

# Considering Abiotic Processes for Integrated Persistence and Environmental Risk Assessment

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**REACH Seminar, Stanhope Gate, London**  
**26 March 2009**



# REACH: Environmental Fate Tests Included in Chemical Safety Report

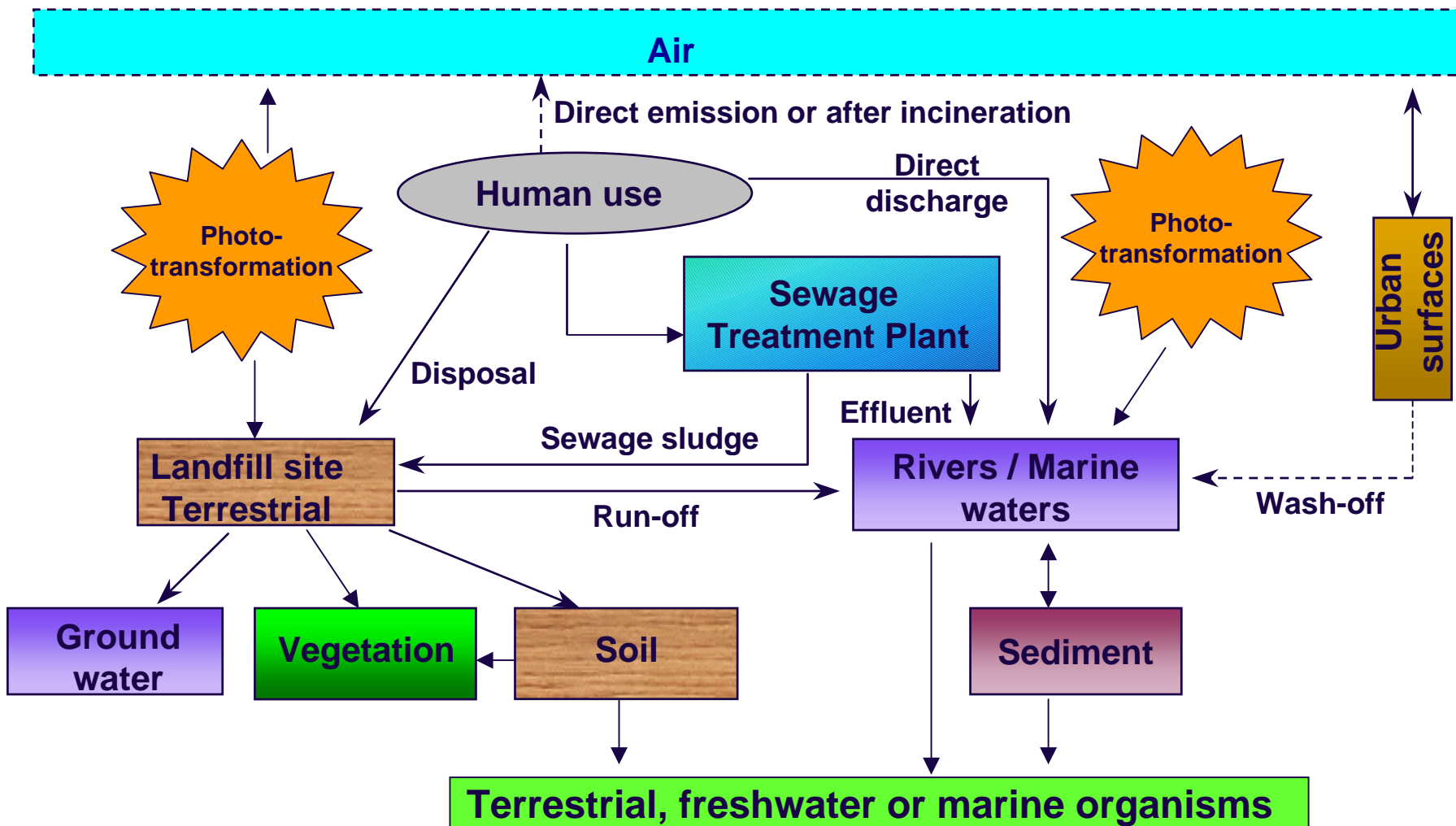
DEGRADATION	
ABIOTIC DEGRADATION	BIODEGRADATION
Hydrolysis	Biodegradation in water *
Phototransformation in air	Biodegradation in sediment
Phototransformation in water	Biodegradation in soil
Phototransformation in soil	

ENVIRONMENTAL DISTRIBUTION	BIOACCUMULATION
Adsorption / desorption	Aquatic bioaccumulation
Volatilisation	Terrestrial bioaccumulation
Distribution modelling	

