TPM8 - Session 4

TPM-related Activities in each Priority Research Area and Future Collaborations

The Management of Refractory Organic Matter in Water Environment

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Content

Ⅰ. The Management of Organic Matter for Water Quality Conservation in Korea

Goals of Water Quality Management

Water Environment Management Master Plan (2006~2015)

- **Object and Vision**

  To create clean water environment where our children can swim with fish

  - Ecologically healthy water environment and safe water free of harmful substances

- **Core indicators**

  - Maintaining the nationwide quality of 85% of the water at high levels under the revised Water Quality Conservation Act
  - Restoring 25% of non-natural stream(21,800) into natural streams
  - Creating 30% of the buffer zones in the upper streams of water quality sources as Riverine Ecobelt

- Number of public health criteria will be increased from 9 to 30

  - Number of specific water quality hazard criteria will be increased from 17 to 35

Goals of Water Quality Management

Securing Fishable and Swimmable Rivers & Lakes

- Perform Basic Research
- Restore Aqua-eco System
- Manage Hazardous Materials
- Extend Basic Infra

Change of Water Quality Standard

- **National Water Quality Management Standard for human health and sound aquatic environment**
- **Water Quality and Aquatic Ecosystem**
  - Water quality chemical standards focus on human health
  - Consider the effect of pollution on aquatic ecosystem
  - 5 grades in the existing category were increased to 7 in **2007** to more specifically explain water quality
    - **Standard for human health protection (17)**
    - **Standard for the living environment (5) / 7th grade**
    - **Water quality biological feature of aquatic ecosystem, 4th grade**

Water Quality Standard (WQS)

- **River and Stream, Lake** (before 2007)
- Physic-chemical and organism-based environmental standard (5 grades)

classification	class	pH	BOD COD*	SS	DO	Total Coliform	TP *	TN *
Living Environment	I	6.5~8.5	≤ 1	≤ 25 ≤ 1 *	7.5 ≥	≤ 50	≤ 0.010	≤ 0.200
	II	6.5~8.5	≤ 3	≤ 25 ≤ 5 *	5 ≥	≤ 1,000	≤ 0.030	≤ 0.400
	III	6.5~8.5	≤ 6	≤ 25 ≤ 15 *	5 ≥	≤ 5,000	≤ 0.050	≤ 0.600
	IV	6.5~8.5	≤ 8	≤ 100 ≤ 15 *	2 ≥	-	≤ 0.100	≤ 1.0
	V	6.5~8.5	≤ 10	No floating matter such as garbage	2 ≥	-	≤ 0.150	≤ 1.5
Protection of human health (9)	Cd ≤ 0.01, As ≤0.05 CN ND, Hg ND, Organic phosphorus ND, Pb ≤0.1, Cr+6 0.05, PCB ND, ABS ≤0.5							

* Lake

Water Quality Standard

Standard for the living environment

- Animated character helps understand the environmental standard easily
- **COD, TP** were included to make up for water quality management from Jan. 2010

Stream and river		State (Character)	pH	**BOD (mg/L)**	**COD (mg/L)**	TP (mg/L)	SS (mg/L)	DO (mg/L)	Coliforms (No/100mL)	
									Total coli.	Fecal coli.
Very Good	Ia		6.5 ~ 8.5	**≤1**	**≤2**	≤0.02	≤25	≥7.5	≤50	≤10
Good	Ib		6.5 ~ 8.5	**≤2**	**≤4**	≤0.04	≤25	≥5.0	≤500	≤100
Fairly Good	II		6.5 ~ 8.5	**≤3**	**≤5**	≤0.1	≤25	≥5.0	≤1,000	≤200
Fair	III		6.5 ~ 8.5	**≤5**	**≤7**	≤0.2	≤25	≥5.0	≤5,000	≤1,000
Fairly Poor	IV		6.0 ~ 8.5	**≤8**	**≤9**	≤0.3	≤100	≥2.0	-	-
Poor	V		6.0 ~ 8.5	**≤10**	**≤11**	≤0.5	1)	≥2.0	-	-
Very Poor	VI		-	**>10**	**>11**	>0.5	-	<2.0	-	-

