An Australian Government Initiative

Introduction to Drinking Water Research at National Cheng Kung University in Taiwan

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Tainan, Taiwan

July 21, 2008

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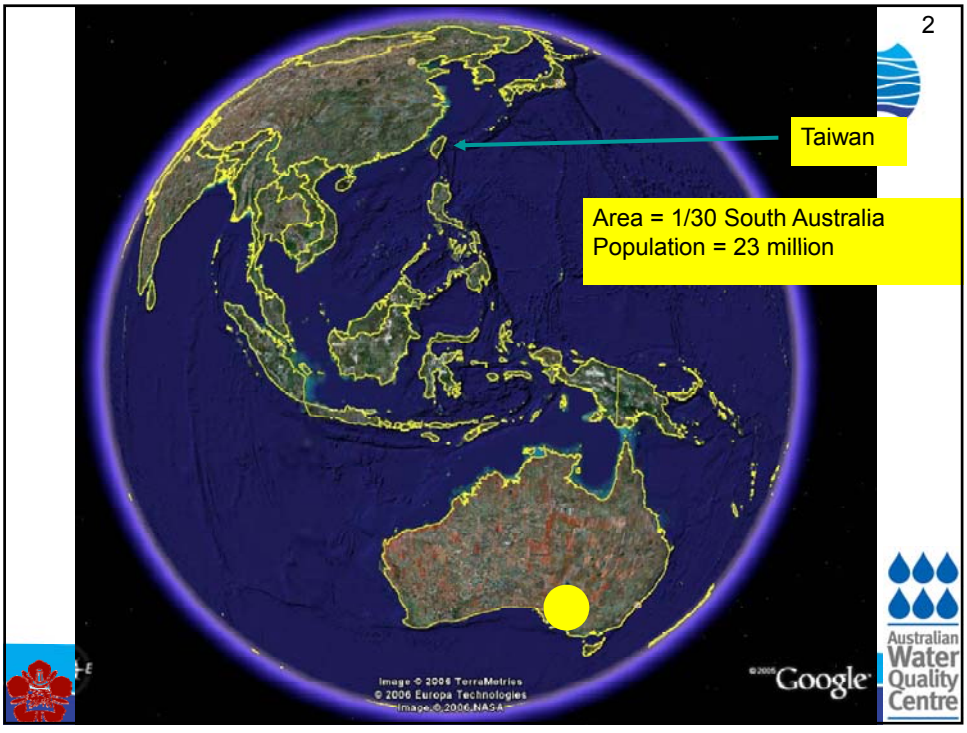

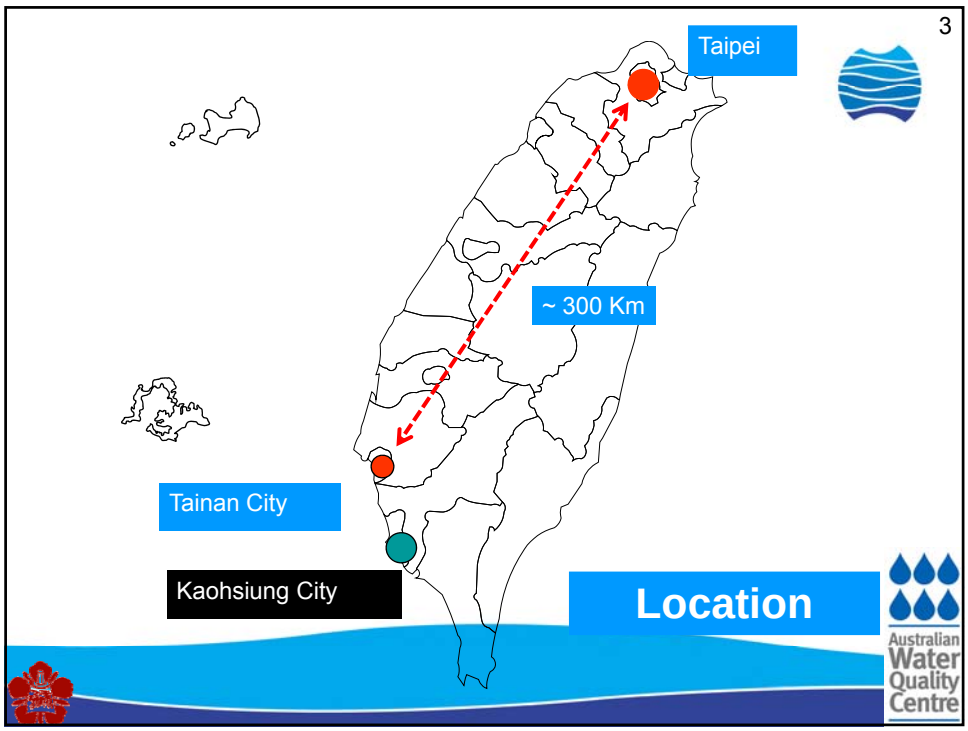
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Taipei
~ 300 Km
Tainan City
Kaohsiung City
Location
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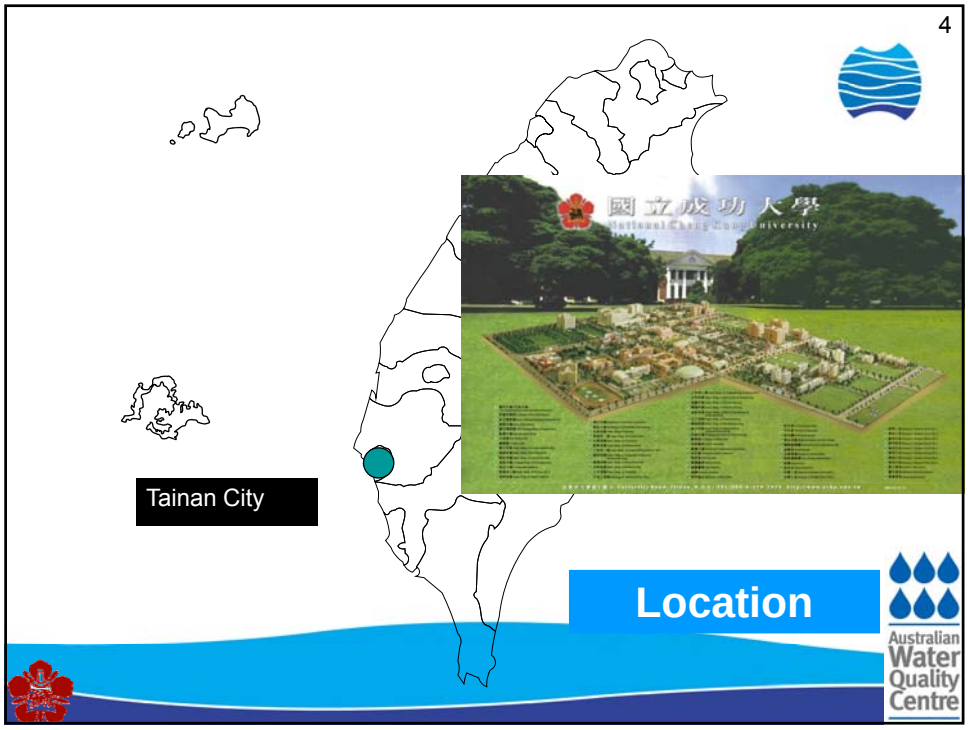
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國立成功大學
Tainan City
Location
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國立成功大學
National Cheng Kung University

