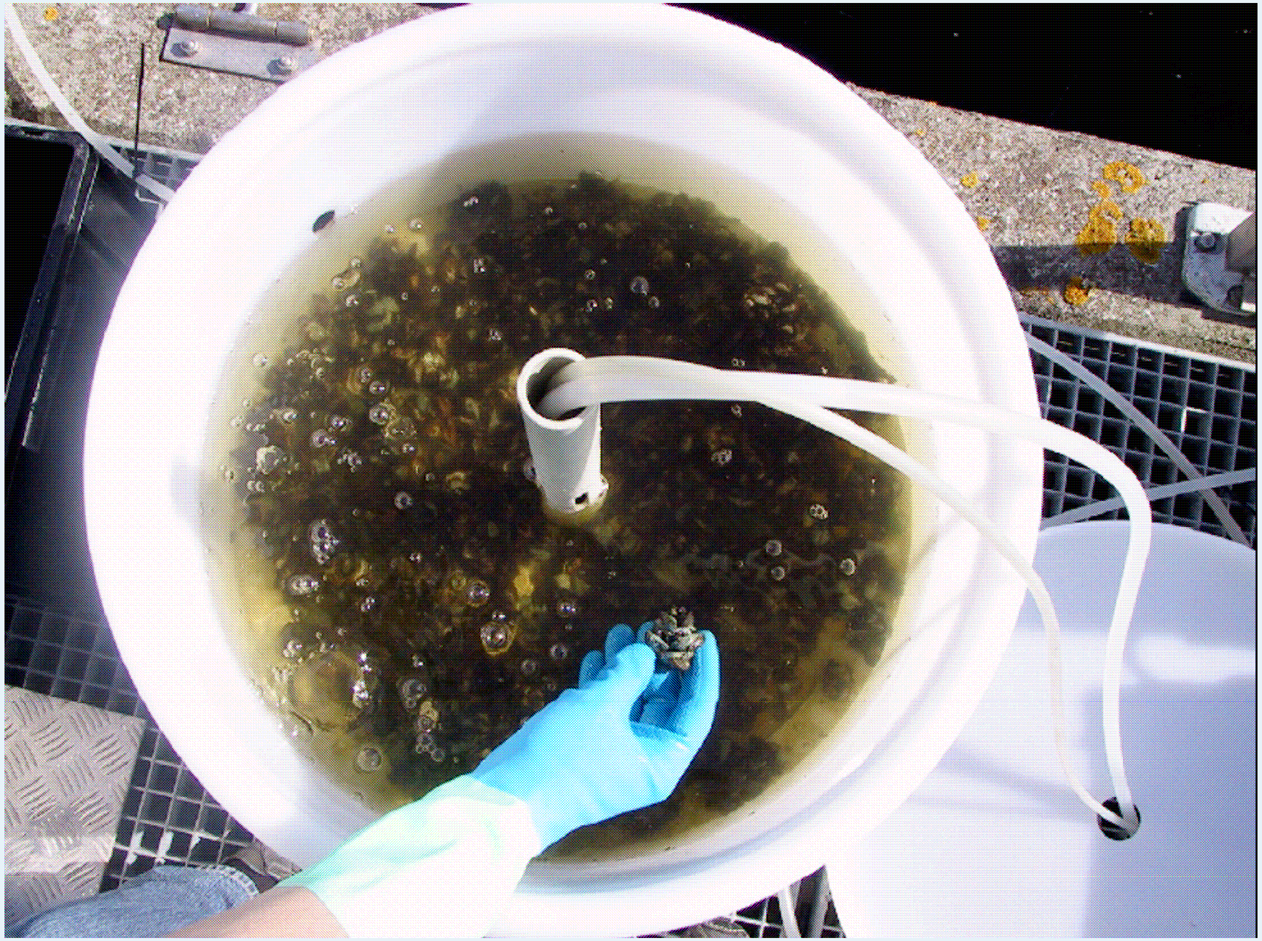
bioaccumulation in mussels

bioaccumulation in mussels

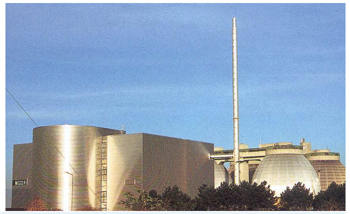




bioaccumulation in mussels

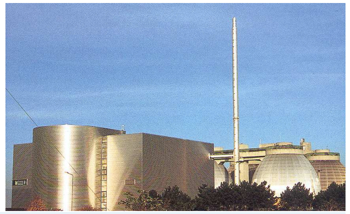


Selected results for bioaccumulation in mussels exposed to Avedoere WWTP effluent in 2002



