

# CVL100:Environmental Science(2-0-0)

Dr. Arun Kumar

Water Treatment-Mass Balance and Big-Picture  
Nov 10<sup>th</sup> 2021 (Part2)



भारतीय प्रौद्योगिकी संस्थान दिल्ली  
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# Recap

## Meta-Analysis of Mass Balances Examining Chemical Fate during Wastewater Treatment

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*Received December 3, 2007. Revised manuscript received June 11, 2008. Accepted June 11, 2008.*

Mass balances are an instructive means for investigating the fate of chemicals during wastewater treatment. In addition

composition of biosolids is important because use of sewage sludge as fertilizer in agriculture, for

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Chemosphere 88 (2012) 17–24

Contents lists available at SciVerse ScienceDirect

**Chemosphere**

journal homepage: [www.elsevier.com/locate/chemosphere](http://www.elsevier.com/locate/chemosphere)

**Occurrence of pharmaceuticals in a municipal wastewater treatment plant: Mass balance and removal processes**

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**ARTICLE INFO**

Article history:  
 Received 2 November 2011  
 Received in revised form 1 February 2012  
 Accepted 2 February 2012

**ABSTRACT**

Occurrence and removal efficiencies of fifteen pharmaceuticals were investigated in a conventional municipal wastewater treatment plant in Michigan. Concentrations of these pharmaceuticals were determined in both wastewater and sludge phases by a high-performance liquid chromatograph coupled to a

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The mass flow calculation can be written as:

$$m_{\text{inf}} = m_{\text{eff}} + m_{\text{bio}} + m_{\text{sor}} \quad (3)$$

*( $m_{\text{lost}} = m_{\text{biodegradation}} + m_{\text{sorbed}}$ )*

where  $m_{\text{inf}}$  ( $\text{kg d}^{-1}$ ) and  $m_{\text{eff}}$  ( $\text{kg d}^{-1}$ ) are mass input and output of the treatment system.  $m_{\text{bio}}$  ( $\text{kg d}^{-1}$ ) and  $m_{\text{sor}}$  ( $\text{kg d}^{-1}$ ) refer to the mass of pharmaceutical lost due to biodegradation and sorption,

**Table 2**

Mass flux of the investigated pharmaceuticals at different treatment units.

Pharmaceuticals	Mass flux (gd <sup>-1</sup> )									(C=100*(B/A))	(E=100*(D/A))	(F=100-(C+E))
	Raw(A)	Pretreatment effluent	Primary effluent	Aeration effluent	Secondary effluent	Final effluent (B)	Primary sludge	Waste sludge	Dewatered sludge(D)	Mass in effluent (%) (C)	Mass in dewatered sludge, R <sub>201</sub> (%) (E)	Mass lost in WWTP, R <sub>bio</sub> (%) (F)
CTC	8.1±8.2	7.7±1.8	5.5±1.1	2.4±0.9	NA	NA	0.2	NA	NA	NA	NA	100
DMC	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DOC	34±25	22±16	20±16	26±25	15±18	17±17	2.3±1.5	1.3±1.3	1.0±0.5	50	3.0	47
OTC	1.3±0.8	0.9±0.6	1.2±0.3	0.9±0.2	0.6±0.4	0.8±0.2	0.1±0.01	0.1±0.03	0.03±0.02	61	2.2	37
TC	14±4.2	5.7±2.0	7.0±2.4	7.0±3.9	NA	NA	NA	3.1±1.7	1.0±0.5	NA	7.1	93
SDZ	1.7±0.5	1.6±0.4	1.6±0.3	2.0±0.3	1.3±0.1	1.2±0.6	0.2±0.04	0.2±0.2	0.1±0.03	73	5.2	22
SMR	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
SMZ	1.2±0.1	NA	NA	NA	NA	NA	NA	0.03±0	0.01±0	NA	0.5	99
SMX	71±26	58±24	59±23	75±32	22±3.9	8.1±6.9	0.1±0.1	0.3±0.2	0.1±0.03	11	<0.1	>89
ERY	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
TYL	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
LCM	2.6±3.6	6.1±7.6	3.4±5.1	2.6±3.5	2.6±2.0	1.6±0.5	0.04±0.05	0.2±0.04	0.03±0.02	60	1.0	39
CBZ	5.0±1.2	5.4±1.2	6.0±1.8	7.7±2.7	7.1±2.2	7.0±2.5	0.1±0.1	0.1±0.05	0.03±0.02	141	0.6	-41
AMP	2800±1493	2644±1099	2561±1238	145±134	3.2±1.6	4.5±3.9	0.3±0.1	0.5±0.3	0.2±0.1	<0.2	<0.01	>99
CAF	1871±550	1737±538	2436±794	138±205	3.3±2.1	3.4±2.7	0.3±0.1	0.4±0.6	0.1±0.05	<0.2	<0.01	>99

NA, not currently available. Mass flux was calculated according to Eqs. (1) and (2). R<sub>bio</sub> and R<sub>cor</sub> were calculated using Eqs. (4) and (5), respectively.

tetracycline (TC), demeclocycline (DMC), chlortetracycline (CTC), oxytetracycline (OTC), doxycycline (DOC), meclocycline (MCC), sulfadiazine (SDZ), sulfamerazine (SMR), sulfamethazine (SMZ), SMX, tylosin (TYL), acetaminophen (AMP), erythromycin (ERY), lincomycin(LCM), carbamazepine (CBZ) and Caffeine (CAF).