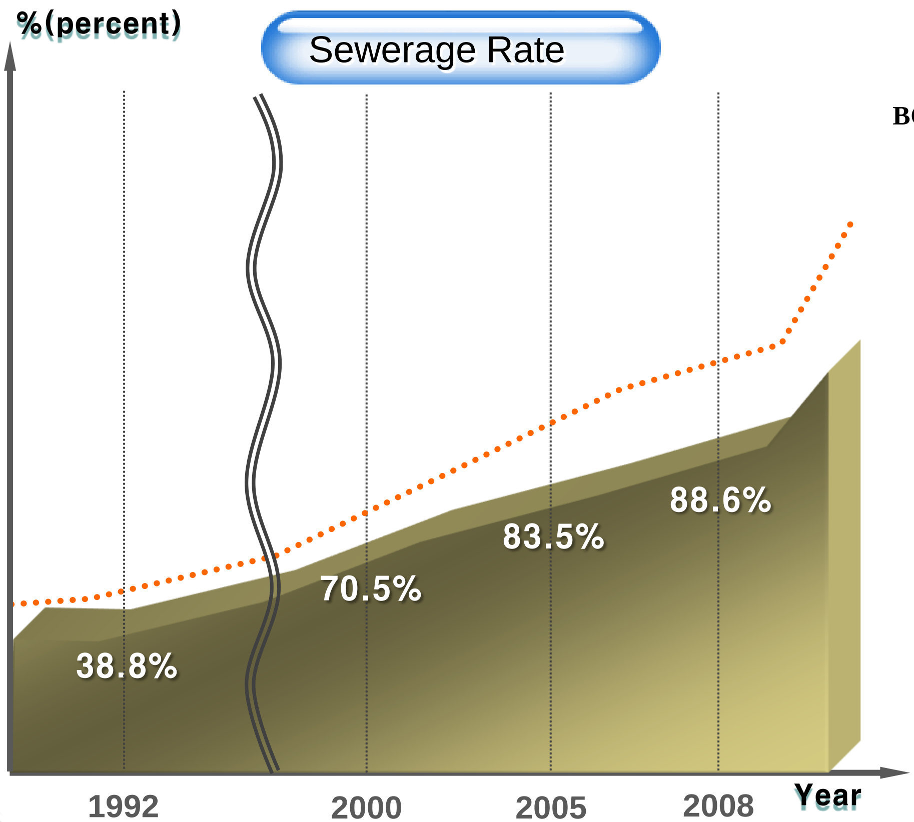
Lake		State	pH	**COD (mg/L)**	SS (mg/L)	DO (mg/L)	TP (mg/L)	TN (mg/L	Chloro phyll-a (mg/m^3)	Coliforms (No/100mL)	
										Total coli.	Fecal coli.
Very Good	Ia		6.5 ~ 8.5	**≤2**	≤1	≥7.5	≤0.01	≤0.2	≤5	≤50	≤10
Good	Ib		6.5 ~ 8.5	**≤3**	≤5	≥5.0	≤0.02	≤0.3	≤9	≤500	≤100
Fairly Good	II		6.5 ~ 8.5	**≤4**	≤5	≥5.0	≤0.03	≤0.4	≤14	≤1,000	≤200
Fair	III		6.5 ~ 8.5	**≤5**	≤5	≥5.0	≤0.05	≤0.6	≤20	≤5,000	≤1,000
Fairly Poor	IV		6.0 ~ 8.5	**≤8**	≤15	≥2.0	≤0.10	≤1.0	≤35	-	-
Poor	V		6.0 ~ 8.5	**≤10**	1)	≥2.0	≤0.15	≤1.5	≤70	-	-
Very Poor	VI		-	**>10**	-	<2.0	>0.15	>1.5	>70	-	-

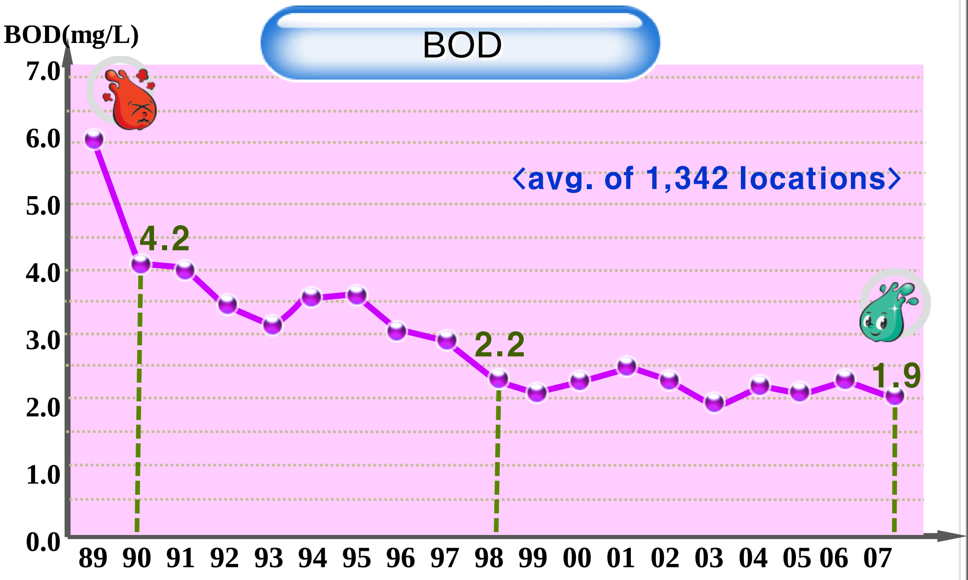
1) No floating matter such as garbage

Ⅱ. Status of Organic matter in Water Environment of Korea

Improvement of Water Quality

- The water quality of 4 major rivers has improved through the comprehensive water measures since 1996.
- Main water supply sources of 4 major rivers are well managed at 1~2 mg/L BOD.



