Odorous Compounds in Wastewater Effluent

identification, occurrence and impact on potable water reuse

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PUB
Water for All : Conserve, Value, Enjoy

de facto Indirect Potable Water Reuse

…occurs wherever treated municipal effluent is discharged into a body of water which serves as public drinking water source at a downstream location.

"effluent-impacted" "effluent-dependent" "effluent-dominated"

Trinity River, Fort Worth, TX [Fono et al., *ES&T*, 2006]

South Platte River, Denver, CO [Bradley et al., *Wat. Resource Res.,* 1995]

Santa Cruz River, Tucson, AZ [Duran & Spencer, *SW Hydrol.* 2004]

Rivers Humber and Wear, England [Jarvie et al., *Sci. Tot. Env.*, 2006]

Osaka River, Japan [Yamamoto, *Env. Poll.,* 1996]

Waskana Creek, Canada [Waiser et al., *Env. Tox. Chem*., 2011]

Notwane River, Botswana [Mladenov et al., *Env. Monitor. Assess*., 2005]

and many more…

Planned Potable Water Reuse

With **advanced treatment** of municipal effluent:

reverse osmosis, deep-bed filtration, UV disinfection, advanced oxidation processes (AOPs), chlorination

Direct Windhoek, Namibia

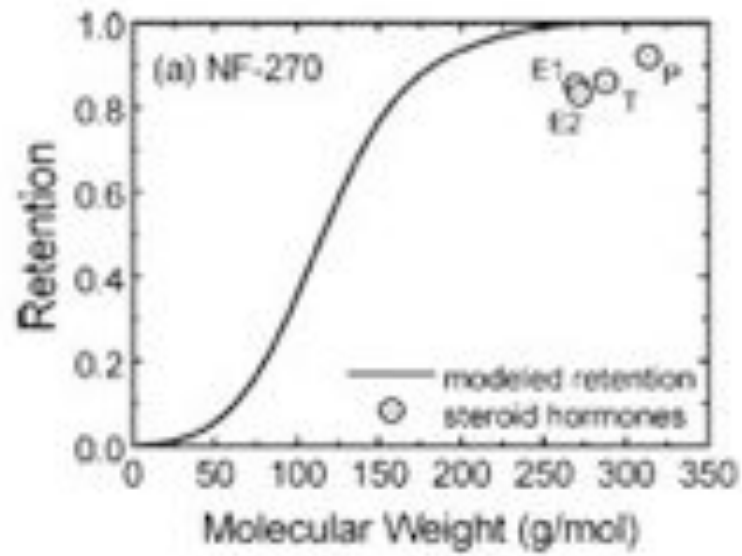
Indirect

Asia	Singapore, Korea
Australia	SE Queensland, Newcastle (NSW), Canberra
US	Southern California, Nevada, Arizona, Florida
Europe	London (England), Veurne (Belgium)

Incomplete Rejection by RO

Apparent % rejection by RO decreases around and below the nominal MW cutoff of ~200 Da.

Bellona et al., *Wat. Res.* 2004



Nghiem *et al*., ES&T, 2004

Reported in the literature:

COMPOUNDS	MW (Da)	%R	
Estrogenic hormones	270-314	80%	Nghiem *et al*., ES&T, 2004
NDMA	74	10-50%	West Basin MWD, WRF 2006
Trihalomethanes	119-252	50-80%	Agus & Sedlak, Water Res., 2010 Agenson *et al*., J Membrane Sci, 2003 Magara *et al*., Water Sci. Tech, 1996

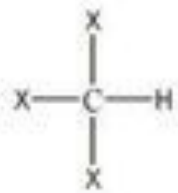
DBPs in Pilot Desalination Plant

Chlorine is used as pretreatment against membrane biofouling.

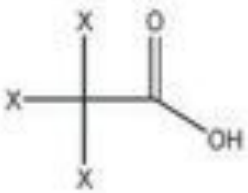
Monitored intake, feed, permeate and concentrated between 2007-2008.

Bromine-substituted DBPs were dominant due to high-salinity and Br content of seawater.

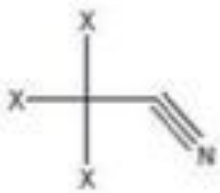
Carlsbad, CA. May 2008



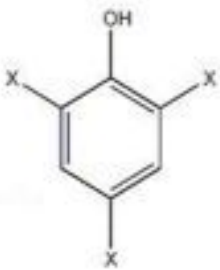
Trihalomethanes



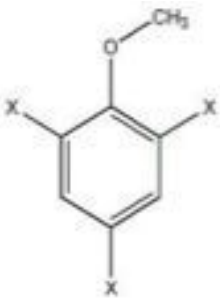
Haloacetic Acids



Haloacetonitriles

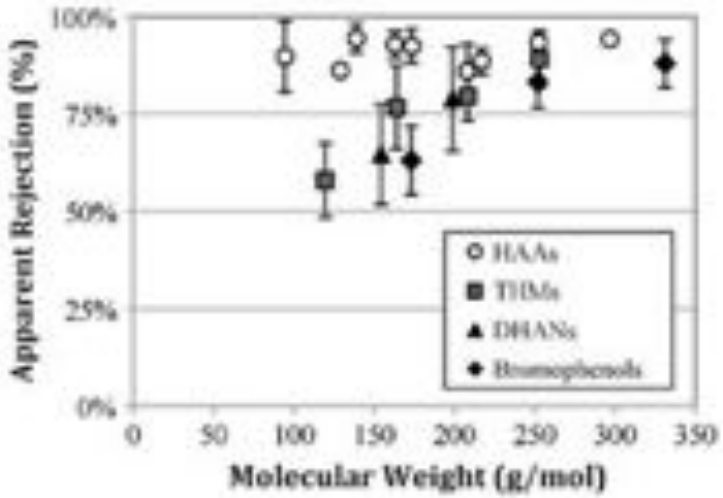


Halophenols



Haloanisoles

Rejection vs MW

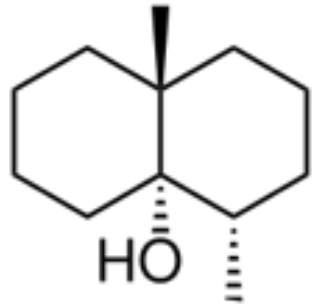


Agus & Sedlak, *Wat. Res.* 2010

For neutral organic compounds, apparent RO rejection rates decrease below the molecular weight cutoff value of 200 Da.

Bellona et al., *Wat. Res.* 2004

DBPs MW range: 94 – 344 Da



Geosmin

MW = 182 Da

no pK_a

log K_{ow} = 2.85

Odor Threshold = 1-10 ng/L

Many potent odorant identified in water have characteristics that indicate incomplete rejection by RO:

low MW, uncharged at circumneutral pH, moderately hydrophobic.

Odorants in Potable Water Reuse

What are they?

Can we describe their odors?

Can we quantify them?

Can we get rid of them?

Framework for Identification

Sniffing panel (FPA) flavor profile analysis by sensory panel per AWWA Standard Method 2170B	Overall odor of water
SPE-GC-MS/Olf solid phase extraction for gas chromatography with full-scan mass spectrometry and olfactory port detection	Characteristic odor peaks
SPE-GC-MS/SIM solid phase extraction for gas chromatography with single ion monitoring mass spectrometry detection	Target odorants

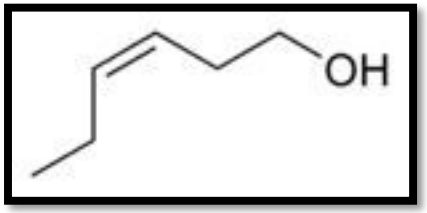
Flavor Profile Analysis

sniffing panel

"grassy"

0 1 2 3 4

none maybe weak mod strong



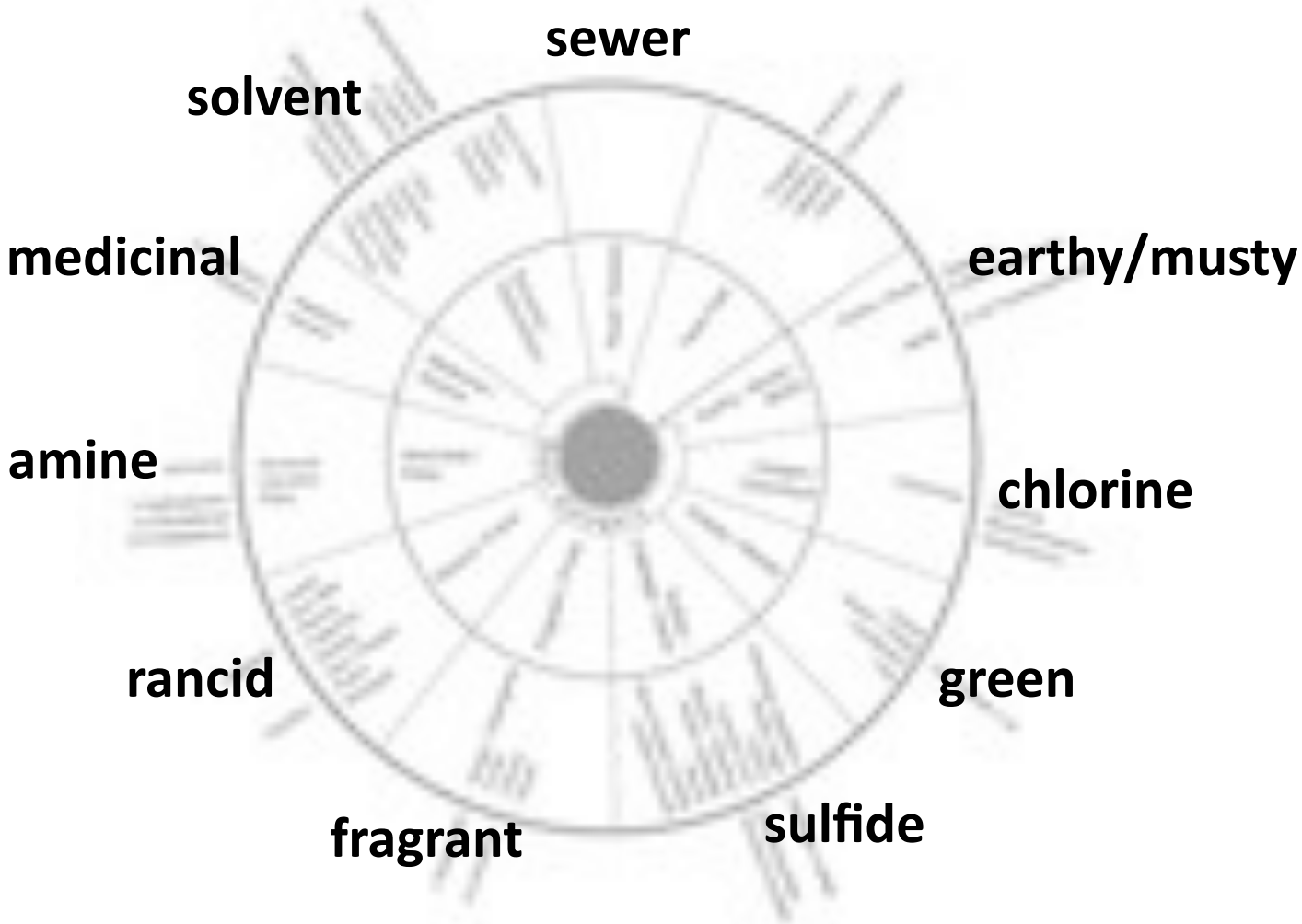
odor reference
cis-3-hexen-1-ol
500 μg/L

Based on Standard Method 2170B:

4-5 trained panelists sniff whole samples at 50°C then recording intensity rating and descriptors according to "calibration" and odor references.