Weeks of exposure	Diethyl-phthalate	DEHP	LAS (C10-C14)	EOX	Cr	Ni
	ug/kg fat		mg/kg TS		mg/kg TS	
0	33	62	< 5	52	0.4	3.5
3	110	39	36	122	0.5	3
7	210	43	13	106	1.8	6

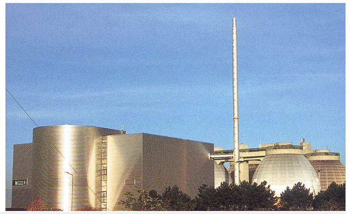
No bioaccumulation was observed for 101 other organic compounds and 8 other heavy metals		
Mussle:	*Dreissena polymorpha*	Exposure period: 28 May - 15 July, 2002

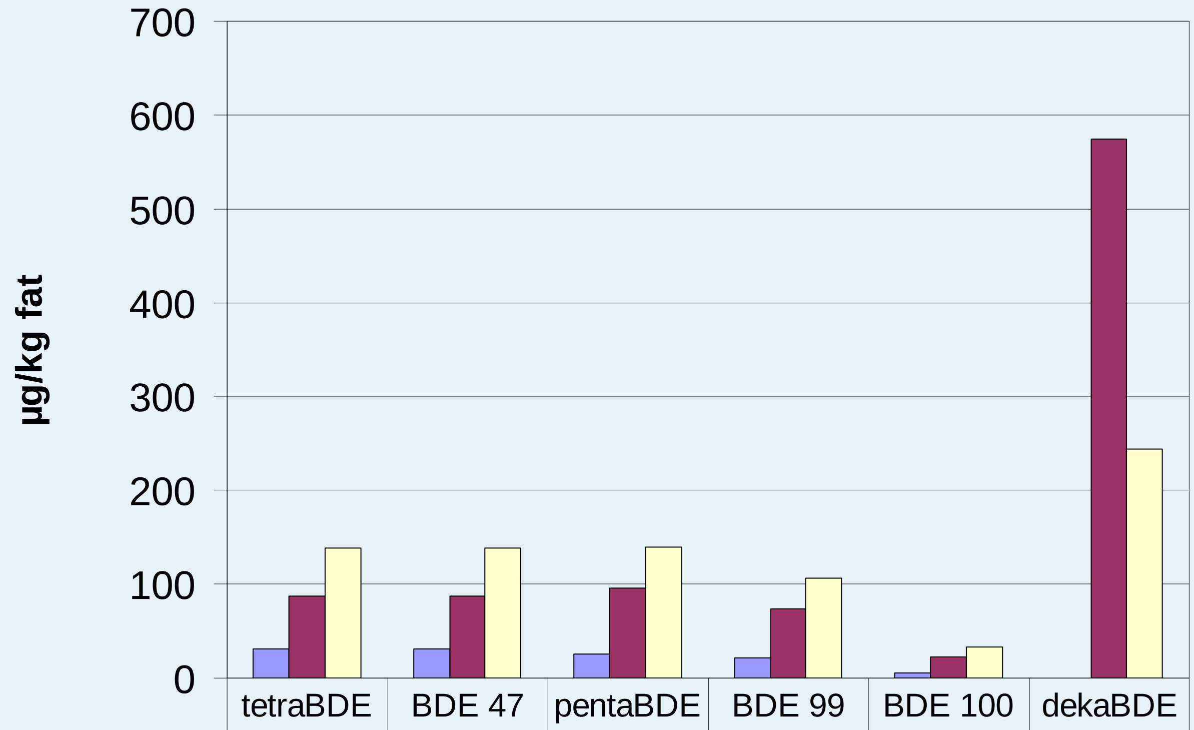


bioaccumulation in mussels

- Observed accumulation in mussels in Avedoere WWTP effluent in 2005:
  - Cr
  - 5 PAH specific compounds
  - Plastic softeners (DEHP)
  - LAS
  - 6 bromated flame retardants
- Observed accumulation in mussels in Koege Bay:
  - Cd, Hg, Cu
  - PAH
  - TBT