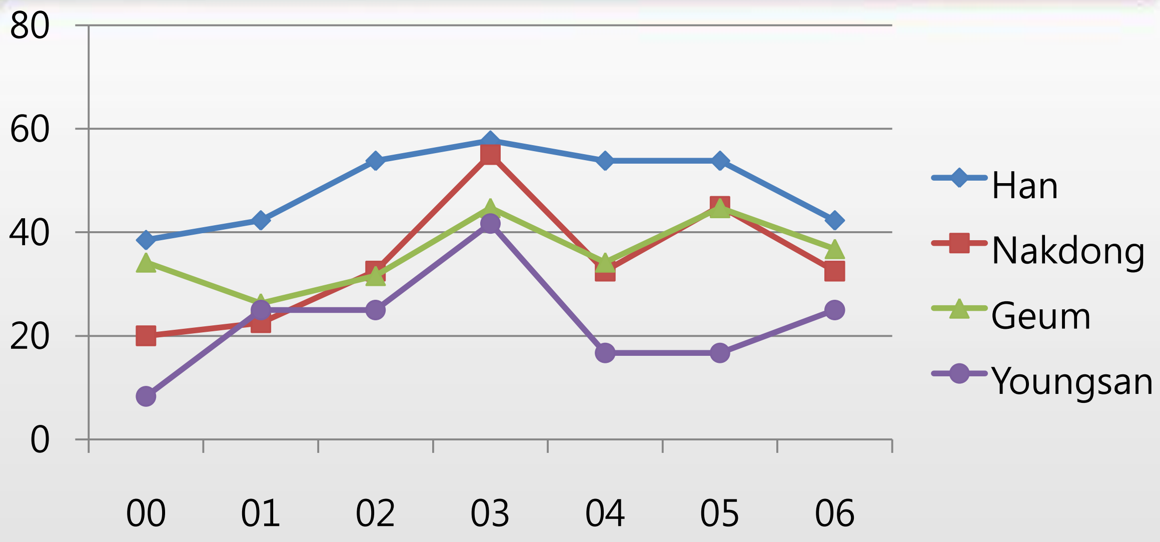


Improvement of Water Quality

Improvement Rate of Aquatic Environmental Standard

- All streams nationwide are classified into 194 sections.
- Improvement rate of the standard focusing on BOD levels was 35.6 % in 2006, up from the 27.6 % in 2000.

Improvement Rate(BOD) in major 4 rivers



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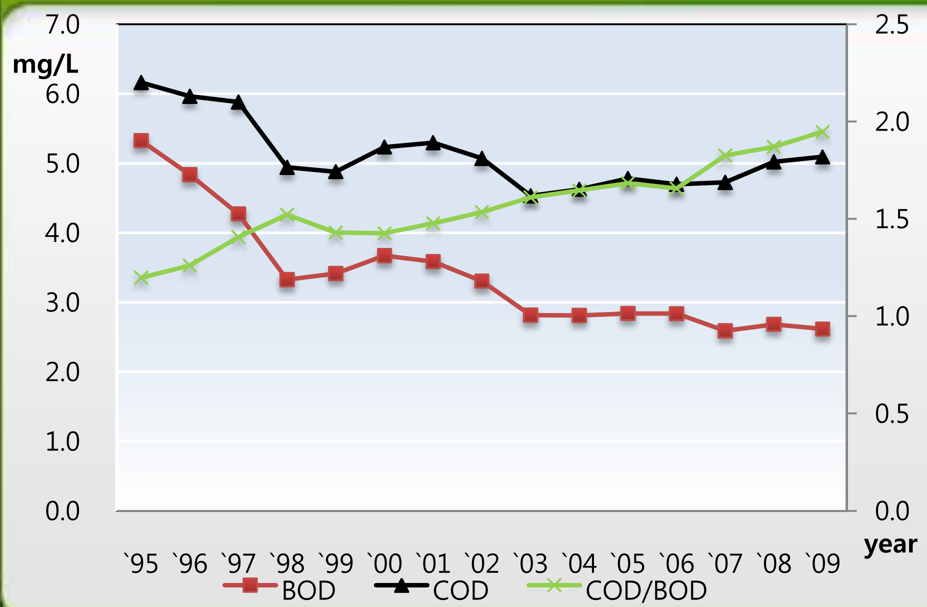
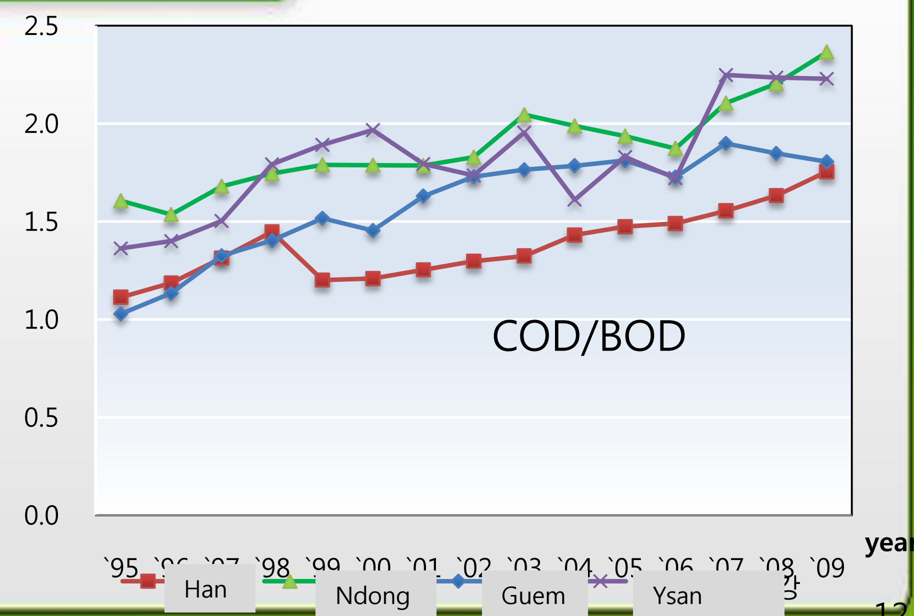
Limitation in Water Quality Improvement