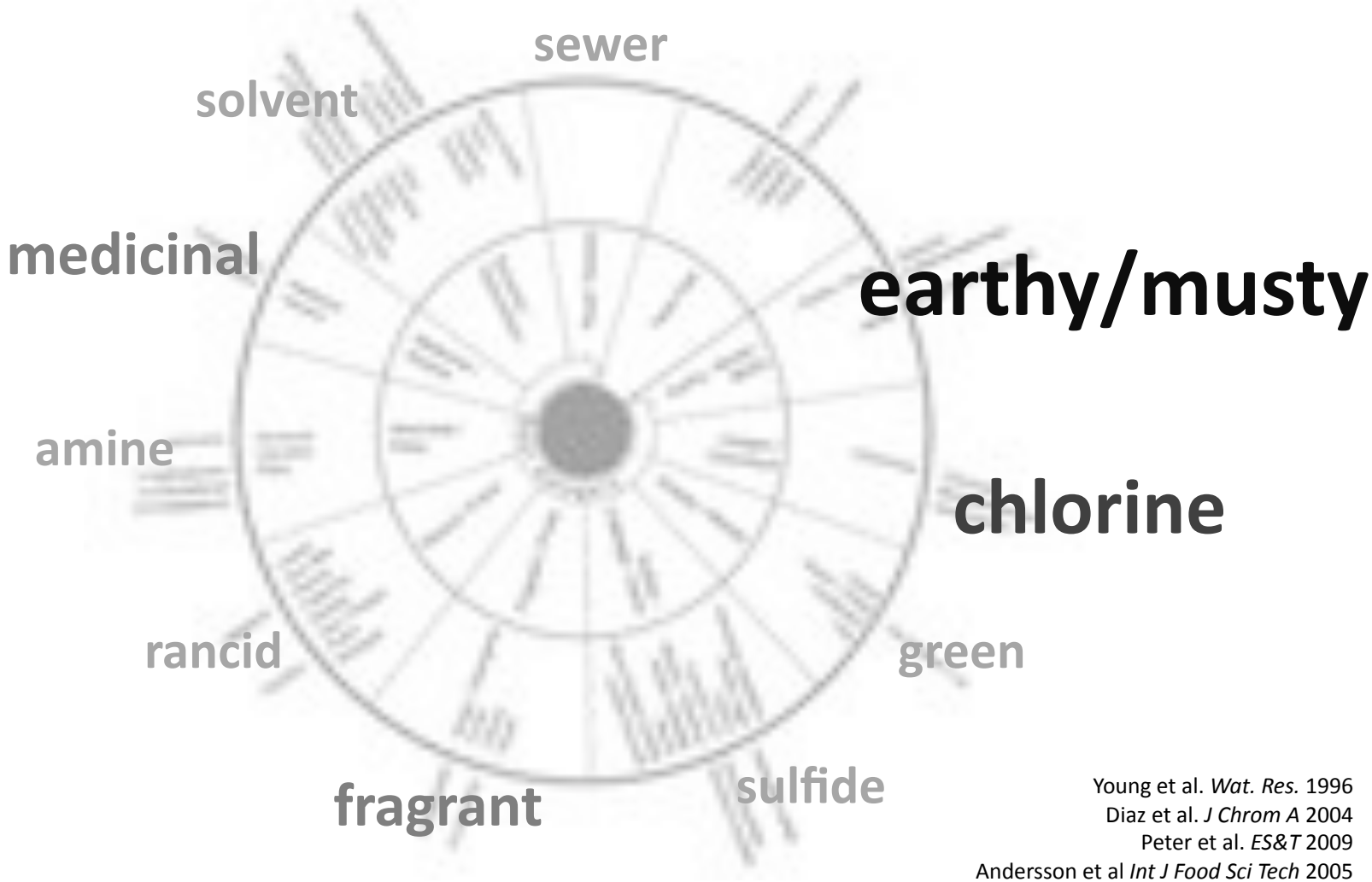
Odor references are based on 2170B and odor wheel.

Water Odor Wheel



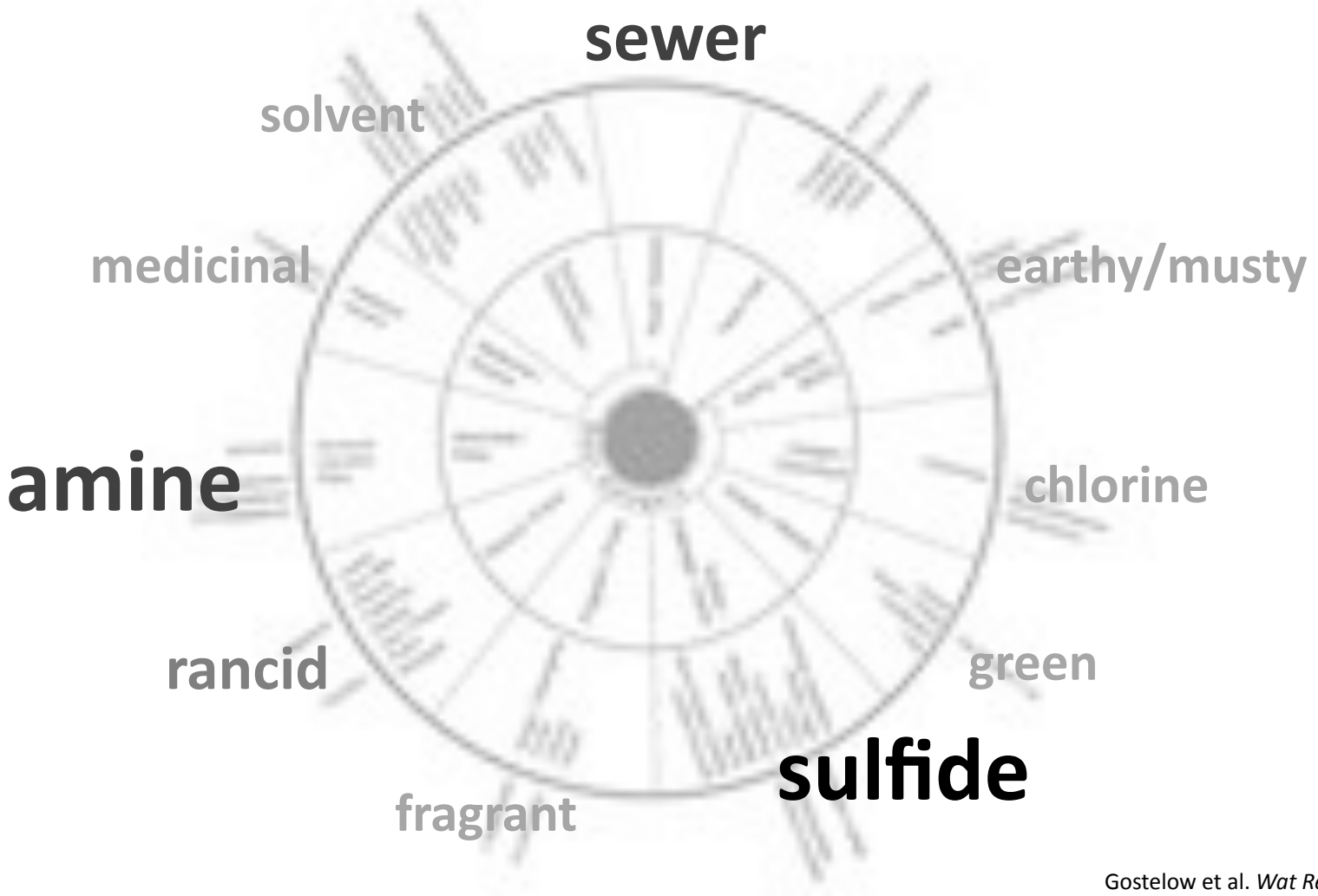
Burlingame et al. *Wat. Sci. Tech* 2004

Drinking Water Odor Wheel



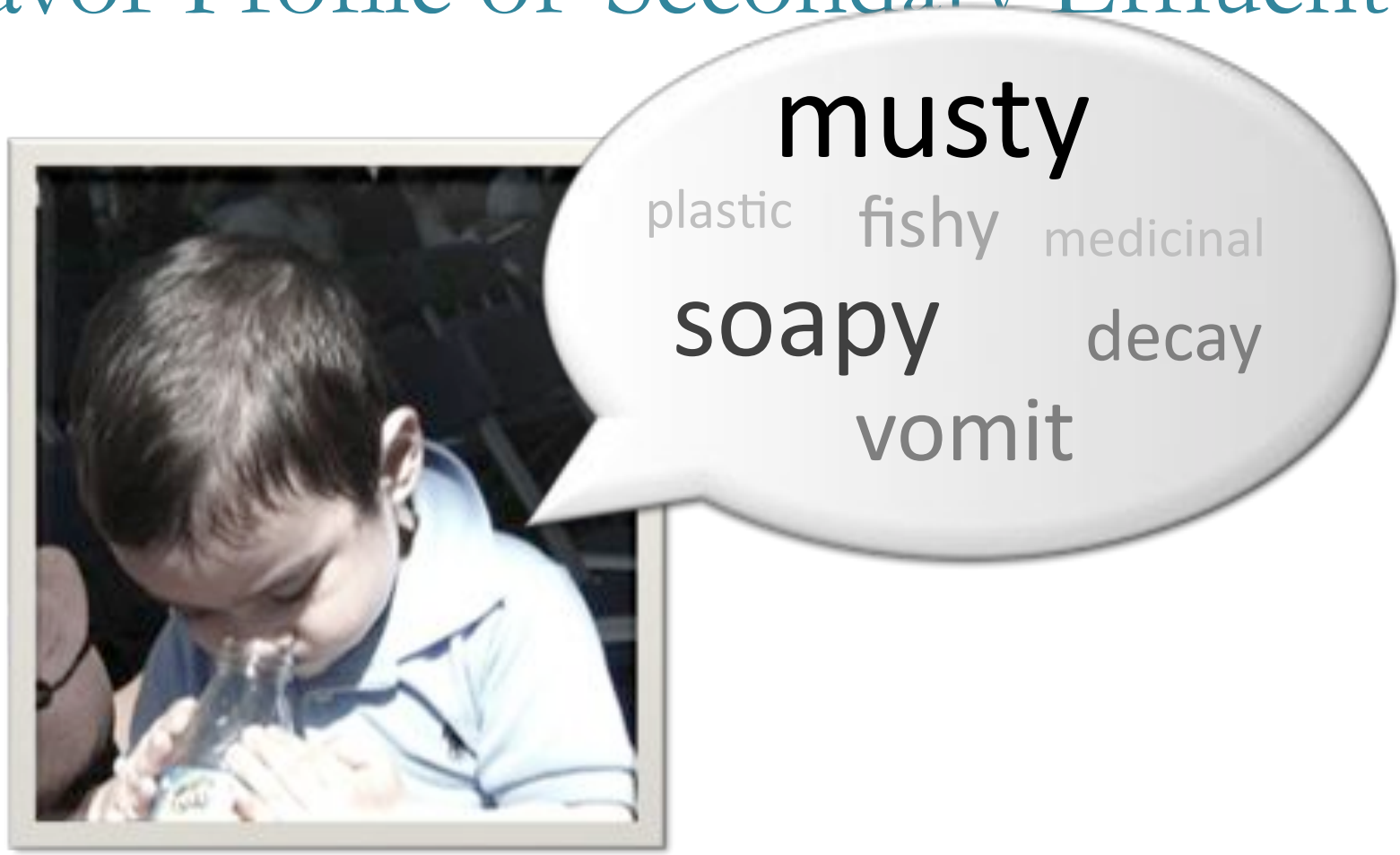
Young et al. *Wat. Res.* 1996
Diaz et al. *J Chrom A* 2004
Peter et al. *ES&T* 2009
Andersson et al *Int J Food Sci Tech* 2005
Burlingame et al. *Wat. Sci. Tech* 2004
Piriou et al. *Wat. Sci. Tech* 2001

Wastewater Works Odor Wheel



Gostelow et al. *Wat Res* 2001
Burlingame et al. *Wat. Sci. Tech* 2004
Lambert et al. *Wat. Sci. Tech* 2000
Stuetz et al. *Wat Res* 1999

