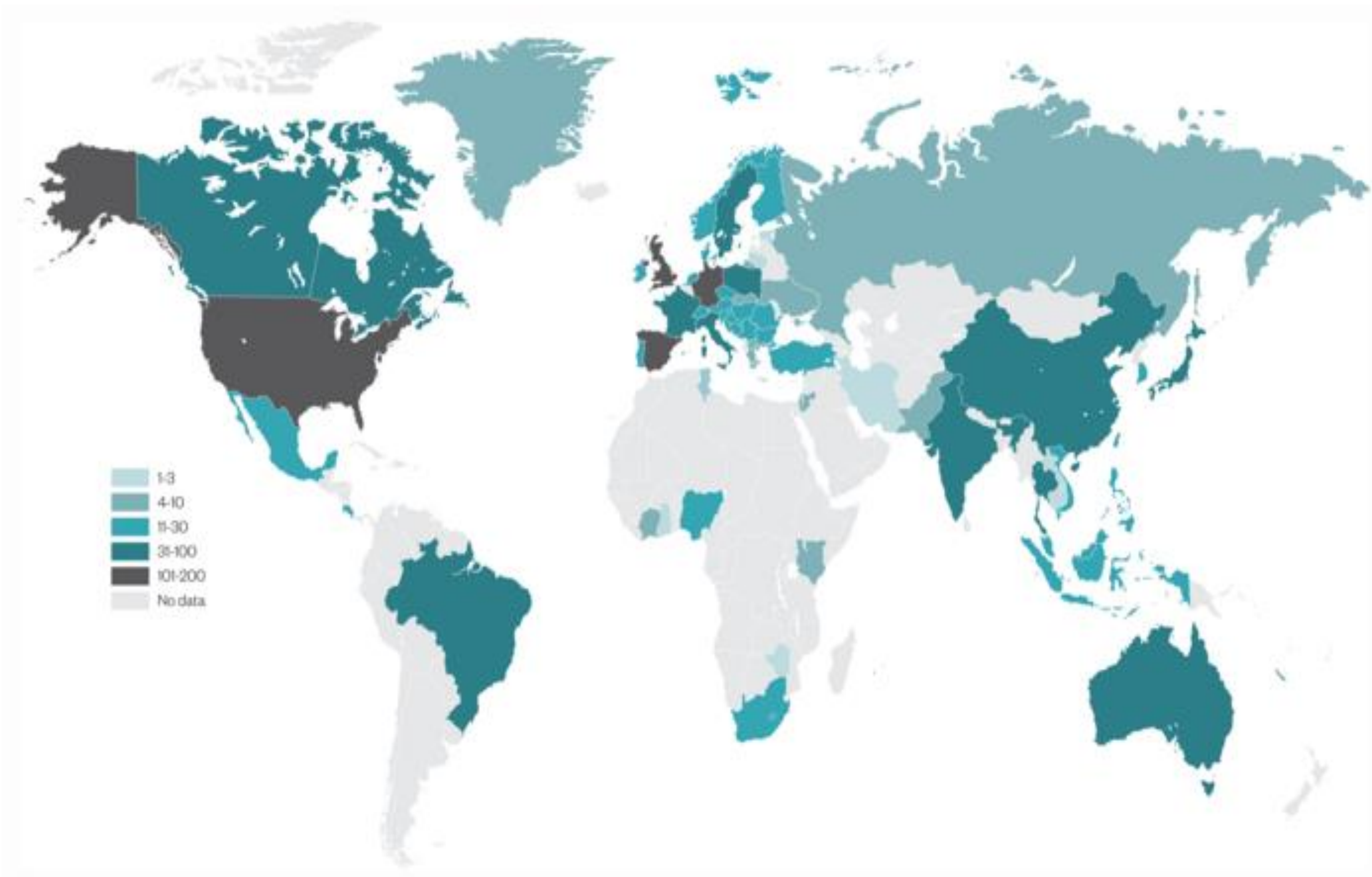
Occurrence, levels and risk assessment of emerging pollutants in fish samples

Leslie Petrik

Waste Khoro 2019 Asbestos and Land remediation summit
Mittah Seperepere Convention Centre Kimberley
18-20 Sept 2019


Level
Chemistry Computer Laboratory 3.10
Tutorial Room 3.08
ENS
Environmental
Nano Sciences

Drinking water in industrialised and populated states is contaminated… ..IWW,2014.



What are Emerging Contaminants (EC)?

- Types of emerging contaminants
  - Pharmaceuticals
    - Antibiotics (sulfamethoxazole
    - Anti-diabetics (sulphonylurea)
    - Anti-epileptic (carbamazepine)
    - Antimicrobials (penicillins)
    - Anti-inflammatories and analgestics (diclofenac, paracetamol)
    - Antimalarial (cinchonidine)
    - Anti-ulcer and antihistamine (ranitidine)
    - Anti-retrovirals (Lamivudine)
    - Antidepressants (benzodiazine-pines)
    - β-blockers (atenolol, metoprolol)
  - Endocrine disrupting compound
    - Phenolic compounds nitrophenol Phenol
    - Xenostrogens; estradiol, 17α-ethinylestradiol bisphenol A
  - Personal care product
    - Disinfectants Triclosan chlorophene
    - Fragrance polycylic musk
    - Preservative (paraben)
  - Nanomaterials
    - TiO_2 ZnO
  - Perfluorinated compounds
    - Perfluorodecanoic acid
  - Pesticides
    - Algicides
    - Herbicides
    - Biocides
    - Fungicides
    - Insecticides
    - Fumigants
    - Attractants

TIJANI, J. O., FATOBA, O. O., BABAJIDE, O. O. AND PETRIK, L. F. (2016). Pharmaceuticals, endocrine disruptors, personal care products, nanomaterials and perfluorinated pollutants: A review. Environmental Chemistry Letters, 14:27-49. DOI 10.1007/s10311-015-0537-z

TIJANI, J. O., FATOBA, O. O., PETRIK, L. F. (2013). A review of pharmaceuticals and endocrine disrupting compounds: sources, effects, removal and detections. Water, Air and Soil Pollution, 224, pp. 1770-1799. DOI 10.1007/s11270-013-1770-3.

What is in our drinking water (Patterton, 2013)

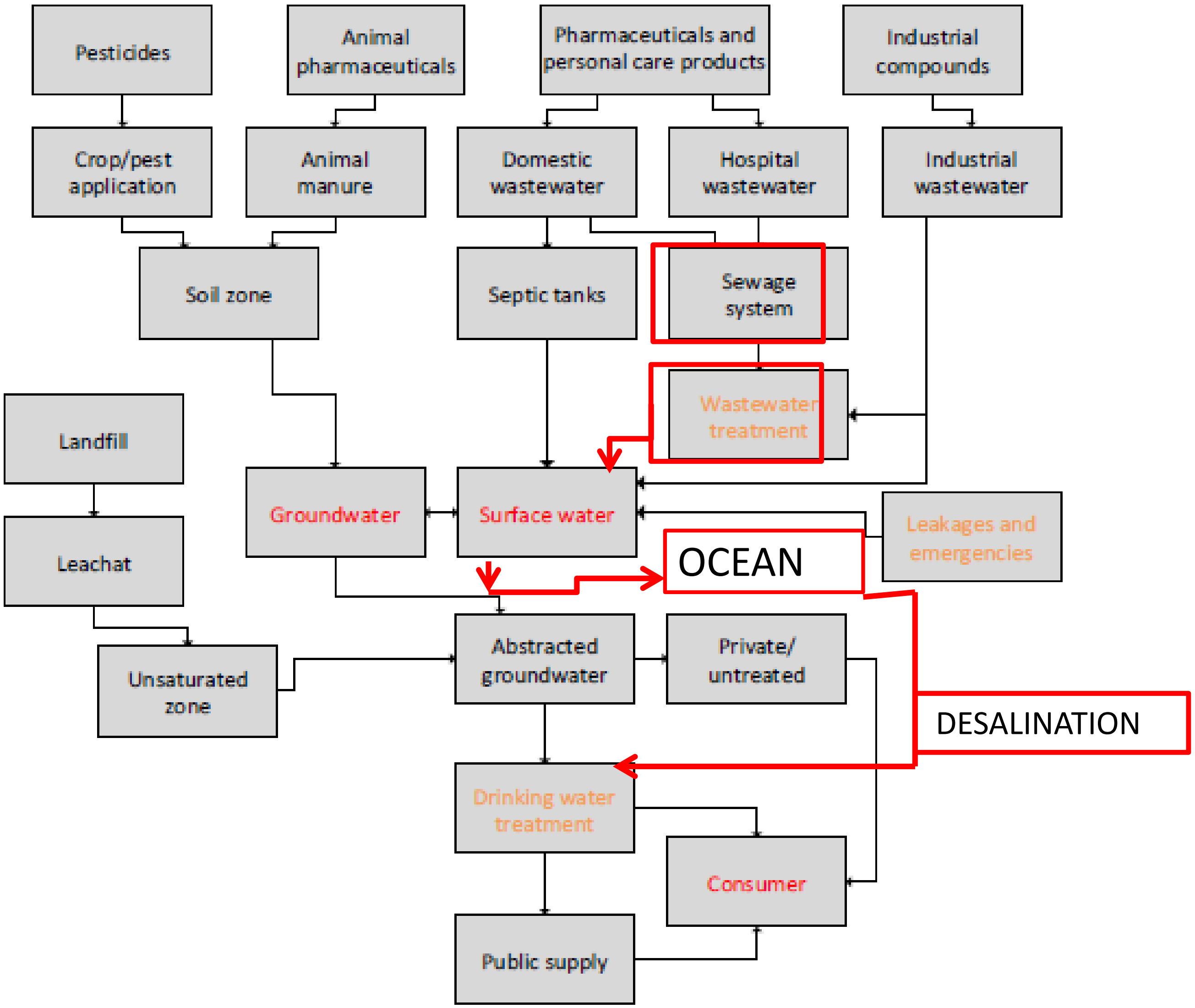
Analyte	Description
Benzocaine	Anaesthetic
Paracetamol	Analgesic
TemazUSEPAm	Antianxiety
Flecainide	Antiarrhythmic
Nalidixic acid	Antibiotic
Sulfisomidine	Antibiotic
Carbamazepine	Anticonvulsant /antiepileptic
Oxcarbazepine	Anticonvulsant /antiepileptic
Phenytoin	Antiepileptic
Fluconazole	Antifungal
Telmisartan	Antihypertensive
Atenolol	Antihypertensive
Minoxidil	Antihypertensive vasodilator
Cinchonidine	Antimalarial
Cinchonine	Antimalarial
Ephedrin	Bronchodilator

Emerging contaminant's impacts

WRC Project No. K5/2369, March 2016

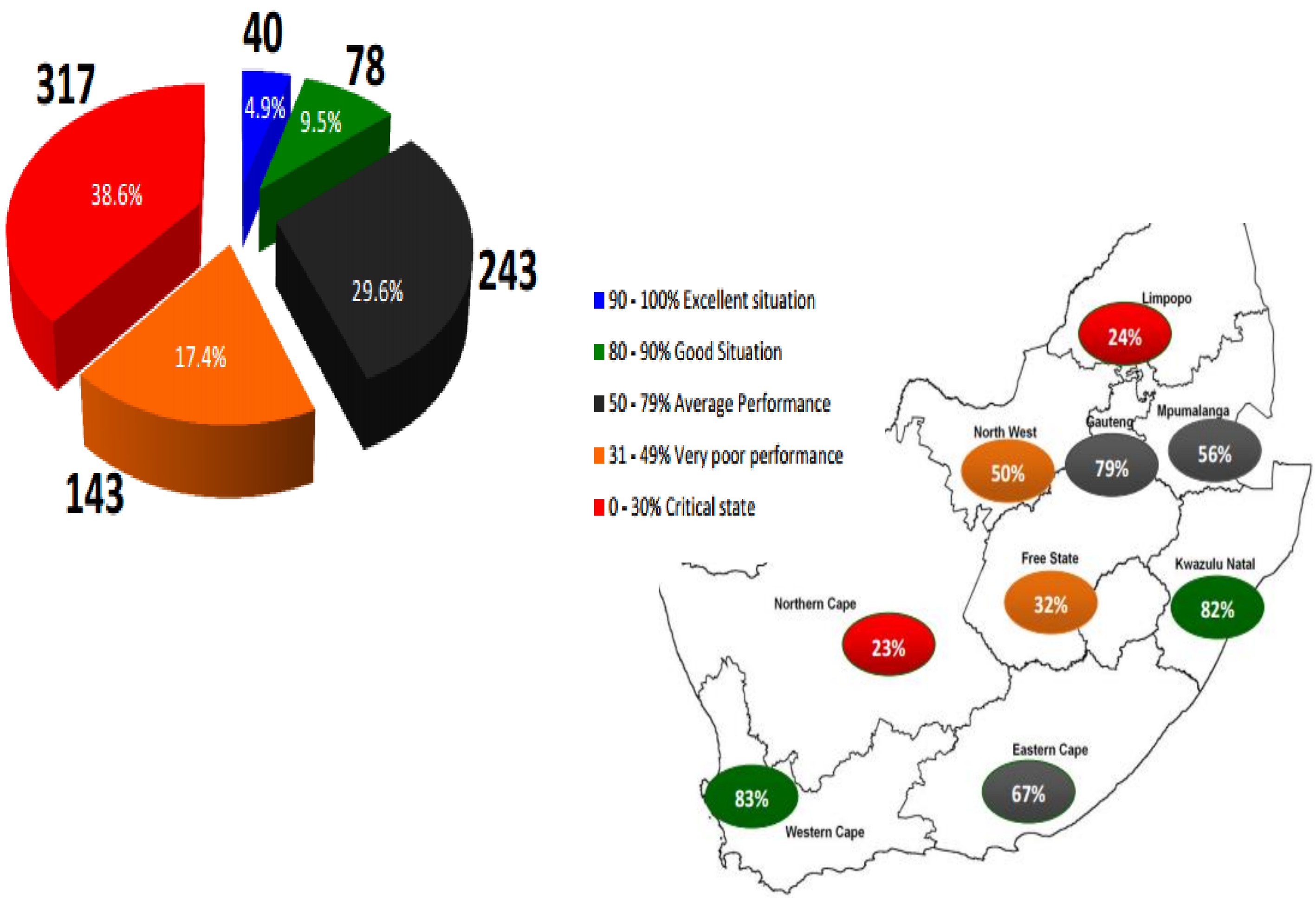
- Feminization and downward trends in semen quality
- Declining sex ratios
- Sexual & Developmental abnormalities
- Reproductive impairments
- Endocrine disruption
- Persistent antibiotic resistance
- Structural deformities
- Gene alteration
- Testicular and thyroid cancers
- Risk depends upon concentration, exposure time, volume, complexity of mixtures, organism type, metabolism rate, etc

CEC pathways and flows

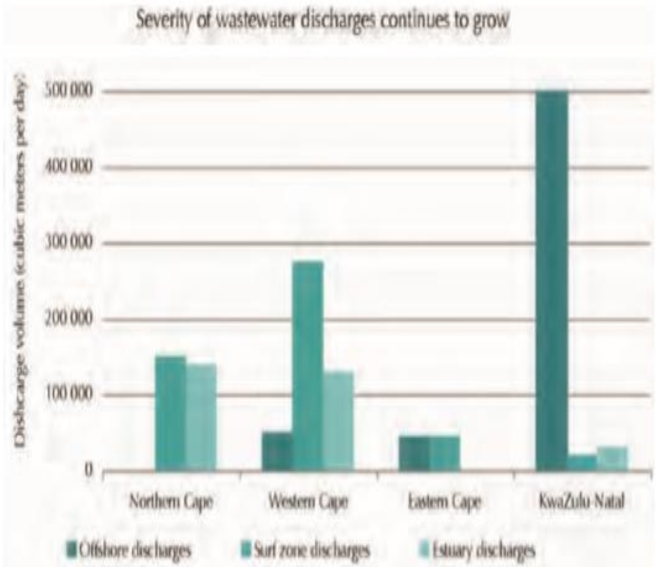


Number of WWTPs (and %) in each performance category

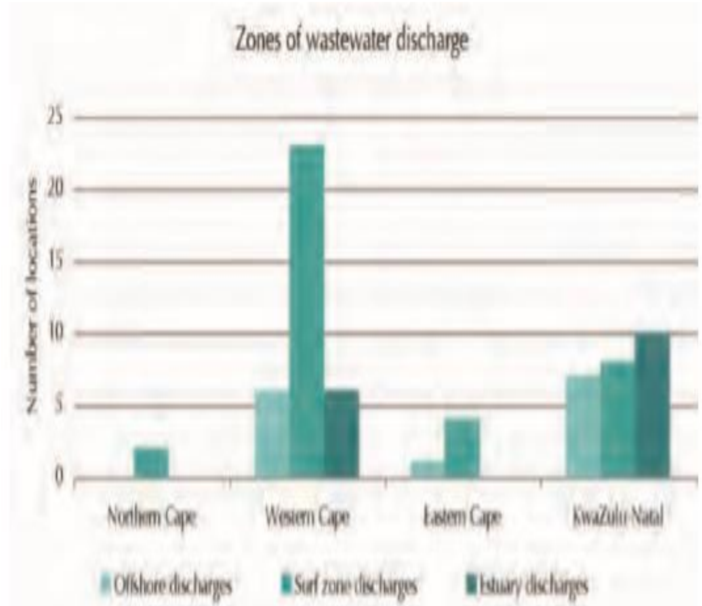
National Green Drop Results for 2010/11



Marine Outfalls, Estuary and Surfzone discharges



Total daily wastewater discharged into the marine environment per coastal province, 2003



Location of coastal wastewater discharge points in the South African marine environment per coastal province, 2003

Source: Department of Water Affairs and Forestry (2004)

Surfzone, riverine and estuary sewage effluent discharges Western Cape

WWTP	Treatment Volume (Ml/d)
Cape Flats	161.0
Athlone	110.0
Zandvliet	73.6
Bellville	56.0
Fisantekraal	58.0
Potsdam	43.9
Mitchells Plain	35.3
Borchards Quarry	35.3
Macassar	30.7
Kraaifontein	28.0
Scottsdene	10.0
Other	~10.0

These partially treated effluents are ultimately discharged into the marine environment.