Limitation for the Management of Refractory Organic Matter in Water Environment

- COD has steadily increased since 2003 based on the data of stream (700 sites), lake(184 sites) during the last 15 years (1995~2009).
- COD/BOD in 4 major rivers is increasing (1.2(‘95) → 1.95(‘05)

BOD, COD and COD/BOD in major 4 river





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Limitation in Water Quality Improvement

Limitation for management of refractory organic matter in water environment

- Improvement rate of COD was lower than BOD in river during the last 5 years (2005~2009).
- Especially, improvement rate of COD in lake is lower than in river
  - COD standard in lake is stricter than river → Different evaluation results

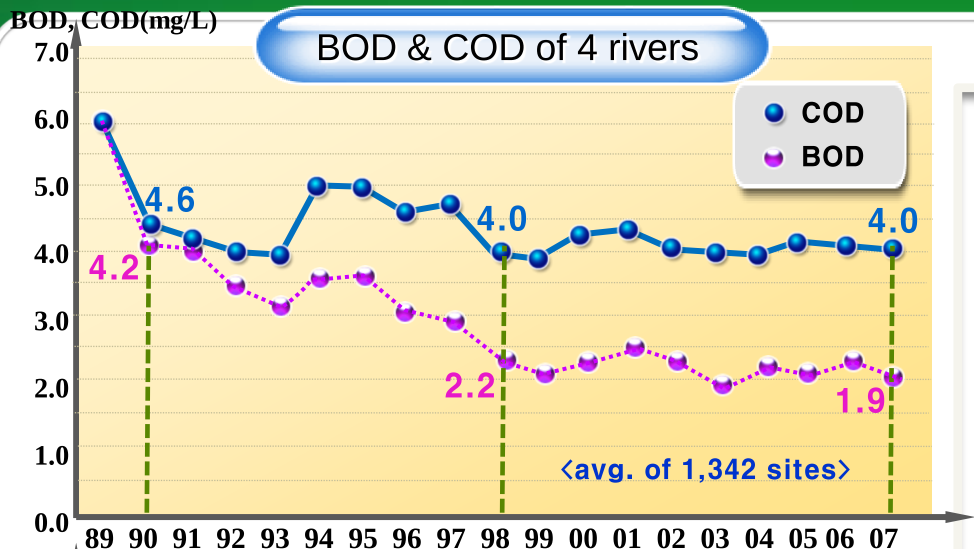
⇒ Integrated standard for lake and river is needed