Flavor Profile of Secondary Effluent



** not an actual trained panelist*

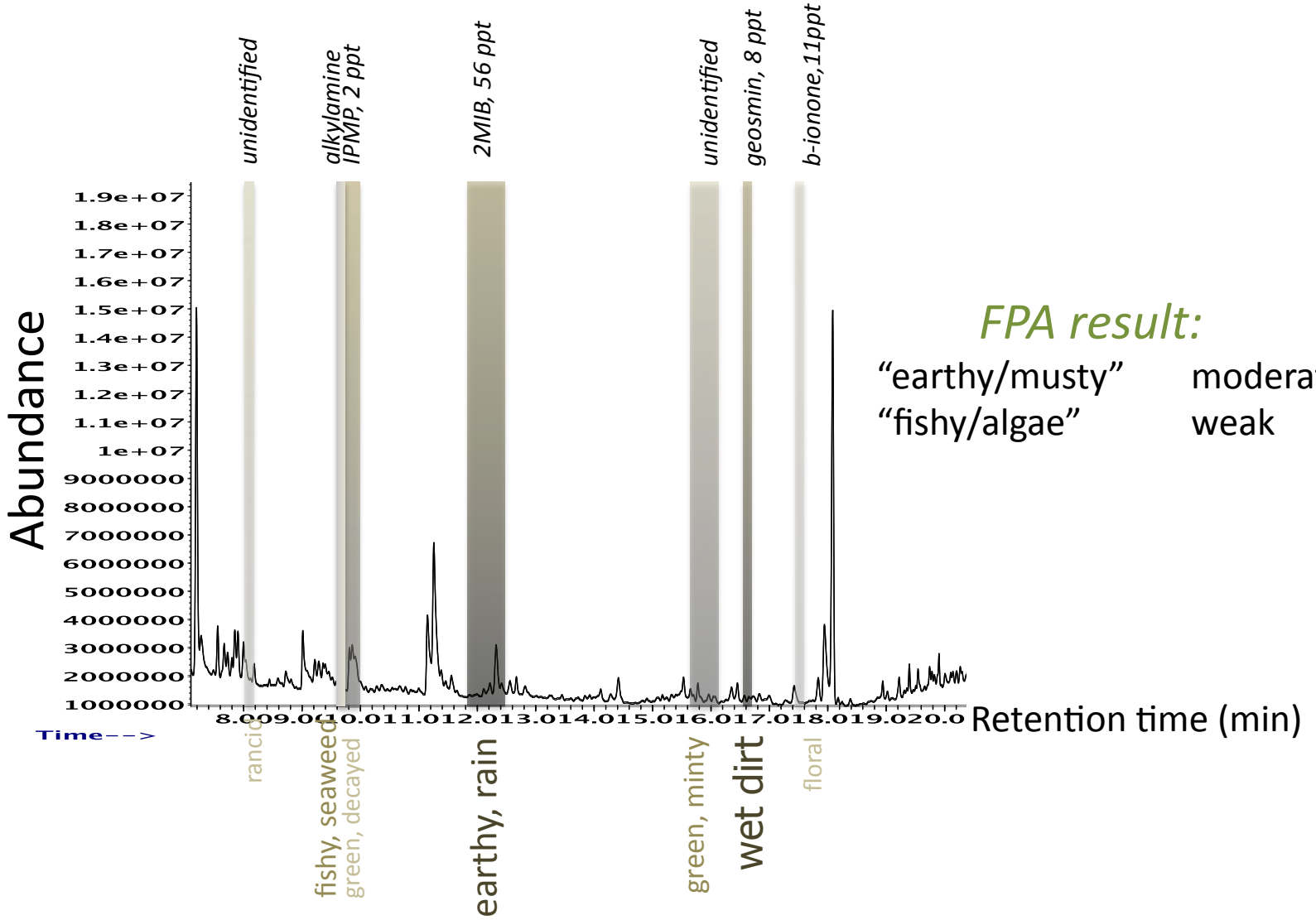
GC-MS/Olfactometry

Screened for ability to sniff and describe odors:

non-smoker	no allergies/sinus congestion
wears no fragrance	food restrictions
good verbal skills	no anosmia/hypersensitivity

Trained to detect odor peaks at specific retention times.

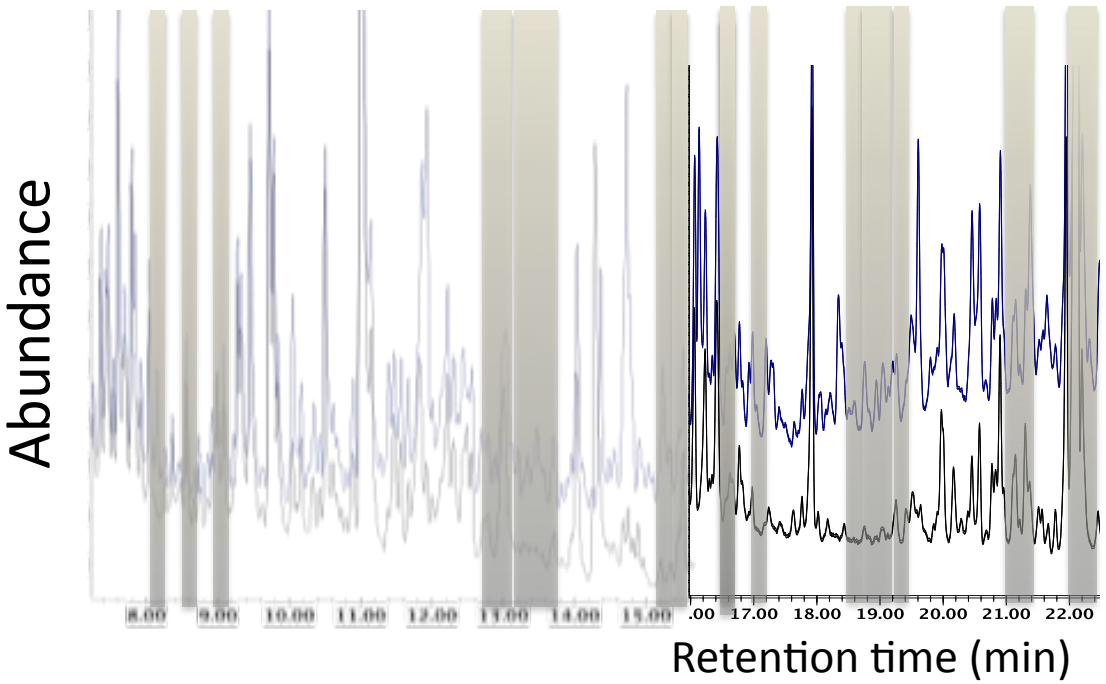
Olfactogram of Reservoir Water



FPA result:

"earthy/musty"	moderate
"fishy/algae"	weak

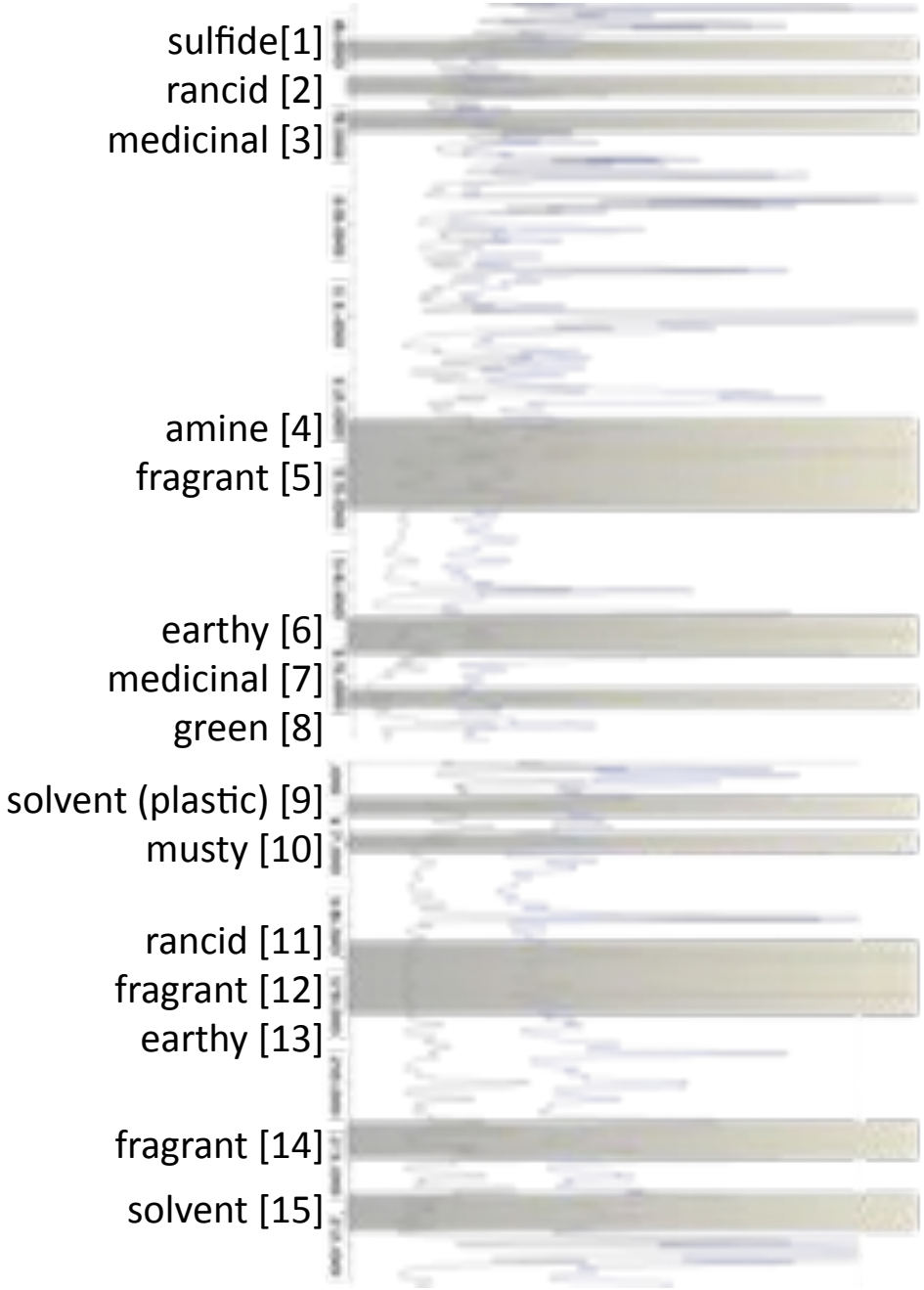
Olfactogram of Secondary Effluent



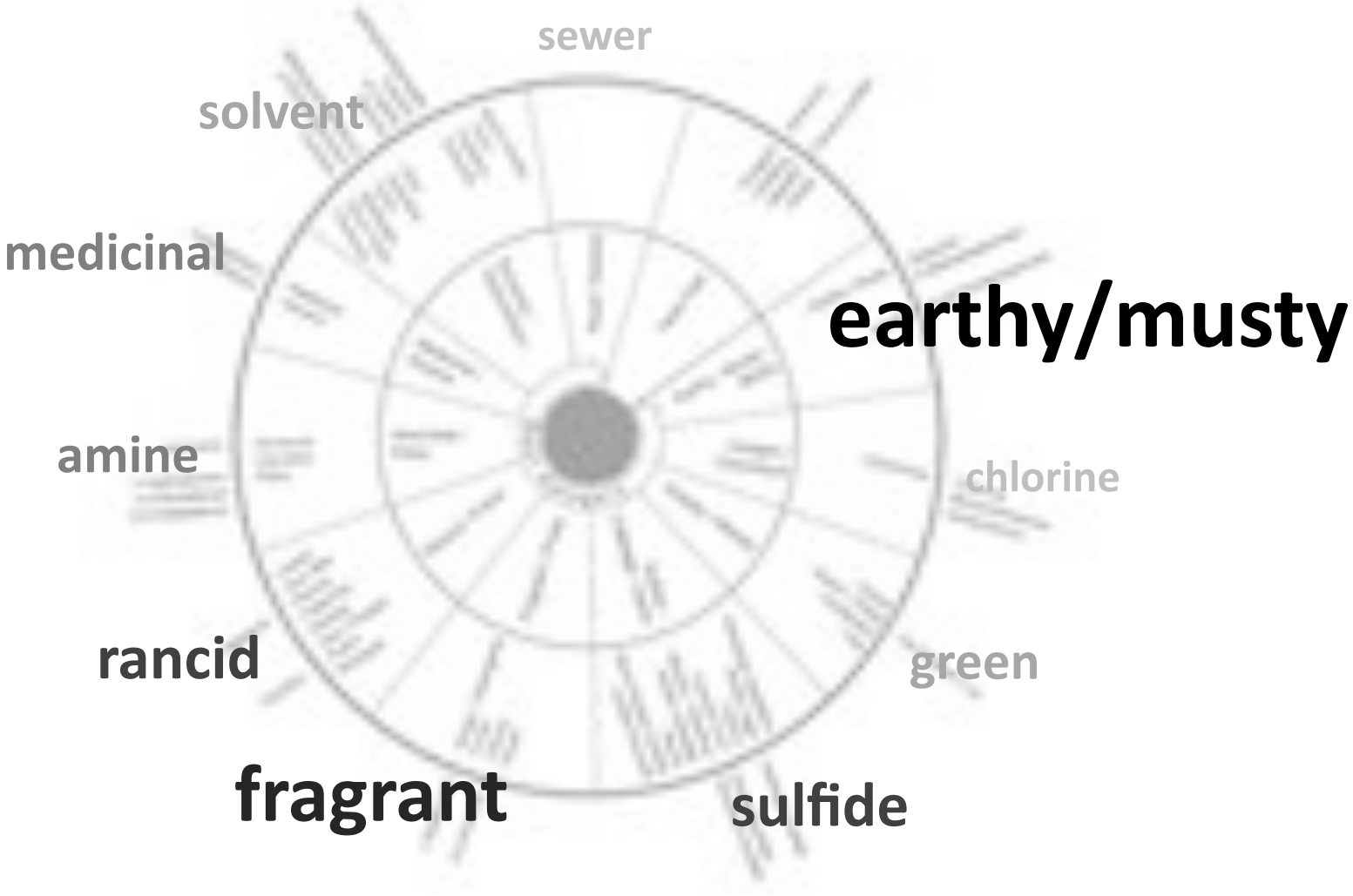
FPA results:

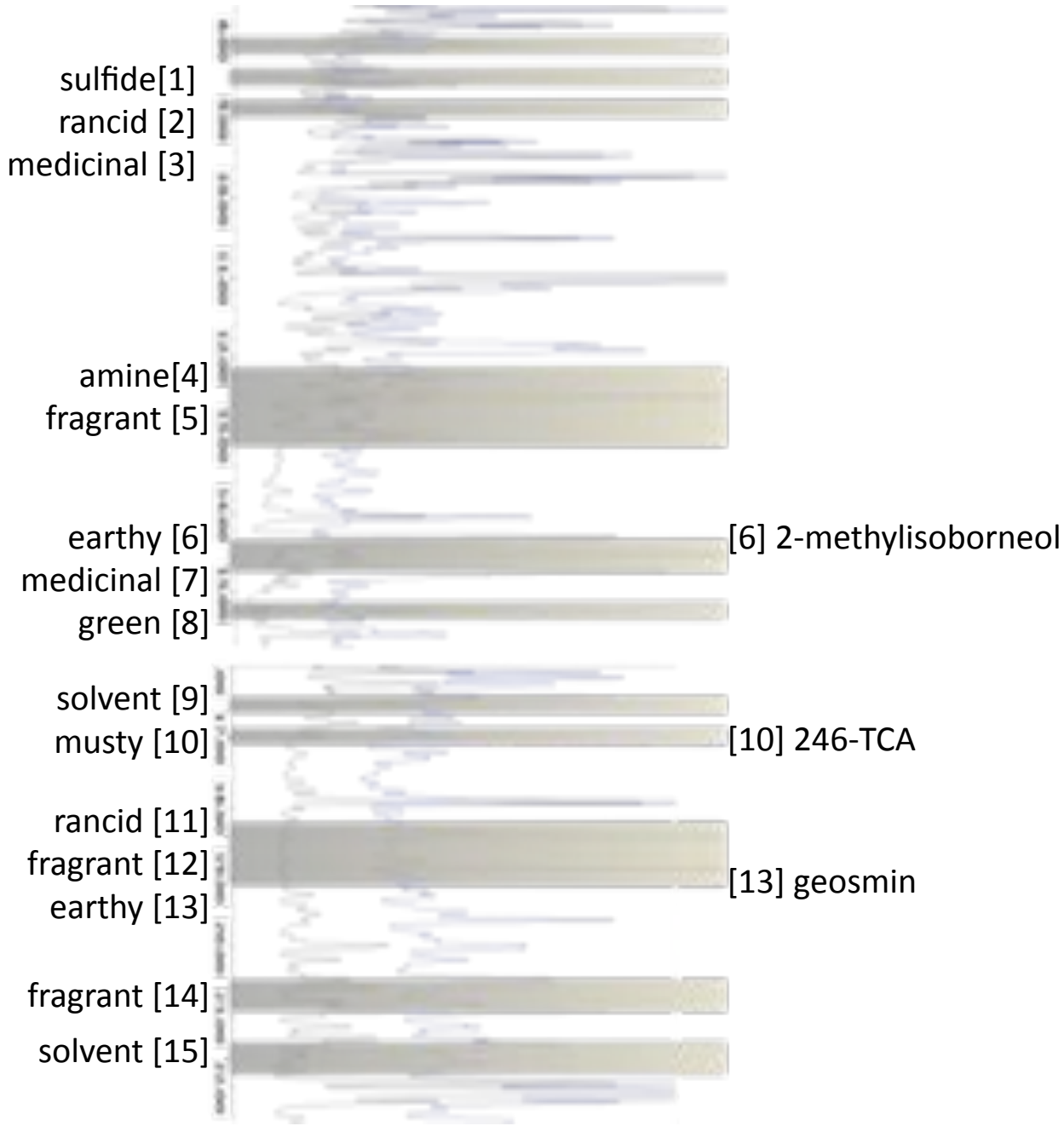
"musty"	strong
"soapy"	moderate

garlic, skunk [1]
gym socks, sweat, rancid [2]
medicinal, fresh paint [3]
rubber, urine, public toilet [4]
caramel, burnt, nougat [5]
rain, grassy, earthy, mothballs [6]
alcohol, clean, bandages [7]
IKEA, woody, forest [8]
corn tortilla, Barbie™, plastic [9]
old cupboard, basement, moldy [10]
sour milk, feta, vomit [11]
fruity, sweet, jasmine, soap [12]
wet dirt, rain [13]
picnic, pine, liqueur [14]
candle, wax, burnt [15]

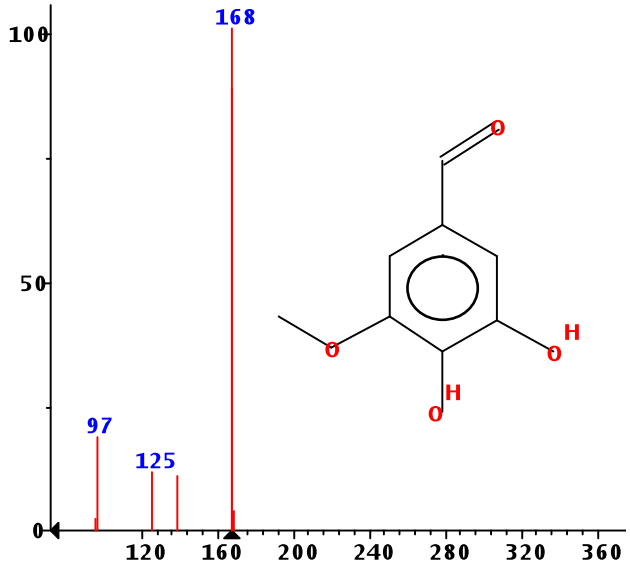

sulfide[1]
rancid [2]
medicinal [3]
amine [4]
fragrant [5]
earthy [6]
medicinal [7]
green [8]
solvent (plastic) [9]
musty [10]
rancid [11]
fragrant [12]
earthy [13]
fragrant [14]
solvent [15]

Secondary Effluent Odor Wheel




sulfide[1]
rancid [2]
medicinal [3]
amine[4]
fragrant [5]
earthy [6]
medicinal [7]
green [8]
[6] 2-methylisoborneol
solvent [9]
musty [10]
[10] 246-TCA
rancid [11]
fragrant [12]
earthy [13]
[13] geosmin
fragrant [14]
solvent [15]

Using the NIST Library: The Good



Fragrant at 20.6 – 21.0 min

Match Probability: 96%

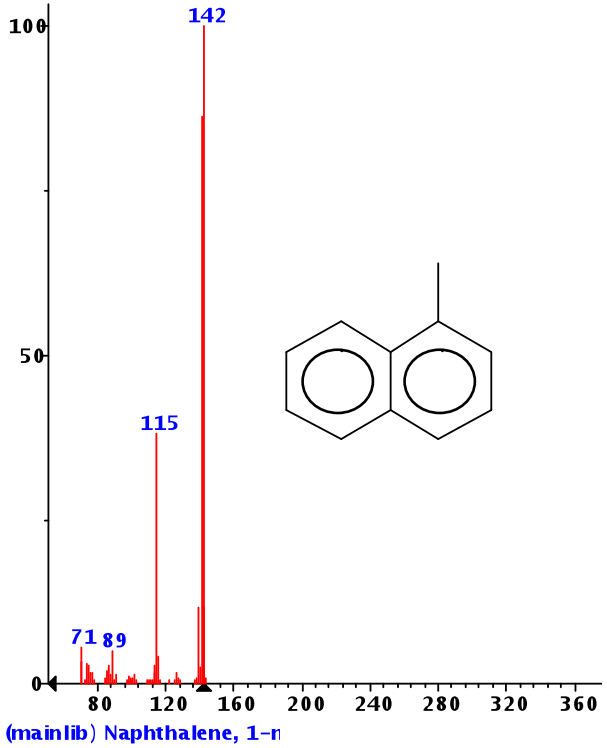
Name: 5-hydroxy-vanillin

Formula: C8H8O4

MW: 168

CAS#: 3934-87-0

Using the NIST Library: The Bad



Plasticky at 16.0 – 16.4 min

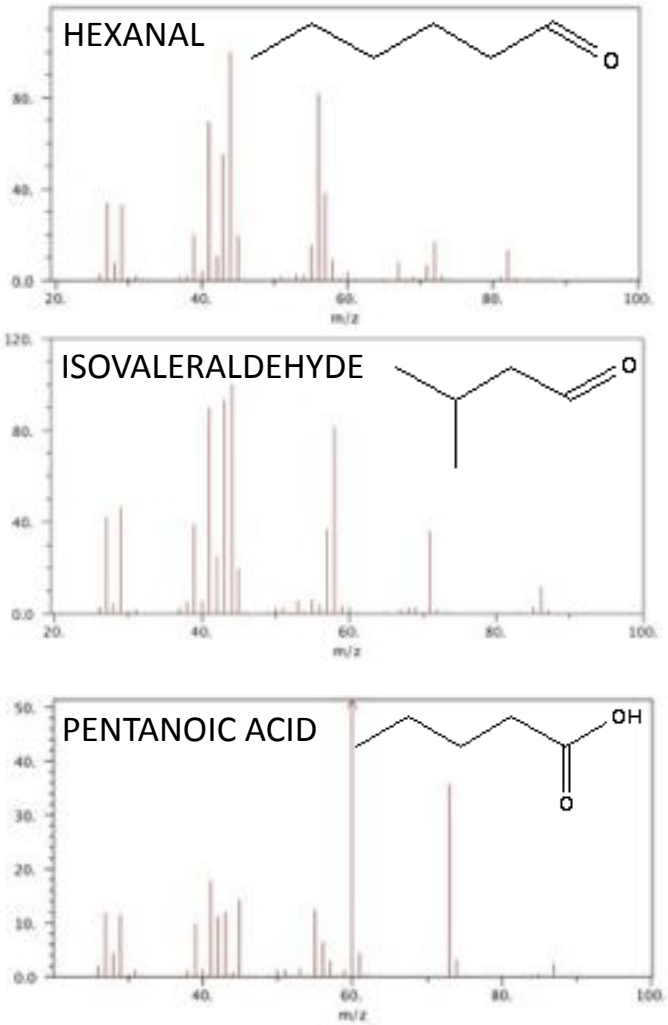
Match Probability: 40%

MANY CONGENERS!

Name: Naphthalene, 1-methyl-
Formula: C11H10
MW: 142 CAS#: 90-12-0

Name: Naphthalene, 2-methyl-
Formula: C11H10
MW: 142 CAS#: 91-57-6

Using the NIST Library: The Ugly



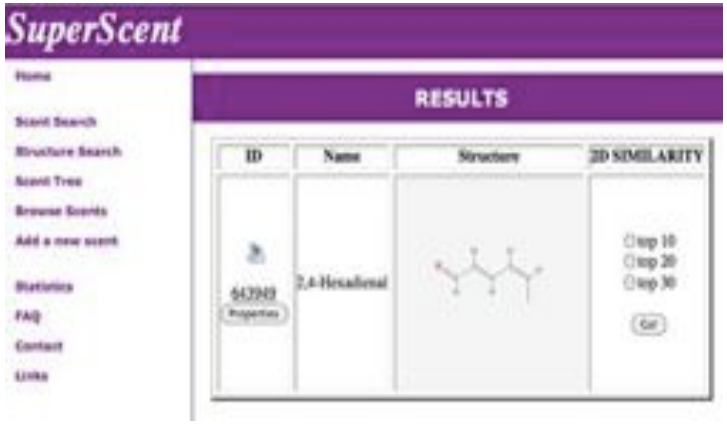
Rancid at 8.0 – 8.2 min

<u>Match Probability</u>: <20%

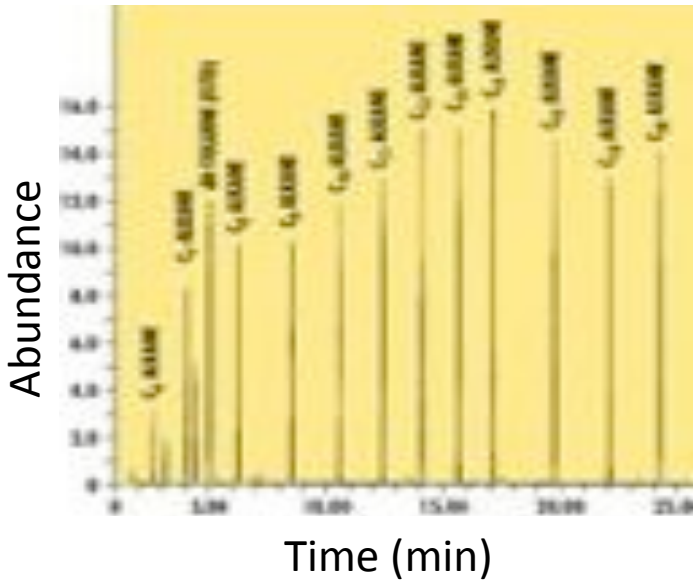
More than 10 different alkyl aldehydes and fatty acids suggested

Match odor descriptors.