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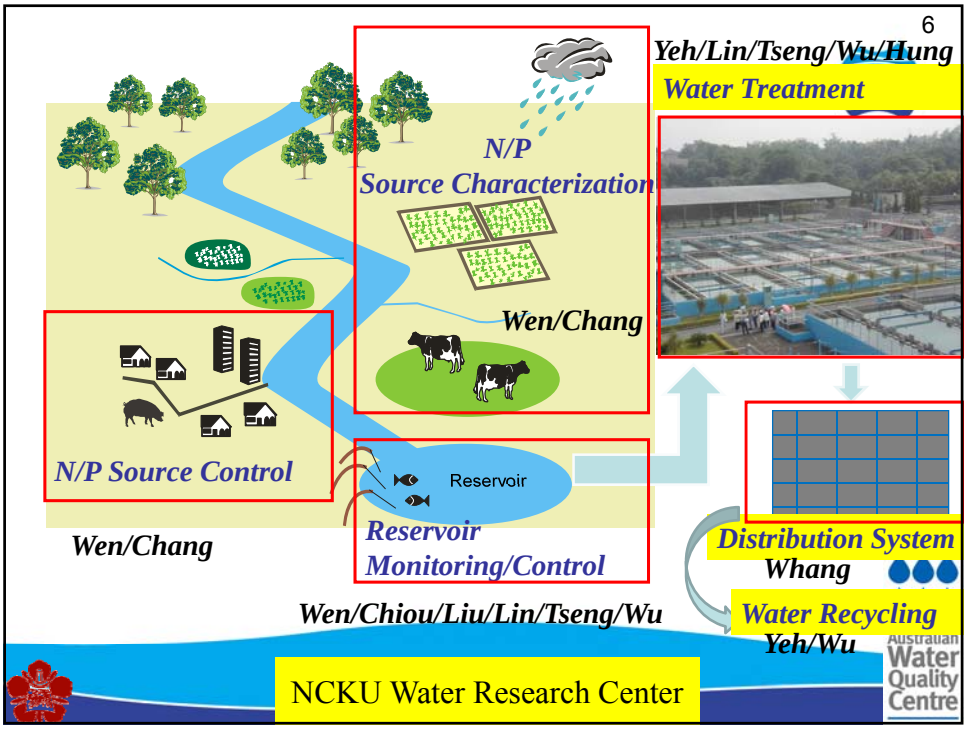
Yeh/Lin/Tseng/Wu/Hung
Water Treatment
N/P
Source Characterization
Wen/Chang
N/P Source Control
Wen/Chang
Reservoir
Reservoir
Monitoring/Control
Wen/Chiou/Liu/Lin/Tseng/Wu
Distribution System
Whang
Water Recycling
Yeh/Wu
NCKU Water Research Center

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Water Quality Research Center @NCKU

Professor Chang (Director), Former EPA Minister

N/P/Organic Source Characterization and Control in Catchment

Professor Weng and Dr. Chang

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Water Quality Research Center @NCKU

Reservoir Water Quality Monitoring and Control

Prof Chiou
Phy. Chemistry

Prof Weng
Env. Eng.

Prof Lin
Env. Eng.

Assoc. Prof Tseng
Microbiology, Algae

Assoc. Prof Liu
Remote Sensing

Asst. Prof Wu
Molecular Bio.

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Water Quality Research Center @NCKU

Water Treatment/Distribution Systems/Water Recycling

Prof Yeh
Env. Eng.

Prof Lin
Env. Eng.

Assoc. Prof Tseng
Microbiology, Algae

Assoc. Prof Whang
Biological Treatment

Asst. Prof Wu
Molecular Bio.

Dr. Hung
DBPs, Organics

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Catchment Control of N, P, and Organics

Wen and Chang

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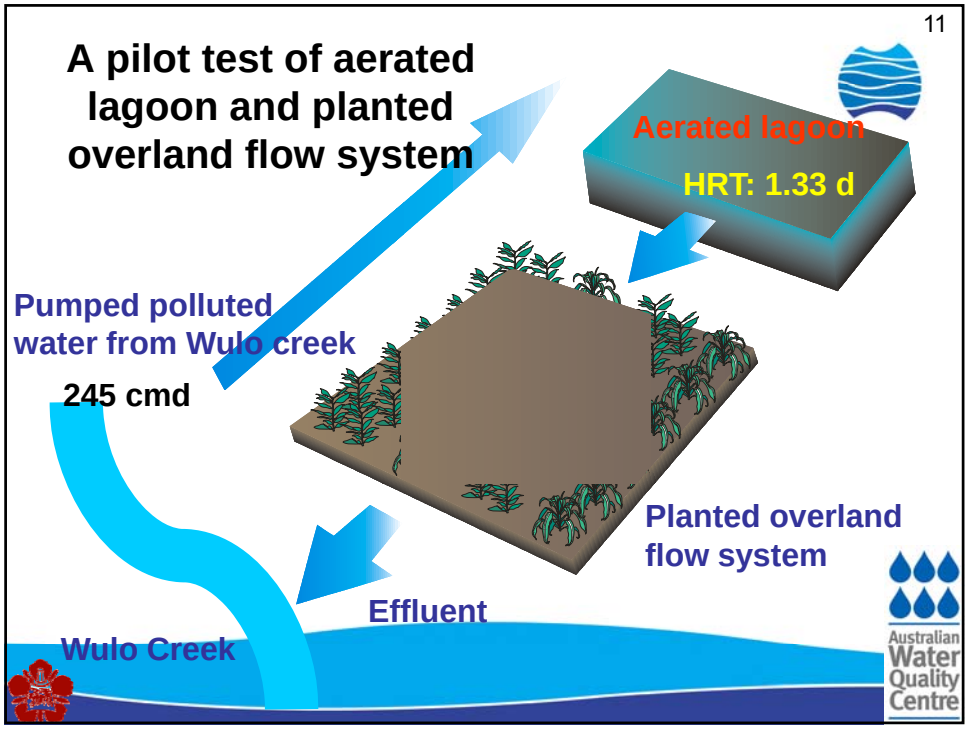
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A pilot test of aerated lagoon and planted overland flow system
Aerated lagoon
HRT: 1.33 d
Pumped polluted water from Wulo creek
245 cmd
Planted overland flow system
Effluent
Wulo Creek
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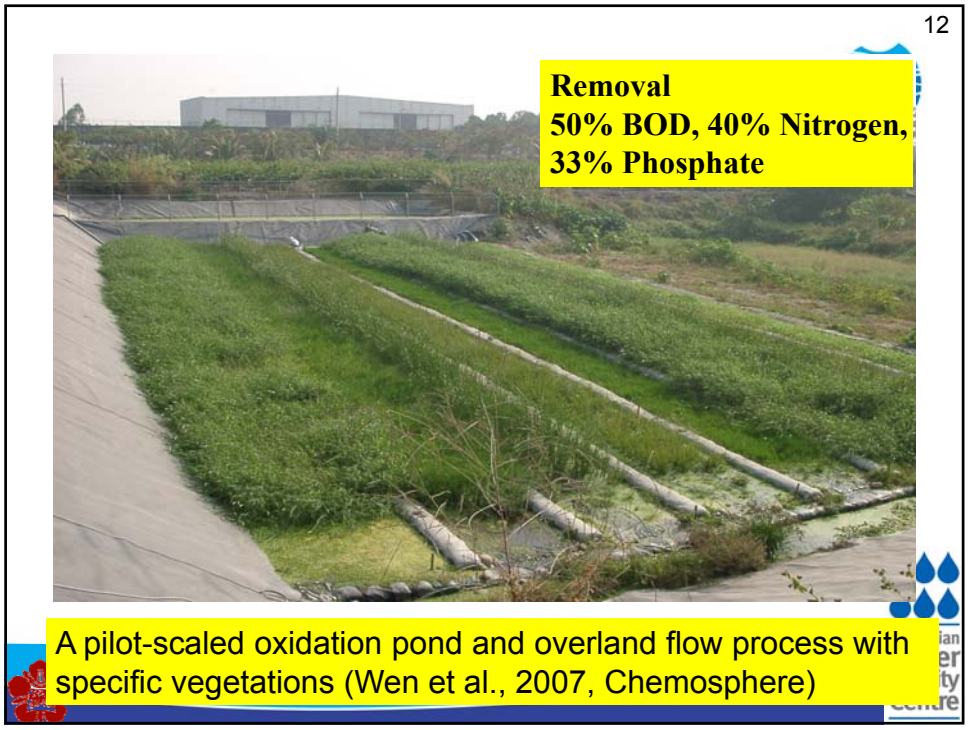
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Removal
50% BOD, 40% Nitrogen, 33% Phosphate
A pilot-scaled oxidation pond and overland flow process with specific vegetations (Wen et al., 2007, Chemosphere)