\* Estimated data, screening tests and simulation tests



# Release Route and Fate Processes in the Environment

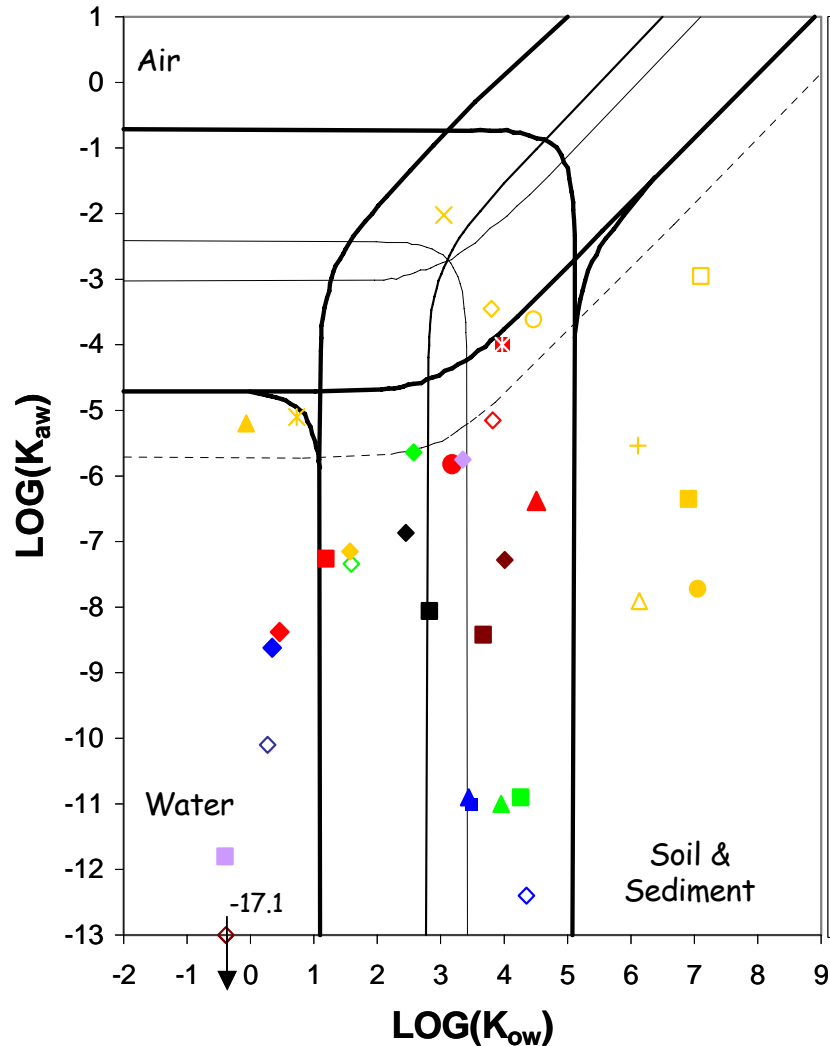


Liu et al. 2004 AZ Environ. Fate Strategy Report



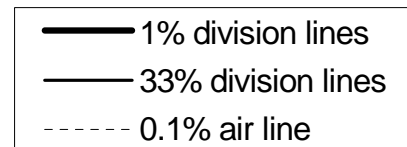
# Partition Map

## Partition Map



## Substances

- |  |  |
|--|--|
| ◆ Acetaminophen (analgesic & anti-inflammatory)        | ◆ Azelaic acid (dicarboxylic acid)     |
| ■ Acetylsalicylic acid (analgesic & anti-inflammatory) | ■ p,p'-DDT (pesticide)                 |
| ▲ Diclofenac (analgesic & anti-inflammatory)           | ▲ Caffeine (stimulant)                 |
| ✕ Ibuprofen (analgesic & anti-inflammatory)            | ● Linoleic acid (unsaturated acid)     |
| ● Naproxen (analgesic & anti-inflammatory)             | ✕ Octanoic acid (short-chain acid)     |
| ◆ Captopril (cardiovascular)                           | ✕ Phthalic acid (aromatic acid)        |
| ■ Propranolol (cardiovascular)                         | + Tetradecanoic acid (long-chain acid) |
| ▲ Quinidine (cardiovascular)                           | ◆ a-HCH (pesticide)                    |
| ◆ Clofibrilic acid (blood lipid regulator)             | □ PCBs (poly-chlorinated biphenyls)    |
| ■ Lovastatin (lipid lowering)                          | ▲ Benzo[a]pyrene (PAH)                 |
| ▲ Mevastatin (lipid lowering)                          | ○ Phenanthrene (PAH)                   |
| ◆ Estradiol (estrogen agonist)                         |  |
| ■ Ethynylestradiol (estrogen agonist)                  |  |
| ◆ Carbamazepine (anti-epileptic)                       |  |
| ■ Diazepam (anti-epileptic)                            |  |
| ◆ Flutamide (anti-neoplastic & immunosuppressant)      |  |
| ■ Mitomycin C (anti-neoplastic & immunosuppressant)    |  |
| ◆ Fluoxetine (anti-depressant)                         |  |
| ◆ Ketoconazole (anti-fungal)                           |  |
| ◆ Nalidixic acid (antibiotic)                          |  |
| ◆ Ofloxacin (antibiotic)                               |  |
| ◆ Ranitidine (gastro-intestinal)                       |  |



Liu Q-T et al. 2004 SETAC Prague



# Degradability ≠ Biodegradability, It's the Function of

- **Diversity of metabolic enzymes**, e.g. bacteria: narrow spectrum in humans, broad spectrum in the environment
- **pH** (municipal sewage 7-9; surface water 7-8, stomach < 2)
- **Redox potential**: gut anaerobic, environment often aerobic
- **Light**: photolysis and photo-induced reactions catalysed by radicals,  $^1\text{O}_2$  and cDOM (light spectrum, intensity)
- **Temperature, etc.**

