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**Final Workshop**

June 4-6, 2013



**Universidade de Brasília**



50<sup>1962</sup>  
2012

# Emerging Pollutants A Brief Overview

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## *Emerging Pollutants*

Emerging pollutants are defined as compounds that are not currently covered by existing water-quality regulations, have not been studied before, and are thought to be potential threats to environmental ecosystems and human health and safety (Farré et al, 2008).

- Not necessarily new compounds
- Some are present in the environment for decades
- Recently “discovered” – improvement of analytical technics
- Environmental and health significance under evaluation

In the US the expression “emerging pollutants” have been substituted by “pollutants of emerging concern”

- Emerging micropollutants
- Emerging contaminants
- Compounds of emerging concern
- Chemicals of emerging concern



## *Who are the emerging pollutants ?*

- Cyanotoxins
- Drugs of abuse
- Industrial additives and agents
- Flame retardants
- Food additives
- Nanoparticles
- Pharmaceuticals (human and vet.)
- Personal care products
- Pesticides
- Steroids and hormones
- Surfactants
- **Metabolites ????**
- **Emerging pathogens**

### Main effects

- Traditional health significance (carcinogenic, teratogenic, toxicity, etc)
- Antimicrobial resistance
- Endocrine disruption
- Unknown new effects



## *Emerging pollutants - Some examples*

### **Industrial additives (examples)**

- Chlorinated solvents
- Polyaromatic hydrocarbons
- Bisphenol A
- Phthalates
- Dioxins

### **Pharmaceuticals (examples)**

- Antibiotics (Ciprofloxacin, erythromycin, tetracycline, sulfamethoxazole)
- Contrast media (Iopromide, iopamidol)
- Prescribed (benzodiazepines, salbutamol, carbamazepine)
- Paracetamol, ibuprofen

### **Personal care products (examples)**

- DEET- insect repellent
- Parabens – Bacteriostatic and fungistatic (cosmetics)
- Triclosan – Biocide (tooth paste, soap, etc)
- Sun-screen agents
- Synthetic musk

### **Steroids and Hormones (examples)**

- Androgens (testosterone, androstenedione, etc)
- Estrogens (estrone, estriol, estradiol)
- Xenoestrogens (ethynilestradiol, diethylstilbestrol)
- Phytoestrogens