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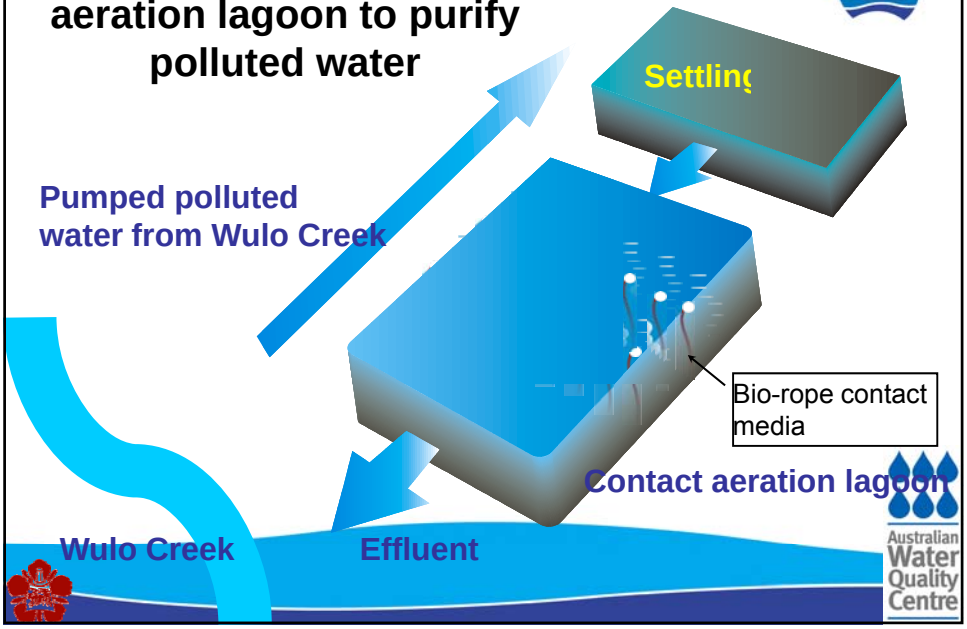
A pilot test of contacted aeration lagoon to purify polluted water



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A pilot-scaled contacted aeration lagoon (Wen et al., 2007, International Conference on Watershed Management and Mountain River Protection and Development)

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Water Quality Monitoring- Remote Sensing

Liu, Wen and Chang

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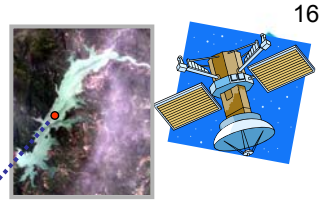
Continuous ground truth observation (CGTO) for linking remote sensing and water quality monitoring



Satellite image

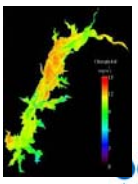
Satellite data calibration

Remotely operated vehicle (ROV) for collecting ground-truth water quality and optical data

HSSR

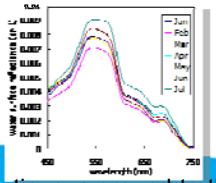
ROV

Retrieval algorithm development



Final product: accurate water quality map

The Hemi-Spherical Spectro-Radiometer (HSSR) with rotating holder



Continuous ground-truth optical data

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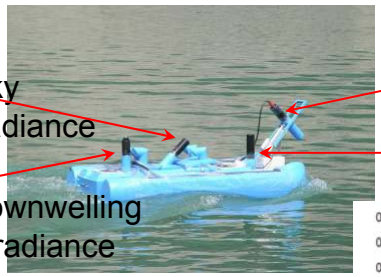
Assembling HyperSAS on ROV



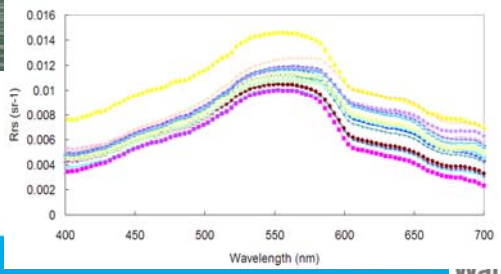
L_i: sky radiance

E_s: downwelling irradiance

Hyper Surface Acquisition System

L_T: total radiance from water surface

THS: tilt heading sensor



Remote sensing reflectance (R_{rs})

Continuous monitoring results on TW Reservoir

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Interrelationships among AOPs, in-water constituents and IOPs

$$R_{rs} = f\left(\frac{b_b}{a + b_b}\right)$$

Apparent Optical Properties
Ocean Colour
Remote sensing reflectance, Rrs

Forward Models

Inverse Models

Inherent Optical Properties
Absorption (a)
Back-scattering (b_b)

Forward Models

In-water Constituents
Phytoplankton, Detritus, CDOM, Sediment

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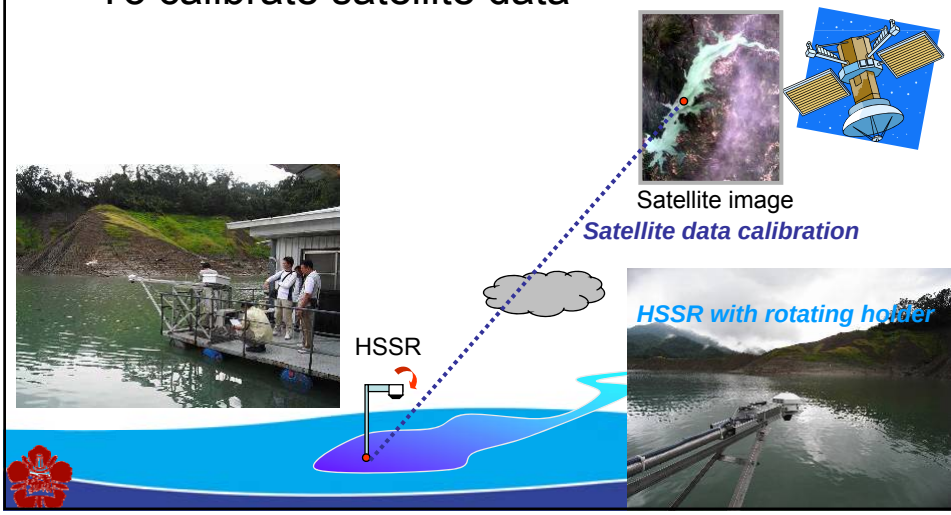
Continuous ground truth observation using Hemi-Spherical Spectro-Radiometer (HSSR)