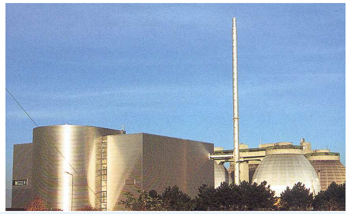
bioaccumulation in mussels (2005)
Bromated flame retardants





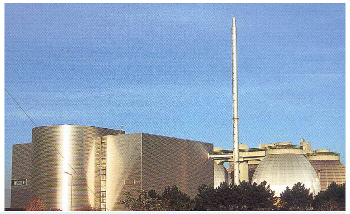
	tetraBDE	BDE 47	pentaBDE	BDE 99	BDE 100	dekaBDE
Start	31	31	26	21	5	0
3 weeks	87	87	96	74	22	574
6 weeks	138	138	140	107	33	244

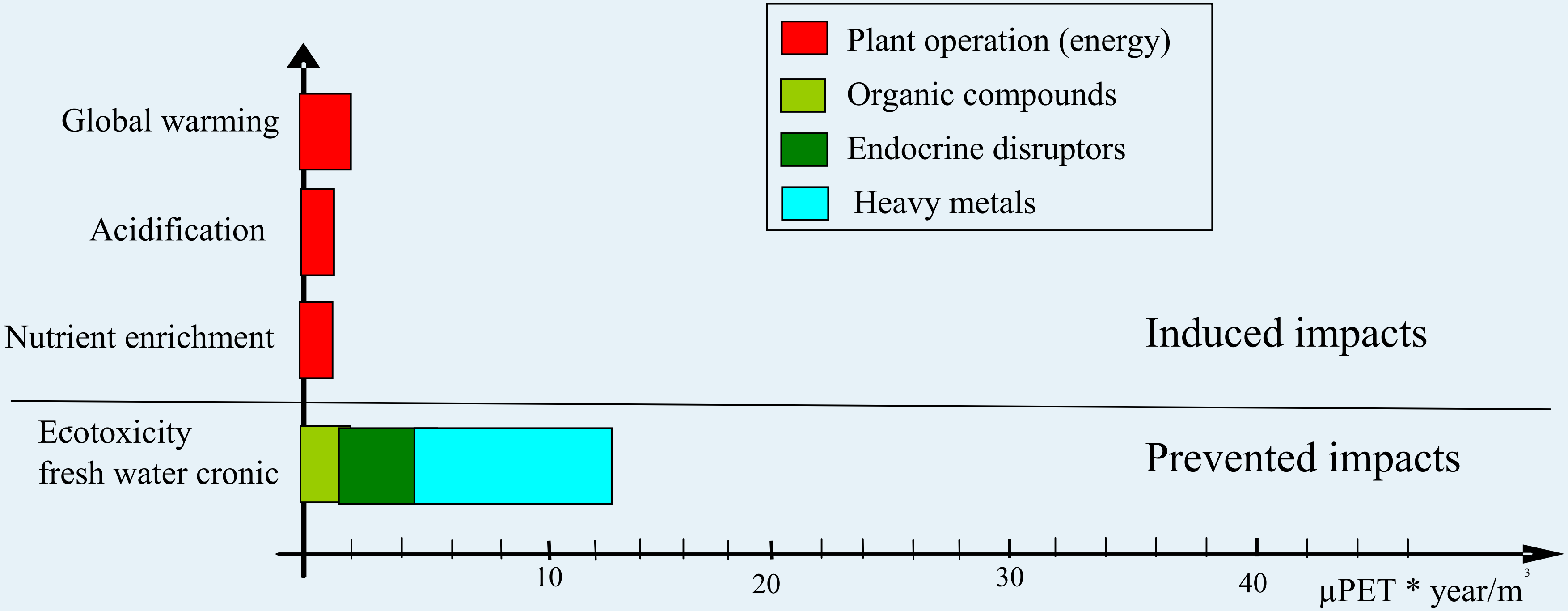
How can we reduce emissions ?