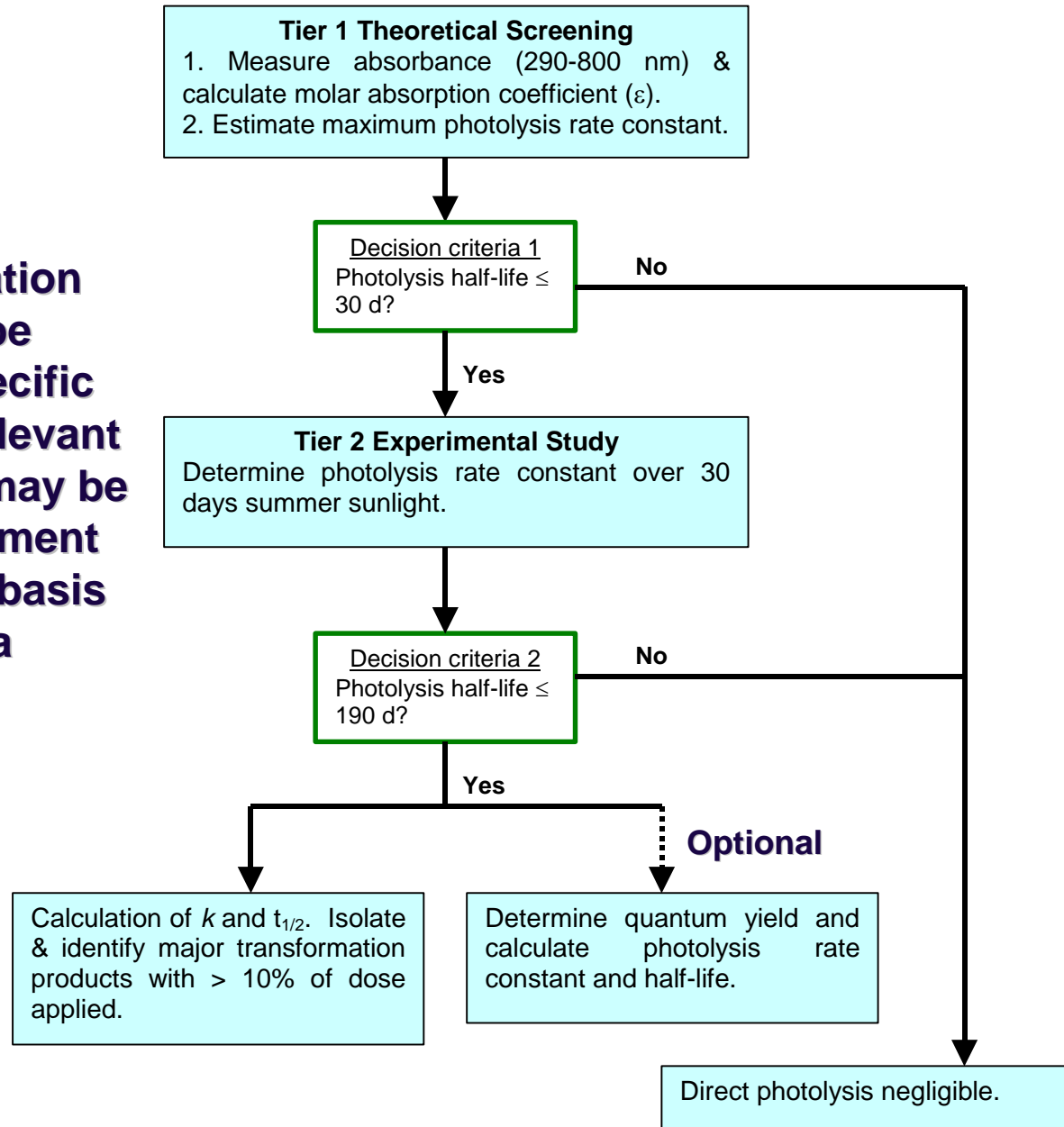
**And the combination of several of them!**



# OECD 316: Direct Photolysis

## REACH R. 7b:

...Where a degradation rate constant can be derived for site specific environmentally relevant conditions, these may be used in the assessment on a case-by-case basis where justified by a knowledge of local conditions.



# Case Study

## Application of an Integrated Fate Testing Approach for Persistence and ERA of Substances in River Waters



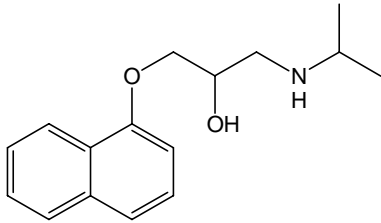
# Comparative In-Stream Depletion Mechanisms: Realistic ERA

- Phototransformation
  - An important removal process of water soluble chemicals from natural surface waters ( $k_p = k_{di} + k_i$ )\*
- Hydrolysis
  - Non-stress conditions
- Biodegradation
  - Not well understood in natural waters
- Environmental Relevance
  - Laboratory test strategy: extrapolation to field
  - Microcosm studies (e.g. Lam et al. 2004)

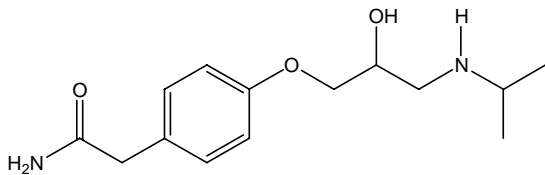
\* Liu et al. NGWA 2004, Liu & Williams Environ. Sci. Technol. 2007, Robinson et al. Chemosphere 2007



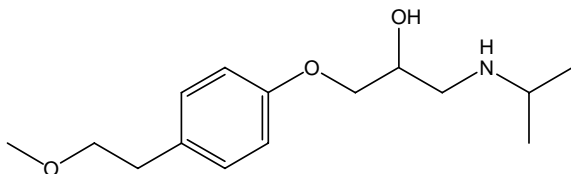
# Test Substances



Propranolol,  
 $\log D_{ow}$ : 0.78 \*



Atenolol,  
 $\log D_{ow}$ : 0.016



Metoprolol,  
 $\log D_{ow}$ : -0.90

- $\beta$ - adrenergic receptors
- Detected in sewage effluent and surface waters at  $\text{ng L}^{-1}$  levels
- Water soluble with one or two aromatic rings
- No significant partitioning to sediment \*
- $\text{PEC}^{**}$  ( $\mu\text{g L}^{-1}$ )                       $\text{MEC}$  ( $\mu\text{g L}^{-1}$ )
  - Propranolol: 0.59                      < 0.004-0.09
  - Atenolol:      0.24                      0.028
  - Metoprolol: 2.2                      0.01-0.39

\* Avdeef et al. 1998; Ternes et al. 2007.

\*\* Cleuvers 2005 *Chemosphere* 59, 199-205.