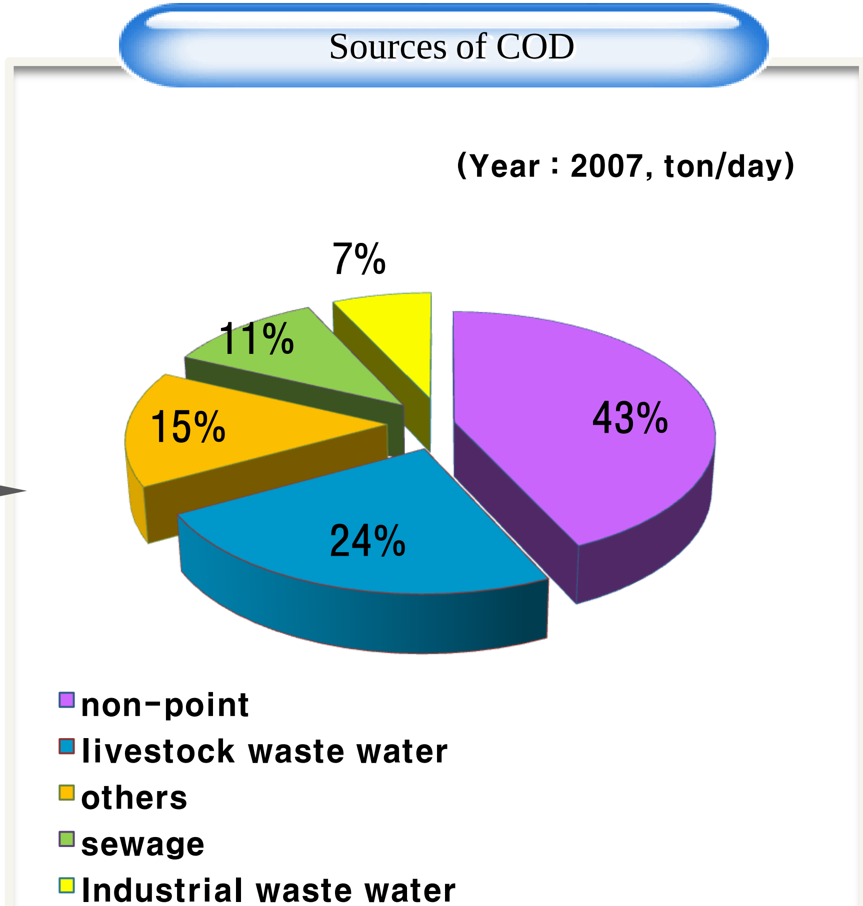
Year	river					lake		
	No. of sites	BOD		COD		No. of sites	COD	
		satisfied sites	improvement rate (%)	satisfied sites	improvement rate (%)		satisfied sites	improvement rate (%)
2005	578	369	**63.8**	292	**50.5**	160	21	**13.1**
2006	585	351	**60.0**	298	**50.9**	169	28	**16.6**
2007	645	449	**69.6**	339	**52.6**	181	20	**11.0**
2008	694	463	**66.7**	298	**42.9**	182	17	**9.3**
2009	696	464	**66.7**	287	**41.2**	182	11	**6.0**

Ⅲ. Discharge Load of Organic Matter

Discharge Load of Organic Matter

- **COD increased** because of increased chemical uses and refractory pollutant influx from non-point sources.