Discharged effluents only comply with a few quality criteria

Source:
WATER SERVICES AND THE CAPE TOWN URBAN WATER CYCLE
August 2018 City of Cape Town

Marine Outfalls

- Seapoint/Greenpoint marine outfall serves the greater CBD from Woodstock to Bantry Bay,
- Discharges 44.0 Ml/d, outfall is 1700 m long and discharges 28 m below sea level
- Campsbay, discharges 10.78 Ml/d
- Houtbay, discharges 5.5.Ml/d
- The sewerage is merely screened through a 3 mm mesh to remove large objects such as nappies
- Maceration may be done- microplastics issue???
- No further treatment occurs before release into our marine environment


Greenpoint Outfall
Direction of Current
Jean Tresfon

Recommended priority list of contaminants of emerging concern (CECs) for assessing water quality for direct potable reuse (Swartz et al, 2017)

GROUP	TYPE	CHEMICALS
Industrial chemicals	Flame retardants	TDCPP and TCEP
	X-ray contrast fluid	Iopromide
	PAH	Benzo(a)pyrene
Pesticides, biocides and herbicides	Herbicide	Atrazine
	Herbicide	Terbuthylazine
	Insecticide	Imidacloprid
	Pesticide	Simazine
Natural chemicals	Stimulant	Caffeine
	Hormone	17-beta estradiol
Pharmaceuticals and metabolites	Antiretroviral drugs	Lamivudine Stavudine
	Anti-epileptic drugs	Carbamazepine
	Anti-malarial drugs	Cinchonidine Cinchonine
	Analgesic	Paracetamol
	Antibiotic	Sulfamethoxazole
Personal care products	Anti-microbial	Triclosan
Household chemicals and food additives	Plasticiser	Bisphenol-A
Transformation products	By-product	N-Nitrosodimethylamine (NMDA)

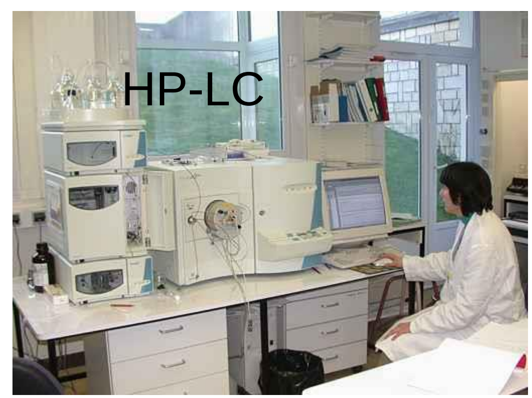
The priority list cannot be seen as an exhaustive list, as each reclaimed potable water reuse project should interrogate the relevance of each of the chemicals

Detection and Quantification of Emerging Micropollutants

There are sophisticated analytical tools available to detect these micropollutants

- PROTOCOL
- Sampling
- Filtration
- Liquid-liquid extraction or solid-phase extraction
- Derivitisation
- Gas liquid Chromatography-Mass Spectrometry (GC-MS)
- High Performance Liquid Chromatography (HP-LC)
- Liquid Chromatography-Mass spectrometry (LC-MS),

GC-MS



Desalination and seawater quality at Green Point, Cape Town: A study on the effects of marine sewage outfalls

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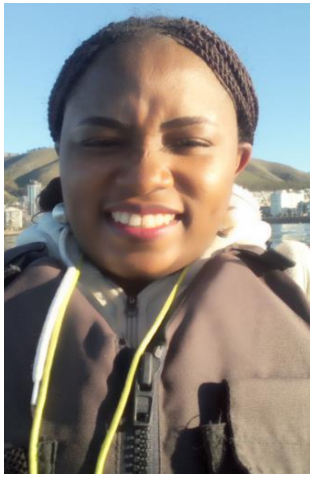
CORRESPONDENCE TO:
Lesley Green

This paper presents our collection methods, laboratory protocols and findings in respect of sewage pollution affecting seawater and marine organisms in Table Bay, Cape Town, South Africa, then moves to consider their implications for the governance of urban water as well as sewage treatment and desalination. A series of seawater samples, collected from approximately 500 m to 1500 m offshore, in rock pools at low tide near Granger Bay, and at a depth under beach sand of 300–400 mm, were investigated for the presence of bacteriological load indicator organisms including *Escherichia coli* and *Enterococcus* bacteria. A second series of samples comprised limpets (*Patella vulgata*), mussels (*Mytilus galloprovincialis*), sea urchins (*Tripneustes ventricosus*), starfish (*Fromia monilis*), sea snails (*Tegula funebralis*) and seaweed (*Ulva lactuca*), collected in rock pools at low tide near Granger Bay, and sediment from wet beach sand and where the organisms were found, close to the sites of a proposed desalination plant and a number of recreational beaches. Intermittently high levels of microbial pollution were noted, and 15 pharmaceutical and common household chemicals were identified and quantified in the background seawater and bioaccumulated in marine organisms. These indicator microbes and chemicals point to the probable presence of pathogens, and literally thousands of chemicals of emerging concern in the seawater. Their bioaccumulation potential is demonstrated.

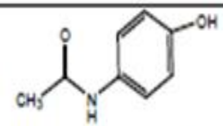
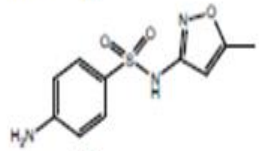
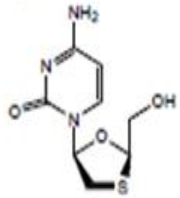
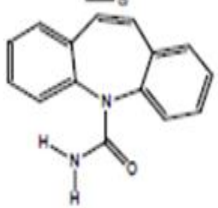
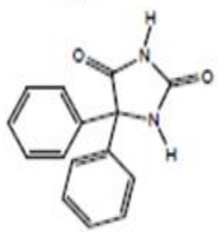
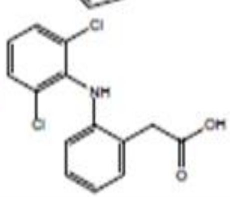
In respect of proposed desalination, the findings indicate that desalinated seawater must be subjected to treatment protocols capable of removing both bacterial loads and organic chemical compounds. The terms of reference for desalination plants must specify adequate testing and monitoring of chemical compounds as well as microorganisms in the intake and recovered water. Drinking water supplied by the proposed seawater desalination plants should be carefully tested for its toxicity.

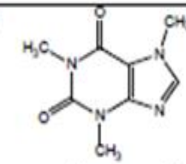
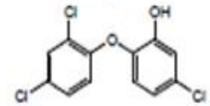
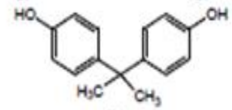
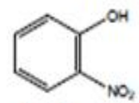
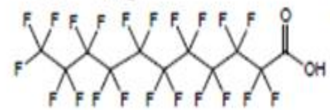
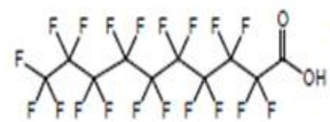
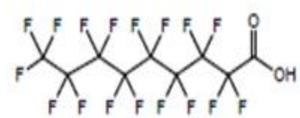
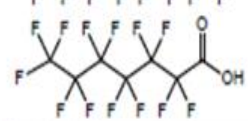
In respect of water management, our findings suggest the need for the City of Cape Town to move to an integrated water and sewage management plan that treats urban water, including seawater, as a circulating system that is integral to the health of the City, and which excludes marine outfalls.



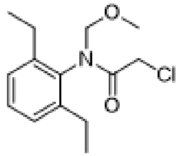
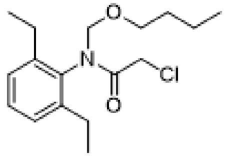
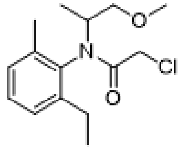
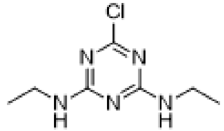
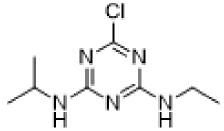
Petrik L, Green L, Abegunde AP, Zackon M, Sanusi CY, Barnes J. Desalination and seawater quality at Green Point, Cape Town: A study on the effects of marine sewage outfalls. **S Afr J Sci. 2017;113(11/12),** Art. #a0244, 10 pages. http://dx.doi. org/10.17159/sajs.2017/a0244

Testing for synthetic chemical compounds of emerging concern

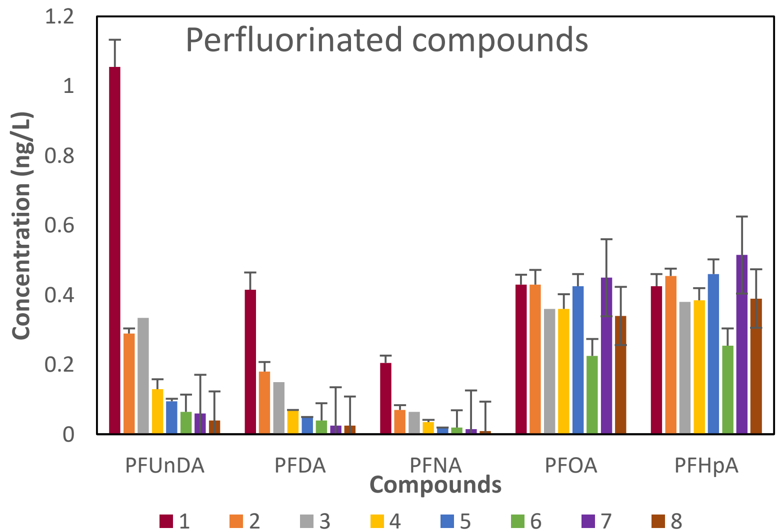
Acetaminophen	Analgesics/anti inflammatory	
Sulfamethoxazole	Antibiotic	
Lamivudine	Antiretroviral	
Carbamazepine	Psychiatric-antiepileptic	
Phenytoin	Anti-epileptic	
Diclofenac	Analgesics/anti inflammatory	

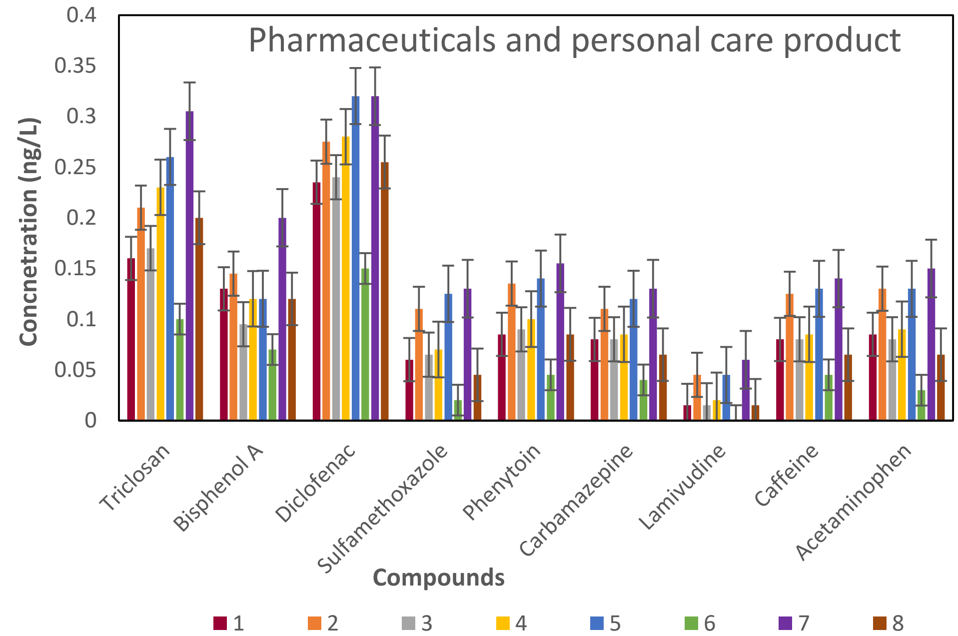
Caffeine	Psychomotor Stimulant	
Triclosan	Disinfectants	
Bisphenol A	Industrial chemical	
2-nitrophenol	Industrial chemical	
Perfluoroundecanoic acid	Industrial chemical	
Perfluorodecanoic acid	Industrial chemical	
Perfluorononanoic acid	Industrial chemical	
Perfluorooctanoic acid	Industrial chemical	
Perfluoroheptanoic acid	Industrial chemical	

Selected Herbicides

Compounds	Molecular mass (g/mol)	Molecular structure
Alachlor	269.8	
Butachlor	311.85	
Metolachlor	283.8	
Simazine	201.6	
Atrazine	215.7	

Green point Seawater samples



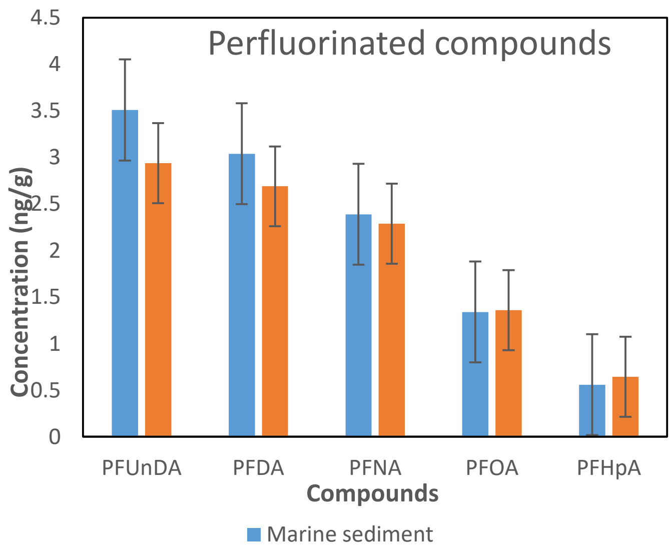


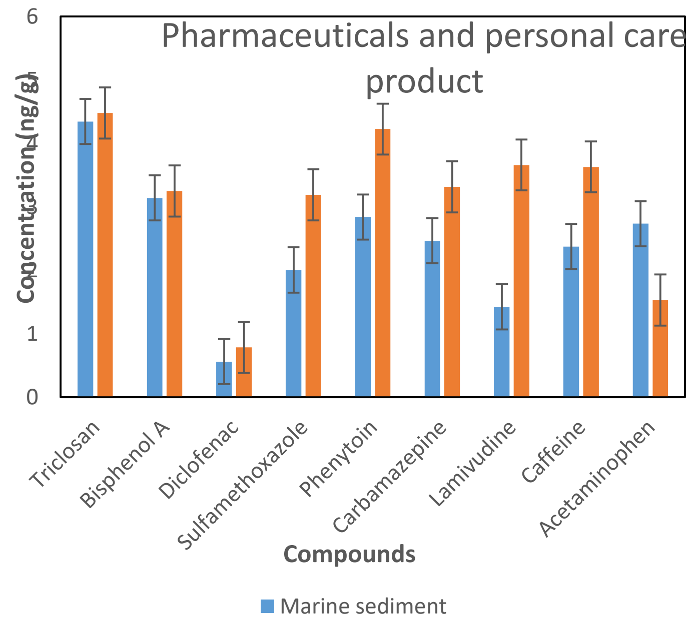
YES-These compounds are found in the seawater close to the marine outfalls!

Concentrations are low but their presence is indicating that many more compounds escape into the environment through the sewage discharges

Are these EC compounds found in marine sediment and beach sand?

Green Point data





Yes, these compounds found in sewage are also contaminating the shoreline

Concentrations on the shoreline are 10-100 times higher than in the seawater

Shows that sewage from the marine outfall flows back to shore

Limpets: *Cymbula granatina* and *C. oculus*

Sea weed: *Ulva sp*

Mussels: *Mytilus galloprovincialis*

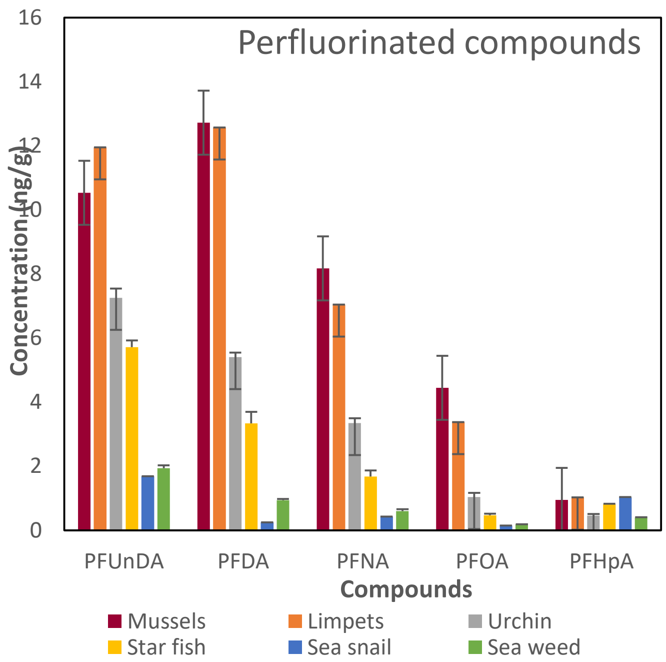
Sea urchins: *Parechinus angulosus*

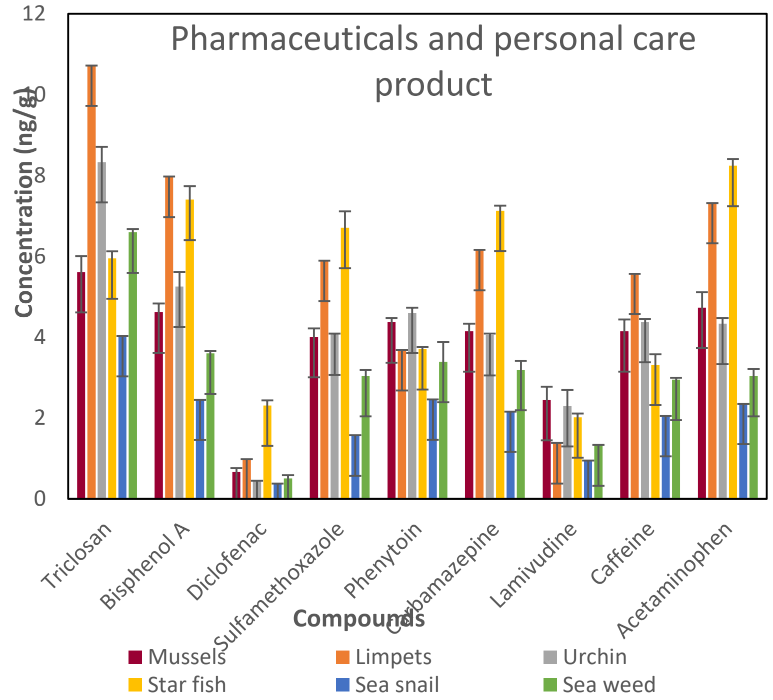
Top shells: Oxystele tigrina

Starfish: *Marthasterias africana*

Are these compounds found in Marine Biota?