# Effect of Light on Environmental Transformation - A Tiered Approach

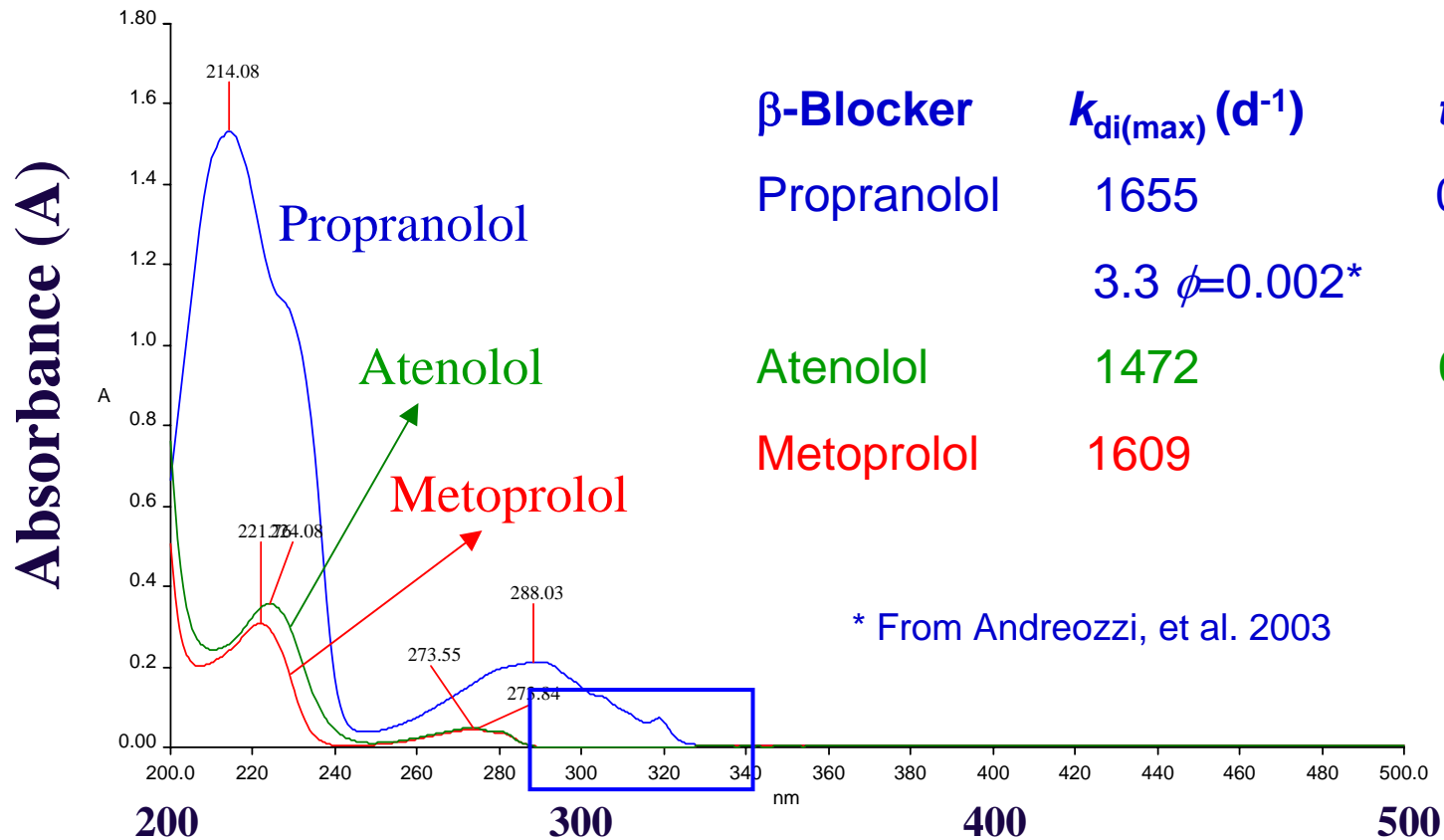
- Estimated rate constant and half-life
- Direct photolysis in deionised water \*
  - Kinetics measurements
  - Sterilised vs. non-sterilised water
- Overall degradation in river waters
  - Kinetics measurements
  - Sterilised vs. non-sterilised water
  - Impact of water parameters on rates
- Identify major degradation products (>10%)
- Impact on Predicted Environmental Concentrations (PECs): river catchment models