- To calibrate satellite data



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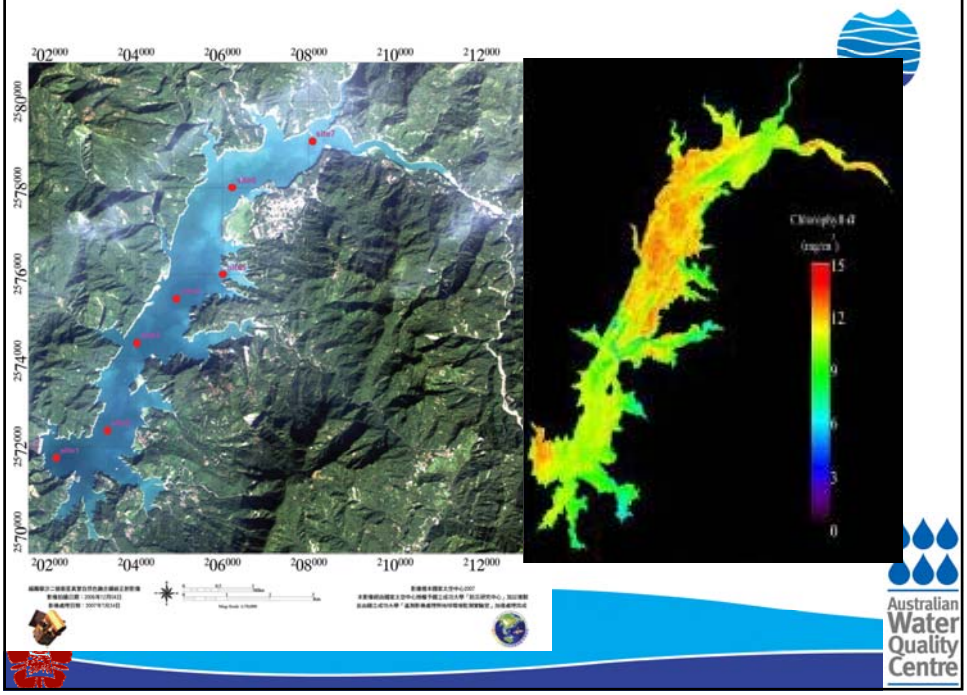

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Average Error

- Chlorophyll-a
  - 34% from water surface
  - 27% from airplane
- Suspended Solid
  - 39% from water surface
  - 70% from airplane

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Emerging Contaminants- Nitrosamines

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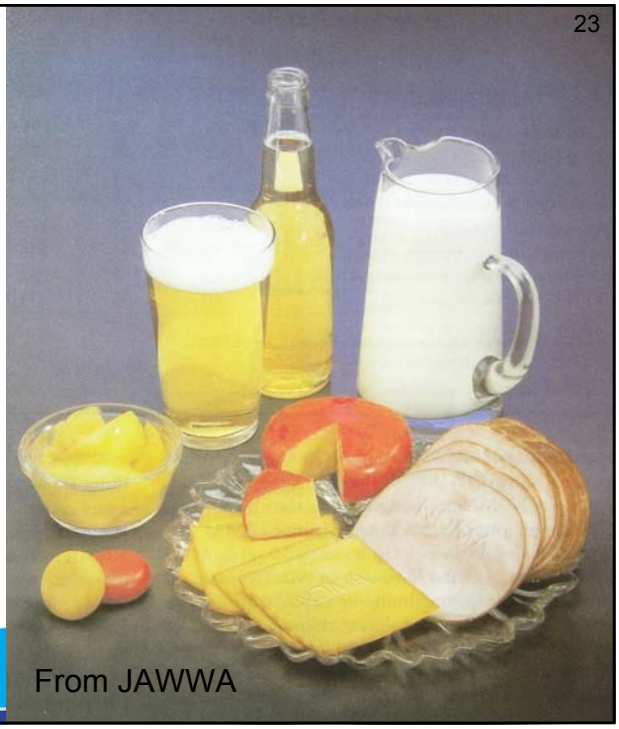
Nitrosamines

with Dr. Hung, HW @WQRC, NCKU



From JAWWA

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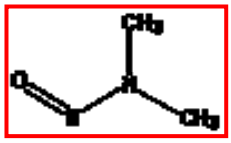
NDMA and Others

- A volatile compound
- Dissolved in water
- Difficult to be removed in conventional WTPs
- Probable human carcinogen
- Found in Drinking Water
- Local limits of NDMA (action level)
  - Ontario, Canada: 9 ng-L^{-1}
  - CA, USA: 10 ng-L^{-1}



N-nitrosodimethylamine

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Nitrosamines

Nitrosamine	Formula	MW	Carcinogenicity
N-nitrosodimethylamine (NDMA)	**$C_2H_6N_2O$**	**74**	**Liver, lung, kidney tumors in rats; liver tumors in hamsters**
N-nitrosomethylethylamine (NMEA)	$C_3H_8N_2O$	88	Liver, lung, esophagus tumors in rats; liver tumors in hamsters
N-nitrosodiethylamine (NDEA)	$C_4H_{10}N_2O$	102	Liver, esophagus, nasal cavity, kidney, forestomach, lung, and larynx tumors in rats; hamsters; guinea pgs; parakeets; and monkeys
N-nitrosopyrrolidine (NPyr)	**$C_4H_8N_2O$**	**100**	**Liver tumors in rats; lung tumors in mice; trachea tumors in hamsters**
N-nitrosopiperidine (NPip)	$C_5H_{10}N_2O$	114	Liver, esophagus, nasal cavity tumors in rats; liver, forestomach, esophagus tumors in mice; trachea tumors in hamsters
N-nitrosomorpholine (NMor)	**$C_4H_8N_2O_2$**	**116**	**Liver, nasal cavity tumors in rats; liver tumors in mice; trachea tumors in hamsters**
N-nitroso- n-dipropylamine (NDPA)	**$C_6H1_4N_2O$**	**130**	**Liver and lung tumors in rats**
N-nitrosodi- n-butylamine (NDBA)	$C_8H_{18}N_2O$	158	

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Methods of Analysis

- Quantified using GC/Positive chemical ionization MS
- Pre-concentration: Conventional Method
  - Liquid-liquid or Solid-phase extraction +
  - Large sample volume
  - Solvents, time-consuming
  - Need 1 day to obtain results
- This study
  - Head space solid-phase microextraction (HSSPME)
  - 1.5 hr SPME + 30 min GC/MS

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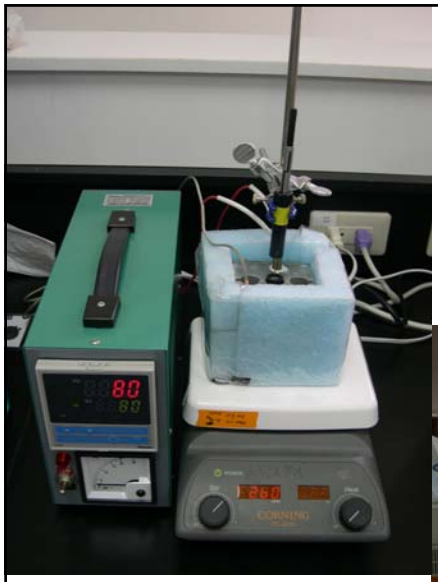

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Parameters for the Analysis of Nitrosamines

segment (min)	nitrosamines	retention time (min)	collision-induced dissociation (volt)	parent ion (*m/z*)	quantification ion (*m/z*)
0-11	Filament/ multiplier delay	-	-	-	-
11-13	NDMA	12.1	0.45	75	44, 47, 58
	NDMA-d_6	12.1	0.43	81	50
13-16	NDEA	14.7	0.40	103	75
16-17.6	NDPA-d_{14}	17.4	0.40	145	97
	NDPA	17.5	0.40	131	89
17.6-18.5	NMor	17.8	0.42	117	86

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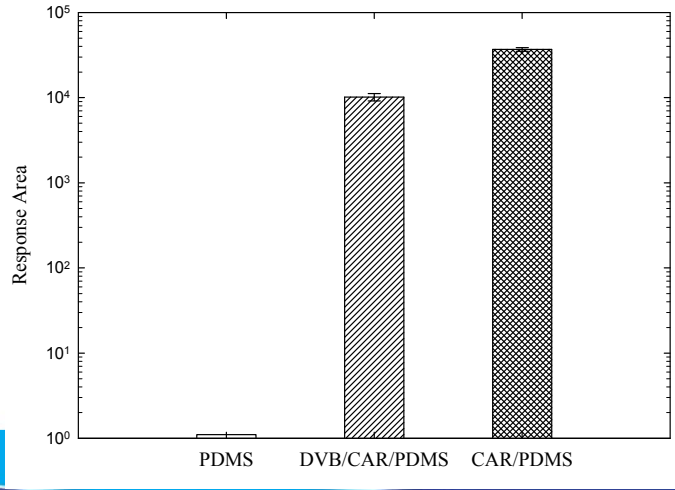
Extraction efficiency of different fibers