## *Emerging pollutants - Survey*

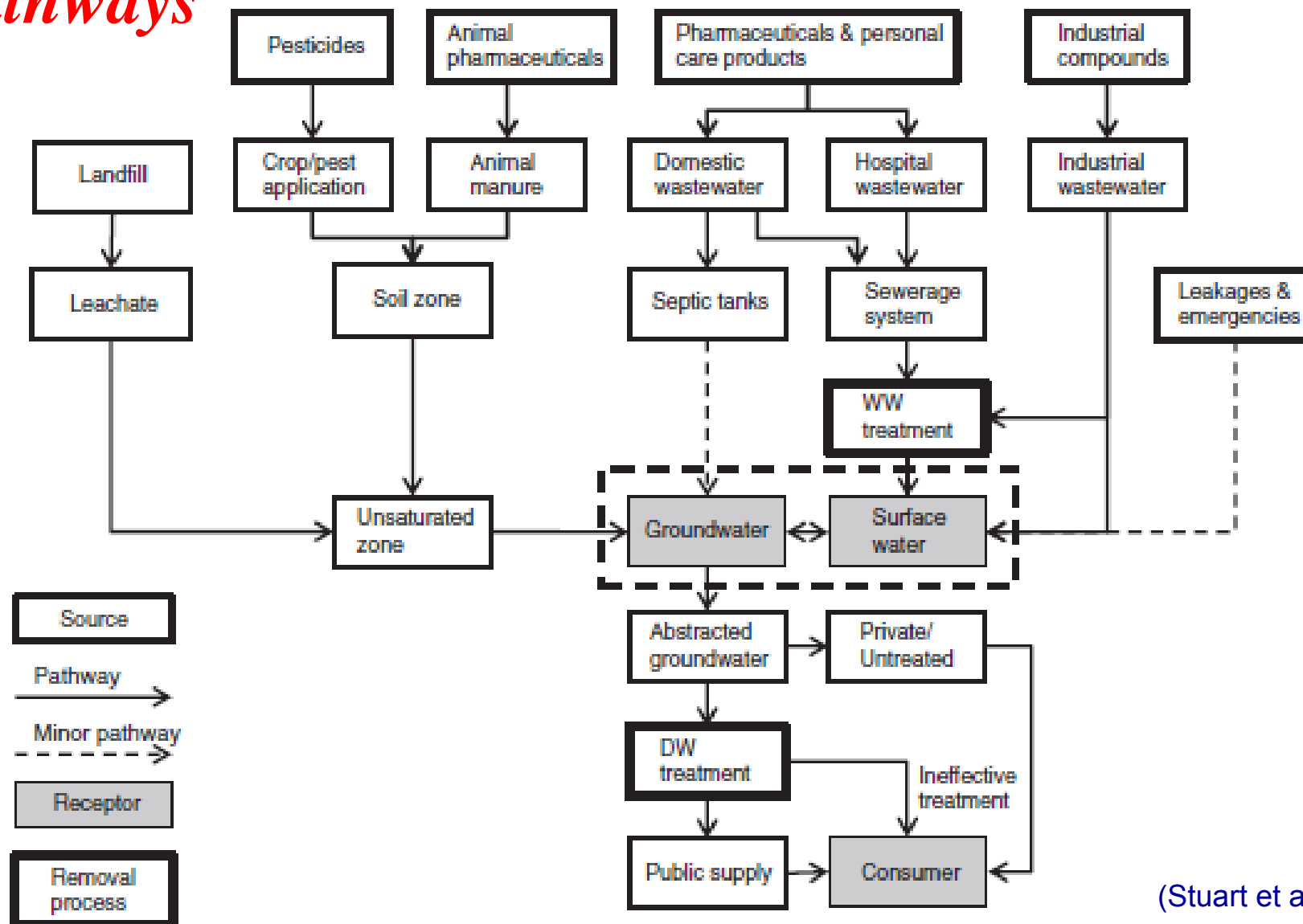
- Algal toxins
- Anticorrosives
- Antifoaming agents
- Antifouling compounds
- Antioxidants
- Biocides
- Bio-terrorism / sabotage agents
- Complexing agents
- Detergents
- DBP (DW)
- Drugs of abuse
- Flame retardants
- Food additives
- Fragrances

### **EMERGING SUBSTANCES MOST FREQUENTLY DISCUSSED (NORMAN, 2011)**

- Gasoline additives
- Industrial chemicals
- Nanoparticles
- Other
- Perfluoroalkylated substances and TPs
- Personal care products
- Pesticides
- Pharmaceuticals
- Plasticisers
- Trace metals and their compounds
- Wood preservatives