\* OECD 2000 draft, modified



# UV Spectra and Estimated $k_{di(max)}$ - Theoretical Screening



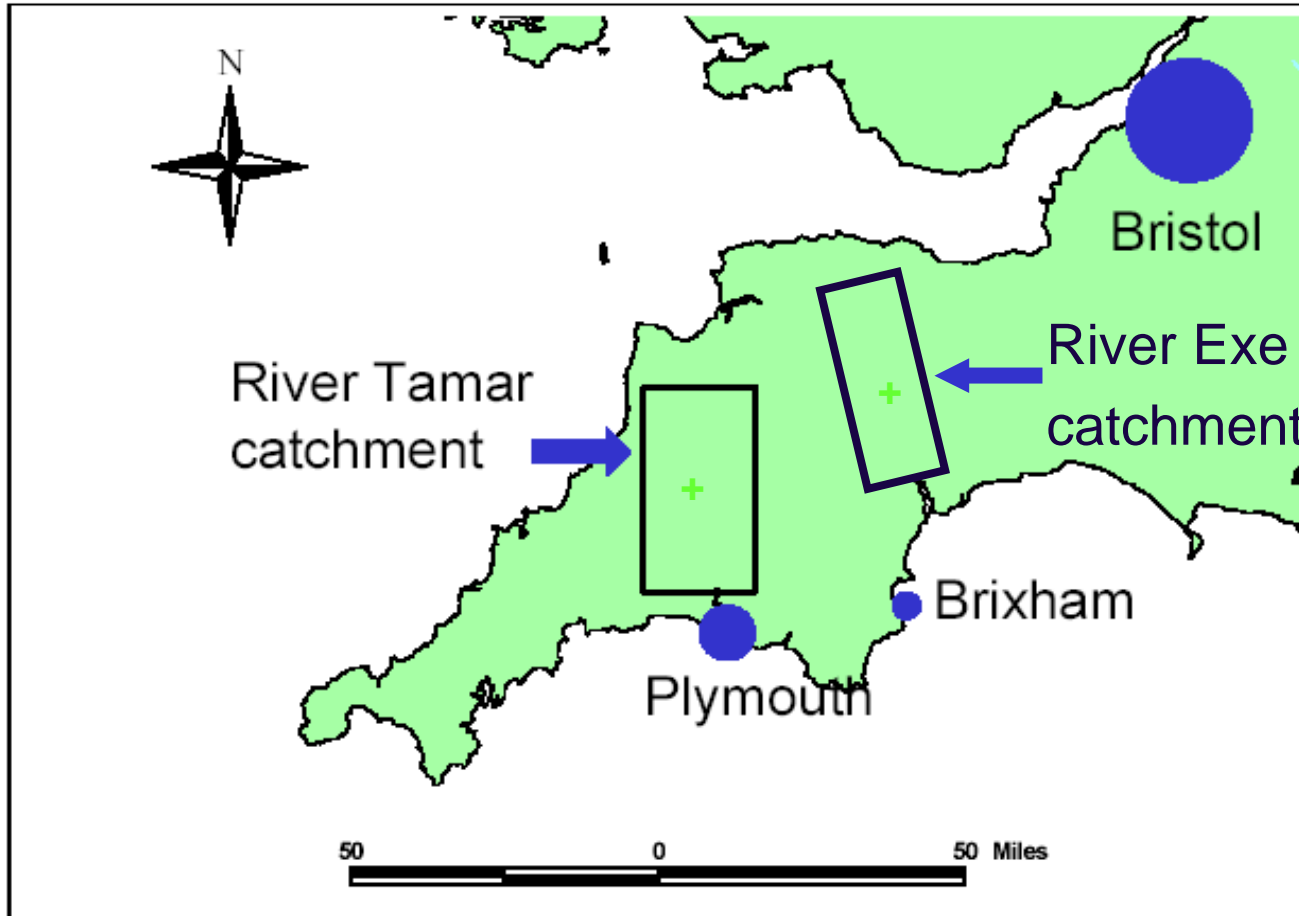
pH 7.0, 10 mg L<sup>-1</sup>

Wavelength (nm)