Odor Descriptor Databases



Kovat's Retention Index



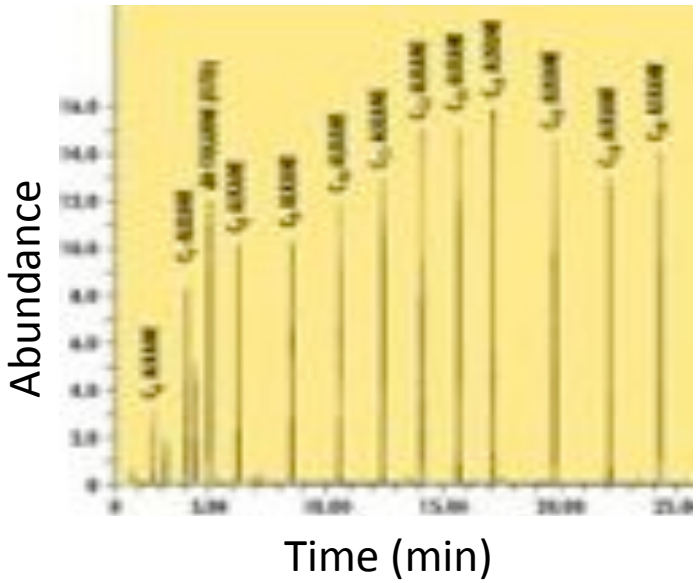
$$RI_{GCX} = \frac{t'_R(X) - t'_R(n)}{t'_R(n+1) - t'_R(n)} \cdot 100 + 100 \cdot n$$

Based on the retention times of n-alkane series in the specific gas chromatography condition.

1. Calculate RI of olfactometry peak
2. Match to published data from NIST WebBook

...if not published

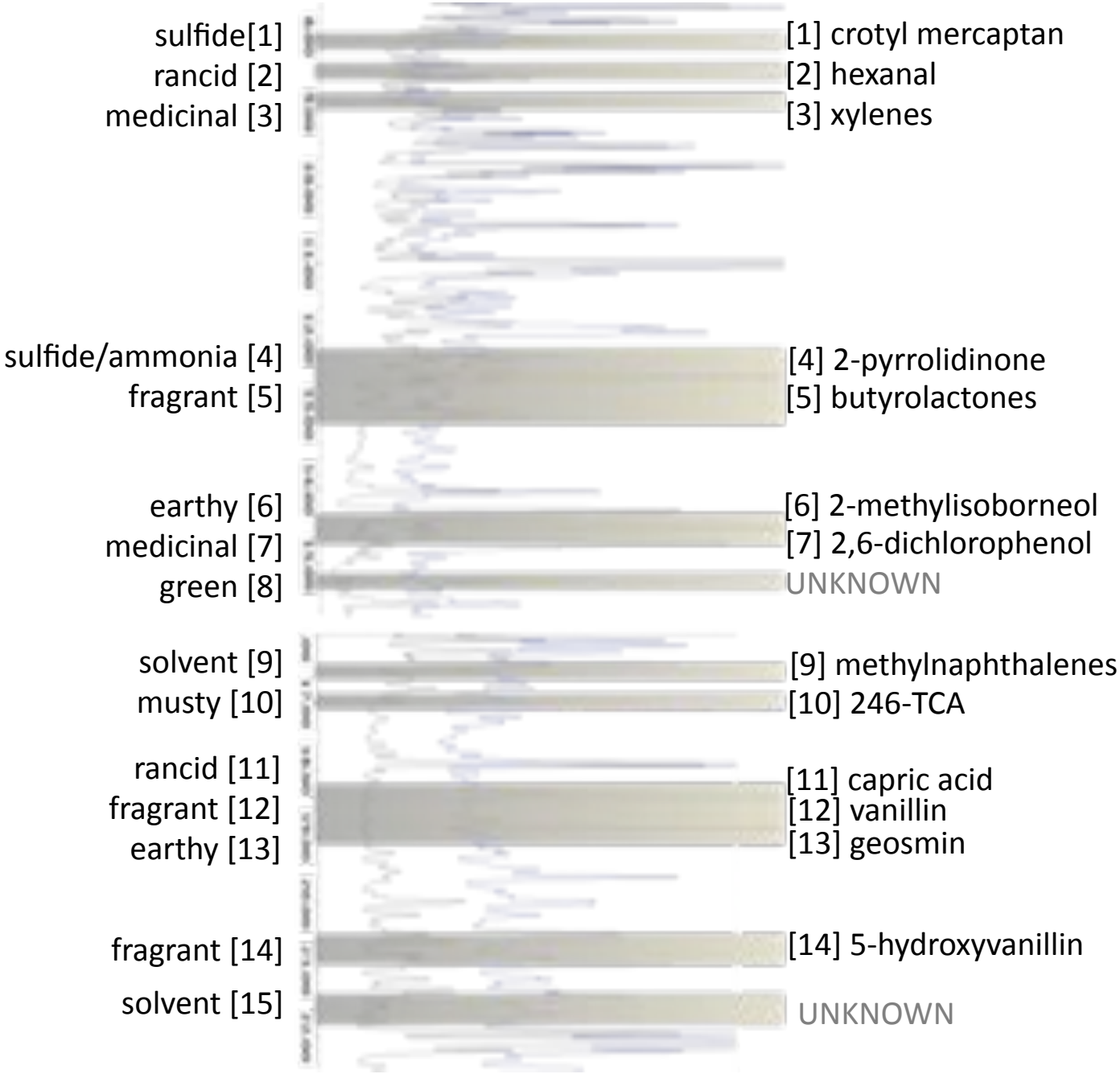
Kovat's Retention Index



$$RI_{GCX} = \frac{t'_R(X) - t'_R(n)}{t'_R(n+1) - t'_R(n)} \cdot 100 + 100 \cdot n$$

Based on the retention times of n-alkane series in the specific gas chromatography condition.

1. Calculate RI of olfactometry peak
2. Match to RI of reference standards


sulfide[1]
rancid [2]
medicinal [3]
sulfide/ammonia [4]
fragrant [5]
earthy [6]
medicinal [7]
green [8]
solvent [9]
musty [10]
rancid [11]
fragrant [12]
earthy [13]
fragrant [14]
solvent [15]
[1] crotyl mercaptan
[2] hexanal
[3] xylenes
[4] 2-pyrrolidinone
[5] butyrolactones
[6] 2-methylisoborneol
[7] 2,6-dichlorophenol
UNKNOWN
[9] methylnaphthalenes
[10] 246-TCA
[11] capric acid
[12] vanillin
[13] geosmin
[14] 5-hydroxyvanillin
UNKNOWN

GC-MS/SIM Target Analytes

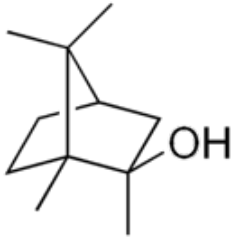
Literature review identified 13 target potent odor compounds with sensory threshold concentrations below 30 ng/L (and 2 precursor compounds).

Compound	OTC (ng/L)	Description
2-methylisoborneol	5 - 10	earthy, rain, camphor
geosmin	1 - 10	earthy, wet dirt
2-isopropyl-3-methoxypyrazine	0.2 - 16	green, floral, decay
2-isobutyl-3-methoxypyrazine	1.0 - 16	green pepper
β-ionone	7	violet, rose
2,6-*E,Z*-nonadienal	20	cucumber
2,4,6-trichloroanisole	0.1-2	musty, moldy, old cupboard
2,3,4-trichloroanisole	0.1-2	musty
2,3,6-trichloroanisole	0.2-2	musty
2,4,6-tribromoanisole	0.15-10	musty
iodoform	30	iodine, medicinal
2-bromophenol	30	medicinal
2,6-dibromophenol	0.5	medicinal, hospital
2,4,6-tribromophenol	600	medicinal, [precursor]
2,4,6-trichlorophenol	> 5,000	chemical, [precursor]

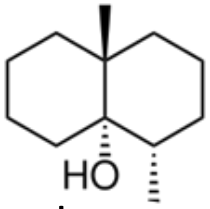
Surface water

Distribution system

Disinfection byproducts

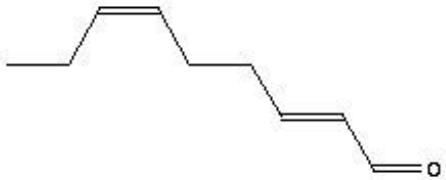


rain

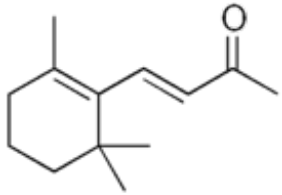


beet

EARTHY

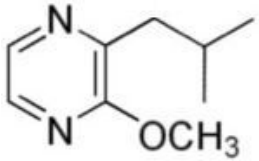


cucumber

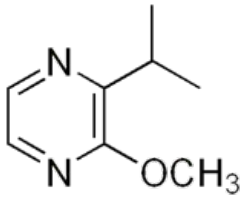


violet, rose

FRAGRANT

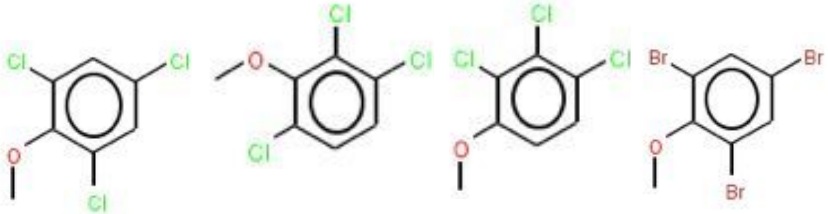


new potato



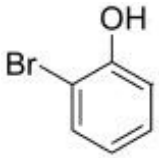
bell pepper

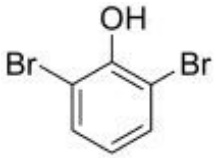
GREEN



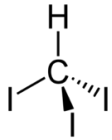
moldy, wet dog, cork taint

MUSTY





hospital



iodine

MEDICINAL

NEWater used as cooling and industrial water, including for semiconductor and biotech companies.

Beginning in 2010, introduced to drinking water reservoirs at up to 6% volume.

As a showcase, NEWater is ozonated and sold as premium bottled water.

Recycled water used in groundwater recharge for barrier to seawater intrusion.

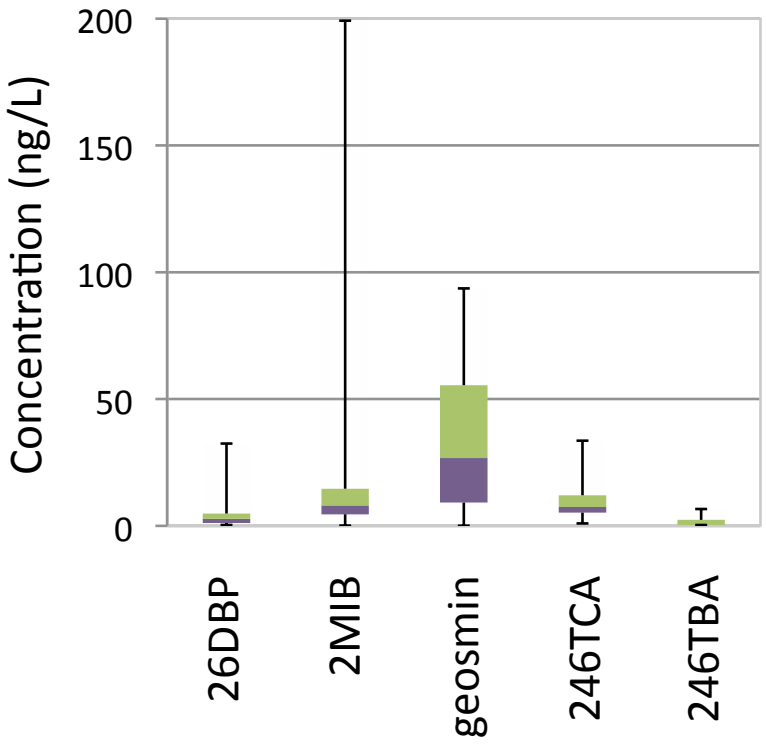
Some directed to agricultural, cooling and refinery use.