## *Pathways*



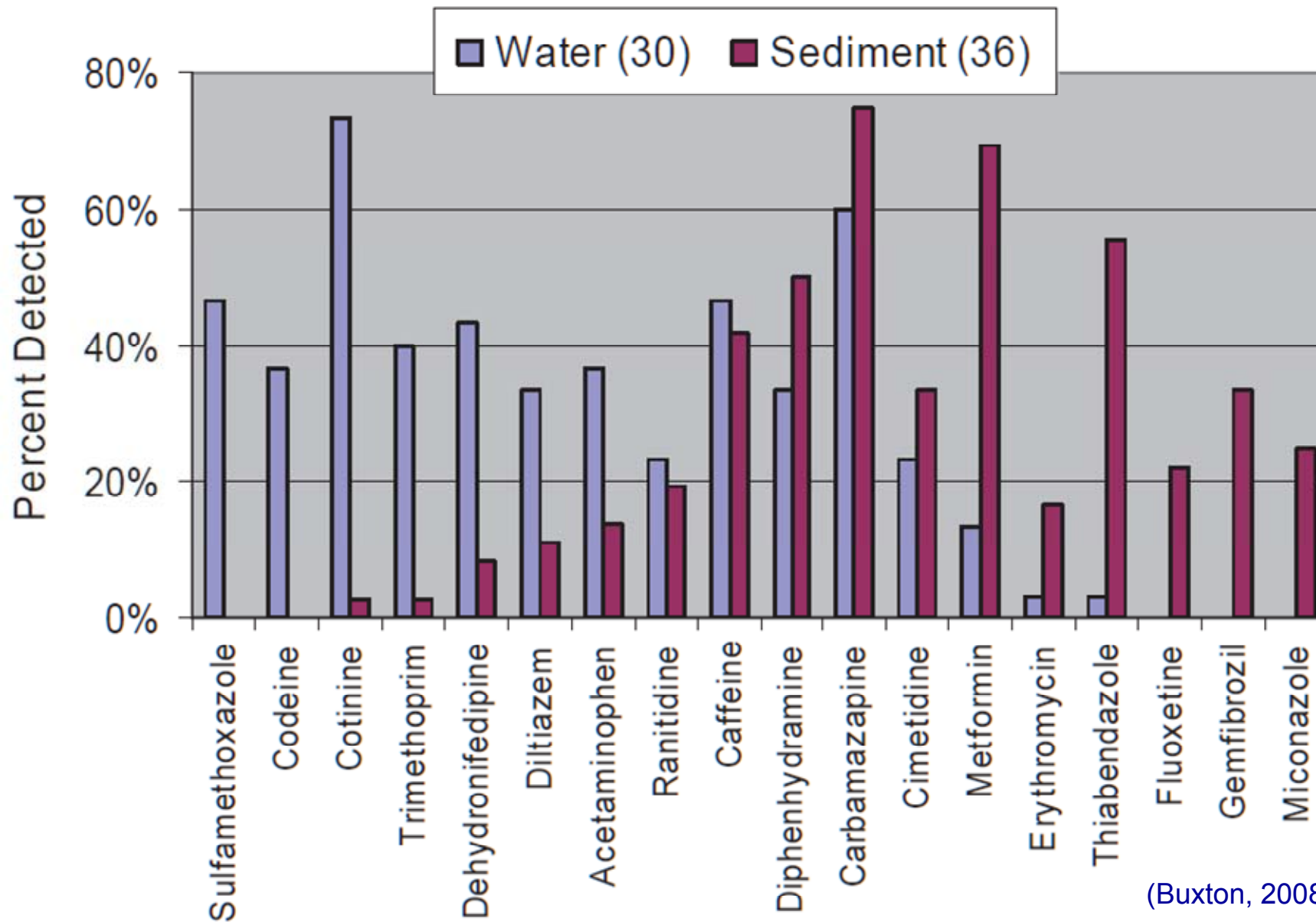
(Stuart et al, 2012)