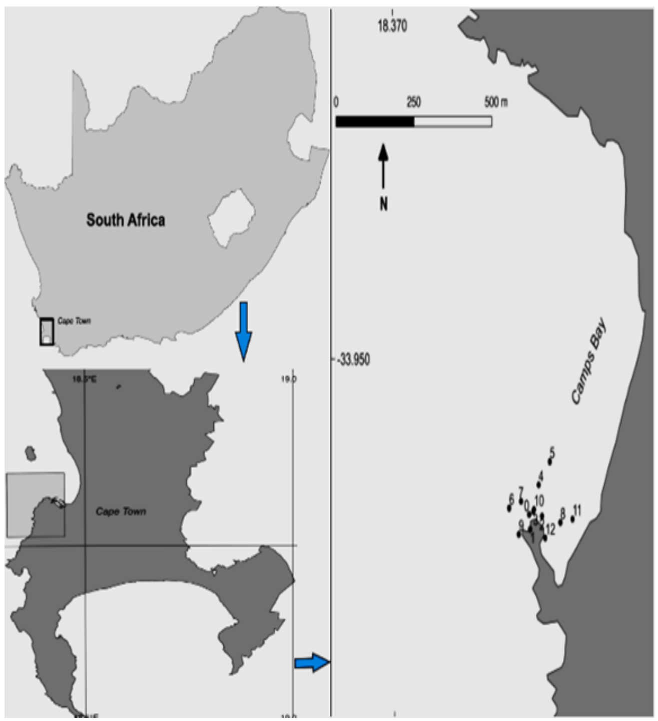
EC Chemicals found in Green Point Marine Biota





Yes- these sewage linked emerging contaminants are present in marine biota
Concentrations are higher than the sea-water and sediment levels
Indicates bioaccumulation
Many other compounds may also be present

Does Camps Bay environment also show impacts of the marine outfall?



5 Perfluorinated compounds
Triclosan (biocide)
Bisphenol-A (plasticizer)
Diclofenac (anti-inflammatory)
Sulfamethoxazole (antibiotic)
Phenytoin (antiepileptic)
Carbamazepine (anticonvulsant)
Lamivudine (antiretroviral)
Caffeine (stimulant)
Acetominophen (painkiller)
2-Nitrophenol (hairdye etc)

PESTICIDES/HERBICIDES
Simazine
Atrazine
Alachlor
Butalaclor
Metalachlor

Does Camps Bay also show impacts of the marine outfall?

CoCT commissioned a study by CSIR in 2016 which showed many chemicals were in the raw sewage being pumped out to sea

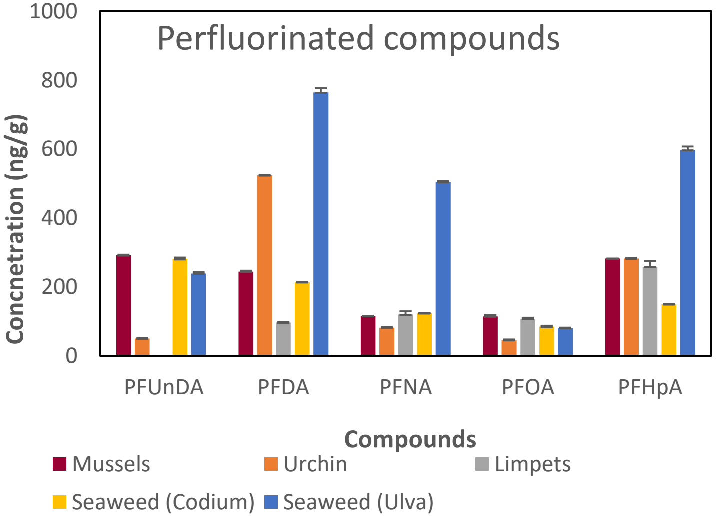
We found these sewage related compounds in CampsBay seawater

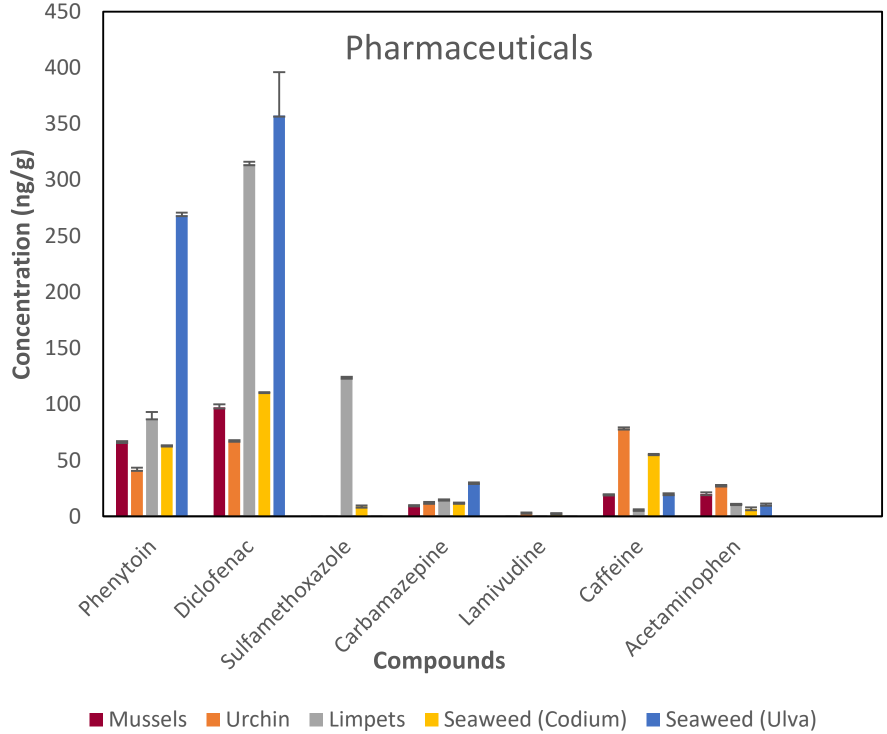
Dilution factor was not the same for different compounds as compounds differ in their properties

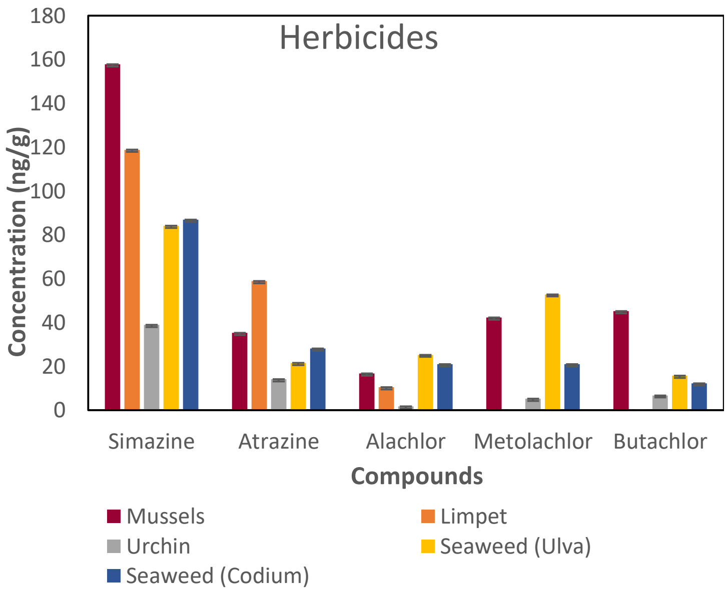
Table 3: Dilution factor of diverse compounds discharged into the marine environment in Camps Bay

Compounds	Sewage at pump station (ng/L)	Seawater (ng/L)	Dilution factor
Carbamazepine	280 – 580	0.05 – 0.14	4142x
Diclofenac	630 – 1500	0.73 – 2.86	524x
Paracetamol	250000 – 950000	0.09 – 0.10	9700000x

EC Chemicals in Campsbay marine biota and seaweed







Diverse chemicals were found in the marine biota at higher levels than at GreenPoint

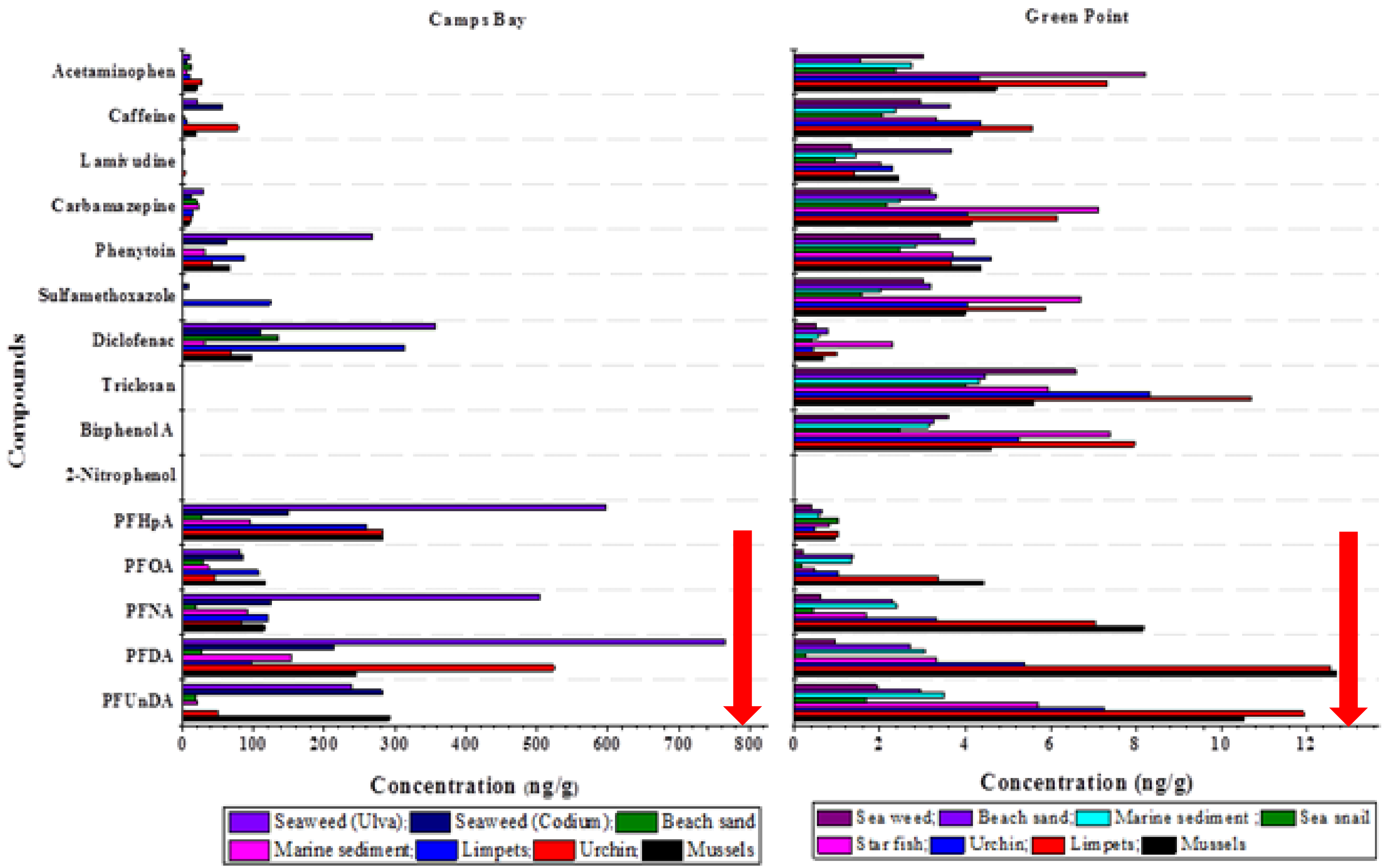
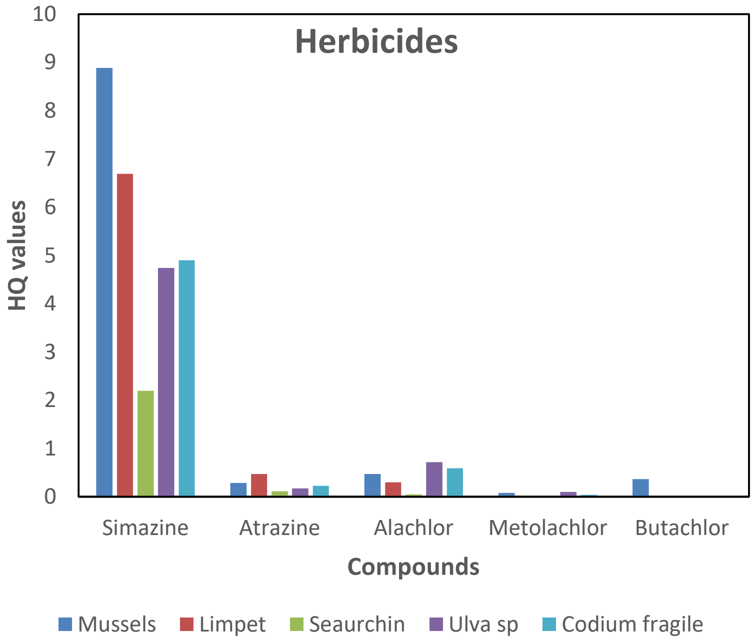
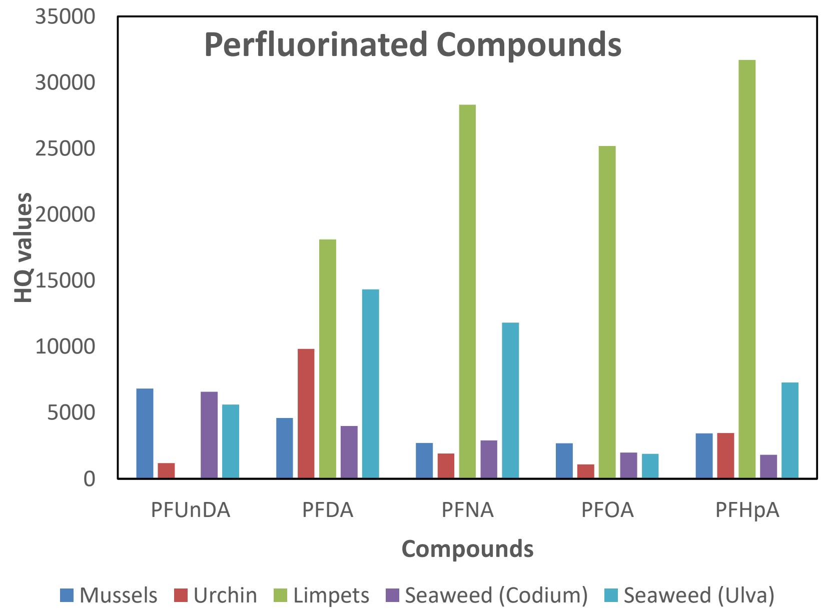


Figure 5: Comparison of concentrations of compounds in sediment, seaweed and marine organisms from Camps Bay and Green Point

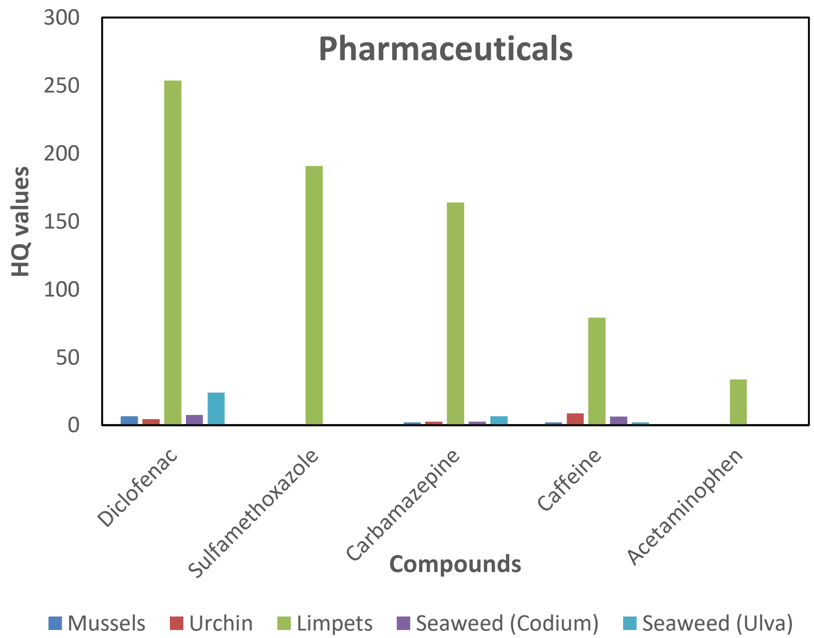
More chemicals found at GreenPoint, **much higher** levels found at CampsBay,
Both seashores and biota were impacted by chemicals in sewage from marine outfalls

Hazard quotient (HQ) for samples from Camps Bay





Much higher than the recommended max value of 1.0



Is the food chain being affected?