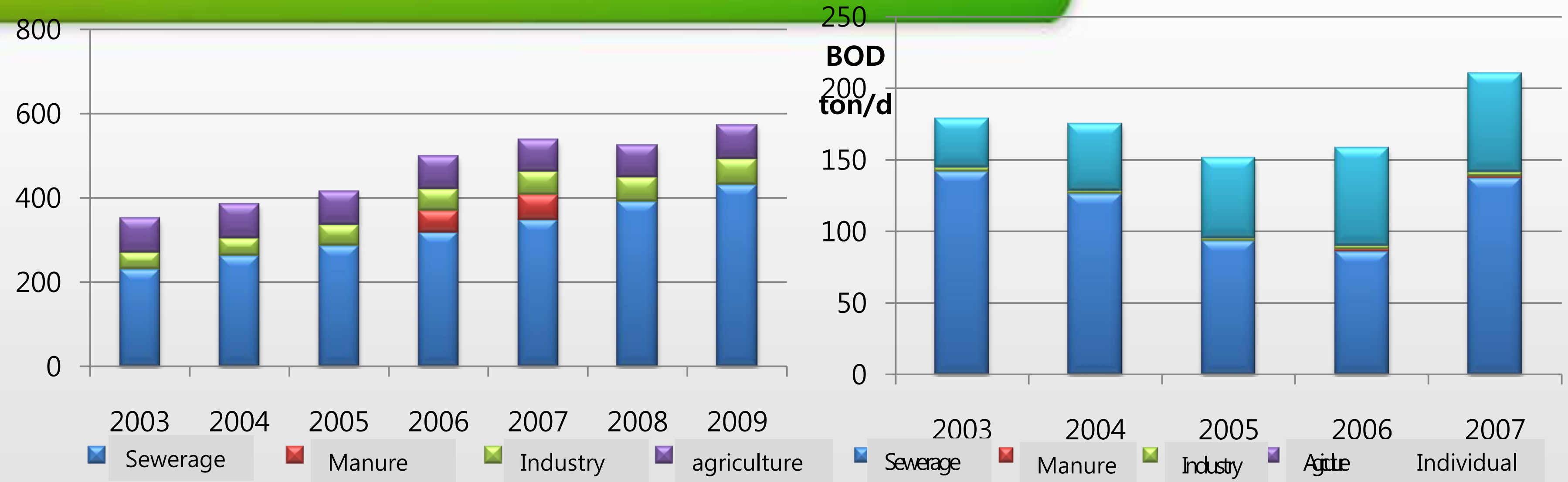




Discharge Load of Organic Matter

The change of treatment facilities

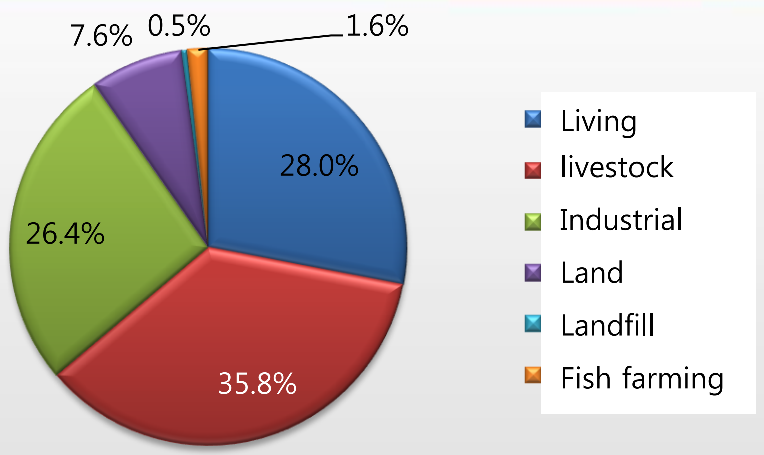
- Treatment facilities have continuously increased from 2003 to 2009.
  sewerage (432), manure (60), wastewater (61), agricultural &industrial (80)
- **BOD loads** of effluent from sewerage and individual wastewater were higher than others (2003~2009)
  BOD load ('07) : sewerage > individual industrial > industrial > agricultural industrial > manure

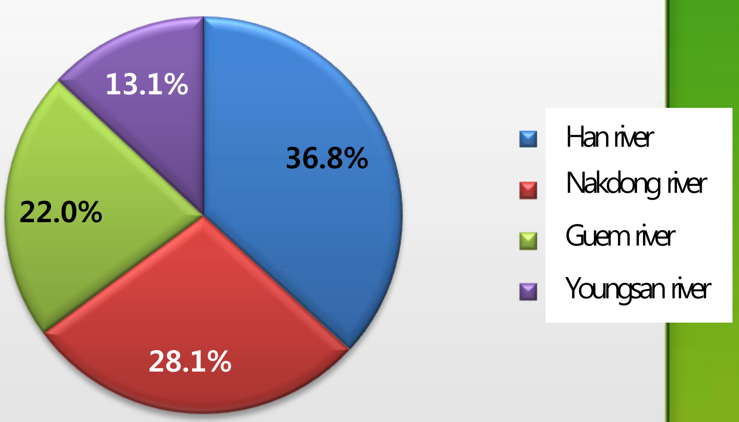


Discharge Load of Organic Matter

Load from discharge sources

- BOD load from 4 major rivers amounts to a total of 8,906,341 kg/day
  - livestock >living > industry > land
  - Han river > Nakdong river > Guem river, Youngsan-sumjin river

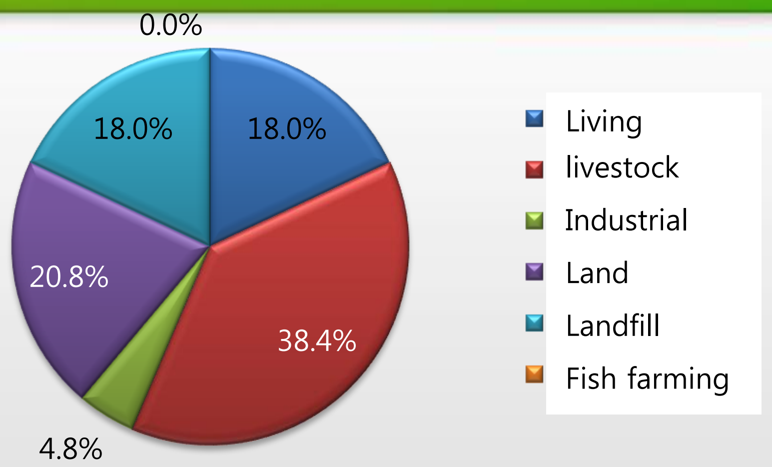


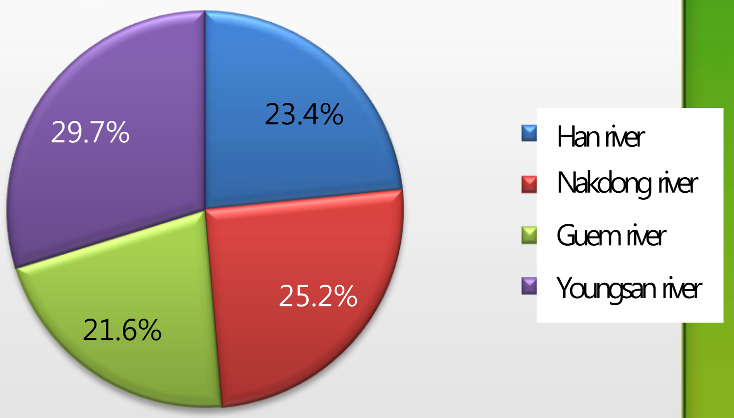


Discharge Load of Organic Matter

Discharge load from sources

- BOD discharge load from 4 major river is 814,217 kg/day, totally
  - livestock > land > living > landfill
  - Youngsan river > Nakdong river > Han river > Guem river
- Variation of discharge load : living 28.0% → 18.0%, industrial 26.4% → 4.8%
  livestock 35.8% → 38.4 %
  land 7.6 % → 20.8%, landfill 1.6%→ 18.0 %