## *Emerging pollutants - What is known\**

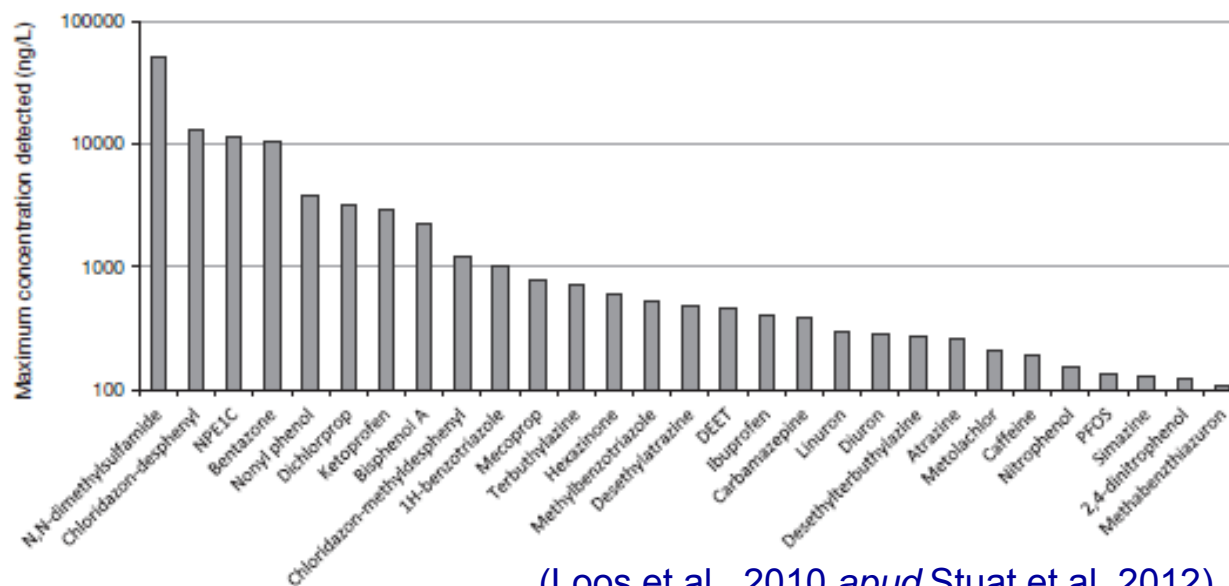
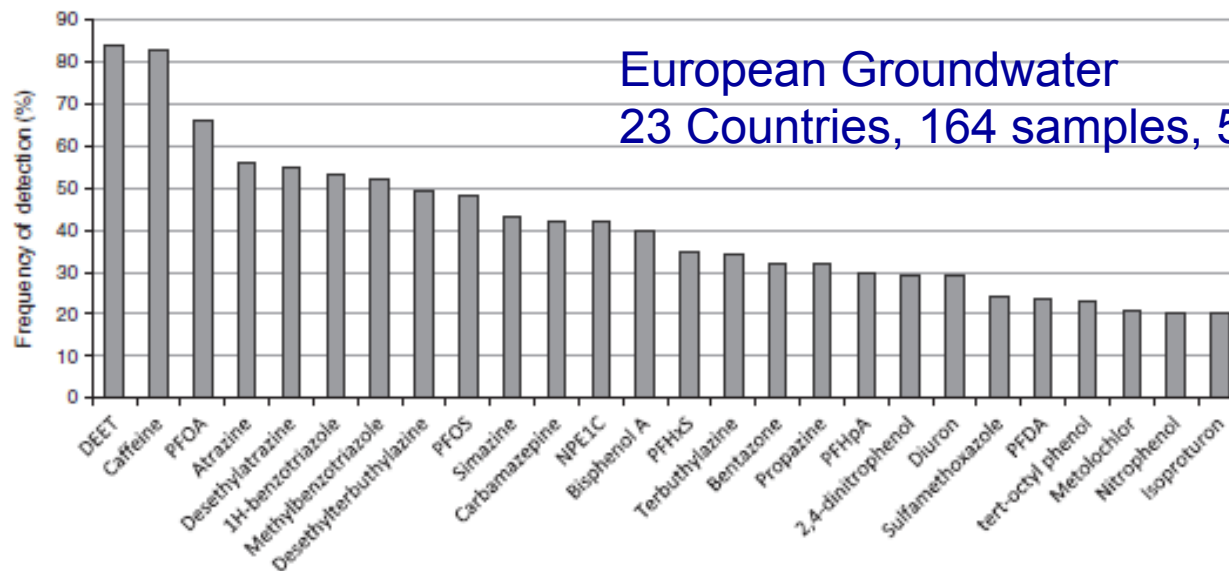
- Present in water at sub-ppb concentrations
- Present as complex mixtures
- Reflect a wide range of human activities
- Some are mobile and persistent
- Present in various environmental media  
(Surface and groundwater, sediments, tissue)





(Buxton, 2008)





(Loos et al., 2010 *apud* Stuart et al, 2012)



## *Emerging pollutants – Endocrine Disruptors*

"An endocrine disruptor is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)population" (European Commission)

### **Chemicals of industrial origin** (Examples)

- Bisphenol A
- Phthalates
- PCBs and Dioxins
- Nonylphenol  
(TP of alkylphenol ethoxylate surfactants)

### **Pesticides** (Examples)

DDT, Atrazine and other chlorinated compounds

### **Hormones**

- Androgens  
(testosterone, androstenedione, etc)
- Estrogens  
(estrone, estriol, estradiol)
- Xenoestrogens  
(ethynilestradiol, diethylstilbestrol)
- Phytoestrogens



## *Endocrine Disruptors – Estrogenic Potential*

| <b>Substance</b>       | <b>Relative estrogenic potential</b>    | <b>Reference</b>               |
|------------------------|---|--------------------------------|
| Estrone (E1)           | 1                                       | Pelissero <i>et al.</i> (1993) |
| Estradiol (E2)         | 1                                       | Pelissero <i>et al.</i> (1993) |
| Ethinylestradiol (EE2) | 1                                       | European Commission(2003)      |
| Progesterone           | $2 \times 10^{-2}$                      | Pelissero <i>et al.</i> (1993) |
| Testosterone           | $1 \times 10^{-2}$                      | Pelissero <i>et al.</i> (1993) |
| Phytoestrogens         | $1 \times 10^{-3}$ a $1 \times 10^{-2}$ | Ghiselli and Jardim (2007)     |
| 4-nonylfenol           | $9 \times 10^{-6}$                      | Jobling and Sumpter (1993)     |
| Bisphenol A            | $1 \times 10^{-5}$                      | European Commission(2003)      |