Environmental Pollution (2019), Environmental Pollution 252 (2019) 562-572 , https://doi.org/10.1016/j.envpol.2019.05.091

Environmental Pollution 252 (2019) 562–572

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

ELSEVIER

Occurrences, levels and risk assessment studies of emerging pollutants (pharmaceuticals, perfluoroalkyl and endocrine disrupting compounds) in fish samples from Kalk Bay harbour, South Africa

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A R T I C L E   I N F O

Article history:
Received 6 January 2019
Received in revised form
7 May 2019
Accepted 17 May 2019
Available online 24 May 2019

Keywords:
Pharmaceuticals
Perfluorinated compounds
Fish
Pollutants
Risk assessment

A B S T R A C T

A comprehensive analysis of 15 target chemical compounds (pharmaceuticals and personal care product, perfluoroalkyl compounds and industrial chemicals) were carried out to determine their concentrations in selected commercially exploited, wild caught small and medium sized pelagic fish species and their organs (*Thyrsites atun* (snoek), *Sarda orientalis* (bonito), *Pachymetopon blochii* (panga) and *Pterogymnus laniarius* (hottentot)) obtained from Kalk Bay harbour, Cape Town. Solid phase extraction (SPE) method based on Oasis HLB cartridges were used to concentrate and clean-up the samples. Liquid chromatography–mass spectrometry analysis of these chemical compounds revealed the simultaneous presence of at least 12 compounds in different parts of the selected fish species in nanogram-per-gram dry weight (ng/g dw) concentrations. The results revealed that perfluorodecanoic acid, perfluorononanoic acid and perfluoroheptanoic acid were the most predominant among the perfluorinated compounds and ranged between: (20.13–179.2 ng/g), (21.22–114.0 ng/g) and (40.06–138.3 ng/g). Also, diclofenac had the highest concentration in these edible fish species out of all the pharmaceuticals detected (range: 551.8–1812 ng/g). The risk assessment values were above 0.5 and 1.0 for acute and chronic risk respectively which shows that these chemicals have a high health risk to the pelagic fish, aquatic organisms and to humans who consume them. Therefore, there is an urgent need for a precautionary approach and the adequate regulation of the use and disposal of synthetic chemicals that persist in aquatic/marine environment in this province and other parts of South Africa, to prevent impacts on the sustainability of our marine environment, livelihood and lives.

DO THESE EC COMPOUNDS ACCUMULATE MORE AT A HIGHER TROPHIC LEVEL?

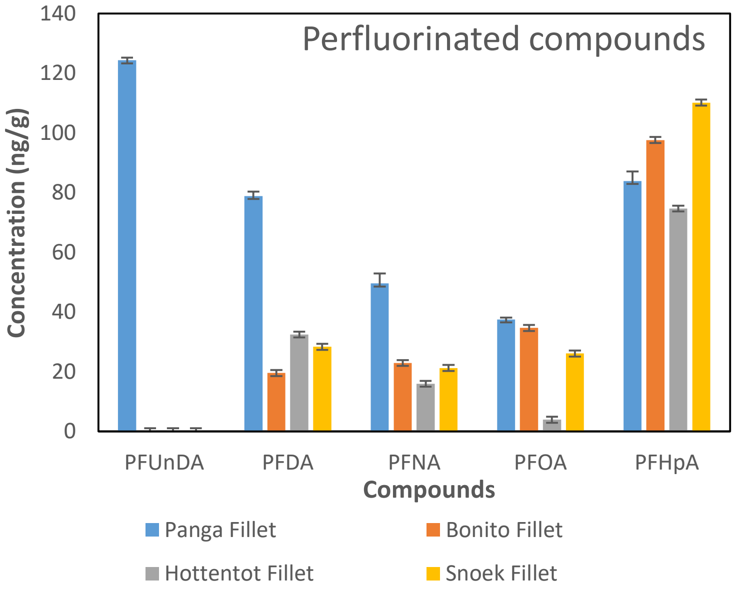
Is False Bay impacted by EC from WWTP sewage effluent discharged into estuaries, surfzones and rivers?

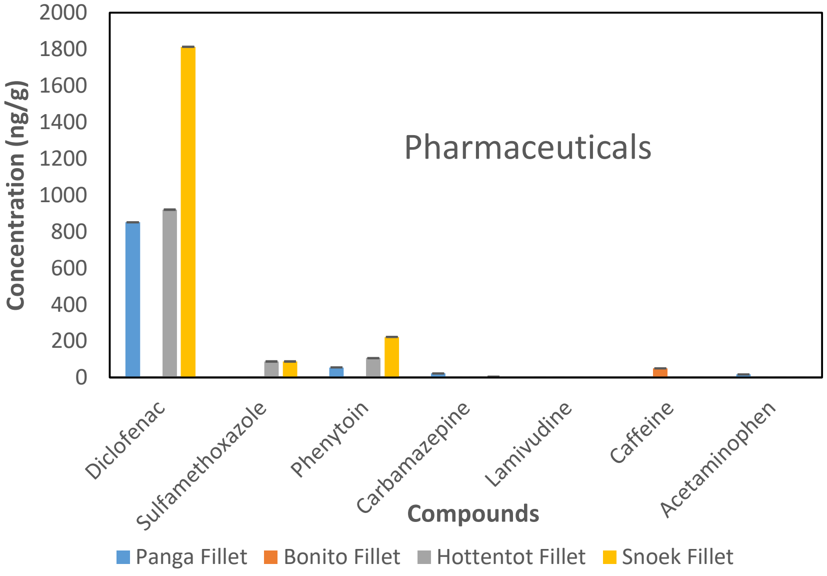
Four species of fish namely:

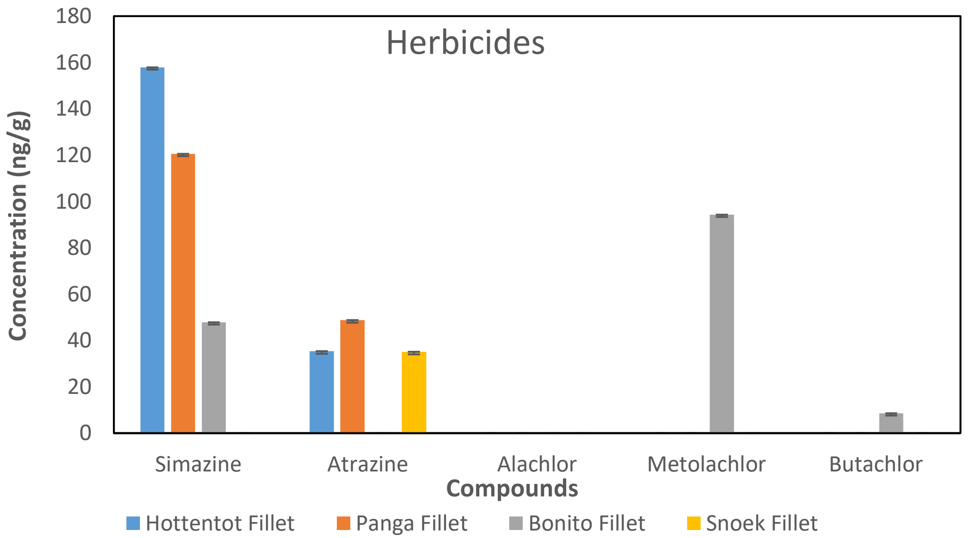
Thyrsites atun (snoek)
Sarda orientalis (bonito)
Pachymetopon blochii (hottentot)
Pterogymnus laniarius (panga)

The samples of fish fillets, intestines and liver and gills were separately evaluated

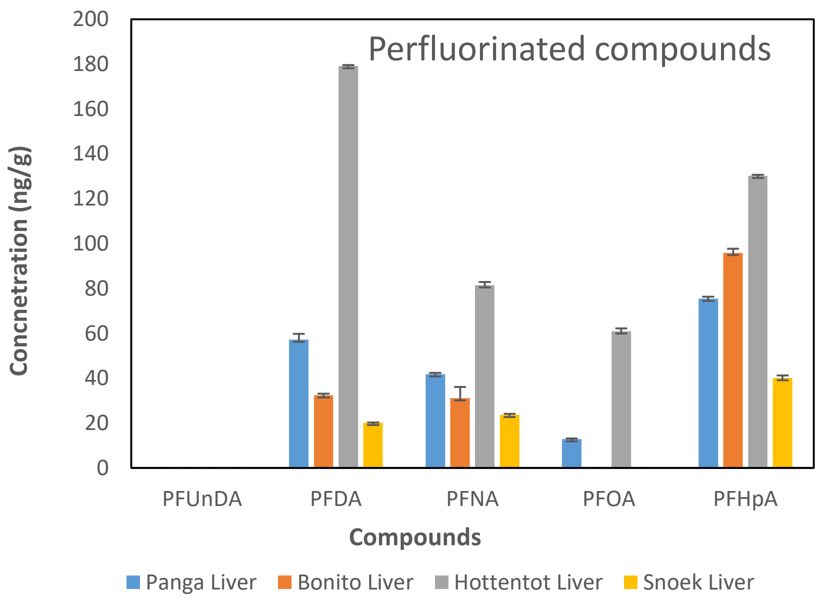
EC Chemicals detected in fillets of fish

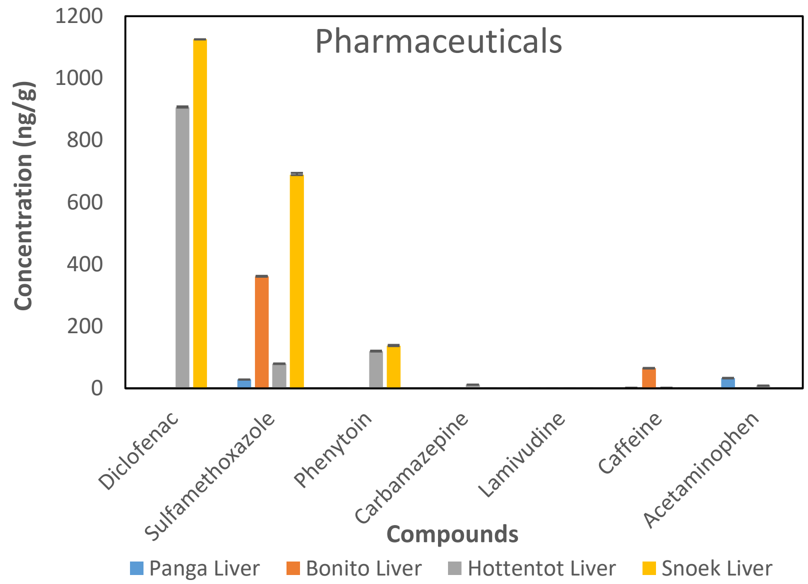


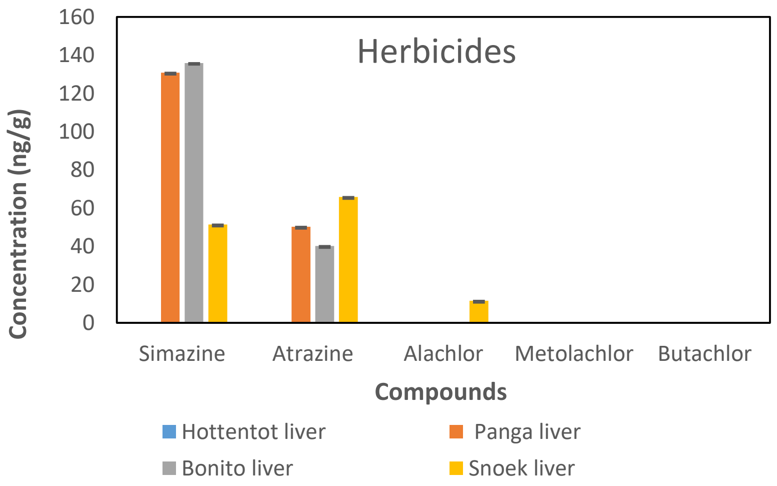




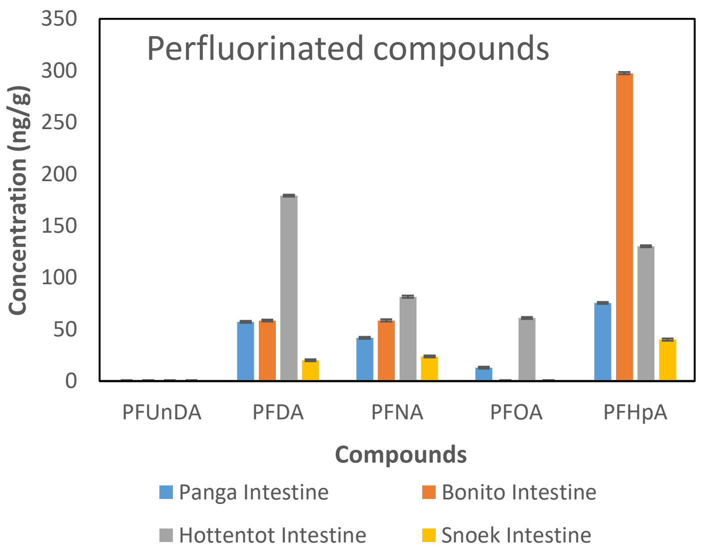
EC Chemicals detected in fish liver samples

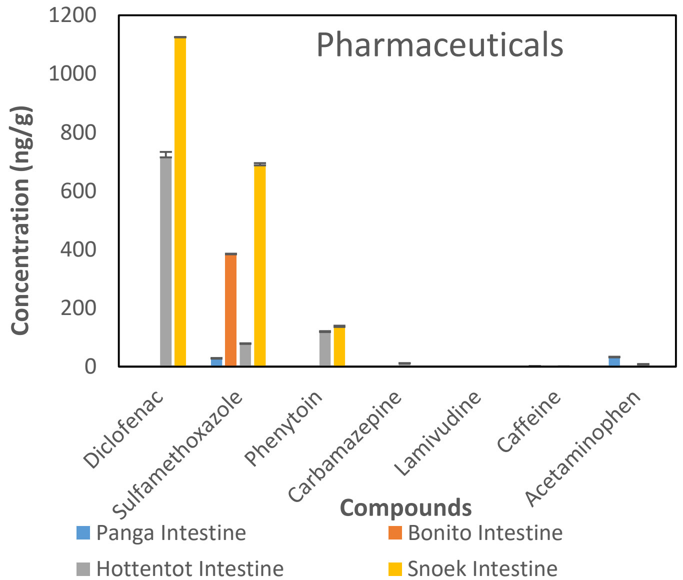


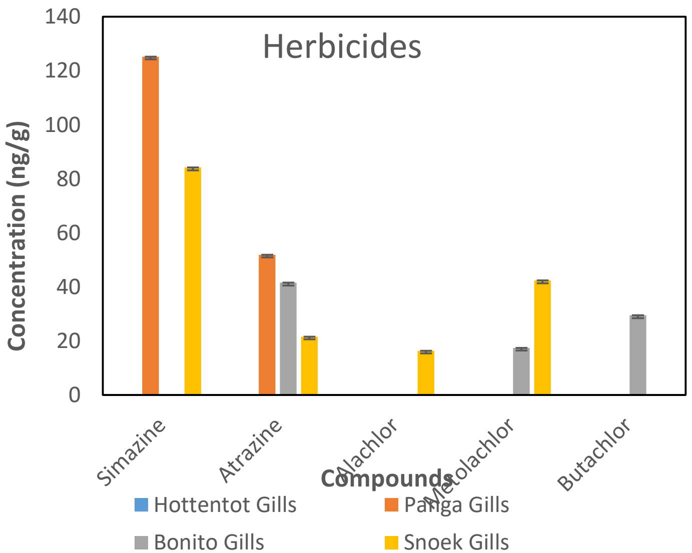




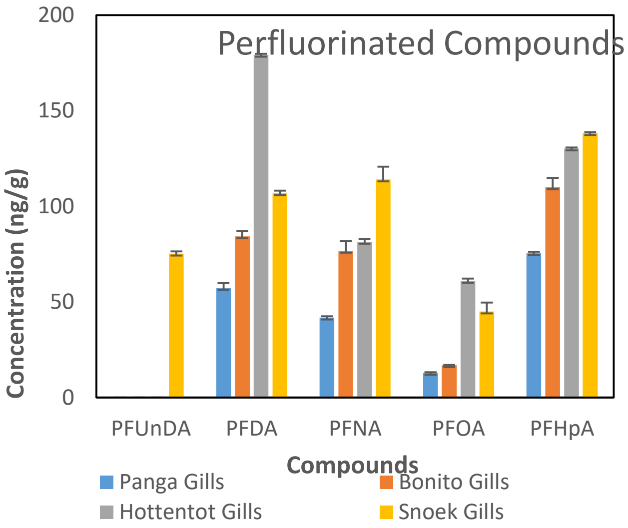
EC Chemicals detected in fish intestine samples

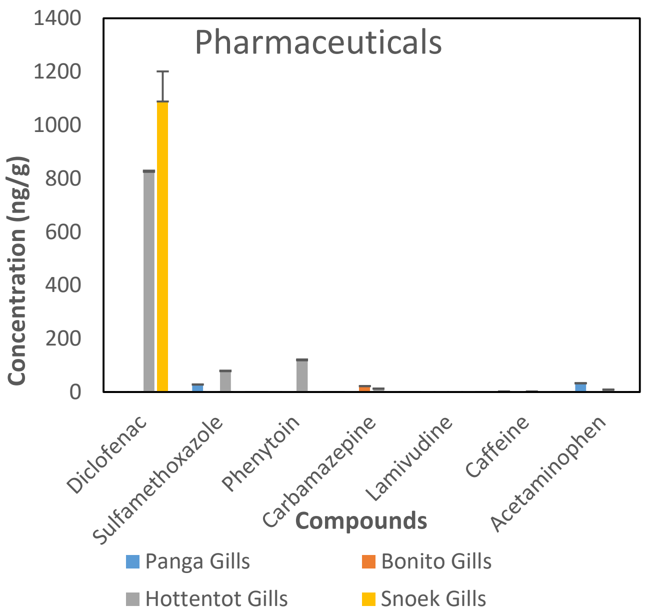


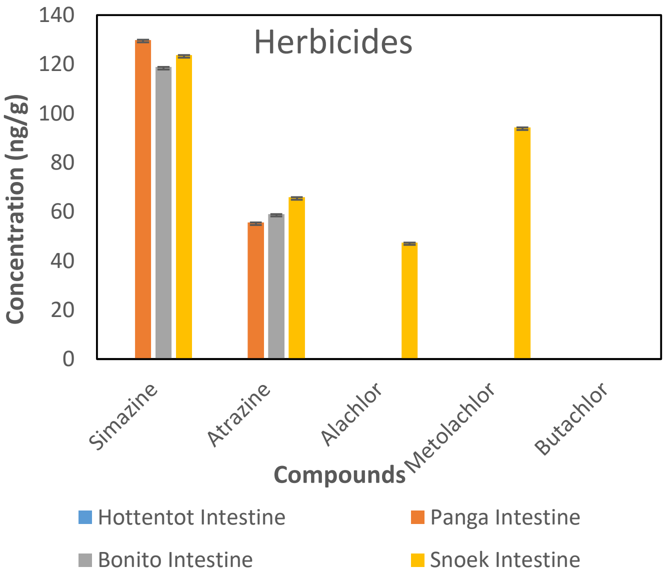




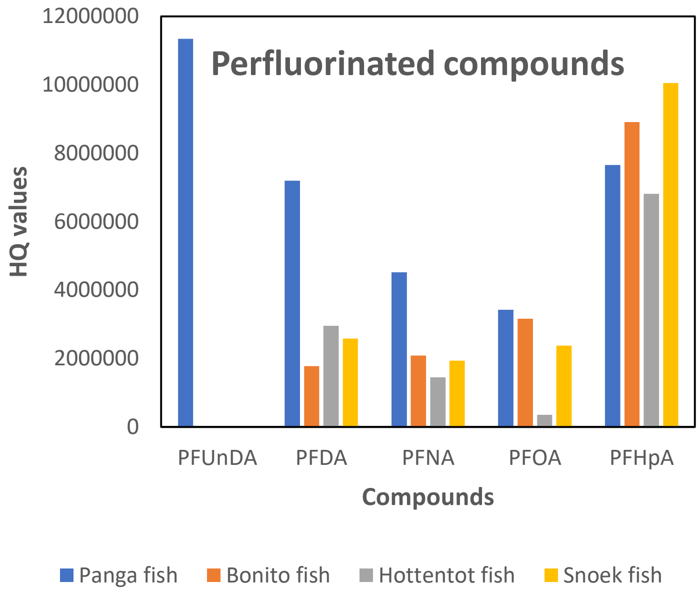
EC Chemicals detected in fish gill samples