- Prevention
  - Product regulation (nationally, internationally, REACH, POP-Convention,..)
  - Affect attitudes / behaviour (campaigns, public awareness activities)
  - Environmental regulation (connection permits for industries, cleaner production methods)
- Improve Treatment
  - Optimisation of WWTP operation (sufficient SRT, ..)
  - Advanved treatment technology (UV, advanced oxidation, membranes, ..)

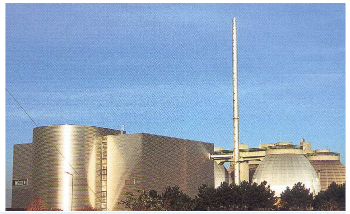
Advanced wastewater treatment ?
Example of LCA evaluation of sand filtration

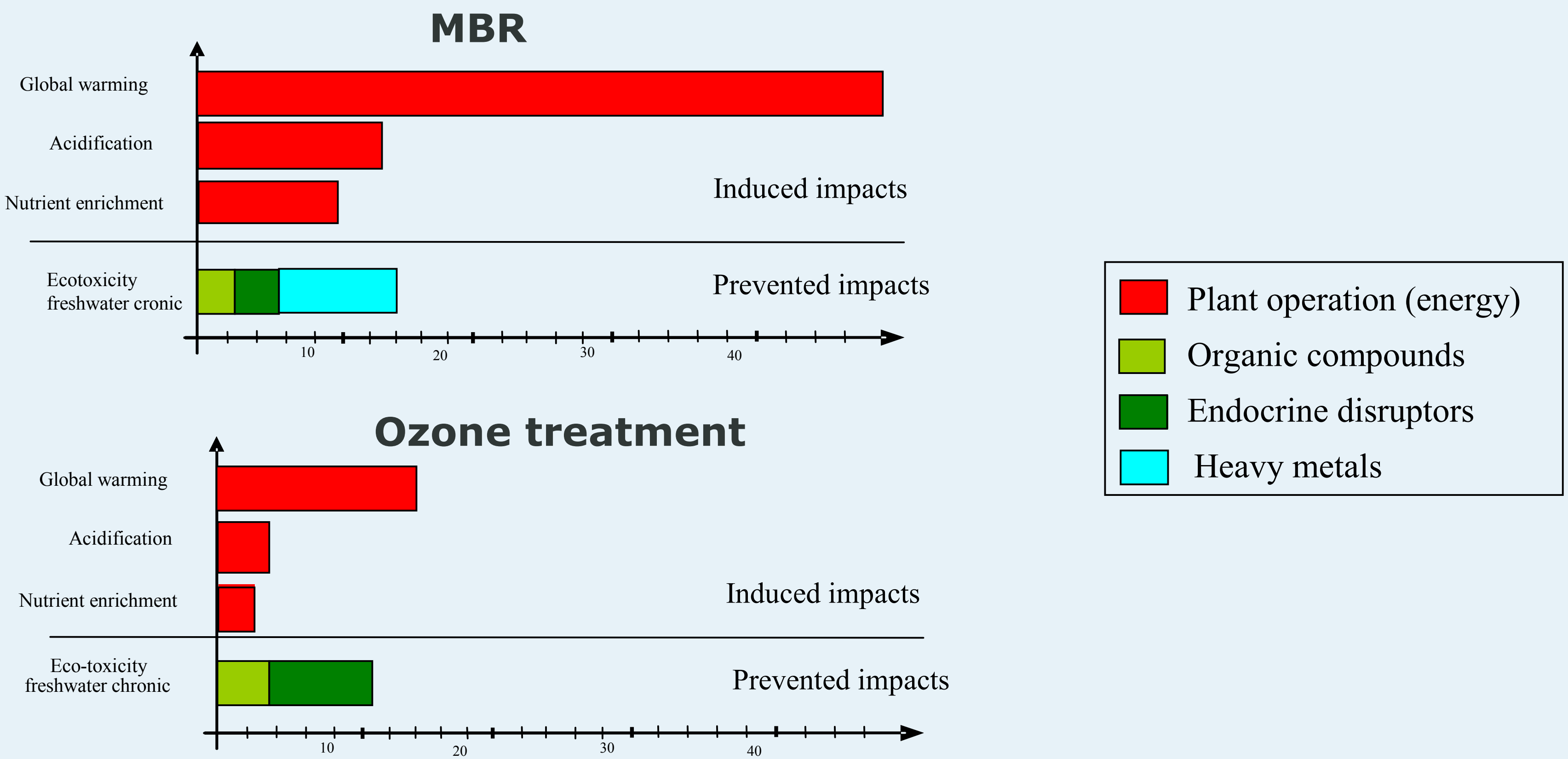




(Høibye et al. 2007)

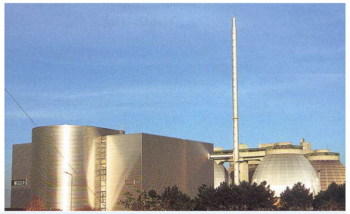
Advanced wastewater treatment ?
Example of LCA evaluation of MBR and ozonation





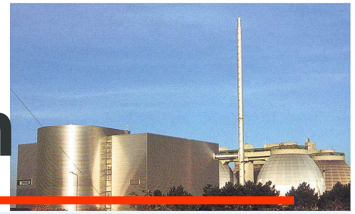
(Høibye et al. 2007)