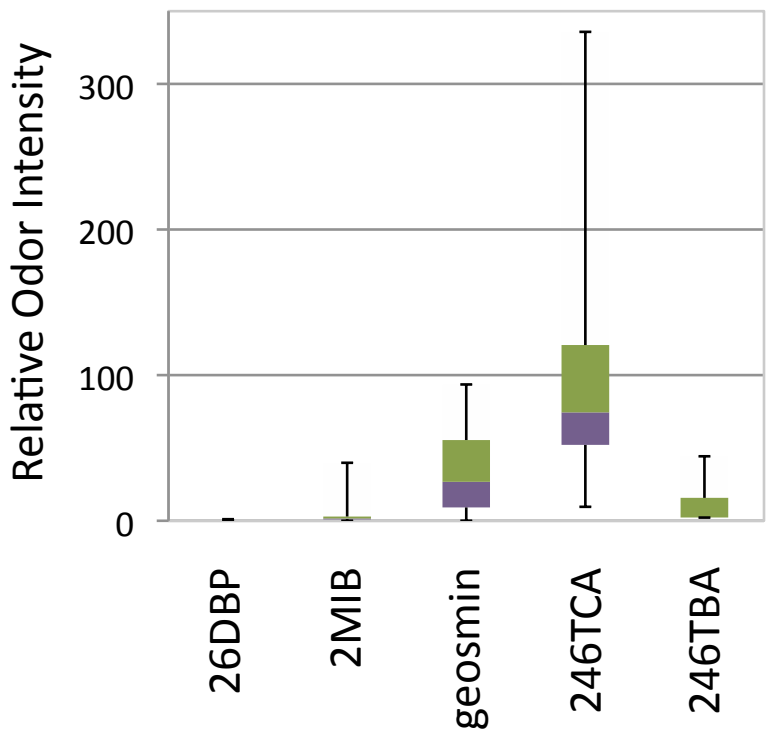
In 2008, a framework for a 50 MGD recycled water purification project was put in place.

Directed for industrial and potable use.

Target Analytes in Secondary Effluent

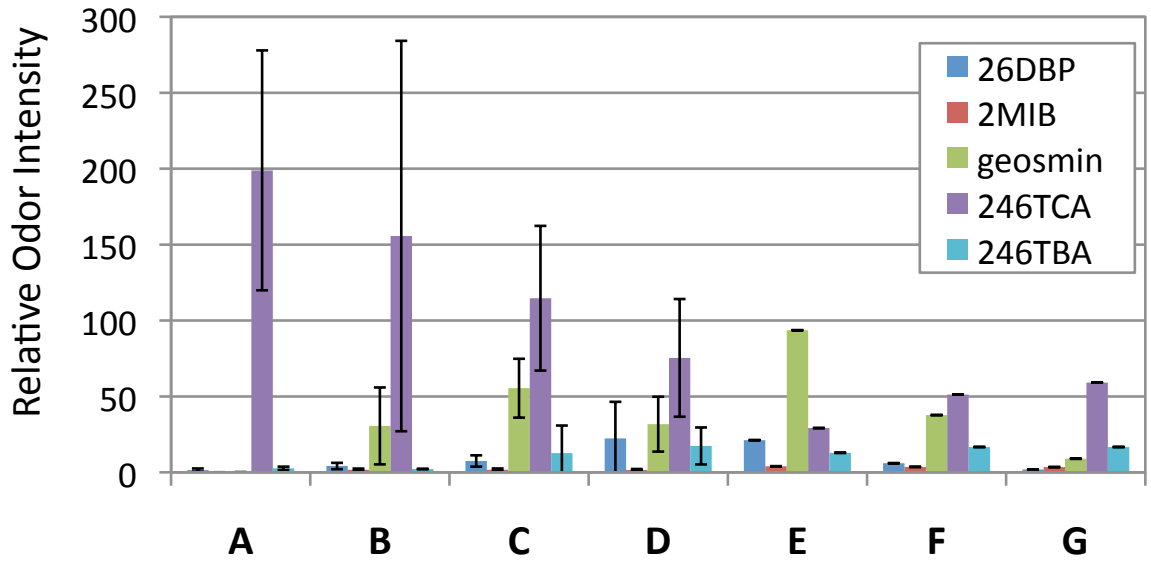
$$\text{Relative Odor Intensity} = \frac{\text{Concentration}}{\text{Odor Threshold}}$$





Dominant: 246TCA and geosmin

Variability among Plants

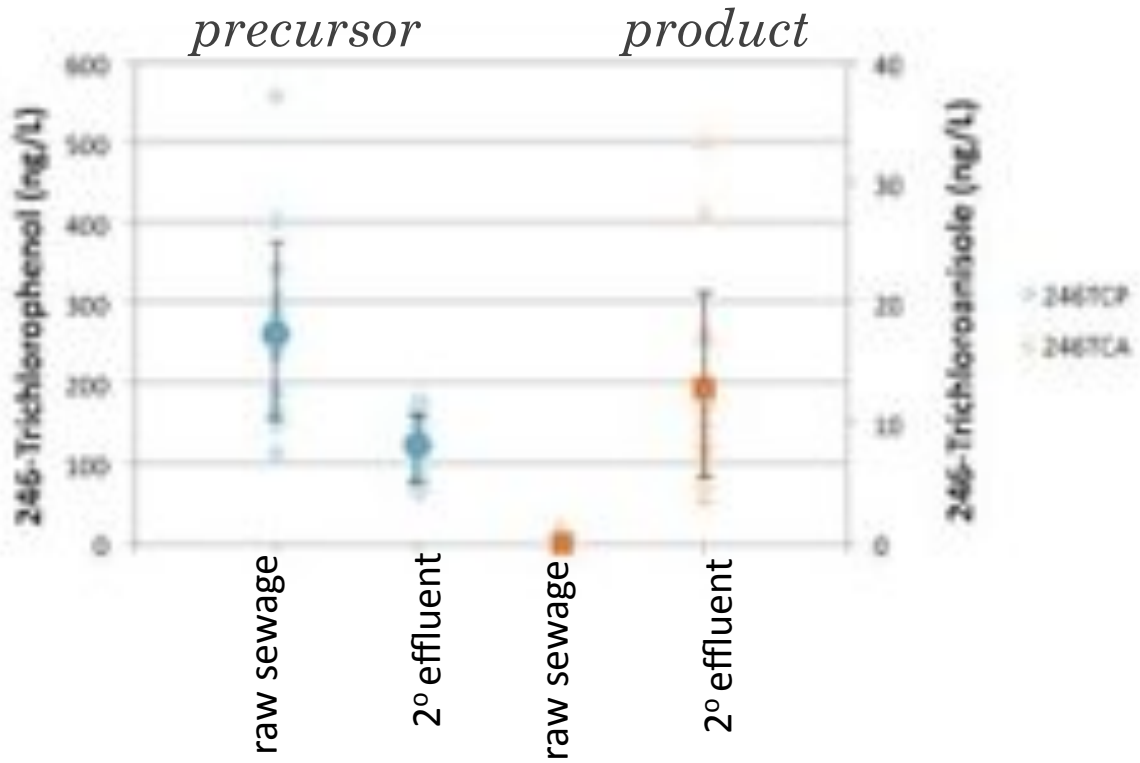


Typical: 246TCA dominant; geosmin at lower intensity.

Plant A: Only 246TCA

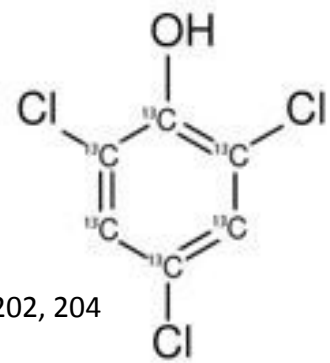
Plant E: geosmin dominant; 246TCA at lower intensity.

Anisole Formation in 2° Treatment



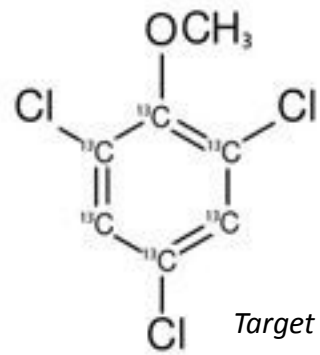
Decrease of known precursor 2,4,6-trichlorophenol was consistently observed along with **formation of 2,4,6-trichloroanisole.**

Anisole Formation in 2° Treatment

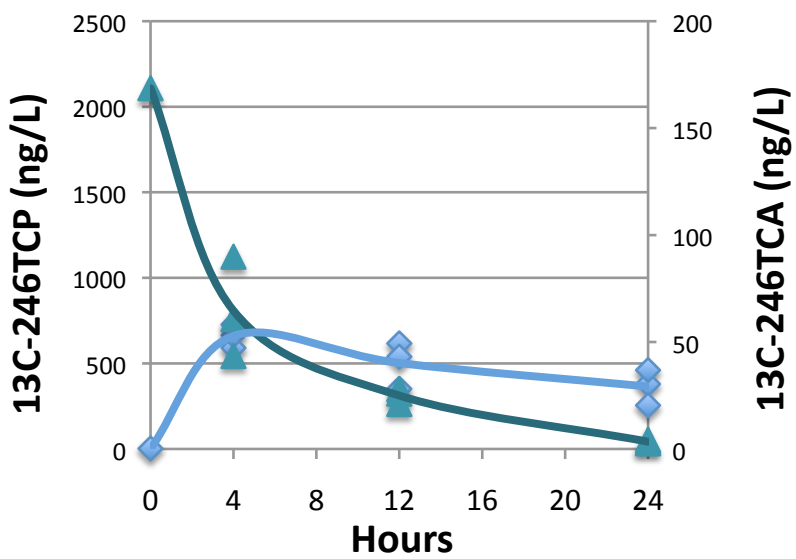


MW: 197.45 + 6
RT: 16.709 min
Target ion: m/z 202, 204

activated sludge



MW: 212.45 + 6
RT: 16.303 min
Target ion: m/z 201, 203

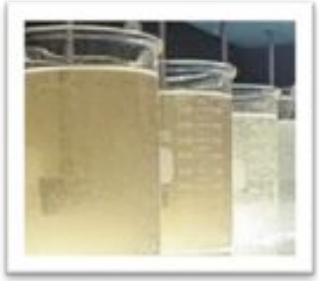


Removing Odorants from Wastewater Effluent

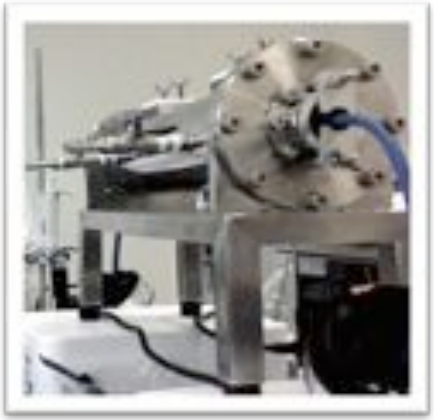
Reverse Osmosis: 6 full-scale plants.

Activated Carbon: 1 pilot-scale plant.

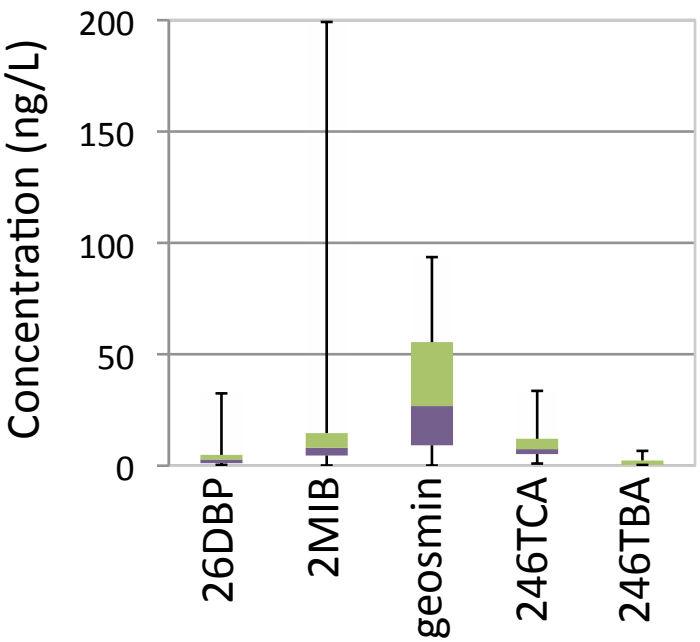
Chlorine: 6 full-scale plants + benchscale.
Chlorine: Benchscale.