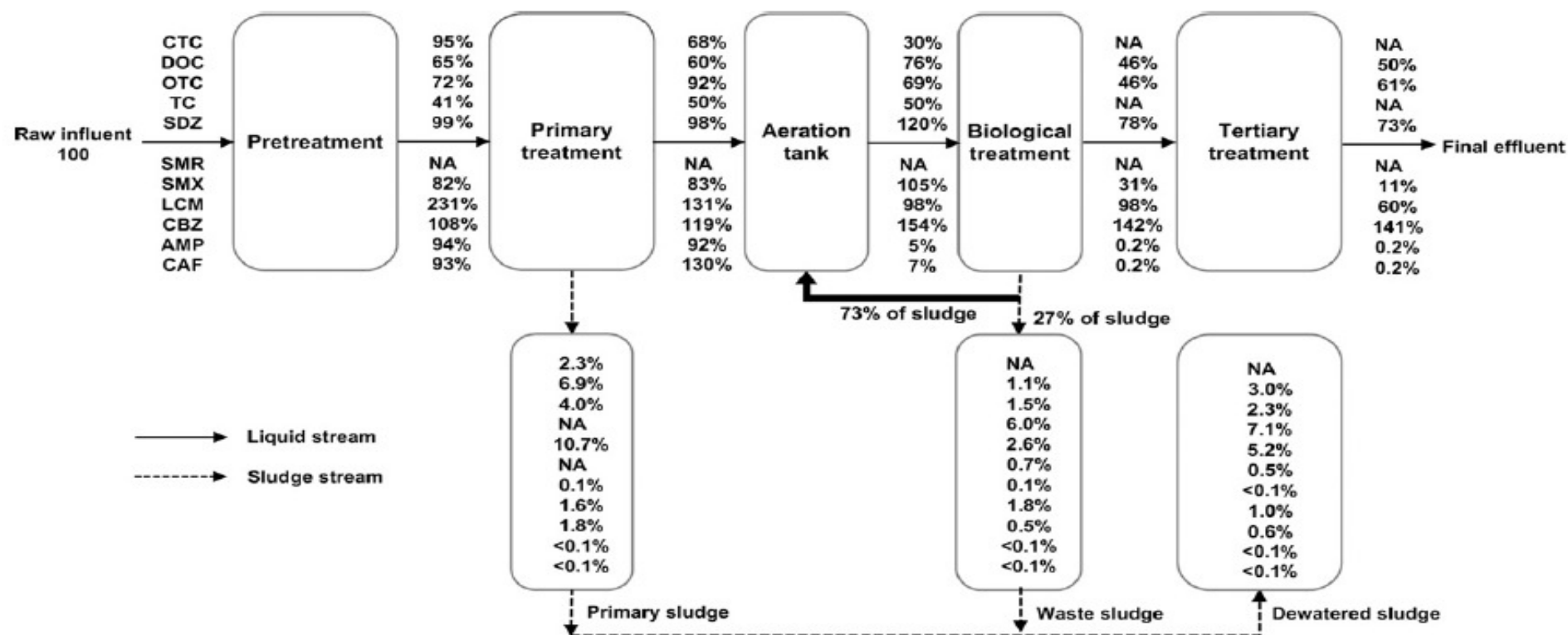


Fig. 4. Percentage ( $R_i$ , %, calculated applying Eq. (6)) of detected pharmaceuticals along the WWTP.

tetracycline (TC), demeclocycline (DMC), chlortetracycline (CTC), oxytetracycline (OTC), doxycycline (DOC), meclocycline (MCC), sulfadiazine (SDZ), sulfamerazine (SMR), sulfamethazine (SMZ), SMX, tylosin (TYL), acetaminophen (AMP), erythromycin (ERY), lincomycin(LCM), carbamazepine (CBZ) and Caffeine (CAF).

- Comment on removal of different organic compounds in different units.
- Which compound is least detected in final effluent and which is mostly detected in final effluent?
- What does it say about their occurrence in sludge?
- Can we relate this to their  $K_{ow}$  and  $K_{oc}$  properties?