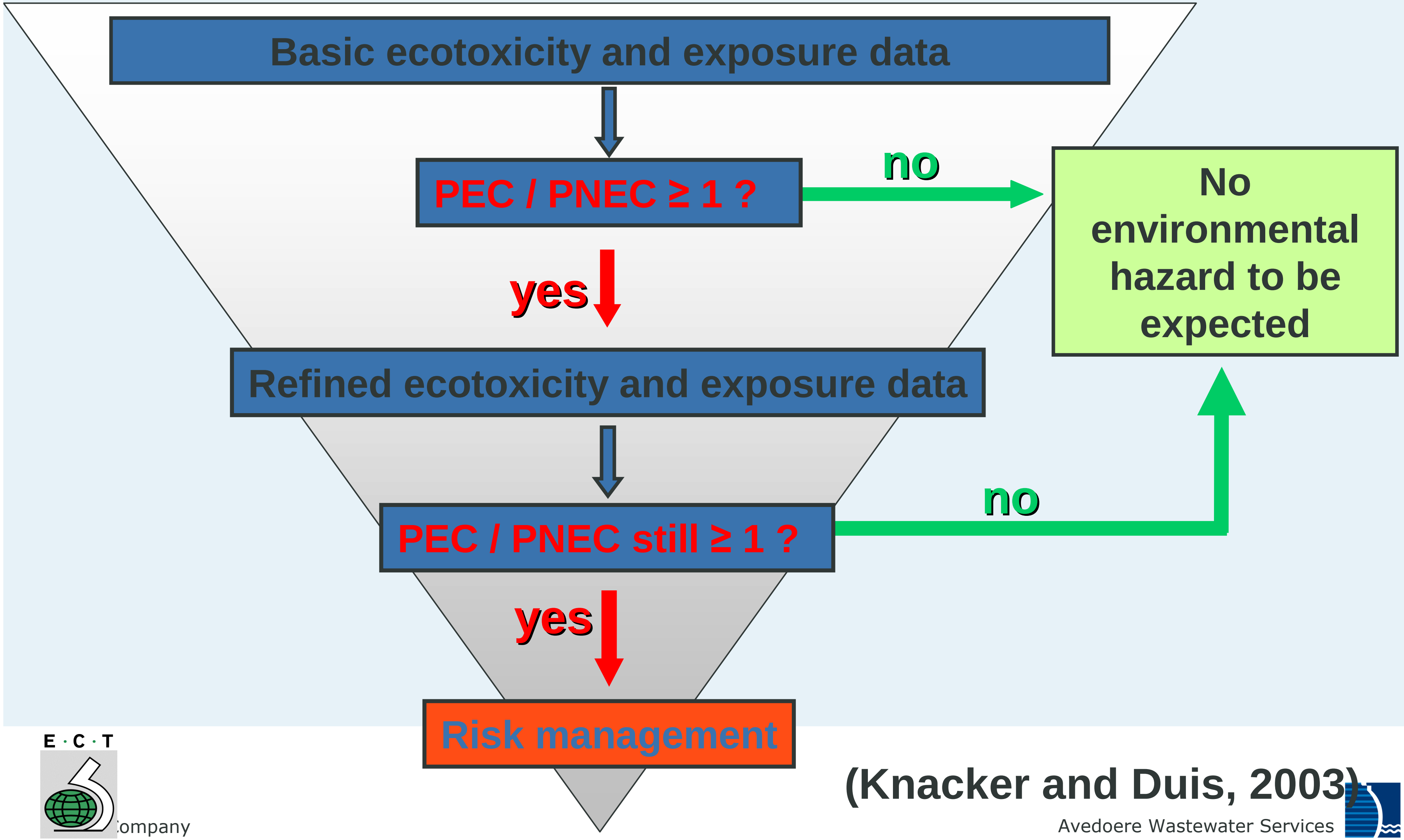
Some regulatory considerations



- Product regulations
  - Are the OECD – tests adequate (field realistic concentration levels)?
- Immission standards
  - Receiving water quality criteria exist – are the analytical methods good enough ?
  - Which time and spatial resolution is needed ?
- Effluent standards for a long lists of specific compounds ?
  - Can we measure everything ?
  - Better to spend resources on treatment technology than on extended monitoring ?
- Whole effluent assessment, including eco-toxicity ?
  - Which toxicity tests should be included ?
  - Are marine toxicity tests representative for brackish waters ?
  - Is it reasonable to base PNEC values on most stringent test results per species ?
  - Can we quantify bioaccumulation and persistance ?
- BAT
  - Should UV and/or membrane treatment technology be mandatory ?
  - Are advanced treatments sustainable in terms of material resource and energy consumptions ?

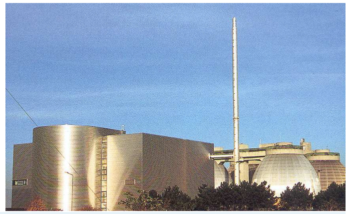
Tiered risk assessment approach





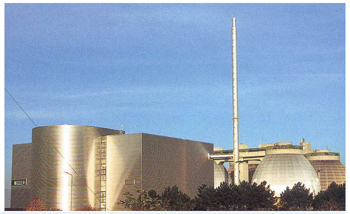
(Knacker and Duis, 2003)

Conclusions (1)

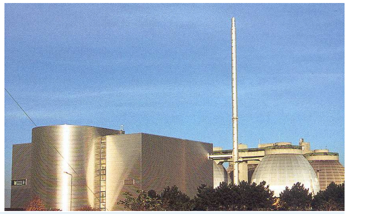


- **WWTP with nutrient removal (long SRT) is quite effective in removal of hazardous substances**
- **Endocrine disruption potential remains but at a low level – hormones >> other EDCs**
- **Good agreement between measured and calculated algal EC50 values – heavy metals major cause**
- **Reasonable agreement between ISO 8692 and Algaltoxkit F$_{TM}$ – mini test may be useful for WWTPs**

Conclusions (2)



- **Combined chemical analyses and biomonitoring give added information value**
- **Bioaccumulation studies of WWTP effluents are useful for shortlisting of specific hazardous substances of concern**
- **Whereas standardised methods have been established for risk assessment of specific substances there is in EU a need for standardised / uniform methods for whole effluent assessment**
- **Future environmental regulations should include initial screening steps and only introduce further risk assessment and/or emission standards for ”problematic” effluents**



Thank you for your attention