(100 ng/L NDMA, Extraction @60min, Temp @85°C)



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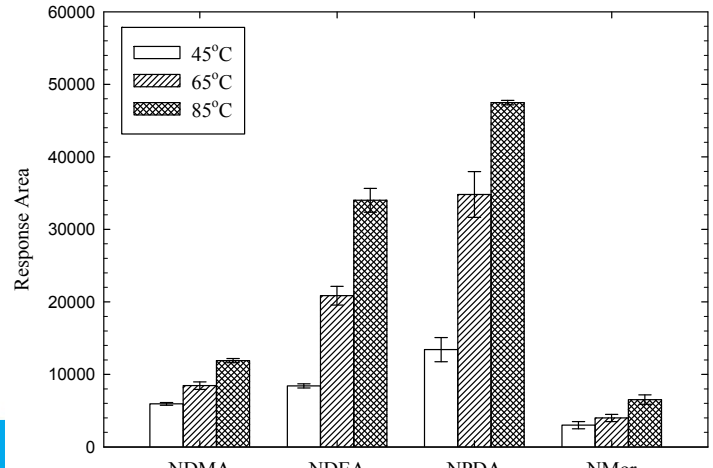
Extraction efficiency of different temp.
(Extraction @60min, CAR/PDMS)



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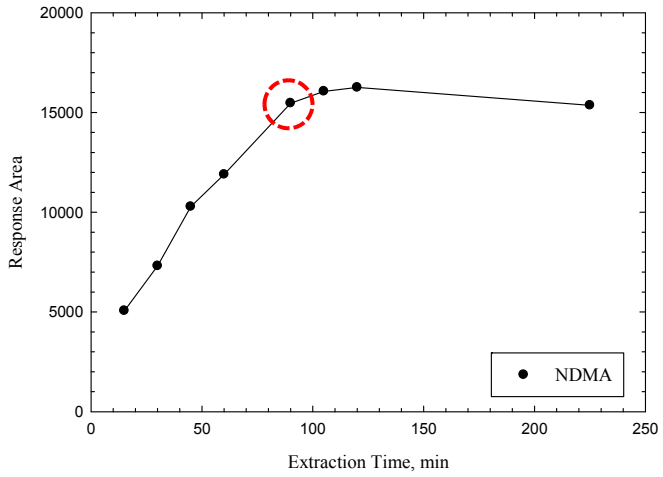
Extraction efficiency at different time (100 ng/L NDMA,Temp @85°C)



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Method Recovery

analyte	SS procedure [a] average accuracy (%) (RSD %)	SS procedure [a] range (%)	IS procedure [b] average recovery (%) (RSD %)	IS procedure [b] range (%)
NDMA-d_6	-	-	109.8 (10.1)	83-118
NDMA	99.7 (9.3)	92-110	99.2 (7.5)	95-107
NDEA	99.4 (3.3)	101-108	97.6 (14.7)	83-112
NDPA	101.3 (15.9)	92-120	96.8 (4.4)	93-101
NMor	106.3 (9.5)	99-122	96.5 (11.6)	84-106

[a] surrogate standard of NDMA-d_6 was spiked at 50 ng/L; [b] internal standard of NDPA-d_{14} was spiked at 20 ng/L.

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Summary for Nitrosamines

- A HSSPME/GC/MS-MS method was developed for the determination of NDMA and other nitrosamines in drinking water
- The detection limit is < 5 ng/L (~ 3 ng/L) for NDMA
- Only small sample volume (4.5 mL) is needed and the results can be obtained within 2 hrs
- The method was successfully employed in analyzing field water samples.
- NDMA > 10 ng/L in some of finished water in Taiwan.

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Preoxidation of Cyanobacteria-Cell Integrity and Metabolite Release

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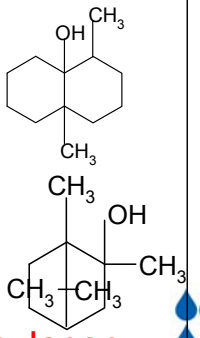
Odorants- Musty and Earthy

- Most commonly observed in DW
- Geosmin: trans-1,10-dimethyl-trans-9-decalol
  - $C_{12}H_{22}O$
  - MW = 182
- 2-MIB: 2-methylisoborneol
  - $C_{11}H_{20}O$
  - MW = 168
- Odor Threshold Concentration
  - ~ 5-10 ng/L
- Drinking Water Standard = 10 ng/L in Japan



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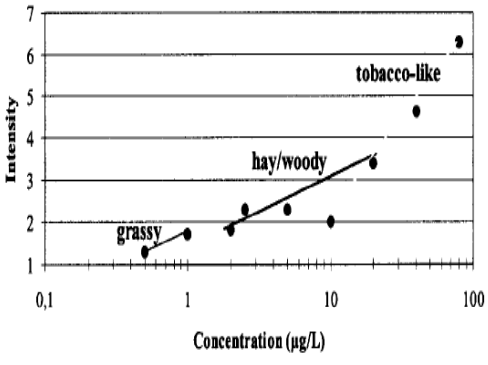
β-cyclocitral



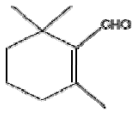


Figure 3. Weber-Fechner plot from FPA for β-cyclocitral.

Source: Young et al. (1999), Identification of a Woody-Hay odor-causing compound in a Drinking water supply.

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Objectives

- To understand the effect of oxidation on the disruption of cyanobcteria cells and their release of metabolites in drinking water treatment plants

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Cell Integrity Determination

- Flow Cytometer
- Epifluorescence Microscope
- With Dyes
  - FDA for cell membranes (Live Cells)
  - Sytox for damaged cells (Dead Cells)
  - Chlorophyll-a for Cyanobateria

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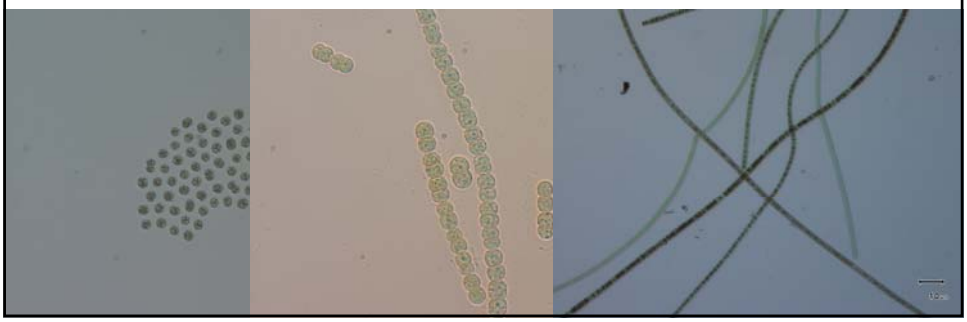
Cyanobacteria Tested

- *Microcystis aeruginosa* (PCC7820)
  MC-LR and β-cyclocitral
- *Anabaena circinalis* - Geosmin
- *Planktothrix raciborskii* – 2-MIB