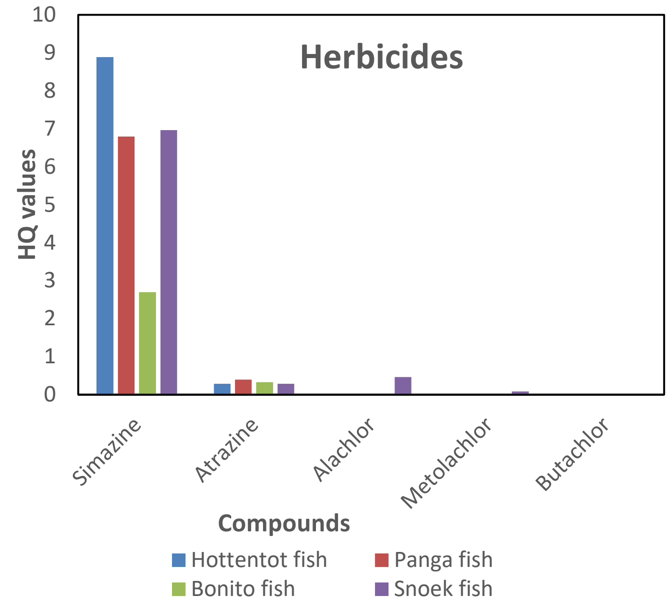


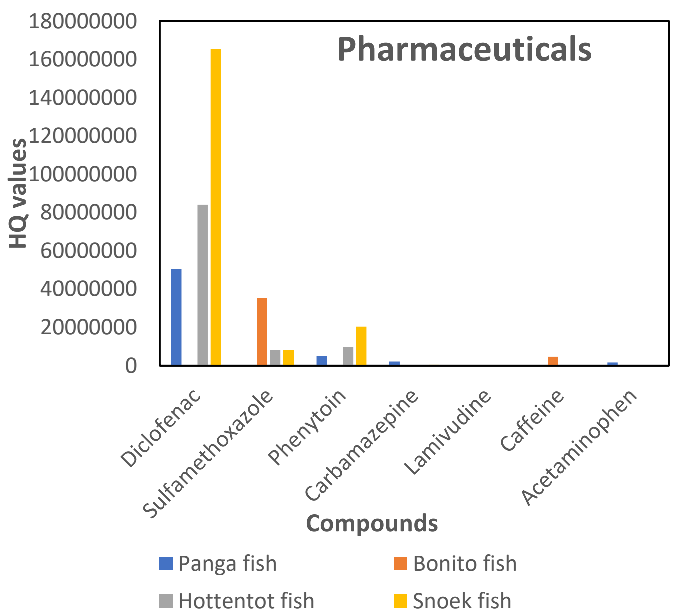




Hazard quotient for fish samples from Kalk Bay harbour







Hazard quotient values: Simazine, perfluorinated compounds and pharmaceuticals higher than the recommended values 1.0

Indicating the severe danger of these pollutants to the ecosystem

There is possibility of people developing non-carcinogenic health issues.

How does Cape Town EC contaminant levels compare with other places?

Comparison of PFAs compounds in fish samples obtained in this study with others in previously published studies.

Location/Compound	PFUnDA	PFDA	PFNA	PFOA	PFHpA	Reference
Hong kong	0.71	–	0.65	–	–	Zhao et al. (2011)
Xiamen	0.59	0.60	0.86	1.0	–	Zhao et al. (2011)
Brazil	<3.0	<1.19	<1.41	1.63	2.34	Quinete et al. (2009)
West coast of Korea	0.04	0.05	0.02	0.06	0.23	Naile et al. (2013)
North Carolina, USA	6.72	15.0	–	–	–	Delinsky et al. (2010)
Greece	1.05	0.65	0.60	–	–	Vassiliadou et al. (2015)
China	1.85	1.22	–	<0.5	–	Shi et al. (2010b)
New York, USA	–	–	–	5.2	–	Sinclair et al. (2006)
Spain	0.71	<0.06	0.51	0.09	<0.08	Domingo et al. (2012)
Ohio, USA	3.50	1.79	0.74	<0.20	0.64	Ye et al. (2008)
Germany	nd	nd	nd	2.3	nd	Hölzer et al. (2011)
This study	12.44	78.86	49.53	37.52	83.86	

Cecilia Y. Ojemaye and Leslie Petrik. 2018. Pharmaceuticals in the marine environment: a review. Environ. Rev. 00: 1–15 (0000) dx.doi.org/10.1139/er-2018-0054

E.G The perfluorinated compounds contaminant levels in fish samples from Cape Town are much higher than reported elsewhere

What is the case elsewhere?

NRC Research Press

REVIEW

Pharmaceuticals in the marine environment: a review

Cecilia Y. Ojemaye and Leslie Petrik

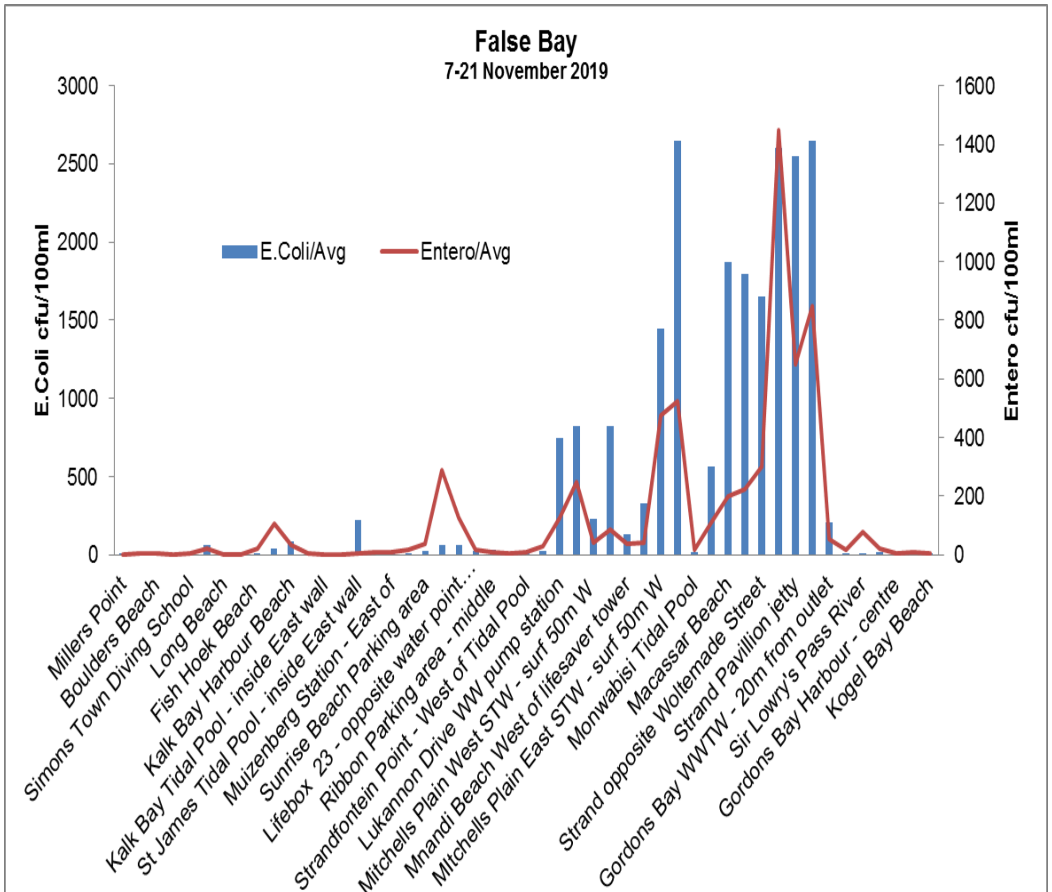
Abstract: Despite the increasing presence of pharmaceuticals in marine environments and their potential negative impacts, little research has been reported on the level and occurrence of these contaminants in the marine ecosystem. This review provides information on the occurrence (level–concentration) of pharmaceuticals in marine environments including seawater, sediments, and organisms within and (or) around this ecosystem. Also, the classification, sources, metabolism, and fate of these contaminants in the marine environment were discussed to identify knowledge gaps. We showed that antibiotics are the most commonly investigated and detected drugs in marine environments. In addition, this review suggested that focused case studies should be a priority for future research and highlighted the need for future assessments of the potential risks of pharmaceuticals to marine species. We also suggested that it is necessary to monitor the level of the most frequent and widespread pharmaceuticals like antibiotics and nonsteroidal anti-inflammatory drugs in sewage and marine outfalls. Finally, we concluded that there is a need for the development of effective treatment methods for the removal of these pollutants from wastewater before their discharge into the receiving marine environment or the main drinking water networks.

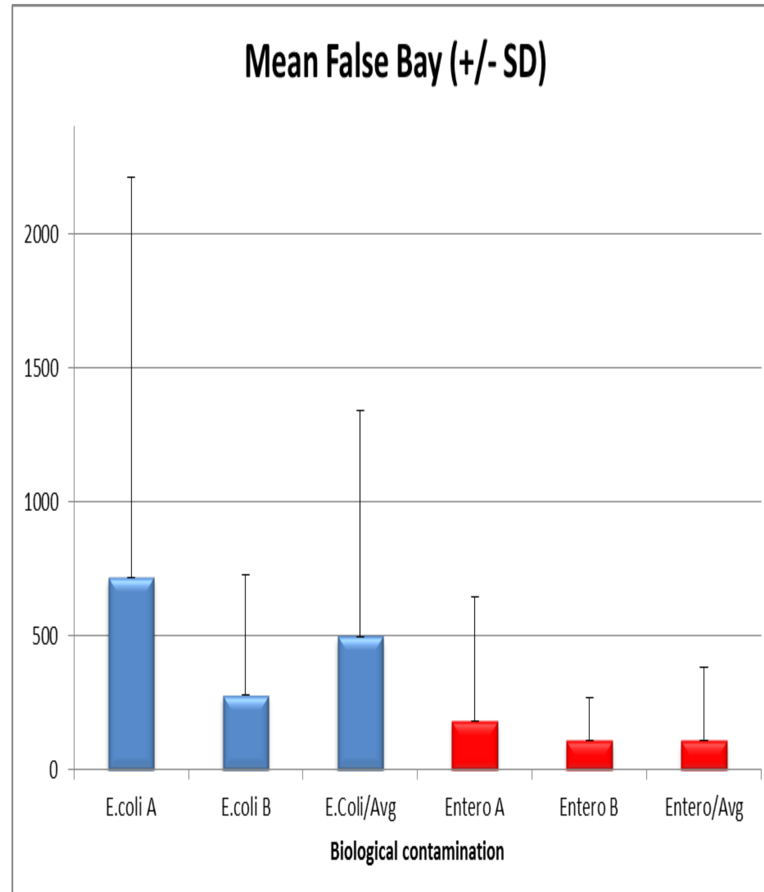
Key words: persistent organic pollutants and contaminants, seawater, sediment, marine organisms.

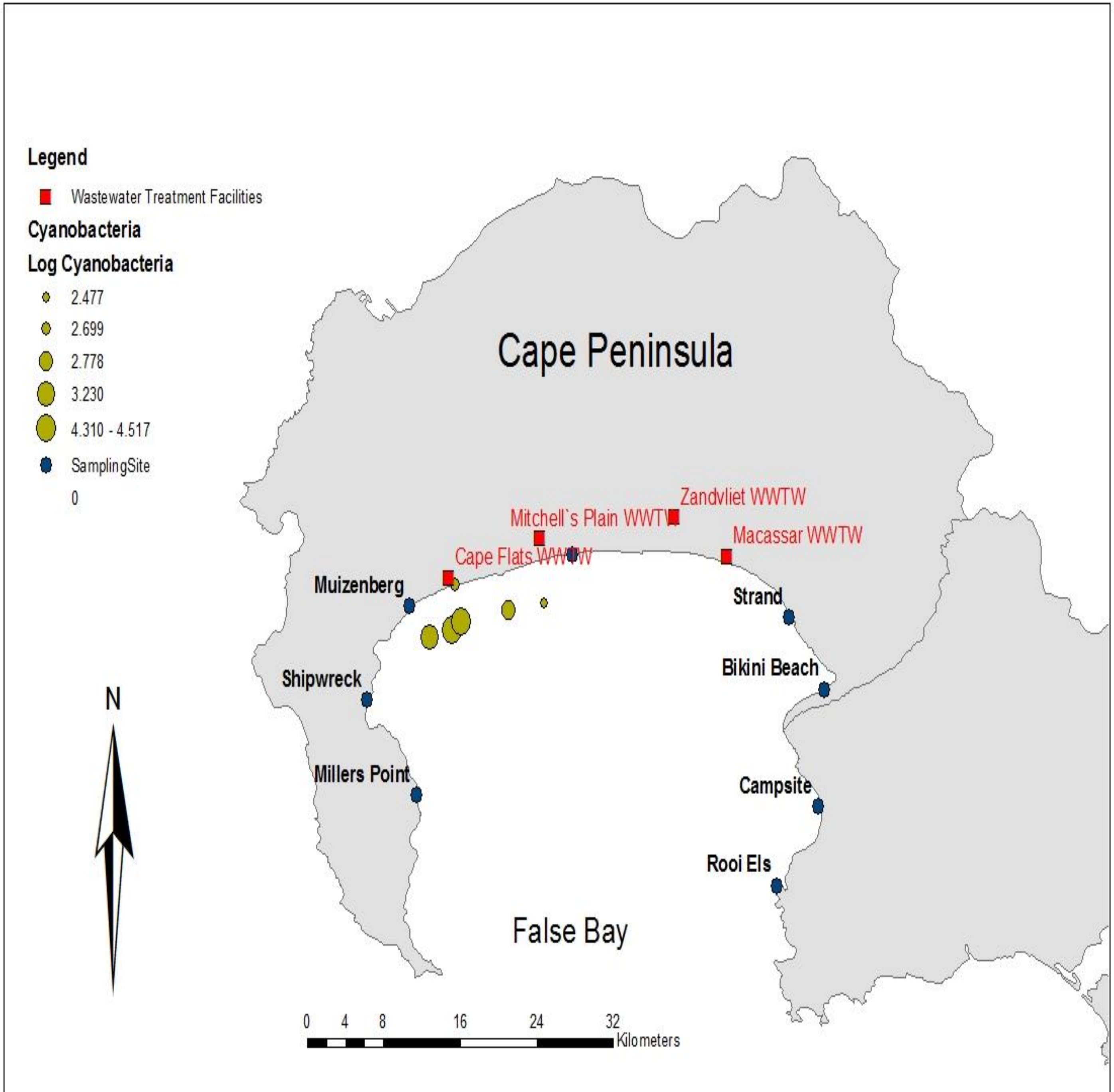
Cecilia Y. Ojemaye and Leslie Petrik. 2018. Pharmaceuticals in the marine environment: a review. Environ. Rev. 00: 1–15 (0000) dx.doi.org/10.1139/er-2018-0054

DESALINATION??