UV: 4 full-scale plants + benchscale.
UV/H_2O_2: 2 full-scale plants + benchscale.



Quantitative and sensory data are BOTH used for assessment of treatment efficacy.



Odor Peak Category	Retention Time	Secondary Effluent		
sulfide	7.0	3	3	3
rancid	7.2	0	2	2
medicinal	7.7	4	4	3
ammonia	11.9, 12.2	4	3	4
fragrant	12.5, 12.7, 12.9	4	2	4
earthy	13.8, 14.0	3	2	3
medicinal	14.3	2	2	3
woody	15.2	0	2	2
chemical	16.3	3	0	2
musty	17.0	2	4	3
rancid	18.0	0	4	3
fragrant	18.2	4	4	4
earthy	18.5	3	4	4
fragrant	20.5	4	4	4
chemical	21.4	2	3	2

← 2MIB

← 246TCA

← geosmin

GC-MS/SIM

GC-Olfactometry

Dilution as Solution

…would take a lot of odorless freshwater.

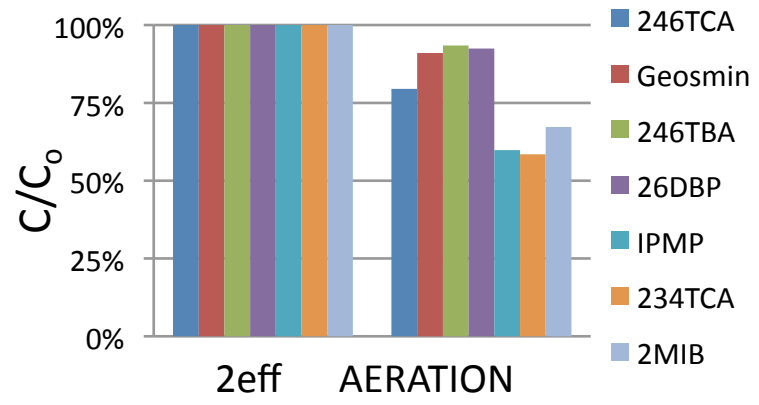
FPA results original strong moderate weak no smell

Dil 0x			Dil 4x			Dil 8x			Dil 32x			Dil 64x			
3	3	3	2	2	3	0	1	2	1	0	0	0	0	0	
0	2	2	0	0	2	0	1	2	0	0	0	0	0	0	
4	4	3	3	2	3	3	3	2	2	1	2	0	0	0	
4	3	4	2	3	3	3	4	3	2	2	3	1	0	0	
4	2	4	3	2	3	2	3	2	0	0	0	0	0	0	
3	2	3	3	3	4	3	3	2	1	0	0	0	0	0	← 2MIB
2	2	3	2	2	3	3	2	2	1	1	2	0	0	0	
0	2	2	4	3	4	0	2	0	0	0	0	0	0	1	
3	0	2	2	3	3	0	1	0	0	0	0	0	0	0	
2	4	3	4	4	4	2	1	2	2	2	3	0	0	0	← 246TCA
0	4	3	2	3	3	2	4	2	0	0	0	0	0	0	
4	4	4	4	3	3	3	3	3	1	2	1	0	0	0	
3	4	4	4	3	4	4	3	3	1	3	3	0	0	0	← geosmin
4	4	4	4	3	4	2	3	3	1	0	0	0	0	0	
2	3	2	3	2	2	2	2	0	1	1	0	0	0	0	

3% effluent

Aeration

2nd effluent			Aeration			
3	3	3	4	0	2	
0	2	2	3	0	0	
4	4	3	4	3	3	
4	3	4	3	3	4	
4	2	4	1	0	0	
3	2	3	4	3	3	← 2MIB
2	2	3	4	2	4	
0	2	2	2	0	0	
3	0	2	1	4	3	
2	4	3	3	2	2	← 246TCA
0	4	3	4	0	0	
4	4	4	3	4	3	
3	4	4	2	4	2	← geosmin
4	4	4	2	3	3	
2	3	2	4	2	4	



Aeration in pilot plant only partially strips away odorants.

RELATED:

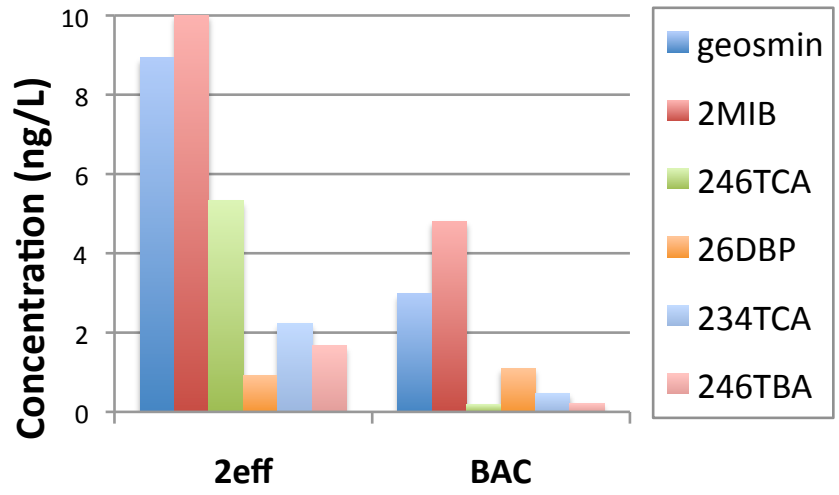
Volatilization depends on mixing conditions in surface water body and water temperature.

For semivolatiles, log 1 removal expected at >>25km downstream.

Rathbun *USGS* 1998

BAC/GAC

2nd Effluent			BAC			
3	3	3	0	1	1	
0	2	2	0	1	0	
4	4	3	2	3	3	
4	3	4	2	3	3	
3	2	4	2	1	2	
3	2	3	2	1	1	← 2MIB
2	2	3	0	2	2	
0	2	2	0	1	1	
3	0	2	2	2	3	
2	4	3	0	0	0	← 246TCA
0	4	3	2	2	2	
4	4	4	1	1	2	
3	4	4	1	1	2	← geosmin
4	4	4	1	1	2	
2	3	2	2	2	2	



Moderately successful for hydrophobic compounds (e.g. haloanisoles)

variable performance was observed on geosmin and 2MIB, depends on organic content and filter condition.

Chen et al, *Wat. Res.* 1997

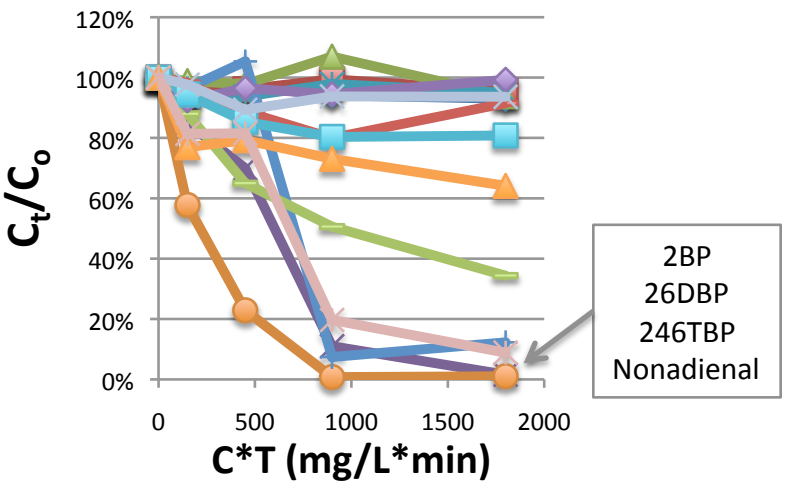
Chlorine

C*T 0			C*T 200			C*T 1000		
1	1	0	3	2	2	2	1	1
3	2	3	2	2	0	1	0	0
4	3	3	3	3	3	2	2	3
4	3	4	2	4	4	3	4	4
4	3	4	2	4	3	3	3	4
3	3	3	3	3	3	2	1	2
2	2	2	2	3	2	2	1	2
3	3	3	2	3	2	1	1	0
4	3	3	1	3	2	3	2	3
3	3	4	2	4	3	2	3	3
2	4	2	2	3	1	1	2	2
4	4	4	2	3	3	4	3	4
3	1	2	2	3	2	4	2	3
3	4	3	2	3	3	3	3	4
4	4	4	3	4	4	3	4	4

← 2MIB

← 246TCA

← geosmin



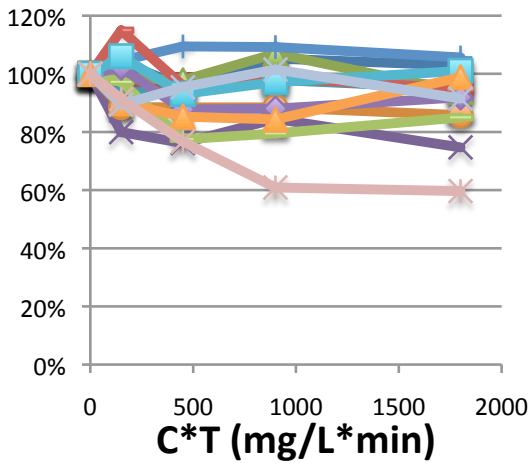
Chloramine

C*T 0			C*T 200			C*T 1000		
1	2	0	2	3	3	1	2	3
3	2	3	2	2	1	3	2	3
4	3	3	4	4	4	3	3	3
4	3	4	3	3	4	3	4	4
4	3	4	3	4	4	2	3	4
3	3	3	3	2	2	2	2	4
2	2	2	3	3	4	2	3	2
3	3	3	3	2	3	2	2	3
4	3	3	4	2	3	2	2	4
3	3	4	2	3	2	2	3	4
2	4	2	4	3	3	3	3	4
4	4	4	4	4	4	3	4	4
3	1	2	3	4		4	2	3
3	4	3	4	4	4	3	2	3
4	4	4	4	4	4	3	4	4

← 2MIB

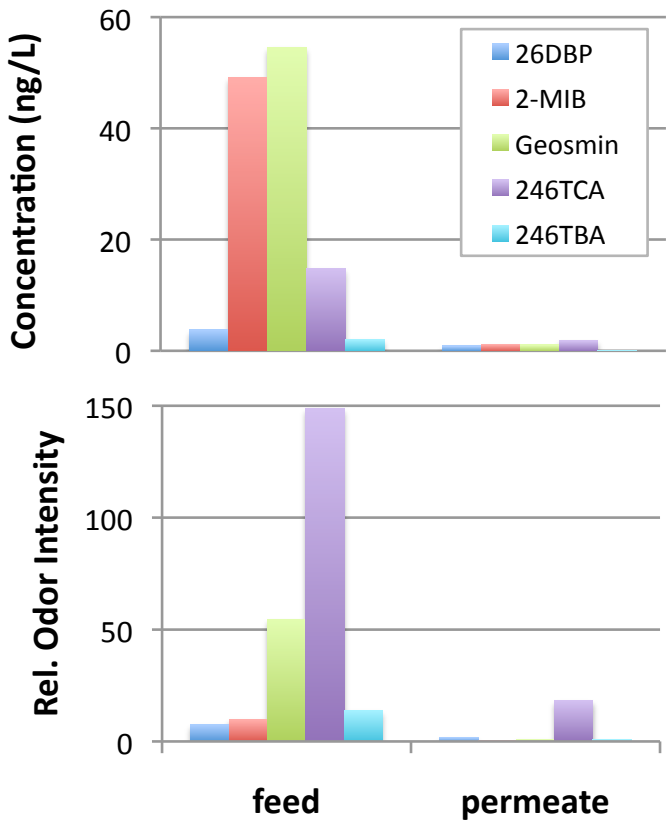
← 246TCA

← geosmin



Reverse Osmosis

Feed			Permeate			
4	4	3	2	3	0	
3	0	0	0	3	0	
4	4	3	1	1	0	
4	4	3	3	3	3	
4	3	4	2	3	1	
2	3	3	2	2	1	← 2MIB
2	4	2	2	1	3	
3	3	4	1	2	0	
2	4	3	2	2	3	
3	4	3	3	3	3	← 246TCA
0	3	2	0	2	3	
2	3	4	2	2	2	
3	3	4	2	3	1	← geosmin
0	4	2	3	1	2	
2	4	2	1	0	0	

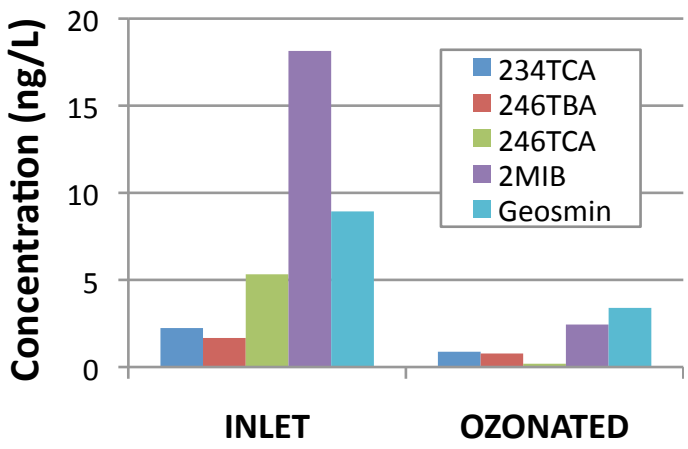


Apparent full-scale plant rejection rate for 246TCA is 87±12%.