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RESULTS AND DISCUSSION

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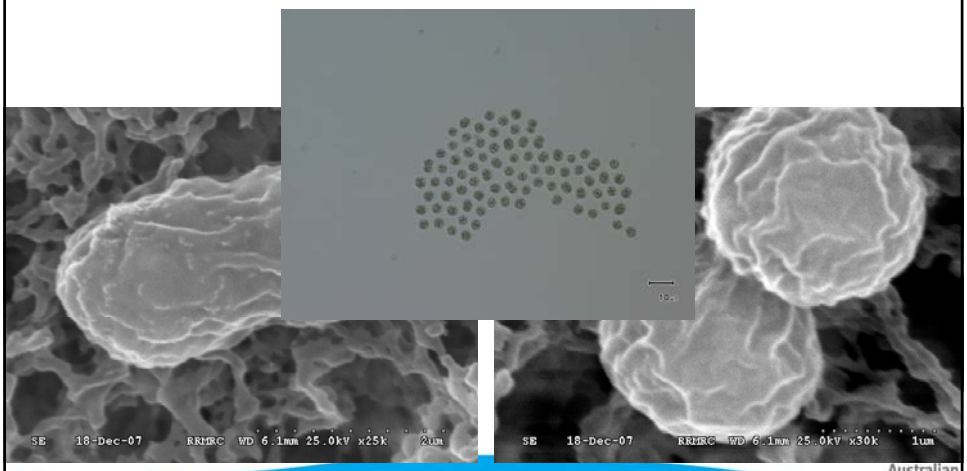
SEM Microphotos of *Microcystis*
(Before Oxidation)



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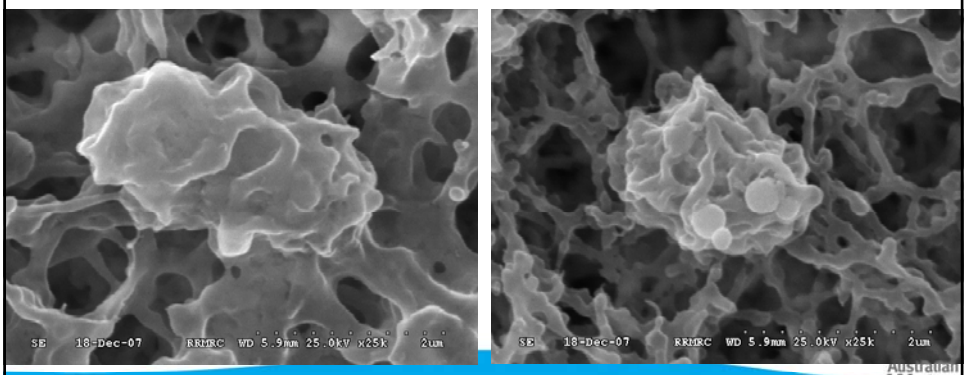
SEM Microphotos of *Microcystis*
(After Chlorination @ 2mg/L and 30 min)



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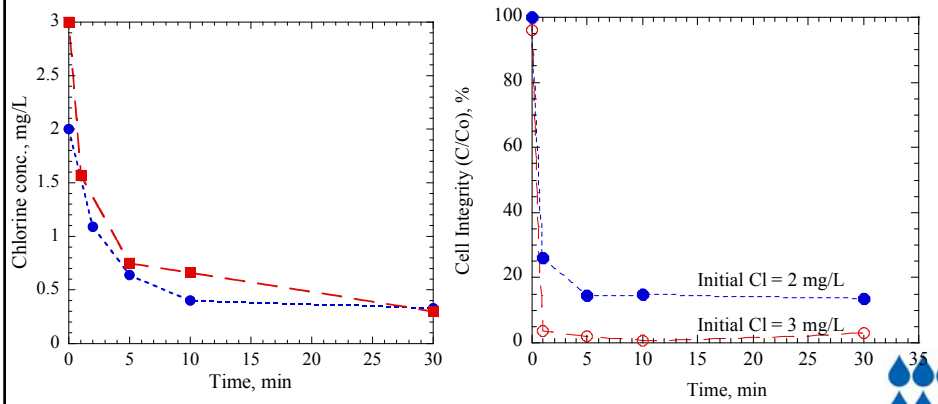
Oxidation of *Microcystis*
(~1,100,000 cells/mL)



Residual chlorine reached constant at 5-10 mins
85-95% cells was ruptured within 5 mins

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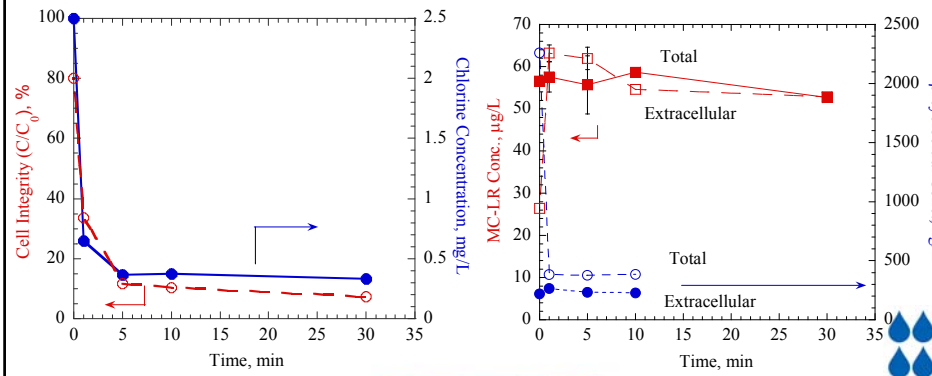
Concentration change of metabolties
(1,100,000 cell/mL)

Initial chlorine conc. 2 mg/L



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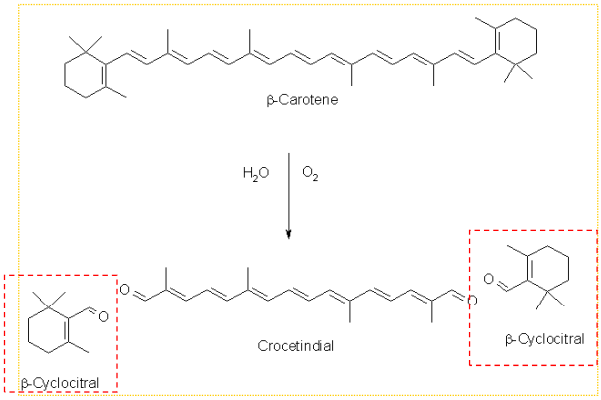
Production of β-cyclocitral



Source: Juttner (1985), Evidence of β- carotene 7,8 (7',8') oxygenase (β-cyclocitral, crocetindial generating) in *Microcystis*

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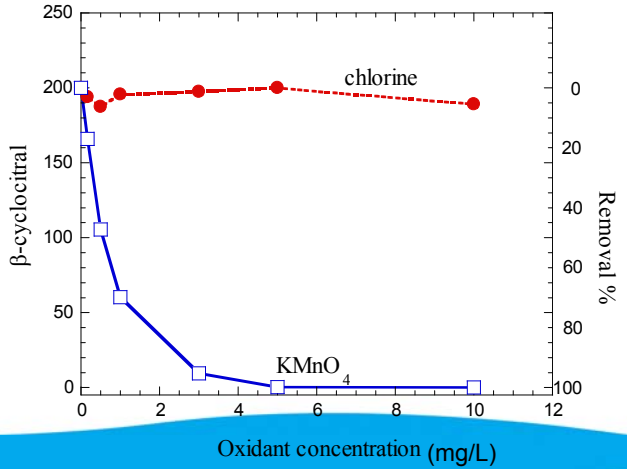
Oxidation of β-cyclocitral