False Bay Preliminary Results: *Escherichia coli* and *Enterococcus* bacteria

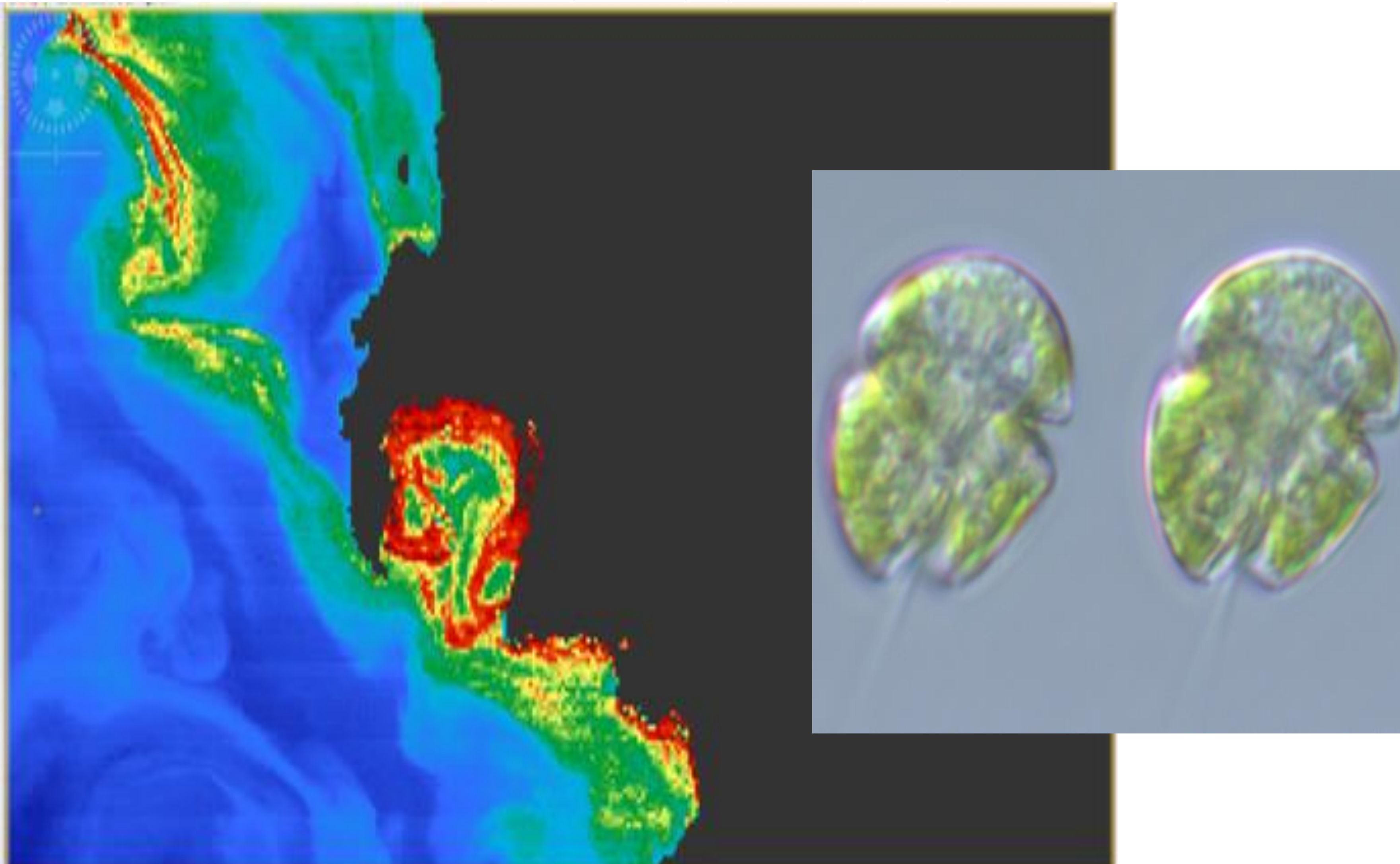




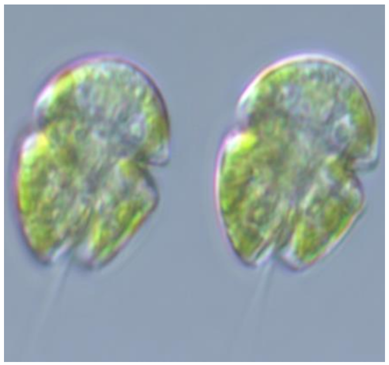


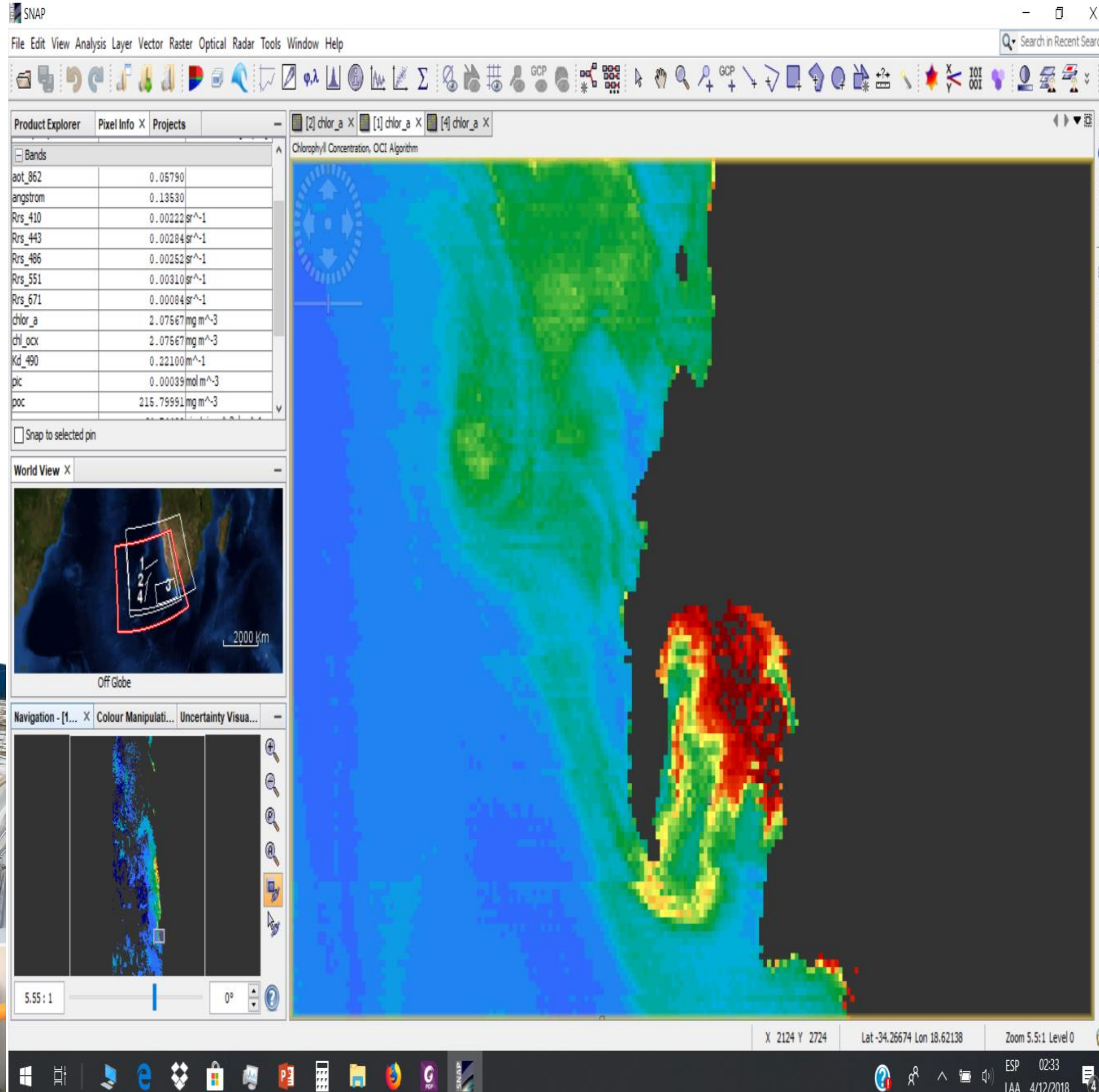
Legend
Wastewater Treatment Facilities
Cyanobacteria
Log Cyanobacteria
2.477
2.699
2.778
3.230
4.310 - 4.517
SamplingSite
0
Cape Peninsula
Zandvliet WWTW
Mitchell`s Plain WWTW
Macassar WWTW
Cape Flats WWTW
Muizenberg
Strand
Shipwreck
Bikini Beach
Millers Point
Campsite
Rooi Els
False Bay
N
0 4 8 16 24 32
Kilometers

False Bay: MicroAlgal blooms November 2018

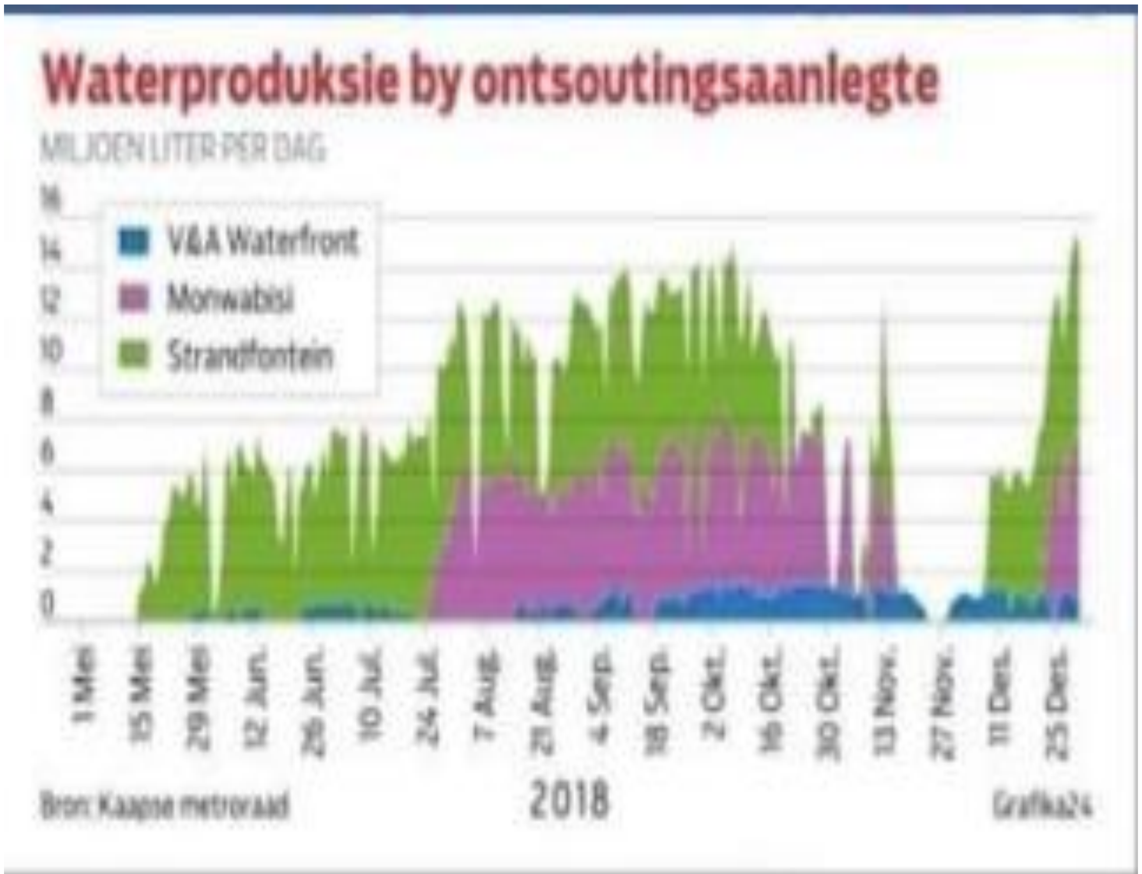


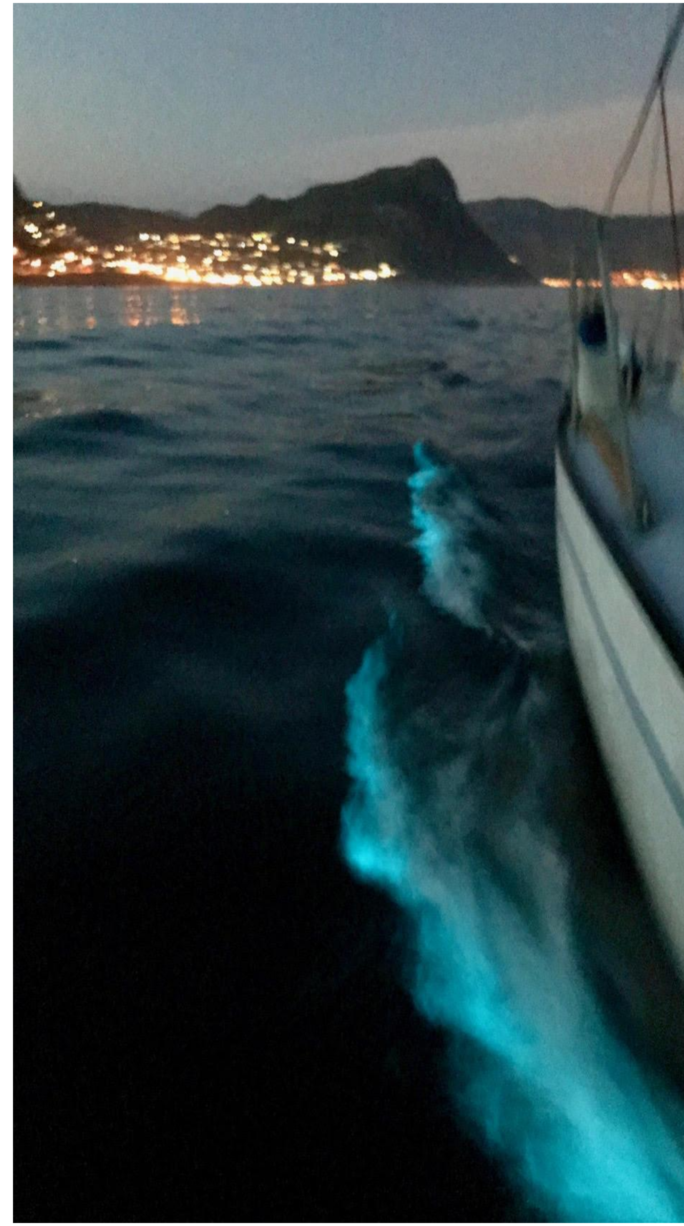
Phytoplankton Bloom in False Bay
around 34.0522 South, 18.7542 E





Desalination outputs





Algal blooms and bacteria

- Bacteria levels show high level of sewage contamination of ocean
- Associated with high load of nutrients
- No harmless scenario of major algal bloom
- Die outs of fish due to lack of oxygen
- Potential toxicities and pathology to humans
- Clogging desalination plants
- Aesthetically a disaster
- Slow response rate and no early warning system
- City and Province no line of communication to public or to scientists
- Data is not made public

STUDY RESULTS

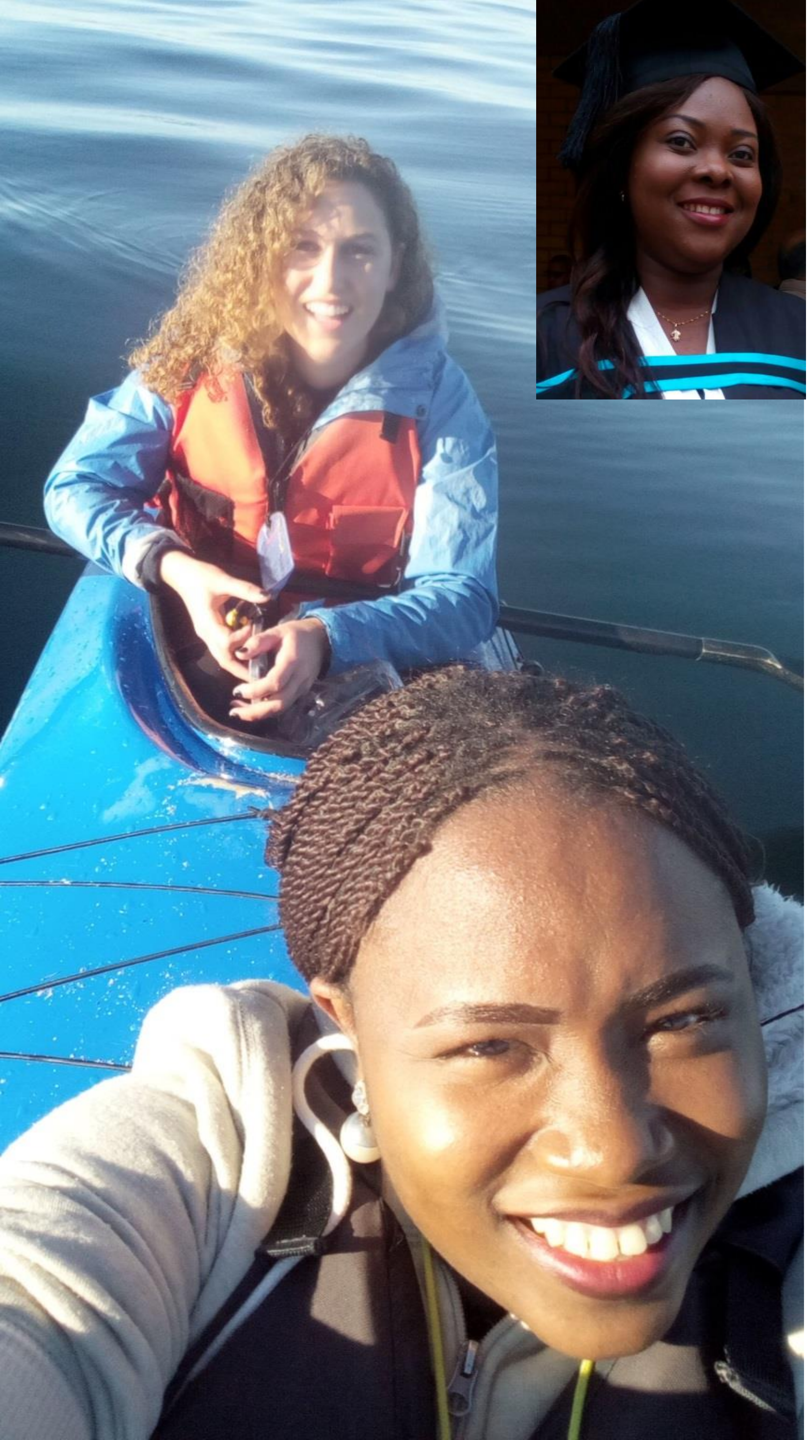
- Measurable presence of selected EC chemicals
- Indicates probable presence of many other EC chemicals
- Combined effects and concentrations are mostly unknown
- Compounds present in organisms' tissues in concentrations much higher than the background level in the ocean
- These compounds thus bio accumulate in marine organisms and up the food chain
- It is clear that, under certain conditions, sewage flows back to shore in detectable quantities that could be harmful
- Sewage is contaminating fish stock wild caught in the marine environment
- Determined by hydrophobicity, molecular mass, hydrogen bonding, polar surface area (PSA), and rotatable bonds, **Lipinski's rule of five**
- Risk =hazard x **exposure**

Conclusions

- The detected compounds **represent a variety of chemical types and therapeutic uses**
- None of these compounds would of themselves be found in seawater and should definitely not be present in these marine organisms.
- With the exception of caffeine, all are manufactured substances
- **High dilution of sewage in seawater did not stop bioaccumulation**

Take home message

- These compounds are in the marine organisms because we use them
- They do not “disappear” after use
- They “reappear” in the environment in unexpected places
- Species die-out partially due to our over use of chemicals
- Many of these chemical compounds come back to us in our food and water….
- Cause all kinds of metabolic problems, birth defects, cancers, feminization, changes in sex ratios etc..
- Please think very carefully about your chemical usage
- **Potable water recovery from unconventional sources needs careful and thorough testing for risk to be determined**



We gratefully acknowledge

Funding from the National Research Foundation (South Africa) for the Human Social Dynamics Grant (HSD141104109103 Grant 96035 titled Race and the Making of an Environmental Public) to Environmental Humanities South at the University of Cape Town.