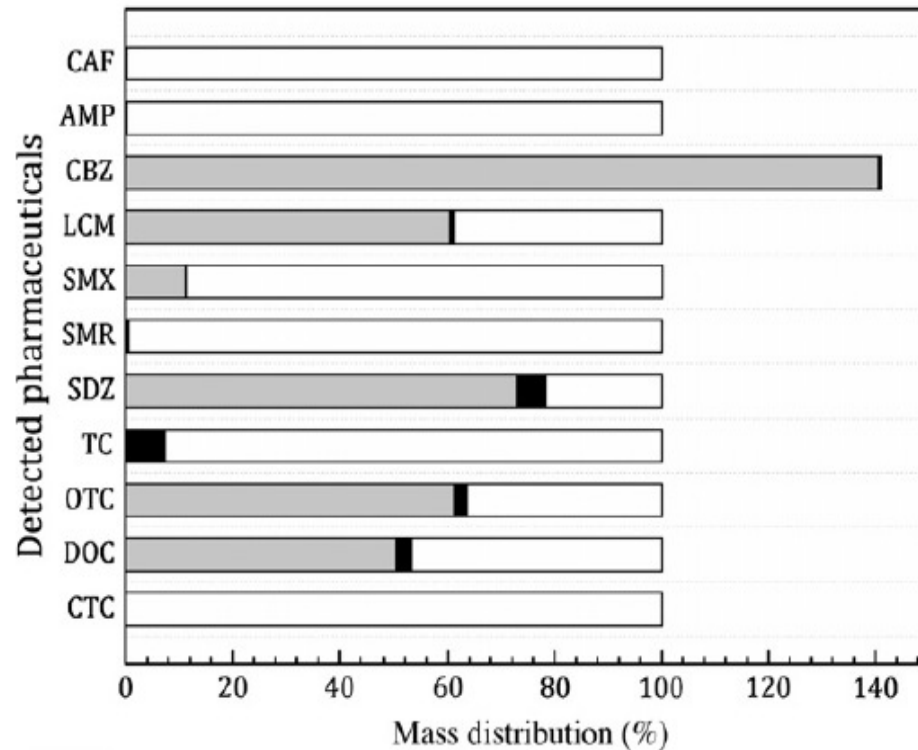
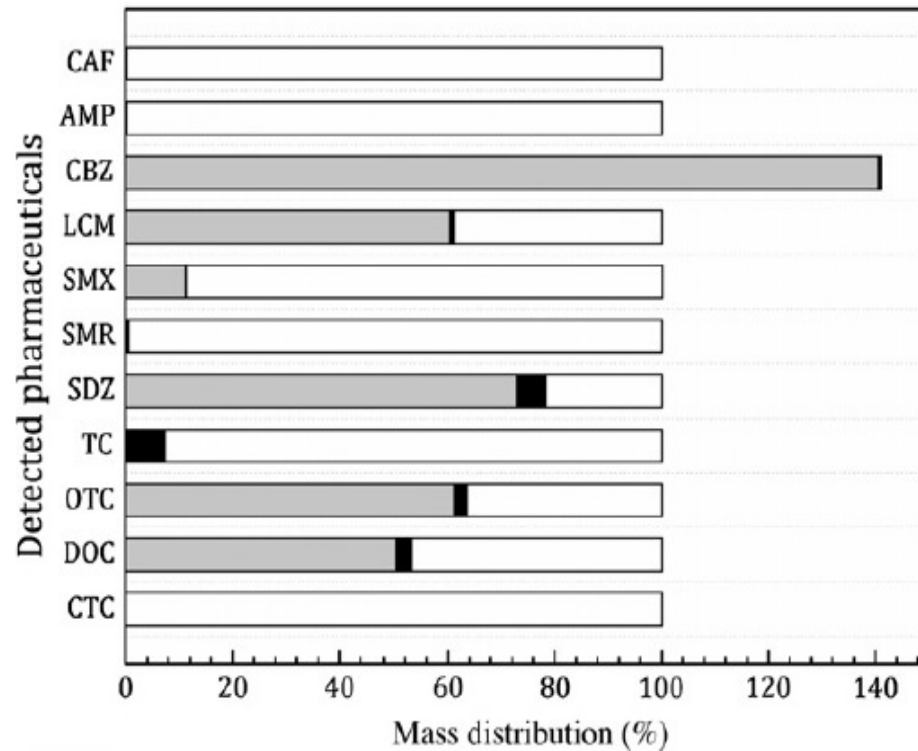


Fig. 3. Mass distribution of the detected pharmaceuticals in the WWTP. The grey-colored bar represents the mass fraction in the final effluent, the black-colored bar represents the fraction in the dewatered sludge, and the white bar represents the loss of pharmaceuticals due to biodegradation.

tetracycline (TC), demeclocycline (DMC), chlortetracycline (CTC), oxytetracycline (OTC), doxycycline (DOC), meclocycline (MCC), sulfadiazine (SDZ), sulfamerazine (SMR), sulfamethazine (SMZ), SMX, tylosin (TYL), acetaminophen (AMP), erythromycin (ERY), lincomycin(LCM), carbamazepine (CBZ) and Caffeine (CAF).

- Q1: Order chemicals in decreasing order of their potential occurrence in final effluent?
- Q2: Which compound is expected to have smallest  $K_{OW}$ ?

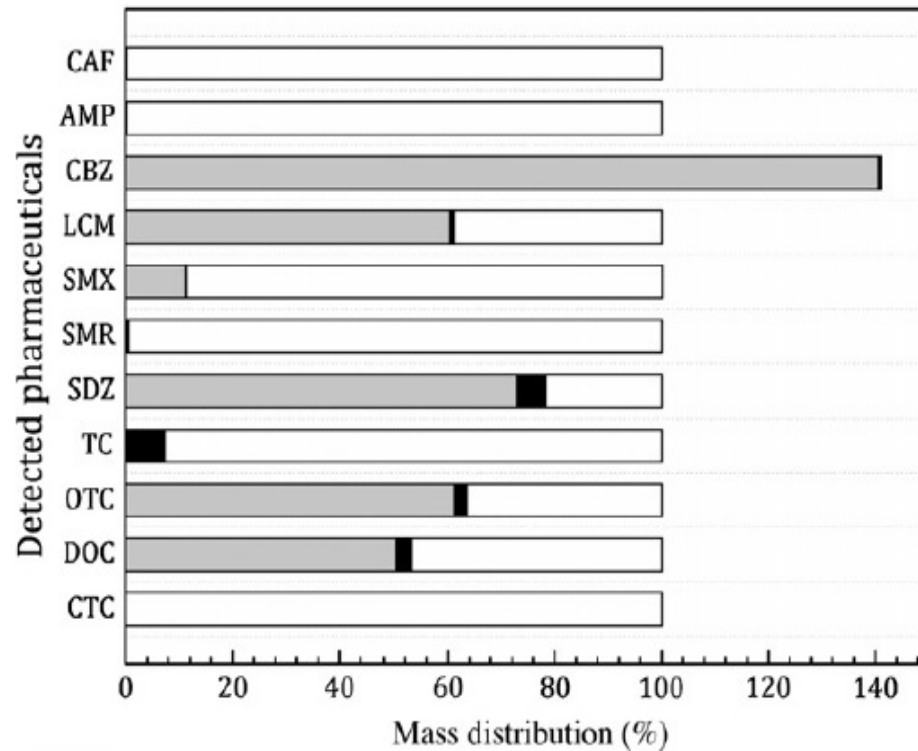




### Presence in final effluent

oxytetracycline (OTC),  
doxycycline (DOC),  
sulfadiazine (SDZ),  
sulfamethoxazole (SMX),  
lincomycin (LCM),  
carbamazepine (CBZ)