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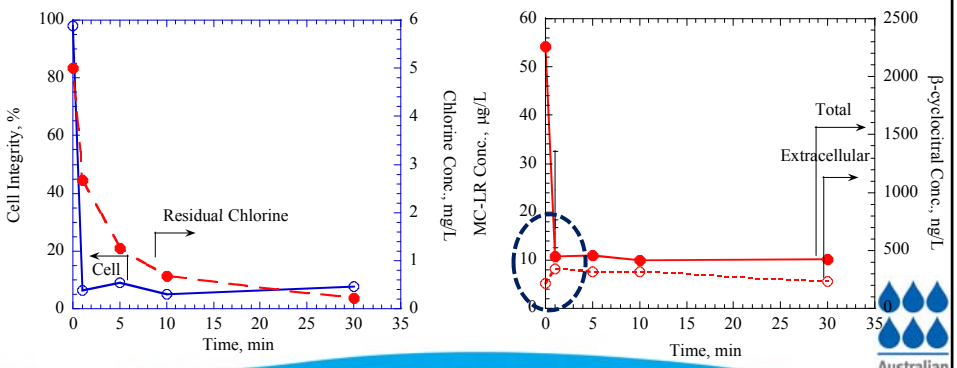
Concentration change of metabolites
(1,100,000 cell/mL)

Initial chlorine conc. 5 mg/L



Chlorine damaged the cells and inhibited the enzymes

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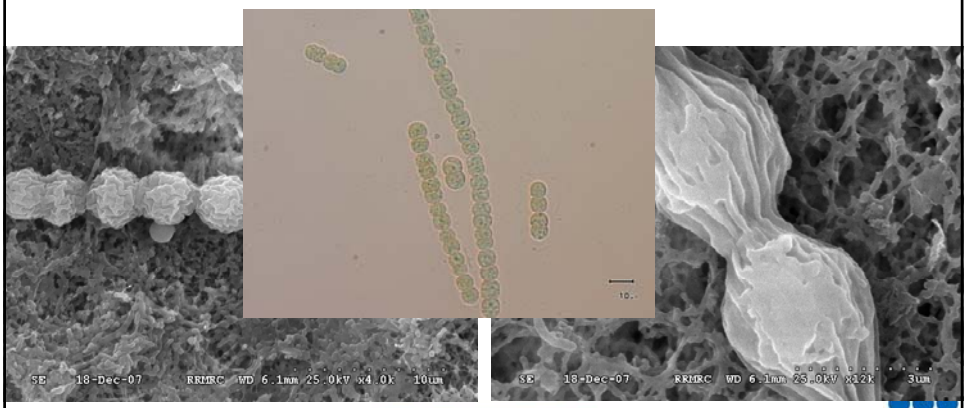
SEM Microphotos of *Anabaena*
(Before Oxidation)



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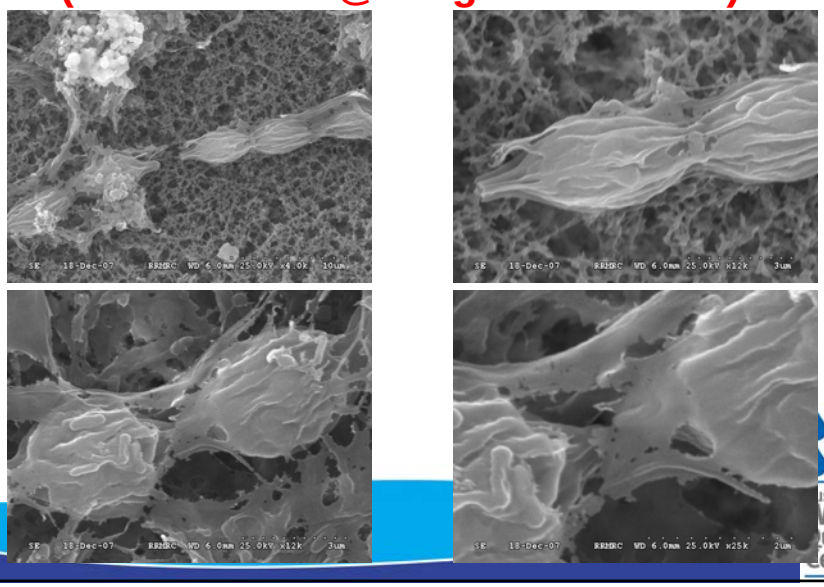
SEM Microphotos of *Anabaena*

(Chlorination @ 1mg/L and 1 min)



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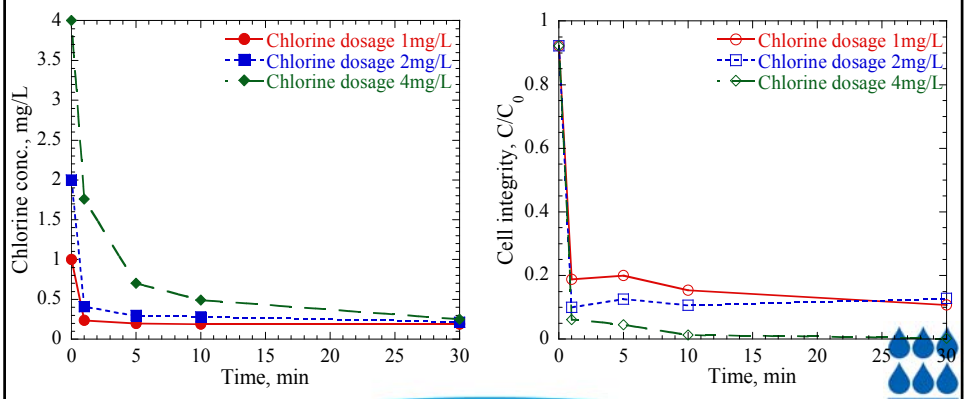
Oxidation of *Anabaena*

(550,000 cells/mL)



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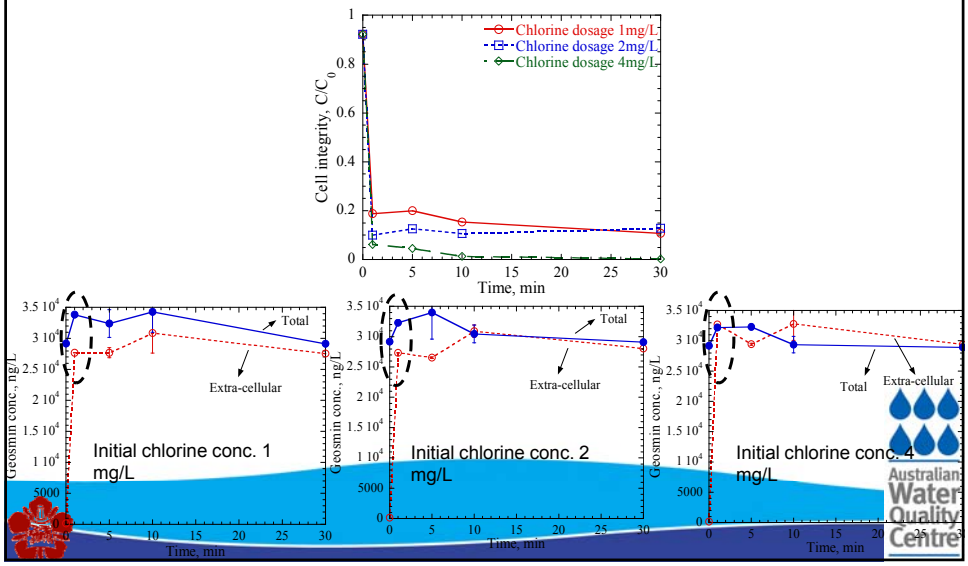
Concentration change of Geosmin (550,000 cell/mL)