# River Water Sampling

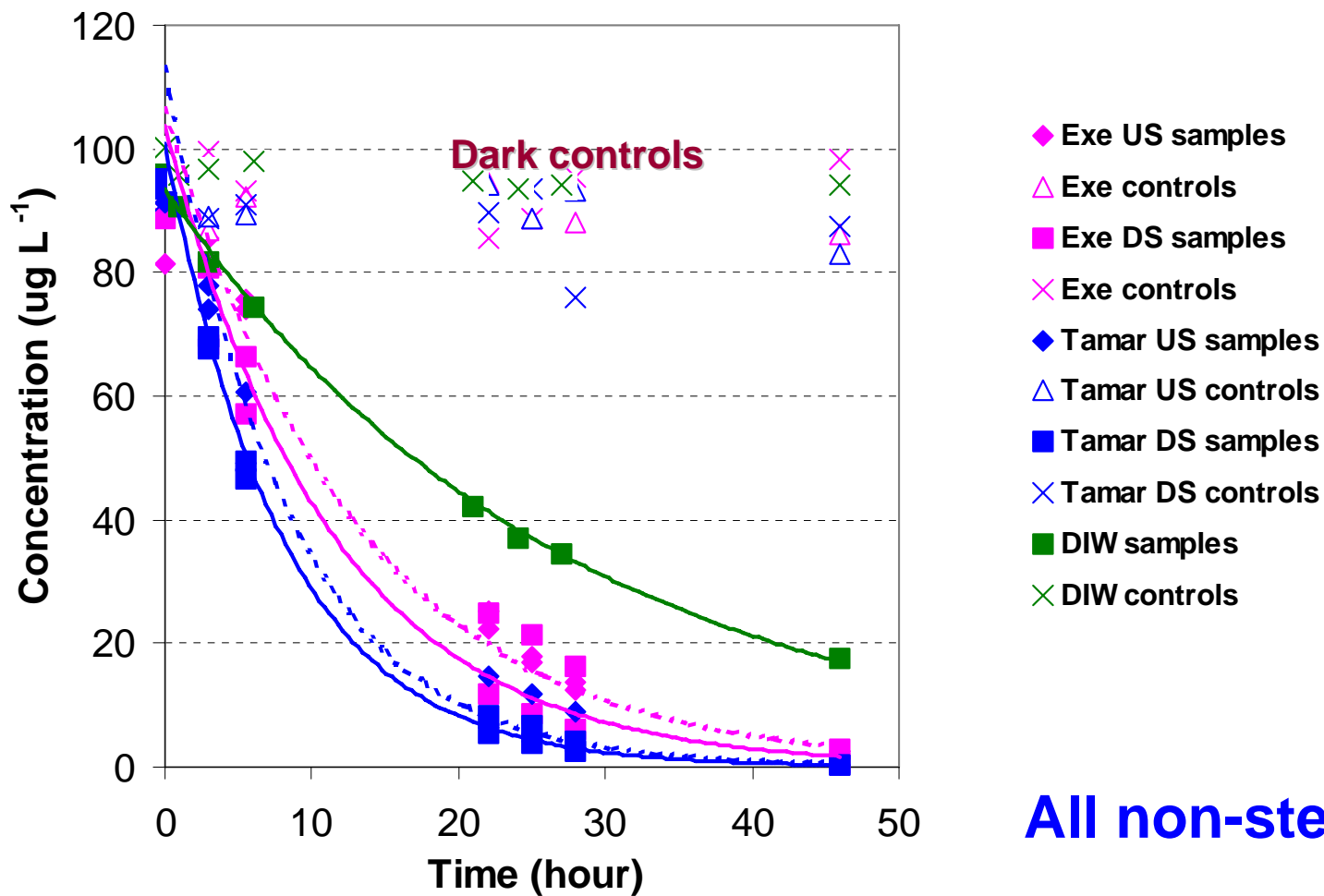
Colne River,  
Urban &  
industrial



Rural &  
agricultural



# Degradation of Propranolol in River Waters

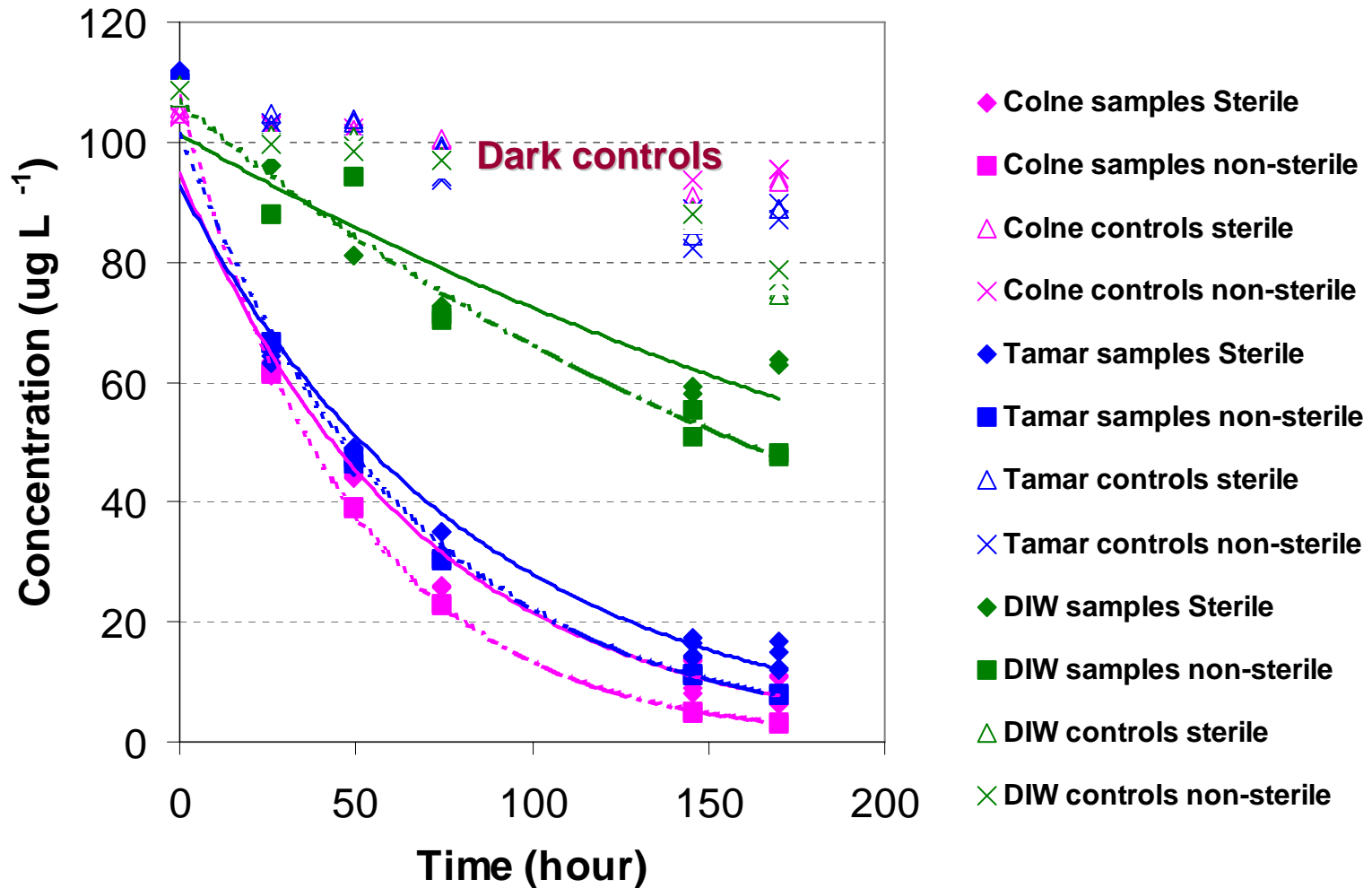