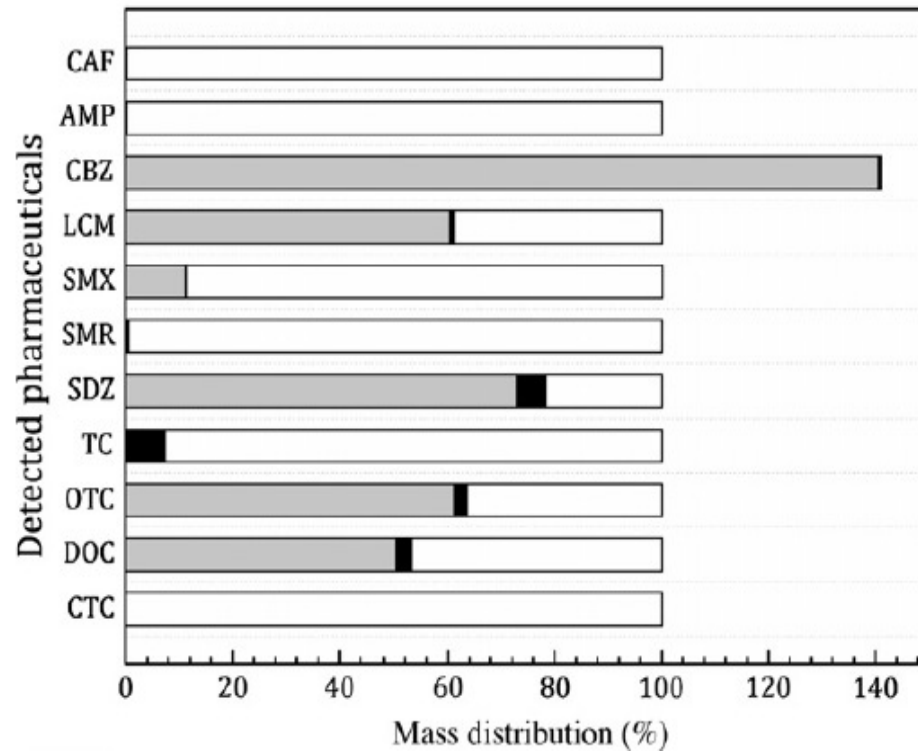
**Fig. 3.** Mass distribution of the detected pharmaceuticals in the WWTP. The grey-colored bar represents the mass fraction in the final effluent, the black-colored bar represents the fraction in the dewatered sludge, and the white bar represents the loss of pharmaceuticals due to biodegradation.



**Check presence in surface water if wastewater effluent is mixed with surface water**

oxytetracycline (OTC),  
doxycycline (DOC),  
sulfadiazine (SDZ),  
sulfamethoxazole (SMX),  
lincomycin (LCM),  
carbamazepine (CBZ)

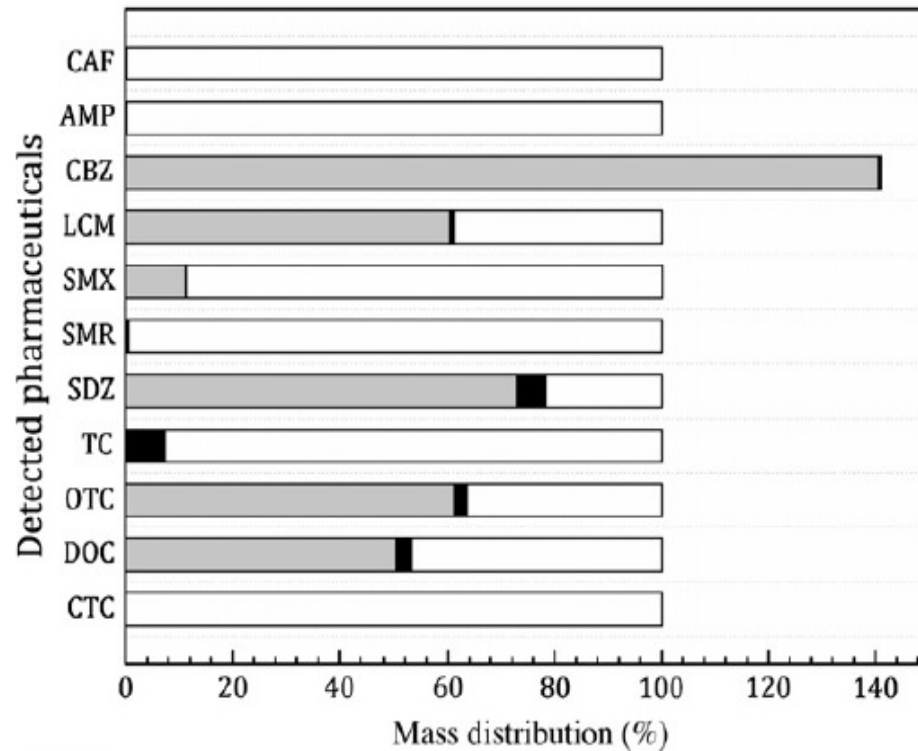
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**Check further removal in drinking water treatment plant if surface water is used as raw source water for making drinking water**

oxytetracycline (OTC),  
doxycycline (DOC),  
sulfadiazine (SDZ),  
sulfamethoxazole (SMX),  
lincomycin (LCM),  
carbamazepine (CBZ)