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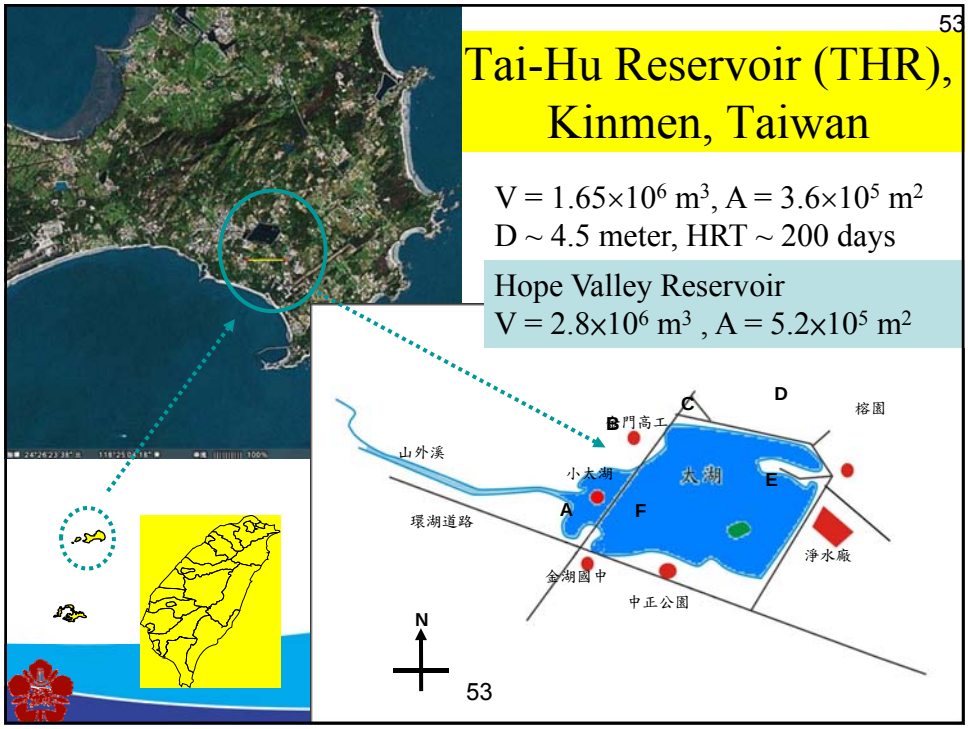
Anabaena: Cell Rupture

Anabaena Conc., cells/mL	Initial Chlorine Conc., mg/L	Reaction Time, min	Cell Integrity, %
60,000	1	1	19
	2	1	10
3,200,000	**2**	**2**	**65**
For *Microcystis*	3	2	45
	4	2	3
3,300,000	1	1	25
	2	1	18
	4	1	9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Tai-Hu Reservoir (THR), Kinmen, Taiwan
V = 1.65×10^6 m^3, A = 3.6×10^5 m^2
D ~ 4.5 meter, HRT ~ 200 days
Hope Valley Reservoir
V = 2.8×10^6 m^3 , A = 5.2×10^5 m^2
A
B
C
D
E
F
太湖
小太湖
山外溪
環湖道路
金湖國中
中正公園
淨水廠
榕園
N
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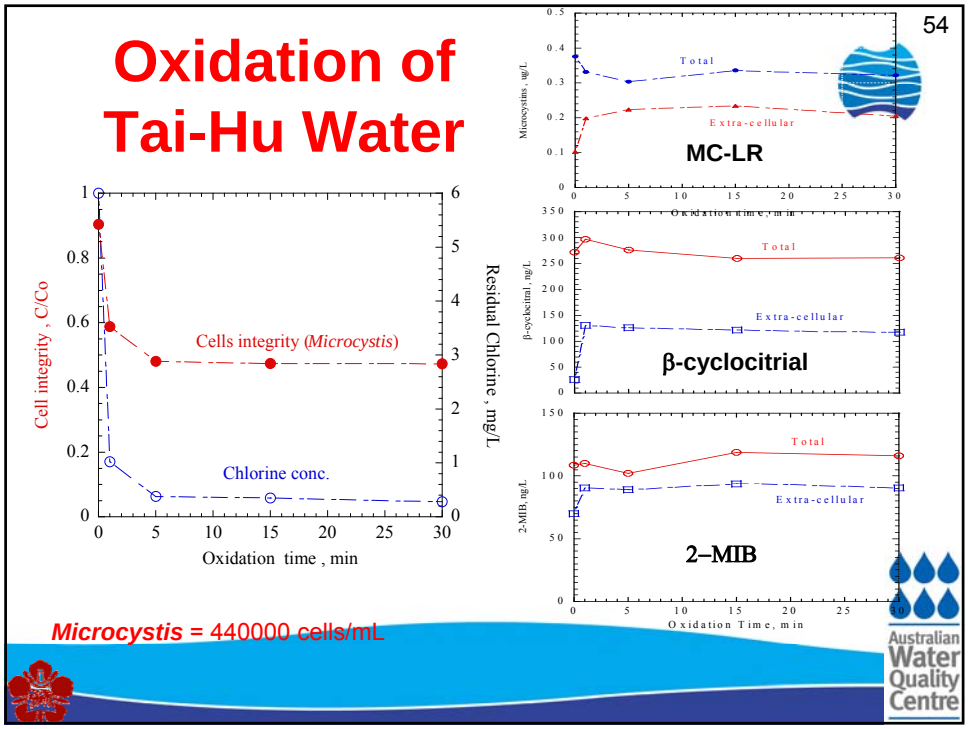
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Oxidation of Tai-Hu Water
Cell integrity , C/Co
Residual Chlorine , mg/L
Cells integrity (Microcystis)
Chlorine conc.
Oxidation time , min
Microcystis = 440000 cells/mL
Total
Extra-cellular
MC-LR
β-cyclocitrial
2–MIB
Oxidation Time, min
Australian Water Quality Centre

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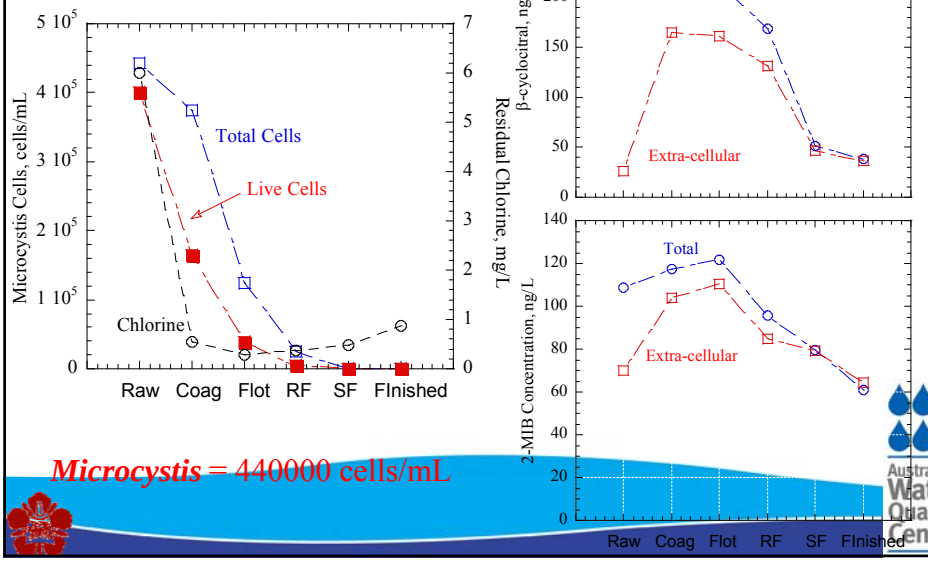
Tai-Hu WTP



Microcystis = 440000 cells/mL

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Conclusions

- Cyanobacteria cells are very fragile to chlorine and ozone
- Order: Anabaena, Microcystis, then Plankthrix
- CT value to damage cells depends on cyanobacteria types and cell concentrations
- Once metabolites released, geosmin, MIB are very resistant to chlorine
- MIB may be destructed by ozone
- β-cyclocitral oxygenase may be inhibited by chlorine and ozone, causing lower b-cyclocitral concentrations

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