Ⅳ. The Effect of Organic Matter in Drinking Water Sources

Organic Matter in Treatment Process

Treatment efficiencies of organic matter in the purification facilities (7)

Classification			1 st		2 nd	
			$KMnO_4$ demand	**TOC**	$KMnO_4$ demand	**TOC**
Advanced treatment process	River	SN2	68.7	41.7	78.1	54.7
		SN3	82.4	71.1	89.2	67.6
		SN4	68.2	40.9	79.3	37.9
		SG	70.9	34.1	78.0	45.2
		SS	69.5	40.1	74.0	41.4
		average	**71.9**	**45.6**	**79.7**	**49.4**
Rapid filtration Process	River	SH	63.2	49.8	-	-
		SN1	59.2	26.9	80.0	57.7
		SP	53.7	7.9	65.3	14.4
	Lake	LP	54.3	29.9	73.1	38.2
		LD	52.5	28.2	78.1	38.2
		LJ	59.2	38.6	-	-
		average	**57.0**	**25.2**	**74.1**	**37.1**

Research

Effect of Organic Matter with CBPs

- **The Relationship of coefficients between CBPs formation and NOM**

Formation	DOC	UV254	SUVA	>100k	<100k	<10k	<1k	N
THMFP	0.38	**0.85**	**0.86**	0.17	0.80	0.38	-	n = 20
HAAFP(2)	0.41	0.54	0.54	0.03	0.99	-	0.99	n = 33

($p > 0.005$)

Ⅴ. The Change of Organic Matter Index

Consideration of New Organic Matter Index

The comparison of organic index

content		BOD_5	COD		TOC
			COD_{Mn}	COD_{Cr}	
Analytical condition	Confirmation of refractory organic matter	×	△	○	○
	Analysis time	×	△	△	○
	Analytical error	×	△	△	○
	Repeatability	×	△	△	○
Application of enforcement	Institutional instrument	○	○	×	×
	Available data	○	○	×	×
	Unit load	○	×	×	×
	Load allocation	○	○	○	○
	Modeling	○	△	×	△
	Connection of water management strategy	×	×	△	○
Score		30	32	26	**36**

(○: good (5), △: fair (3), ×: poor (1))

Consideration of New Organic Matter Index

Advantage of new index

COD_{Cr}	TOC
- Possible to measure total organic matter including refractory organic matter - Good repeatability with high degradability of organic matter - Very effective to consider design of treatment facility and treatment efficiency - Easy to manage data related to wastewater	- Precise method to measure organic carbon including refractory and autochthonous organic matter - Possible to control and manage the treatment facilities with rapid measurement - Automated system - Predict formation potential of disinfection byproduct in drinking water - Rapid response to emergency accidents and real - time monitoring

Consideration of New Organic Matter Index

Disadvantage of new index

COD_{Cr}	TOC
- Lack of nationwide data - Depends on characteristic of sample - Secondary pollution such as chromium and mercury - Data-conversion is needed for water quality modeling - Bigger Error range in lower concentration	- Lack of source data such as industrial and sewerage facilities - Data-conversion is needed for water quality modeling - High costs for buying and maintaining instrument - Potential instrumental errors

Consideration of New Organic Matter Index

Application of Modeling to simulate Water Quality

Subject	Model	DO	BOD	COD	TOC	DOC	Labile DOC	Refractory DOC	POC	Labile POC	Refractory POC	TIC
RIVER /LAKE	QUAL2E	O	O									
	QUALKO2	O	O	O								
	QUAL-NIER	O	O		**O**	**O**						
	WASP	O	O		**O**	**O**			**O**			
	EFDC	O		O	**O**	**O**			**O**	**O**	**O**	
	CE-QUAL-W2	O			**O**	**O**	**O**	**O**	**O**	**O**	**O**	O
BASIN	AnnAGNPS				**O**							
	ANSWERS				**O**							
	SWMM	O	O	O								
	SWAT	O	O									
	MOHID	O			**O**	**O**	**O**	**O**	**O**			O
	HSPF	O	O									O
	CAMEL	O		O	**O**	**O**	**O**	**O**	**O**	**O**	**O**	O

Consideration of New Organic Matter Index

Comparison of scores from CODcr and TOC

content	COD_{Cr}	TOC
International application[1]	3	4
Representativeness[1]	3	3
Monitoring program[1]	1	4
Analytical technique[1]	4	4
Precision/Accuracy [1]	3	3
Analytical time[1]	2	3
Instrument price [1]	3	1
Handling of operation[1]	2	3
Relation with byproduct[1]	1	3
Relation with present index	2	2
Foreign data availability	3	4
Analytical experience	1	2
Survey of unit load	0	2
Total score	**28**	**38**

Level score : 0. none,
1 very poor
2 poor
3 fair
4 good

※ Chang E. E.(2005) "Evaluation of Source Water Quality Standards for Total Coli forms, TOC, and COD in Taiwan"

Consideration of New Organic Matter Index

Coefficient relationship with each item in monitoring data

- Coefficient relationship with BOD and COD was high in surface water over the past 10 years (2000~2009) .
- SS, TP, PO_4-P, Chl-a were more correlated with COD rather than with BOD .