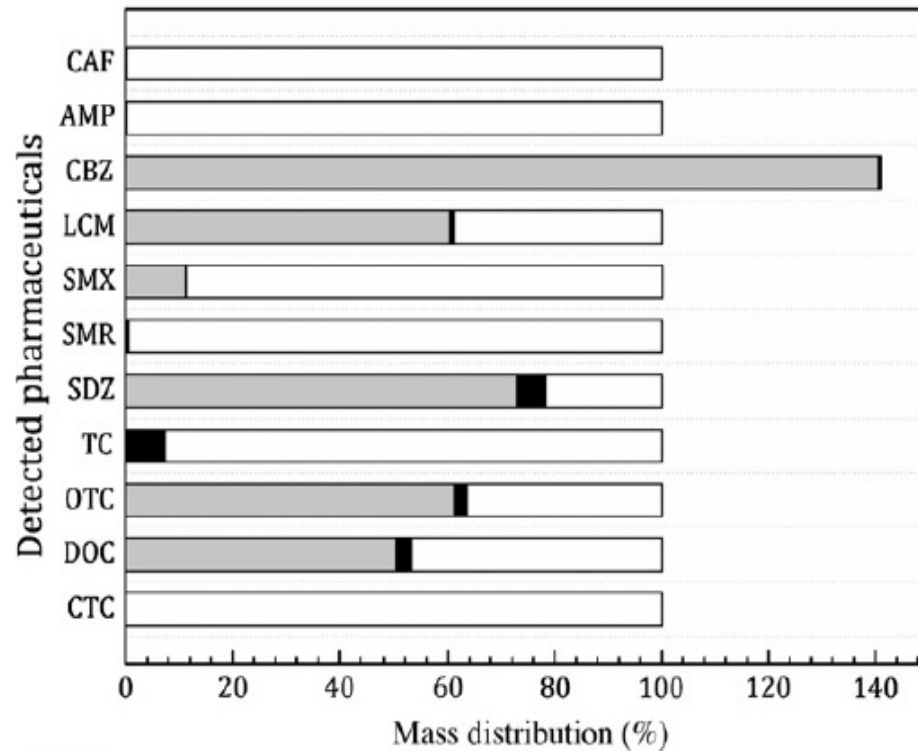
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## Presence in sludge

oxytetracycline (OTC),  
doxycycline (DOC),  
sulfadiazine (SDZ),  
lincomycin(LCM),  
Tetracycline(TC)

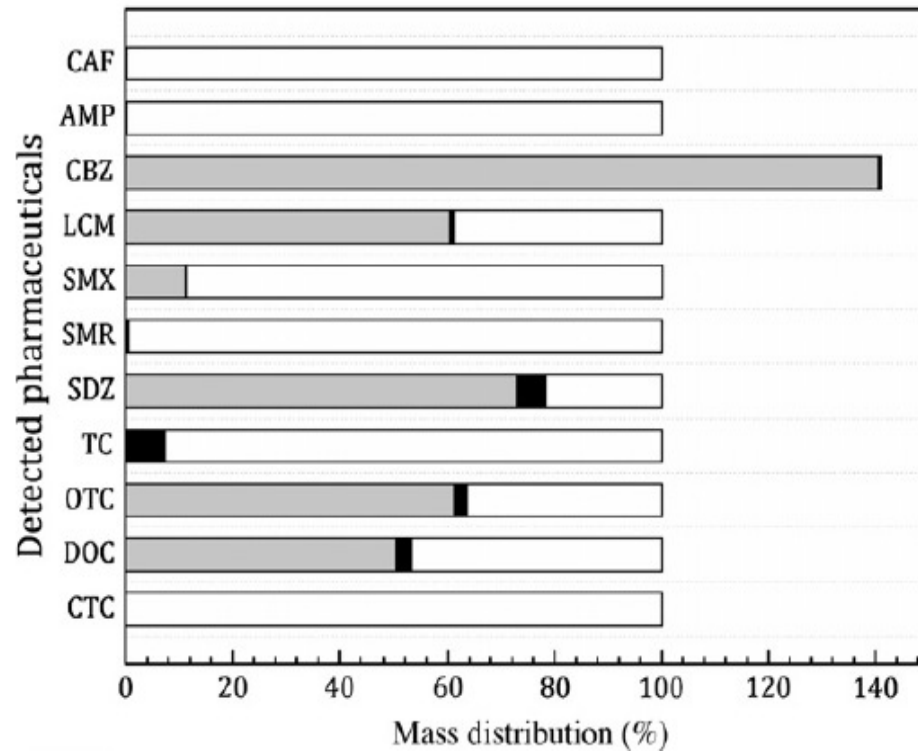
**Fig. 3.** Mass distribution of the detected pharmaceuticals in the WWTP. The grey-colored bar represents the mass fraction in the final effluent, the black-colored bar represents the fraction in the dewatered sludge, and the white bar represents the loss of pharmaceuticals due to biodegradation.



**Check presence in land if  
sludge is applied there as  
nutrient source**

oxytetracycline (OTC),  
doxycycline (DOC),  
sulfadiazine (SDZ),  
lincomycin(LCM),  
Tetracycline(TC)