All non-sterilised

Liu et al. 2009 *Photochem. Photobiol. Sci.* DOI:10.1039/b817890a



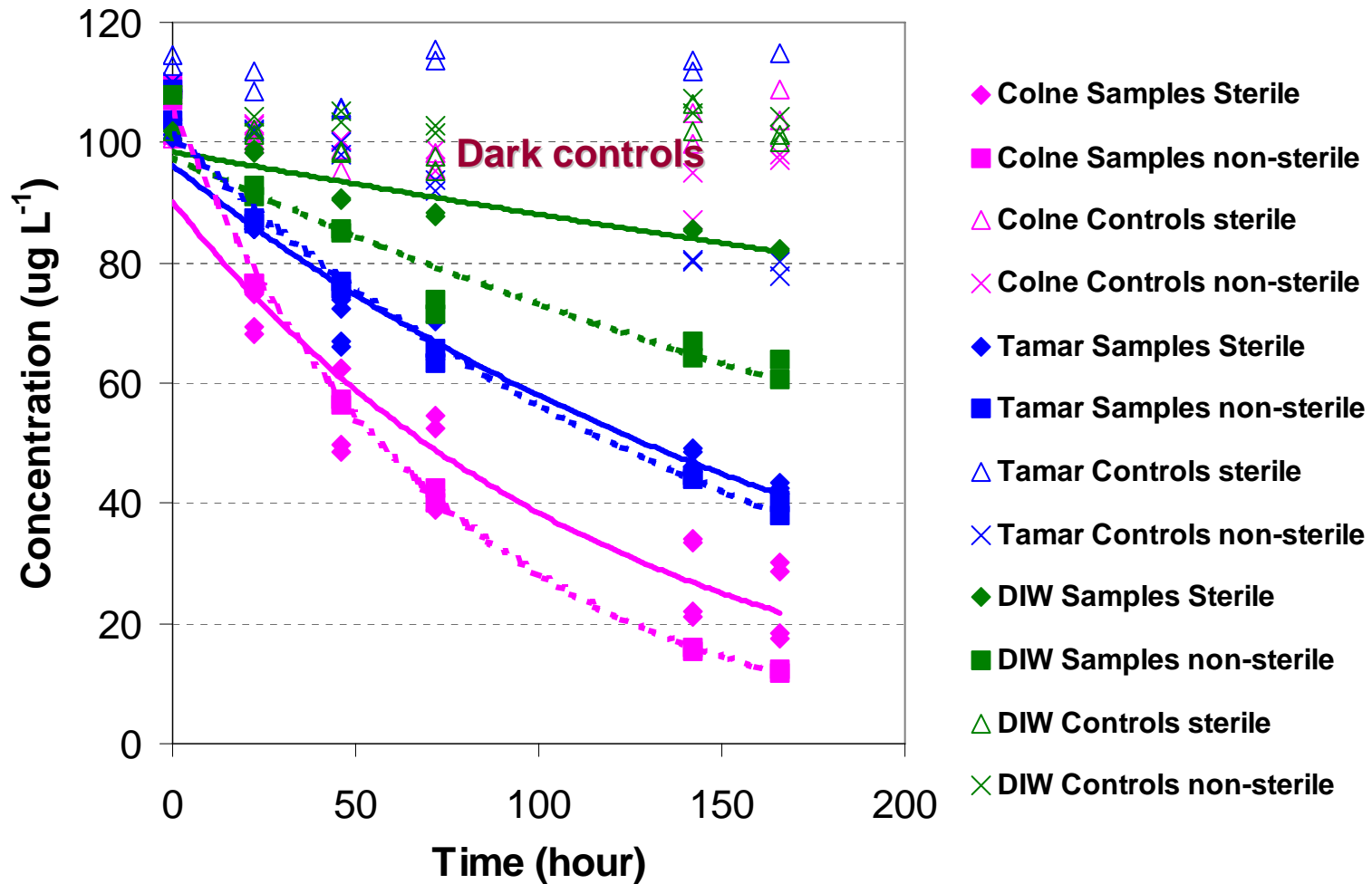
# Degradation of Metoprolol in River Waters