Not enough to reduce permeate concentration to ROI < 1.

Ozone

2nd effluent			O3			
3	3	3	0	0	0	
0	2	2	0	0	0	
4	4	3	3	3	3	
4	3	4	2	3	2	
3	2	4	4	3	4	
3	2	3	0	1	2	← 2MIB
2	2	3	1	2	1	
0	2	2	0	0	0	
3	0	2	0	0	0	
2	4	3	0	0	0	← 246TCA
0	4	3	1	0	1	
4	4	4	0	0	0	
3	4	4	2	2	1	← geosmin
4	4	4	0	0	0	
2	3	2	1	0	0	



246TCA and 246TBA removed to below odor thresholds.
2MIB and geosmin only partially removed.

Also observed in ozonation of RO permeate (full-scale plant).

UV

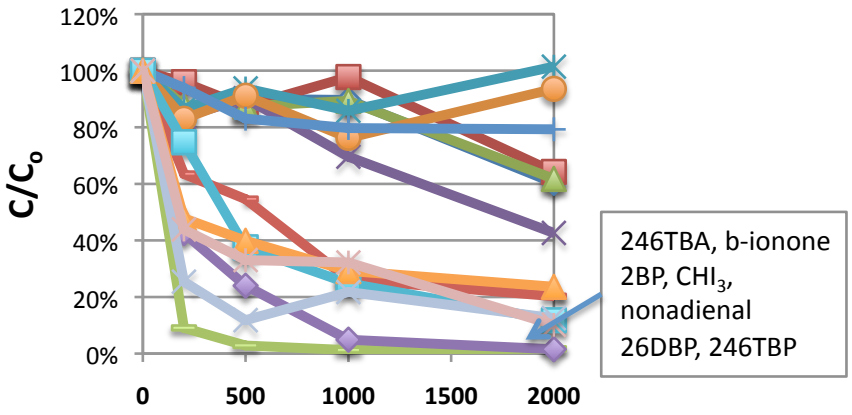
0 mg/L H_2O_2

Fluence 0			Fluence 500			Fluence 2000		
3	3	3	3	3	3	4	2	3
0	2	2	3	3	2	3	3	3
4	4	3	4	3	2	3	4	3
4	3	4	4	3	3	2	1	4
4	2	4	2	3	3	2	4	3
3	2	3	2	2	2	2	4	2
2	2	3	3	2	3	2	4	3
0	2	2	3	3	3	2	2	2
3	0	2	3	3	3	2	0	3
2	4	3	3	3	3	2	2	0
0	4	3	4	3	3	3	3	4
4	4	4	4	2	3	2	0	2
3	4	4	3	3	3	3	3	3
4	4	4	3	3	3	1	0	2
2	3	2	3	2	3	3	1	2

← 2MIB

← 246TCA

← geosmin



UV & H_2O_2

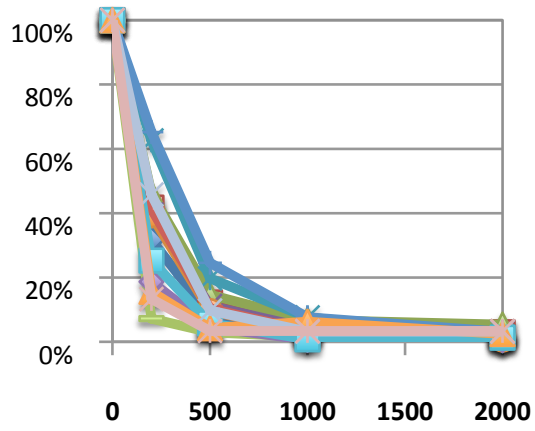
5 mg/L H_2O_2

Fluence 0			Fluence 500			Fluence 2000		
2	0	3	2	2	2	0	1	2
4	4	3	2	3	2	3	0	2
4	4	4	3	2	1	2	2	1
3	3	1	2	3	2	2	0	1
3	2	2	3	4	3	3	3	2
3	4	3	2	2	1	0	0	1
3	2	3	2	2	1	1	0	1
3	3	3	2	3	3	1	0	1
3	2	3	3	2	2	1	1	0
4	4	3	2	2	3	0	0	1
2	4	1	1	1	2	0	0	0
3	4	3	2	3	2	1	2	0
3	4	3	3	3	2	2	0	0
4	4	4	2	2	2	1	1	1
4	2	3	1	1	2	1	1	1

← 2MIB

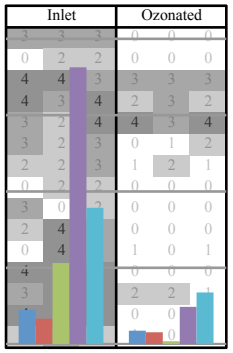
← 246TCA

← geosmin

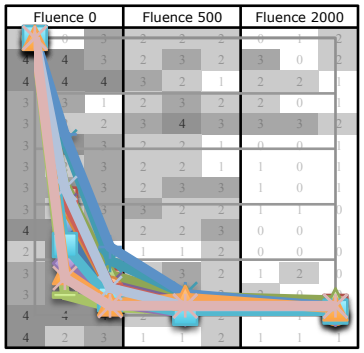


Treatment Summary

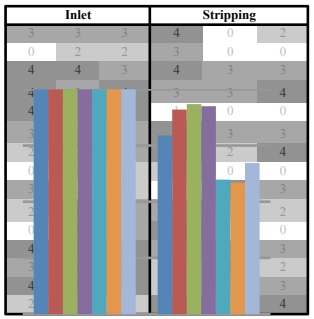
OZONE



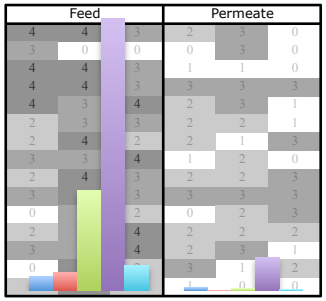
UV-PEROXIDE



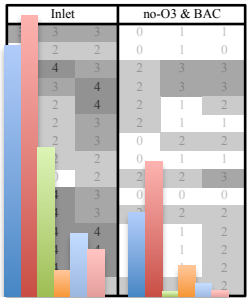
AERATION



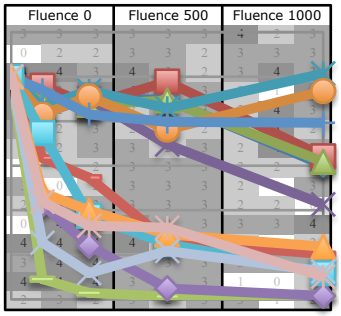
RO FILTRATION



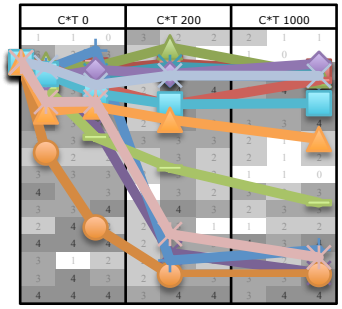
BAC/GAC



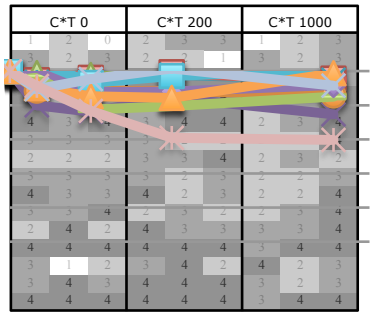
UV PHOTOLYSIS



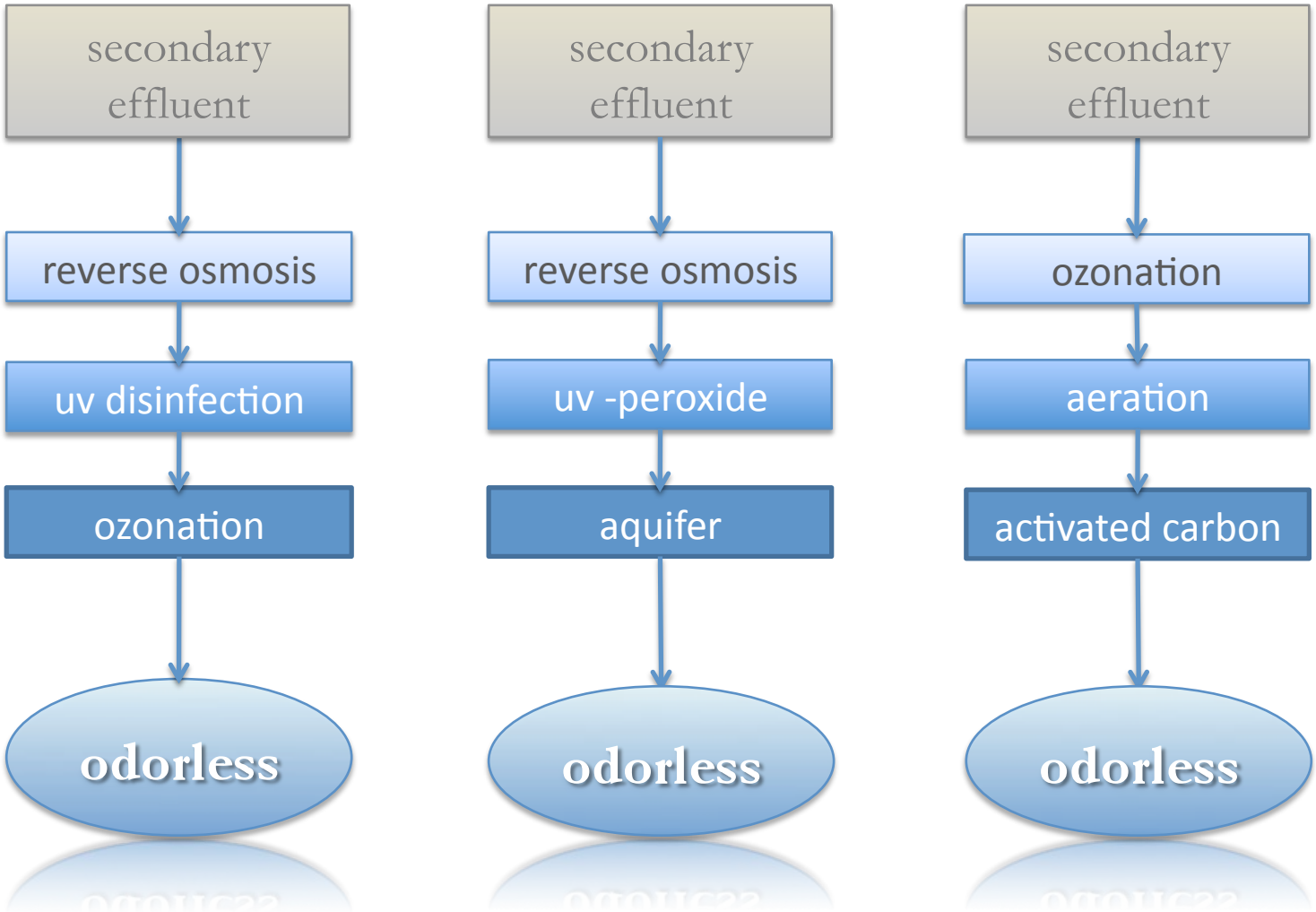
CHLORINE



CHLORAMINE



Multiple Barrier Treatment



Take home messages…

Potent odor compounds in recycled water sources affect public perception.

Effluent-derived odorants are different from drinking water odorants.

Natural attenuation and dilution are often not enough.

No silver bullet to remove all odorants.

Potable water reuse project must adopt a multiple-barrier approach to achieve odor removal.

Singapore Public Utility Board

Mong Hoo Lim, Zhang Lifeng

Sensory team: Qian Xiaoqing, Wu Jingming, Xiao Yongjun, Emily See, Wen Wei She, Ray Tan

AOP guru: Mylene Gomez

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