## *Endocrine Disruptors - Effects*

### **Wildlife species**

- Molluscs, crustacea, fish, reptiles, birds and mammals
- Abnormalities and impaired reproductive performance in some species, and to be associated with changes in immunity and behavior and skeletal deformities

### **Human**

Limited evidence and controversy

- Effect suggested: Declining sperm counts; Increased incidences in numbers of male children born with genital malformations; Increases in incidences of certain types of cancer that are sensitive to hormones
- More research is needed: Large-scale human epidemiology studies relating specific health effects with exposure to EDs; Mechanisms of EDs; Effects of different types of exposure in the environment which may lead to unexpected effects e.g. mixtures of endocrine disruptors, long-term low dose exposure; Exposure at different ages to see if humans are vulnerable to EDs at any particular stage of life; Exposure of individuals who may be especially susceptible.



## *Endocrine Disruptors – Worldwide Occurrence*

| <b>Author</b>                    | <b>Local</b>                                      | <b>Endocrine Disruptor (Concentration)</b>   |
|----------------------------------|---|--|
| Ternes <i>et al.</i><br>(1999)   | Raw sewage RJ                                     | 17b-estradiol (0,021mg/L)<br>Estrone (0,040mg/L)   |
| Ternes <i>et al.</i><br>(1999)   | Raw sewage<br>Frankfurt                           | 17b-estradiol (0,015mg/L)<br>Estrone (0,027mg/L)   |
| Ternes <i>et al.</i><br>(1999)   | Raw sewage<br>(Canada)                            | 17b-estradiol (Higher than German sewage)<br>Estrone (Lower than German sewage)<br>17a-ethinylestradiol (average - 0,009 mg/L)               |
| Azevedo <i>et al.</i><br>(2001)  | Surface water<br>(Portugal)                       | Isomers de 4-nonylfenol (0,2 to 30,0mg/L)<br>Bisphenol A (0,2 e 4,0mg/L)   |
| Furuichi <i>et al.</i><br>(2004) | Tama river<br>(Japan)                             | Estradiol            Estrone<br>Nonylphenol        Octylphenol        Bisphenol A  |
| Kolpin <i>et al.</i><br>(2002)   | Surface waters<br>EUA                             | Several Antibiotics  |
| Sodré <i>et al.</i><br>(2010)    | Drinking water<br>Campinas (São<br>Paulo, Brasil) | Estigmasterol (0.34± 0.13µg/L), cholesterol<br>(0.27±0.07µg/L), caffeine (0.22±0.06µg/L),<br>bisphenol A (0.16±0.03µg/L), estrone, estradiol |