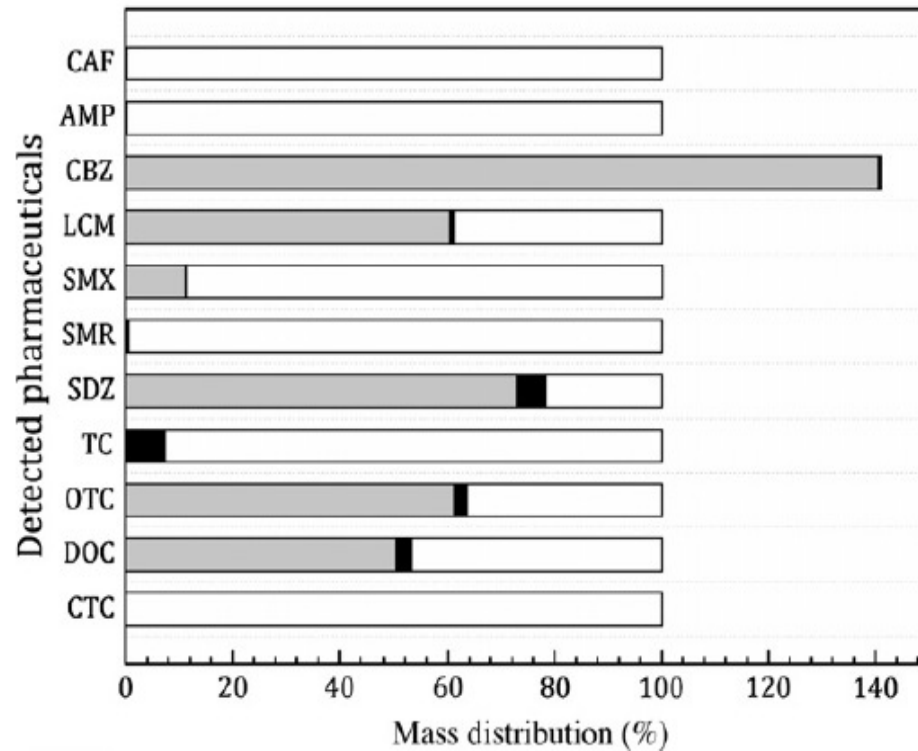
**Fig. 3.** Mass distribution of the detected pharmaceuticals in the WWTP. The grey-colored bar represents the mass fraction in the final effluent, the black-colored bar represents the fraction in the dewatered sludge, and the white bar represents the loss of pharmaceuticals due to biodegradation.



**Check chance of contamination of soil, surface water through runoff and groundwater through percolation if sludge is applied on land as nutrient source**

oxytetracycline (OTC),  
doxycycline (DOC),  
sulfadiazine (SDZ),  
lincomycin(LCM),  
Tetracycline(TC)

**Fig. 3.** Mass distribution of the detected pharmaceuticals in the WWTP. The grey-colored bar represents the mass fraction in the final effluent, the black-colored bar represents the fraction in the dewatered sludge, and the white bar represents the loss of pharmaceuticals due to biodegradation.



**Fig. 3.** Mass distribution of the detected pharmaceuticals in the WWTP. The grey-colored bar represents the mass fraction in the final effluent, the black-colored bar represents the fraction in the dewatered sludge, and the white bar represents the loss of pharmaceuticals due to biodegradation.

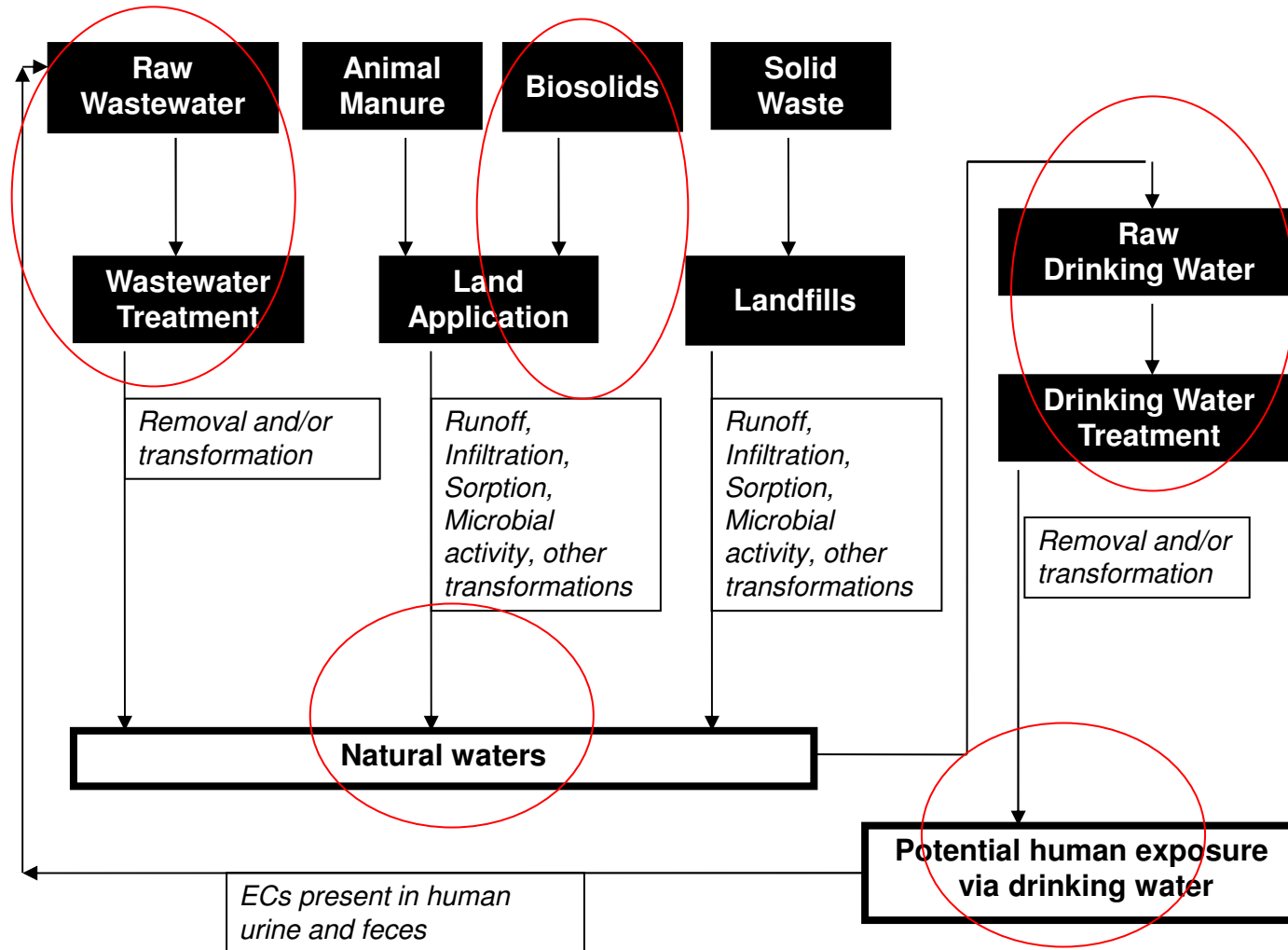
**Lost due to biodegradation  
(i.e., compound can be  
degraded by bacteria)**

CAF  
AMP  
LCM  
SMX  
SMR  
SDZ  
TC  
OTC  
DOC  
CTC

Some can be biodegraded  
more  
And some can be biodegraded  
less.