We are indebted to

Tracy Fincham and Billy Fisher at Kaskazi Kayaks for guiding the sampling team and for the use of kayaks

to the SABS Rosebank for *E. coli* and *Enterococcus* results;

to the laboratories at Stellenbosch University and the University of the Western Cape for analysis;

to Nicholas Lindenberg for assistance with the map.

Acknowledgements

UNIVERSITY of the WESTERN CAPE

The Research Council of Norway

WATER RESEARCH COMMISSION

University of Cape Town • iYunivesithi yaseKapa • Universiteit van Kaapstad

SOUTH AFRICA – NORWAY COOPERATION ON OCEAN RESEARCH INCLUDING BLUE ECONOMY, CLIMATE CHANGE, THE ENVIRONMENT AND SUSTAINABLE ENERGY (SANOCEAN)

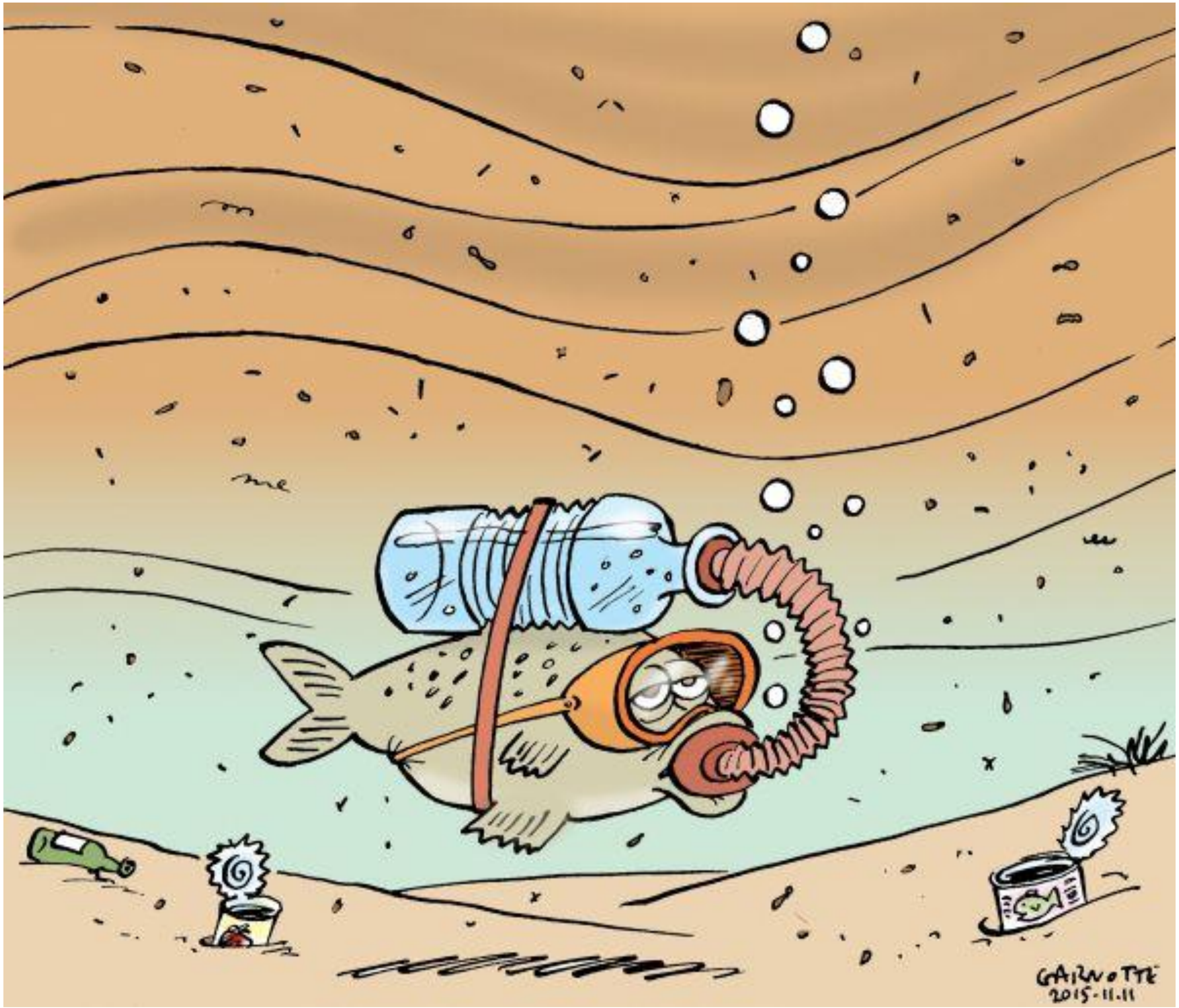
ENS Environmental Nano Sciences

University of Stavanger

NRF National Research Foundation

South African Weather Service

ANY QUESTIONS?

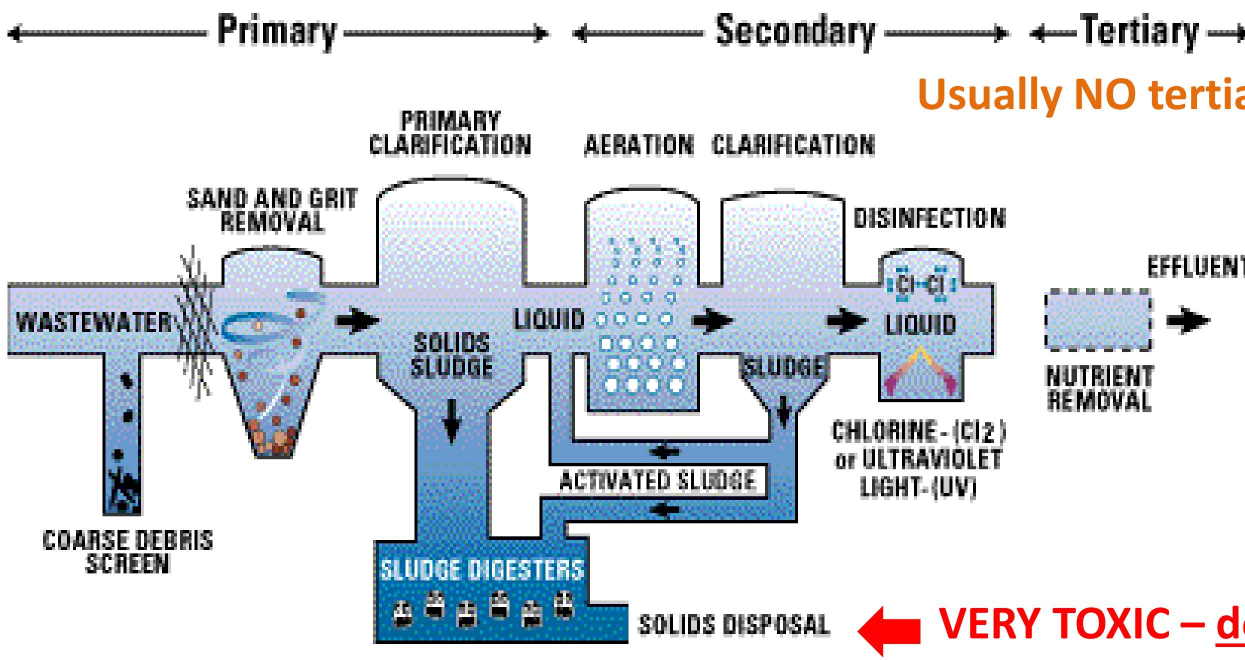


TREATMENT: Can we remove these compounds??

Physicochemical treatment

- **CONVENTIONAL**
- ✓ Chlorination
- ✓ Reverse Osmosis
- ✓ Coagulation/flocculation
- ✓ Adsorption (activated carbon)
- ✓ Filtration
- ✓ Ion Exchange
- ✓ Biological

Typical Wastewater Treatment Plant (WWTP) Process



Usually NO tertiary treatment

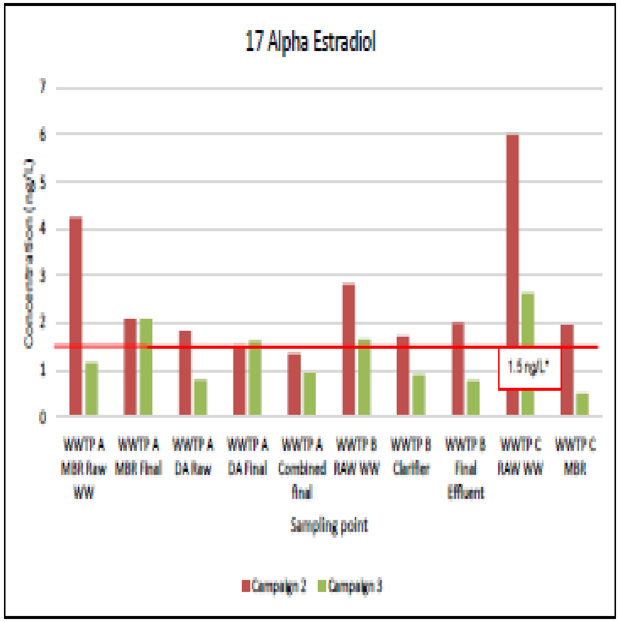
VERY TOXIC – do not dispose solids on agricultural land

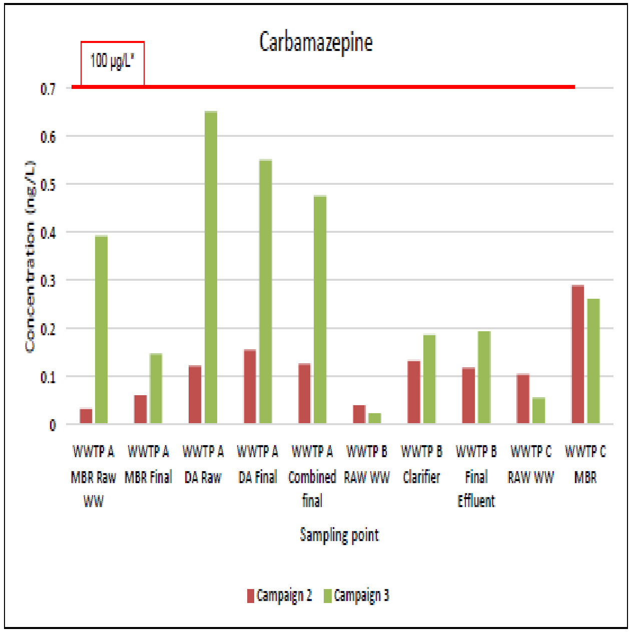
WWTPs TESTED: WRC Project No. K5/2369, March 2016

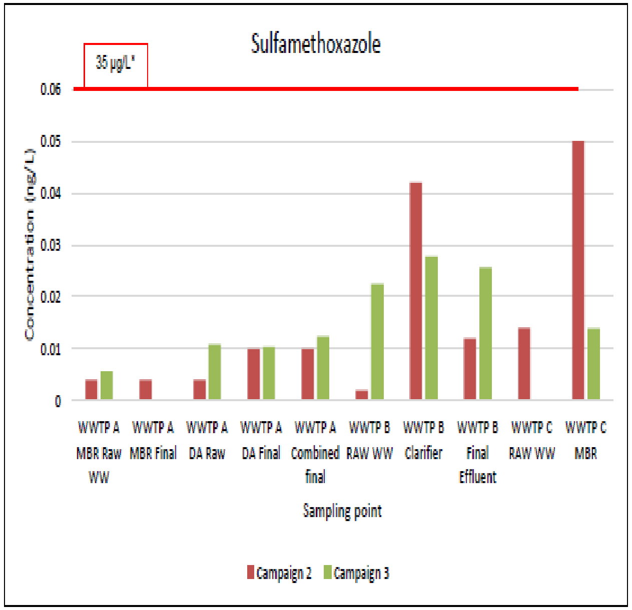
WWTP A (Beaufort West): Primary+ Secondary + Tertiary treatment process (ultrafiltration, reverse osmosis, and UV/H_20_2)
WWTP B (Zandvliet): Primary + Secondary (CAS + MBR)
WWTP C (Bellville): Primary + Secondary (CAS)
WWTP D (Scottsdene): Primary + Secondary (CAS)

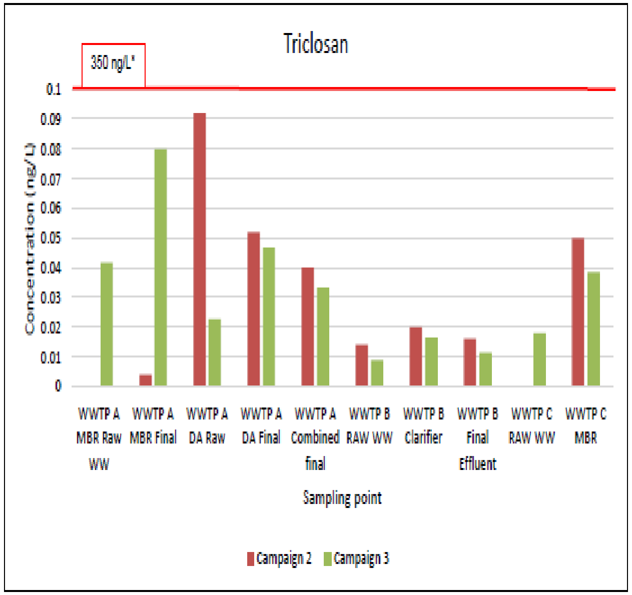
Our study showed poor EC removal from sewage effluents by WWTPs

WRC Project No. K5/2369, March 2016



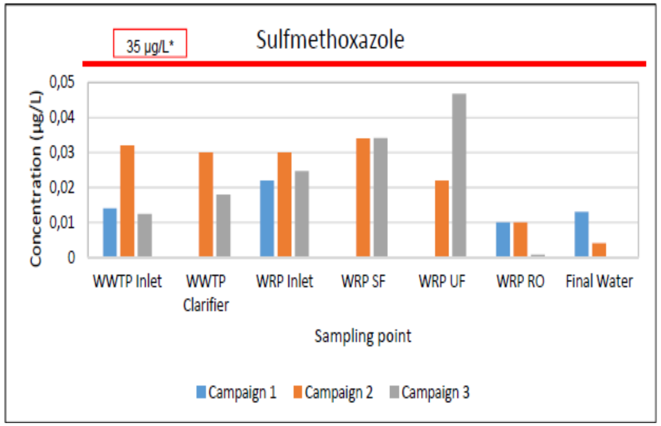


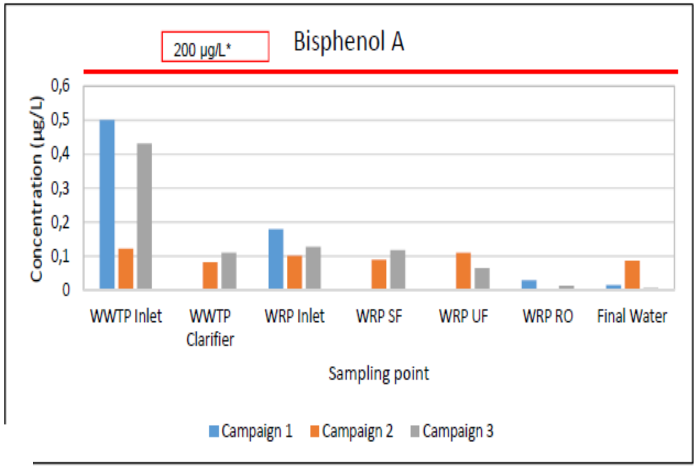




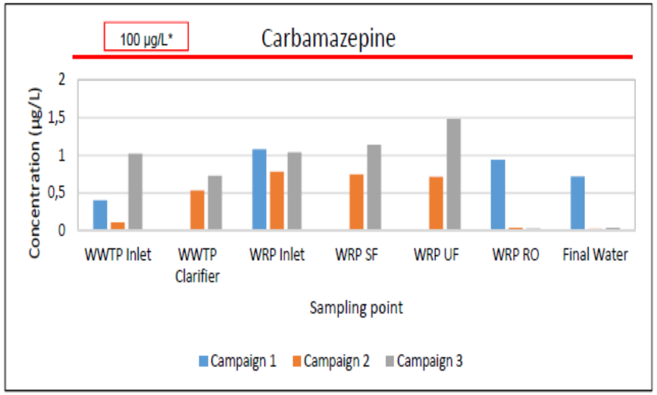
Potable reuse?