Item	DO	BOD	COD	SS	TN	TP	PO_4-P	Chl-a
pH	0.2	0.08	0.08	0.06	0.03	0.01	-0.02	0.18
DO	1	-0.10	-0.18	-0.25	0.01	-0.15	-0.13	-0.07
BOD		1	**0.80**	0.57	0.49	0.65	0.55	0.51
COD			1	**0.68**	**0.46**	**0.70**	**0.59**	**0.58**
SS				1	0.36	0.60	0.45	0.51
TN					1	0.65	0.65	0.19
TP						1	0.86	0.40
PO_4-P							1	0.26

Consideration of New Organic Matter Index

Coefficient relationship with TOC in monitoring data

- TOC showed good coefficient relationship with BOD and COD with statistical significance level in major water monitoring sites (more than 8,000 data) in 2010.

item	BOD	COD	SS	TP	chl -a
TOC	**0.73**	**0.81**	0.58	0.70	0.49
BOD	1.00	**0.82**	0.63	0.72	0.64
COD		1.00	0.69	0.76	0.61
SS			1.00	0.73	0.58
TP				1.00	0.52

Consideration of New Organic Matter Index

Coefficient relationship with TOC in monitoring data

- TOC showed good coefficient relationship with BOD and COD with statistical significance level in **TMDL(total management daily load) monitoring sites** (more than 15,320 data) during 2007~2010.7.
- TOC was more correlated with COD rather than with BOD by all monitoring data

item	DO	BOD	COD	SS	TN	TP	TOC	Flow
pH	0.21	-0.05	-0.07	-0.06	-0.17	-0.15	-0.10	0.04
DO	1.00	-0.14	-0.22	-0.34	0.04	-0.24	-0.22	-0.20
BOD		1.00	**0.88**	0.67	0.57	0.78	**0.83**	0.05
COD			1.00	**0.72**	**0.56**	**0.82**	**0.92**	0.11
SS				1.00	0.36	0.68	0.66	0.33
TN					1.00	0.67	0.54	-0.01
TP						1.00	0.79	0.12
TOC							1.00	0.07

Consideration of New Organic Matter Index

Coefficient relationship with TOC in sewerage wastewater

- Both TOC and DOC showed good coefficient relationship with BOD and COD with statistical significance level in effluent from sewerage facility(Dalseo) .

Item	BOD	COD	SS	T-N	T-P	TOC	DOC
COD	0.48	1					
SS	0.81	0.65	1				
T-N	0.70	0.54	0.81	1			
T-P	0.63	0.79	0.58	0.44	1		
TOC	**0.85**	**0.83**	0.05	0.00	**0.65**	1	
DOC	**0.86**	**0.91**	0.08	0.02	**0.75**	0.98	1

Consideration of New Organic Matter Index

Establishment of TOC for WQS

- TOC distribution in surface water, achievement of goal level, disinfection byproduct formation potential
- Consider TOC standard or guideline in other countries

Level		State (character)	River and Stream		Lake	River/Lake
			BOD	**COD**	**COD**	**TOC**
Very good	Ia		1	2	2	?
Good	Ib		2	4	3	?
Fair good	II		3	5	4	?
Fair	III		5	7	5	?
Fair poor	IV		8	9	8	?
Poor	V		10	11	10	?
Very poor	VI		> 10	> 11	> 10	?

Ⅵ. Research Project

Now

Revision of TOC in Water Quality Standard Method

- Comparison of combustion type and UV-persulfate type for TOC analysis of freshwater

  - Quality control

  - Oxidation rate of refractory organic matter by these types

    Urea, Tartaric acid, L-glutamic acid, Sodium dodecylbenzenesulfonate, Caffeins, L-leucine, Fumaric acid

  - Interference effect of inorganic carbon, Salinity

  - Correction by existence of turbidity and algae

  - Instrumental difference by filter size

Establishment of TOC standard to conserve water quality and aquatic ecosystem

Future Study

- **A study on source of organic matter and background level**
  - Investigation of authochthonus and allochthonous natural organic matter(NOM) in watershed
  - Behavior mechanism of natural organic matter and the relation with refractory organic matter
  - Investigation of TOC background level by soil characteristic, sediment and forest
  - Estimation on variation of organic matter depending on climate change
- **A study on establishment of TOC effluent standard in sewerage treatment facility and industrial wastewater treatment**
  - Treatment efficiency of TOC by specific type of industry
  - Best available treatment of TOC
  - Establishment of TOC standard for sewerage treatment and wastewater treatment facility

Thank you for your attention