# Fate of pharmaceuticals in environment and our exposure



# A big picture overview

```
graph TD
    CI[COSMETIC INDUSTRY] --> MW[MUNICIPAL WASTEWATER]
    EI[ELECTRONIC INDUSTRY] --> IW[INDUSTRIAL WASTEWATER]
    PI[PHARMACEUTICAL INDUSTRY] --> IW
    MW --> WTP[WASTEWATER TREATMENT PLANT]
    IW --> WTP
    WTP --> S[SLUDGE]
    WTP --> WE[WASTEWATER EFFLUENT]
    S --> SC[SOIL CONDITIONER]
    SC --> AL[AGRICULTURE LAND]
    WE --> IW2[IRRIGATION WATER]
    WE --> RW[RIVER WATER]
    WE --> FI[FOOD INDUSTRY]
    WE --> H[INDUSTRIAL WASTEWATER]
    IW2 --> AL
    RW --> F[FISHES]
    F --> FI
    AL -- UPTAKE --> P[PLANTS]
    P --> H
    P --> H1[HERBIVORES]
    H1 --> C[CARNIVORES]
    C --> H
    FI --> H
    FI --> NSP[NANOSUPPLEMENTS/STORAGE/PACKAGING/NANO DELIVERY]
    NSP --> H
    NSP --> DF[DENTAL FILLING]
    NSP --> TP[TOOTHPASTE]
    DW[DRINKING WATER] --> H
    AD[ATMOSPHERIC DUST ON FOOD] --> H
```

The flowchart illustrates the pathways of nanomaterials from various industries to humans. At the top, three industries (Cosmetic, Electronic, and Pharmaceutical) contribute to Municipal and Industrial Wastewater. These wastewaters are treated at a Wastewater Treatment Plant, which produces Sludge and Wastewater Effluent. Sludge is used as a Soil Conditioner in Agriculture Land, while Wastewater Effluent is used for Irrigation Water, River Water, and as input to the Food Industry. Agriculture Land leads to Plants, which are then consumed by Herbivores, Carnivores, and Humans. The Food Industry produces Nanosupplements/Storage/Packaging/Nano Delivery, which is used in Dental Fillings, Toothpaste, and consumed by Humans. Drinking Water and Atmospheric Dust on Food also contribute to Human exposure.