## *Emerging pollutants – Pharmaceuticals (156)*

| <b>EMERGING SUBSTANCES MOST FREQUENTLY DISCUSSED (NORMAN, 2011)</b>  | <b>USE</b>                           |
|--|--------------------------------------|
| Acetaminophen (paracetamol)  | Analgesic                            |
| Codeine, Hydrocodone   | Drugs of abuse (2)                   |
| Fenfluramine   | Anorexic (1)                         |
| Ivermectin,  | Anthelmintic (1)                     |
| Amoxicillin, Ampicillin, Azithromycin, Chloramphenicol, Chlortetracycline, Ciprofloxacin, Iarithromycin, Cloxacillin, Danofloxacin, Dicloxacillin, Doxycycline (anhydrous), Doxycycline (monohydrate), Enoxacin, Enrofloxacin, Erythromycin, Flumequine, Josamycin, Lincomycin, Methicillin, Minocycline, Norfloxacin, Novobiocin, Ofloxacin, Oleandomycin, Oxacillin, Oxytetracycline, Penicillin G, Penicillin V, Roxithromycin, Spiramycin, Sulfadiazine, Sulfamerazine, Sulfamethazine | Antibacterial (33)                   |
| Sulfamethoxazole, Sulfapyridine, Carbamazepine, Primidone  | Anticonvulsant (4)                   |
| Tetracycline, Tiamulin, Citalopram, Escitalopram, Sertraline, Fluoxetine, Fluvoxamine, Paroxetine  | Antidepressant (8)                   |
| Glyburide (glibenclamid; glybenzcyclamide), Metformin  | Antidiabetic (2)                     |
| Diphenhydramine  | Antiemetic (1)                       |
| Loratadine   | Antihistaminic (1)                   |
| Nadolol, Verapamil   | Antihypertensive (2)                 |
| Aceclofenac, Acemetacin, Acetylsalicylic acid (aspirin), Alclofenac, Diclofenac, Fenoprofen, Fenoprofen calcium salt dihydrate, Ibuprofen, Indomethacin, Ketoprofen, Meclofenamic acid, Mefenamic acid, Naproxen, Phenylbutazone, Phenazone, Propyphenazone, Tolfenamic acid   | Anti-inflammatory (17)               |
| Clotrimazole   | Antimicrobial agents (1)             |
| Cyclophosphamide, Cyclophosphamide (anhydrous form), Daunorubicin, Doxorubicin, Epirubicin, Fluorouracil, Ifosfamide   | Antineoplastic (7)                   |
| Famotidine, Lansoprazole, Omeprazole, Ranitidine, Acyclovir  | Antiulcerative (5)                   |
| Alprazolam, Bromazepam, Diazepam, Lorazepam, Medazepam, Meprobamate, Nordiazepam, Oxazepam, Temazepam  | Anxiolytic and Psychiatric drugs (9) |
| Acebutolol, Atenolol, Betaxolol, Bisoprolol, Carazolol, Metoprolol, Oxprenolol, Pindolol, Propranolol, Sotalol, Timolol  | Beta-Blockers (11)                   |
| Pentoxifylline   | Blood viscosity agents (1)           |
| Albuterol, Albuterol sulfate, Clenbuterol, Fenoterol, Salbutamol, Terbutaline  | Bronchodilators (6)                  |
| Caffeine, Furosemide, Hydrochlorothiazide  | Diuretic (3)                         |
| Bezafibrate, Clofibrac acid, Etofibrate, Fenofibrate, Fenofibrac acid, Gemfibrozil, Lovastatin, Mevastatin, Pravastatin, Simvastatin   | Lipid regulators (10)                |
| Acecarbromal, Allobarbital, Amobarbital, Butalbital, Hexobarbital, Pentobarbital, Aprobarbital, Secobarbitol sodium  | Sedatives, hypnotics (8)             |
| 17-alpha-Estradiol, 17-alpha-Ethinylestradiol, 17-beta-Estradiol, Beta-sitosterol, Cholesterol, Diethylstilbestrol, Estriol, Estrone, Estrone sulfate, Prednisolone, Dexamethasone, Betamethasone, Mestranol   | Steroids and hormones (13)           |
| Amityptiline, Doxepine, Imapramine, Zolpidem   | Psychiatric drugs (4)                |
| Diatrizoate, Iohexol, Iomeprol, Iopamidol, Iopromide,  | X-ray contrast media (5)             |



# Pharmaceuticals Life Cycle





## *Pharmaceuticals in Drinking Water WHO Working Group Report (2012)*

### **Human health risk assessments (UK, Australia and USA):**

Margins of exposure (MOEs) **versus** Acceptable Daily Intake (ADI) or Minimum Therapeutic Dose (MTD) or Drinking-Water Equivalent Level (DWEL).

Concentrations of pharmaceuticals in drinking-water are generally more than 1000-fold below the MTD, which is the lowest clinically active dosage. The findings suggest that appreciable risks to health arising from exposure to trace levels of pharmaceuticals in drinking-water are extremely unlikely - **the development of formal guideline values for pharmaceuticals in the WHO Guidelines for Drinking-water Quality is unwarranted**

Human exposure through DW can be reduced through preventive measures, such as take-back programs, regulations, public guidance and consumer education to encourage the proper disposal of unwanted pharmaceuticals and minimize the introduction into the environment.





## *Emerging Pollutants - Final Remarks More Questions than Answers*

- Threats to wild life is recognized.
- Concerns about human exposure (biological plausibility):
  - Long-term effect
  - Mixture of compounds
  - Effect on different ages
- Environmental water quality guidelines maybe more urgent.
  - Detection limits of analytical methods are a barrier?
- Environmental guidelines will protect human health?