Swartz et al, 2017
WRC Project No. K5/2369
EMERGING CONTAMINANTS IN **WASTEWATER TREATED FOR DIRECT POTABLE RE-USE**: THE HUMAN HEALTH RISK PRIORITIES IN SOUTH AFRICA

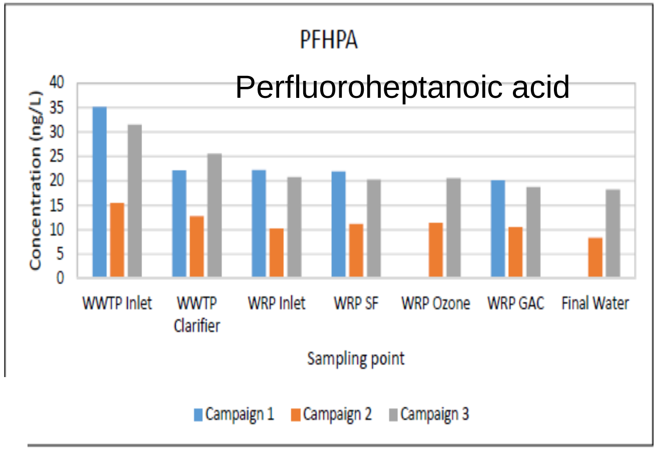




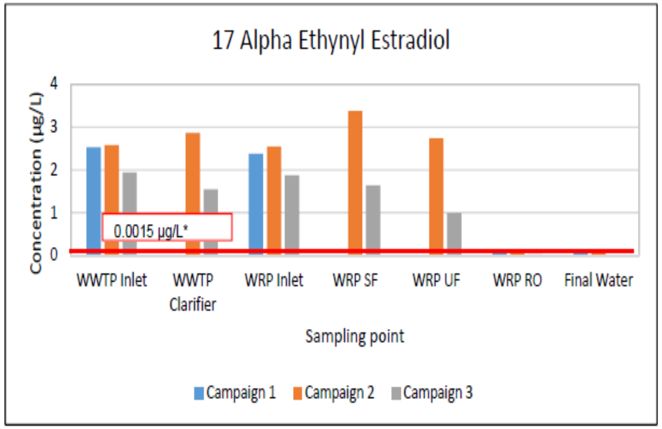
Bisphenol A for all the sampling campaigns for WRP A. * Limit proposed for potable water



Carbamazepine for all the sampling campaigns for WRP A. * Limit proposed for potab water (NRMMC, 2008 Guideline value)



PFHPA for all the sampling campaigns for WRP A



17 Alpha Ethynyl Estradiol for all the sampling campaigns for WRP A. * Limit proposed for potable water (NRMMC, 2008 Guideline value)

This **water reclamation** plant makes use of the **modern dual-membrane** treatment process treated using a sand filter, ultrafiltration (UF) reverse osmosis (RO) membranes and finally advanced oxidation before blending with treated water from a WTP, and then distributed to the public

Conventional systems?????

- Some EC chemicals removed by WWTP but inconsistent removal
- Removal was highly variable and different for different compounds
- Chemicals moved from liquid to solid in some cases = phase change
- Phase transfer means that **solids are highly toxic**
- % Removal from waste water is NOT destruction, but = transformation
- Could not test for transformed secondary byproducts
- Waste water treatment, even in best operational system, is not adequate
- Reverse osmosis is not 100% effective for potable water recovery + brine is very toxic (e.g.Beaufort West)
- Potable water from waste water is highly problematic
- Single advanced oxidation system (e.g.UV or peroxide) is not adequate
- Need a tertiary treatment stage including combined advanced oxidation

WHAT IS THE SOLUTION? ADVANCED OXIDATION

Advanced oxidation systems work by producing short-lived highly reactive free radicals

- ✓ UV
- ✓ Photocatalysis UV/TiO_2,
- ✓ Ozonation
- ✓ Fenton Process Fe^{2+}/H_2O_2
- ✓ Electrochemical oxidation
- ✓ Electrohydraulic discharge or DBD
- ✓ cavitation
- ✓ Combined:
  - UV/O_3,
  - UV/H_2O_2,
  - Fe^{2+}/H_20_2/UV,
  - UV/H_2O_2/TiO_2,
  - UV/O_3/TiO_2
  - UV/OH/H2O2

The radical is non-selective, highly reactive, powerful oxidant compared to other known oxidising agents like potassium permanganate etc

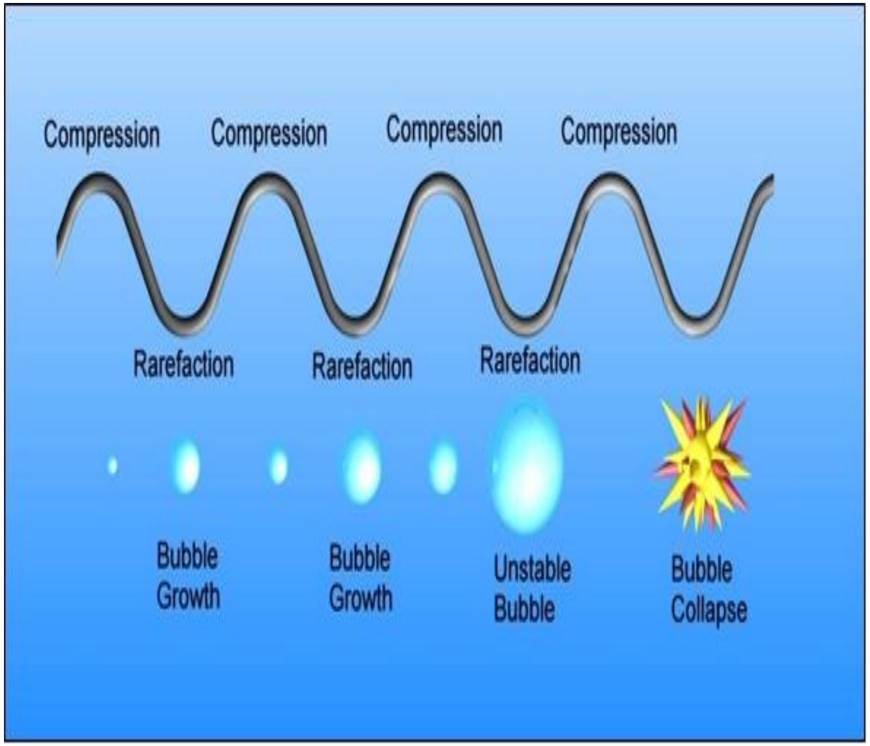
- **Reactions**
- $O_3 + hv \rightarrow O_2 + O(^1D)$ **ozonation**
- $O(^1D) + H_2O \rightarrow 2\,OH\cdot$
- $H_2O_2 + hv \rightarrow 2\,OH\cdot$ **Fenton process**
- $Fe^{3+} + H_2O + UV \rightarrow Fe^{2+} + H^+ + OH^\cdot$
- **Photo-Fenton**
- $TiO_2 + hv \rightarrow e^- + h^+$ ***Heterogeneous photocatalysis***
- $H_2O + h^+ \rightarrow OH^\cdot + H^+$
- $H_2O \quad H^\cdot + OH^\cdot$ **ultrasound**

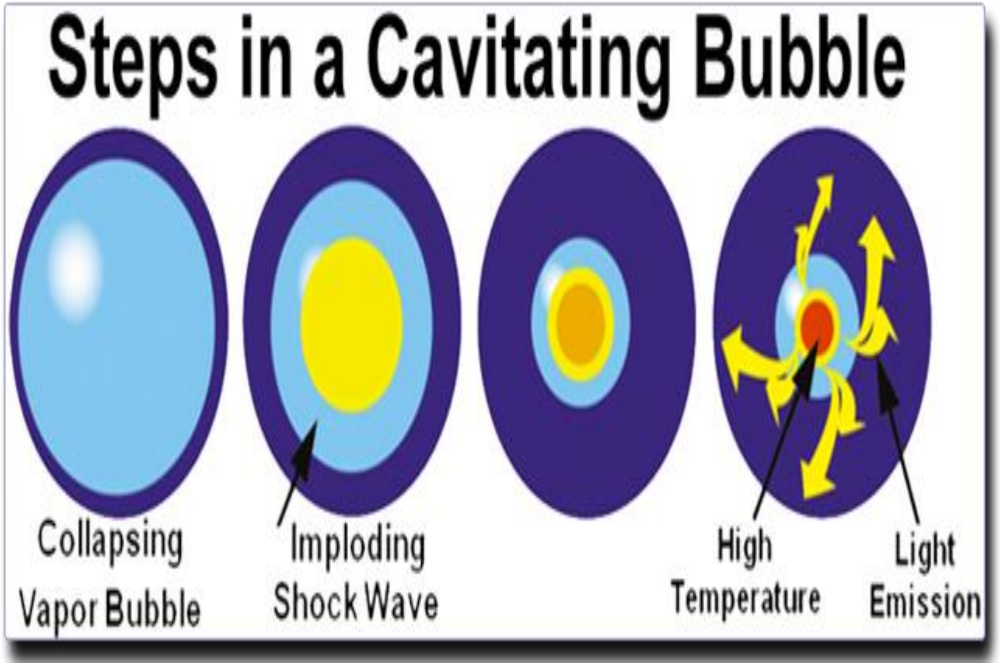
Combinations of three work better than single or double systems

Non-chemical

Cavitation

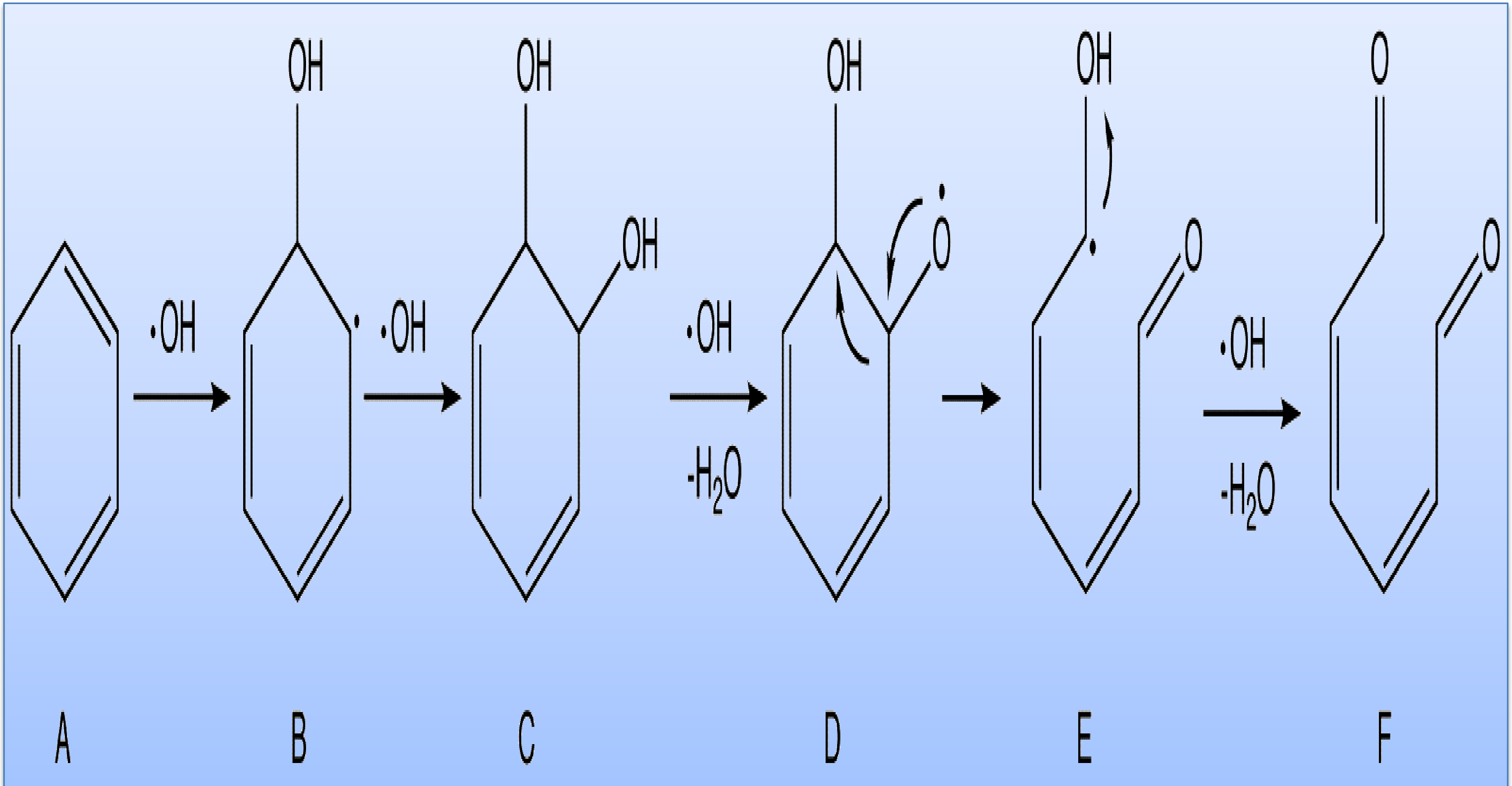
Jet loop Cavitation

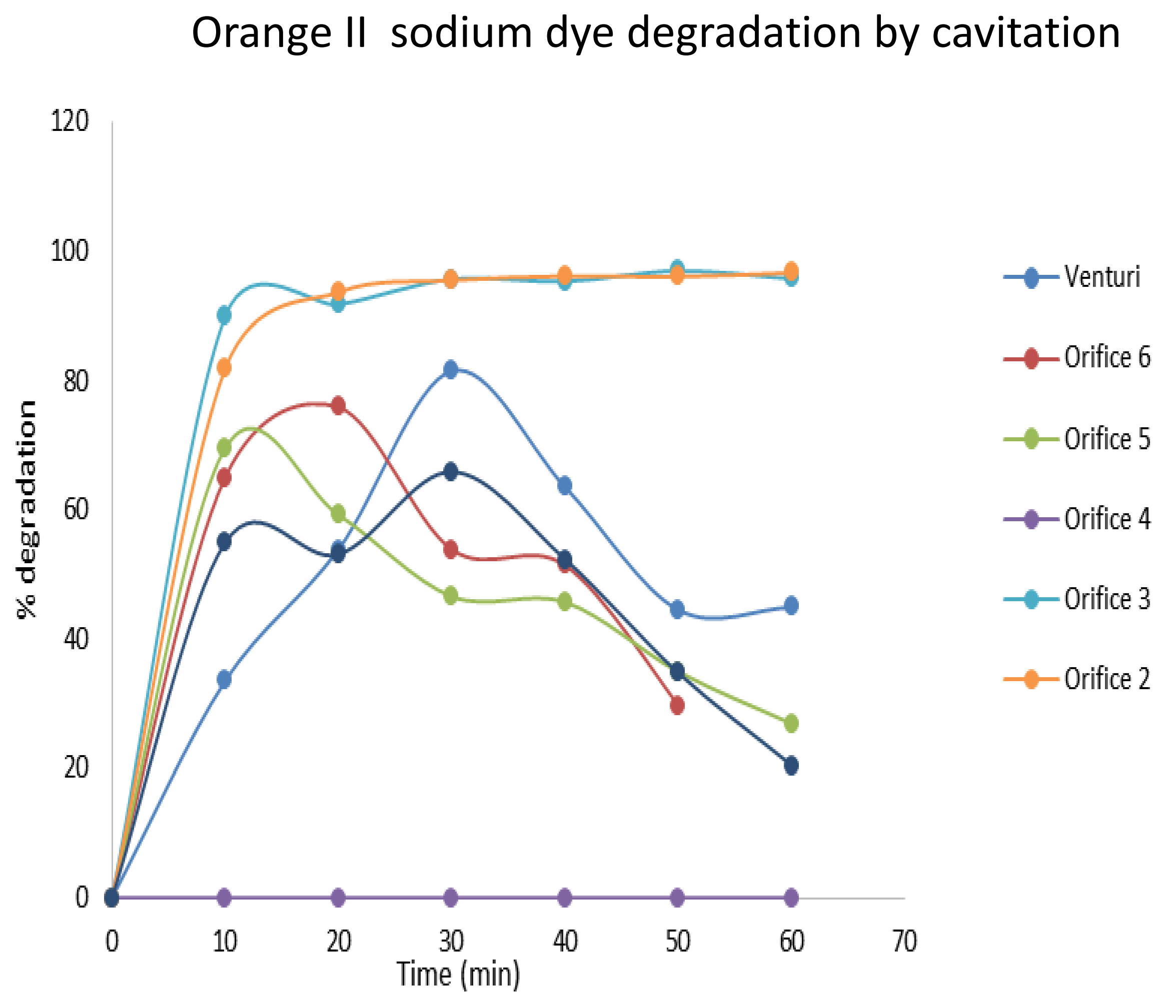




Advanced Oxidation Process

OH radical as nonselective oxidant




Orange II sodium dye degradation by cavitation
% degradation
Time (min)
0
20
40
60
80
100
120
0
10
20
30
40
50
60
70
Venturi
Orifice 6
Orifice 5
Orifice 4
Orifice 3
Orifice 2

Environmental Science and Pollution Research (2018) 25:7299–7314
https://doi.org/10.1007/s11356-017-1171-z

REVIEW ARTICLE

Treatment of persistent organic pollutants in wastewater using hydrodynamic cavitation in synergy with advanced oxidation process

Kassim Olasunkanmi Badmus[1] · Jimoh Oladejo Tijani[2] · Emile Massima[1] · Leslie Petrik[1]

Received: 27 September 2017 / Accepted: 26 December 2017 / Published online: 19 January 2018

Abstract
Persistent organic pollutants (POPs) are very tenacious wastewater contaminants. The consequences of their existence have been acknowledged for negatively affecting the ecosystem with specific impact upon endocrine disruption and hormonal diseases in humans. Their recalcitrance and circumvention of nearly all the known wastewater treatment procedures are also well documented. The reported successes of POPs treatment using various advanced technologies are not without setbacks such as low degradation efficiency, generation of toxic intermediates, massive sludge production, and high energy expenditure and operational cost. However, advanced oxidation processes (AOPs) have recently recorded successes in the treatment of POPs in wastewater. AOPs are technologies which involve the generation of OH radicals for the purpose of oxidising recalcitrant organic contaminants to their inert end products. This review provides information on the existence of POPs and their effects on humans. Besides, the merits and demerits of various advanced treatment technologies as well as the synergistic efficiency of combined AOPs in the treatment of wastewater containing POPs was reported. A concise review of recently published studies on successful treatment of POPs in wastewater using hydrodynamic cavitation technology in combination with other advanced oxidation processes is presented with the highlight of direction for future research focus.

Keywords Persistent organic pollutants · Advance oxidation process · Wastewater · Degradation · Cavitation · Fenton and intermediates

Environmental Science and Pollution Research (2018) 25:7299–7314 https://doi.org/10.1007/s11356-017-1171-z

Recommendations

- Prevent release of untreated or partially treated sewage to surface waters and ocean
- Include limits for indicator ECs in drinking water guidelines
- Make WWTW discharge standards stricter
- Initiate a chemical awareness campaign to consumers
- Practise great caution with unconventional water sources for potable reuse
- Employ combined advanced oxidation as tertiary treatment
- Treat the retentate from RO as highly hazardous
- Treat sludges from sewage plants as highly hazardous
- Implement barriers, monitoring programmes and assessment programmes to eliminate or minimise the risks
- Carefully test drinking water from the seawater desalination plants or reused sewage water for toxicity, which need not be costly
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