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# Big-picture

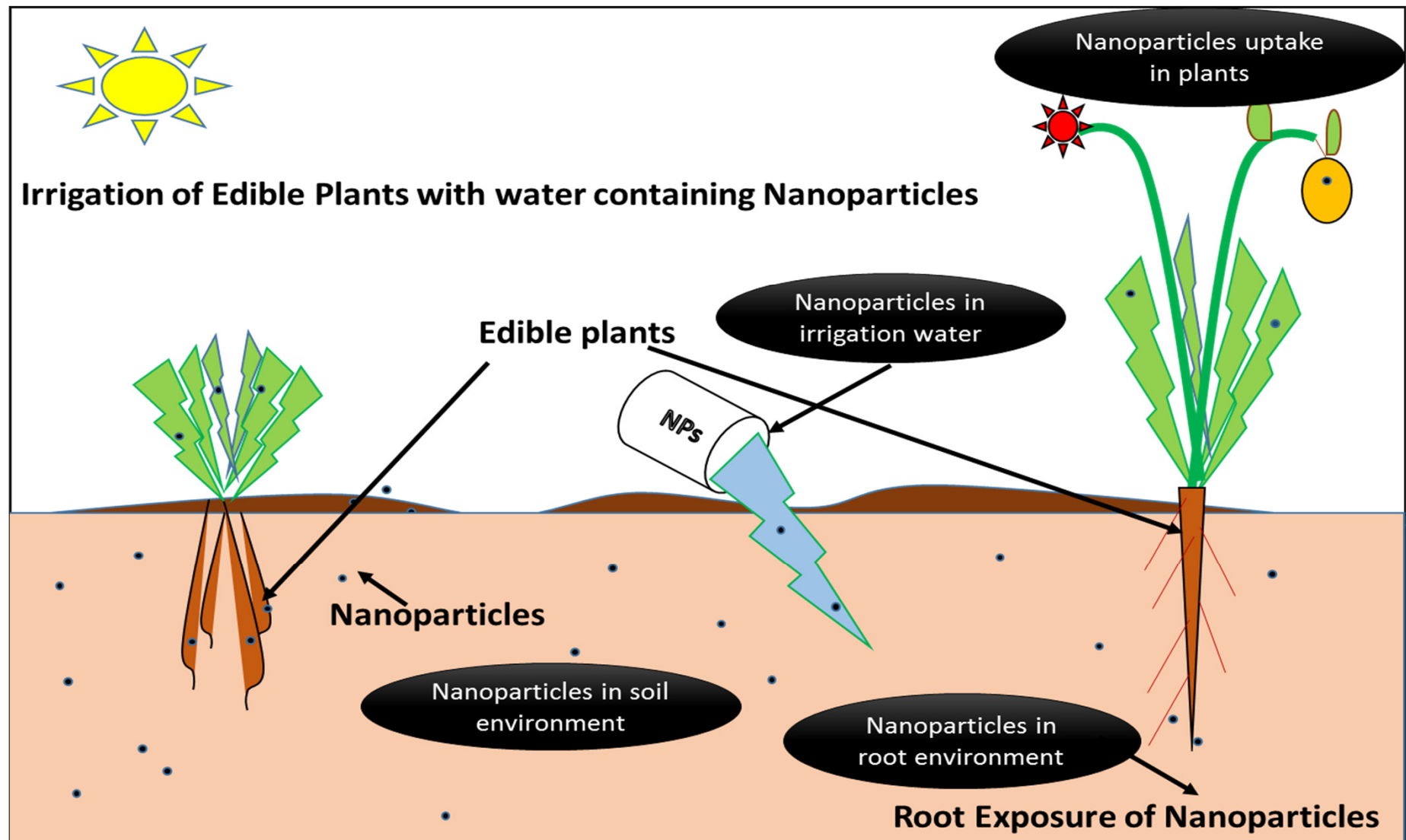
## *Emerging Water Contaminants (EWCs)*

1. Pharmaceuticals, Endocrine-disrupting chemicals(ex: triclosan; Bisphenol-A)
2. Nanoparticles (nanosilver, nanoparticles:  $\text{TiO}_2$ ,  $\text{CuO}$ , Carbon nanotubes)
3. Micro-plastics
4. Viruses and bacterial pathogens
5. Bioaerosols

**Some of these are not regulated**

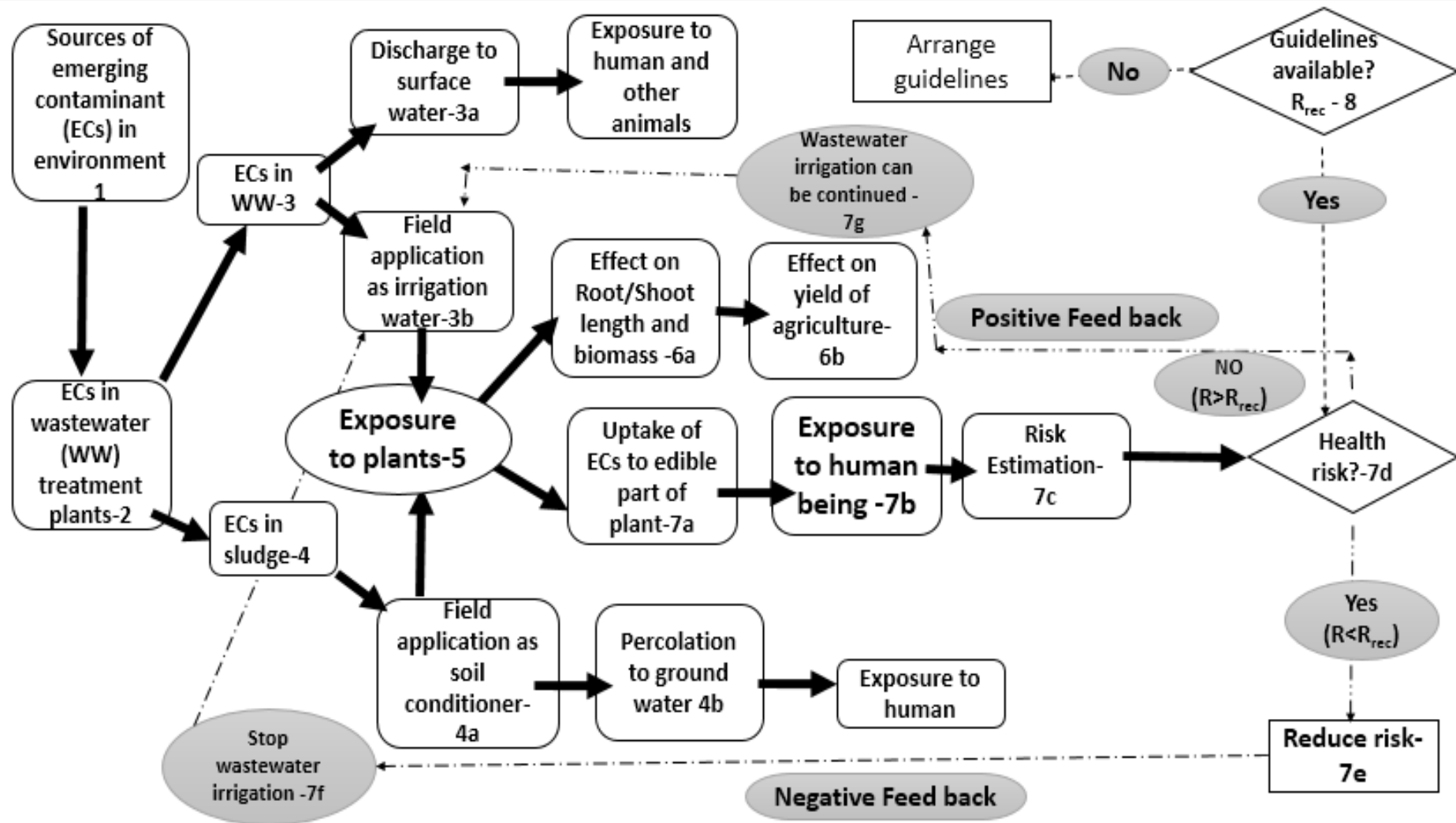
Snyder et al. (2007); Kumar and Xagorarakis (2010a); Boone and Gerba (2007)

# Big- Picture Overview



Adapted from the Singh, D. and Kumar, A. **Understanding effect of interaction of nanoparticles with roots on uptake in plants** Environmental Nanotechnology (Book Chapter - (in press)\*

# Pieces



## *EWCs: Why to worry now?*

1. Occurrence (although low concentration)
2. Toxic nature (long-term toxicity unknown)
3. Long-term implications unknowns
4. How to go about? Additional costs? Additional benefits?  
Cost-benefit? Can we afford?

**Solution:**  
**Environmental solutions with the help of all areas**