Liu et al. 2009 *Photochem. Photobiol. Sci.* DOI:10.1039/b817890a



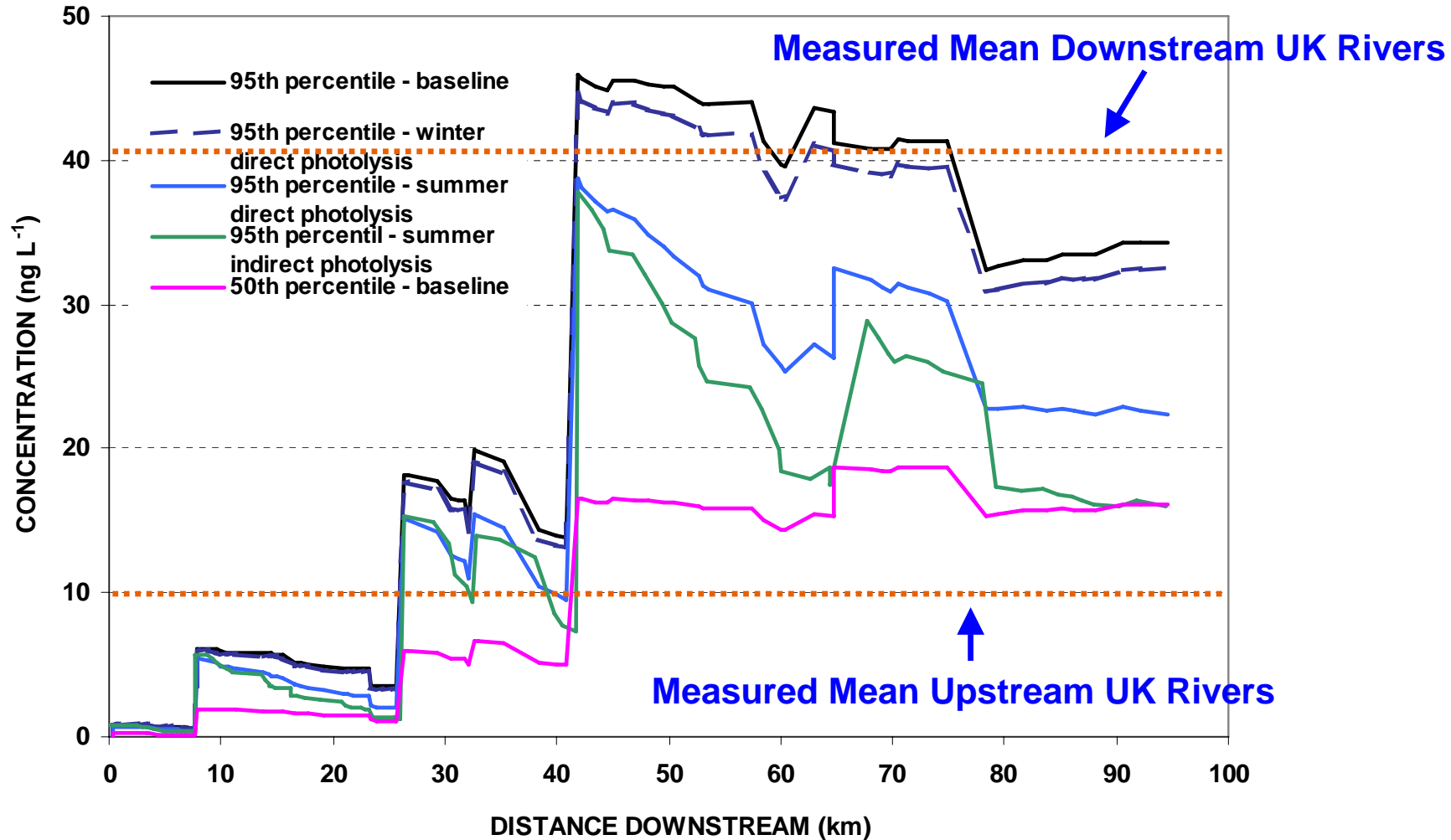
# Degradation of Atenolol River Waters



Liu et al. 2009 *Photochem. Photobiol. Sci.* DOI:10.1039/b817890a



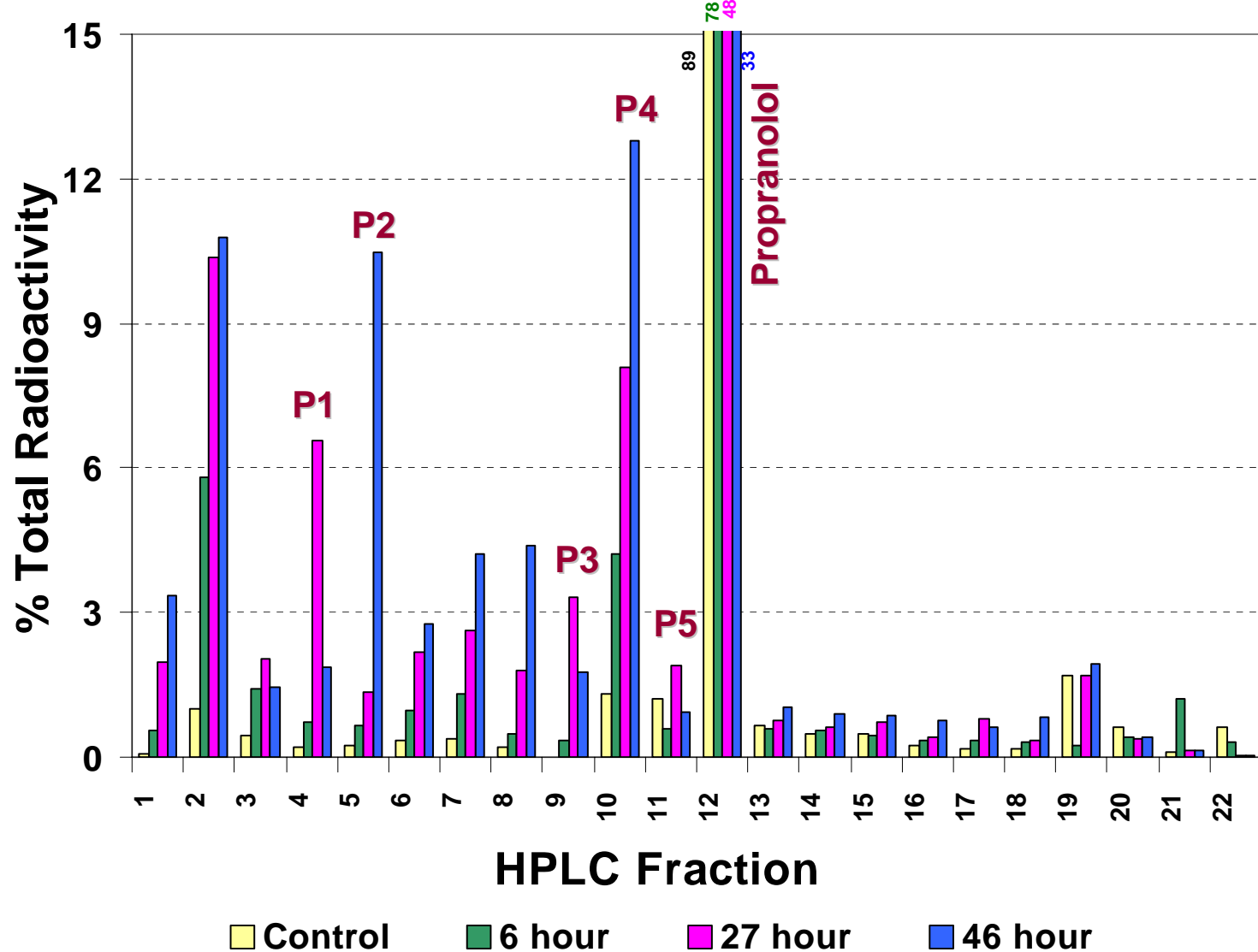
# Including Phototransformation for PEC Refinement



**Propranolol: GREAT-ER model results in Aire / Calder**  
**PECs: Predicted Environmental Concentrations**  
**Robinson et al. 2007 *Chemosphere*, 66, 757-766**



# Mass Balance of $^{14}\text{C}$ -Propranolol and Its Transformation Products

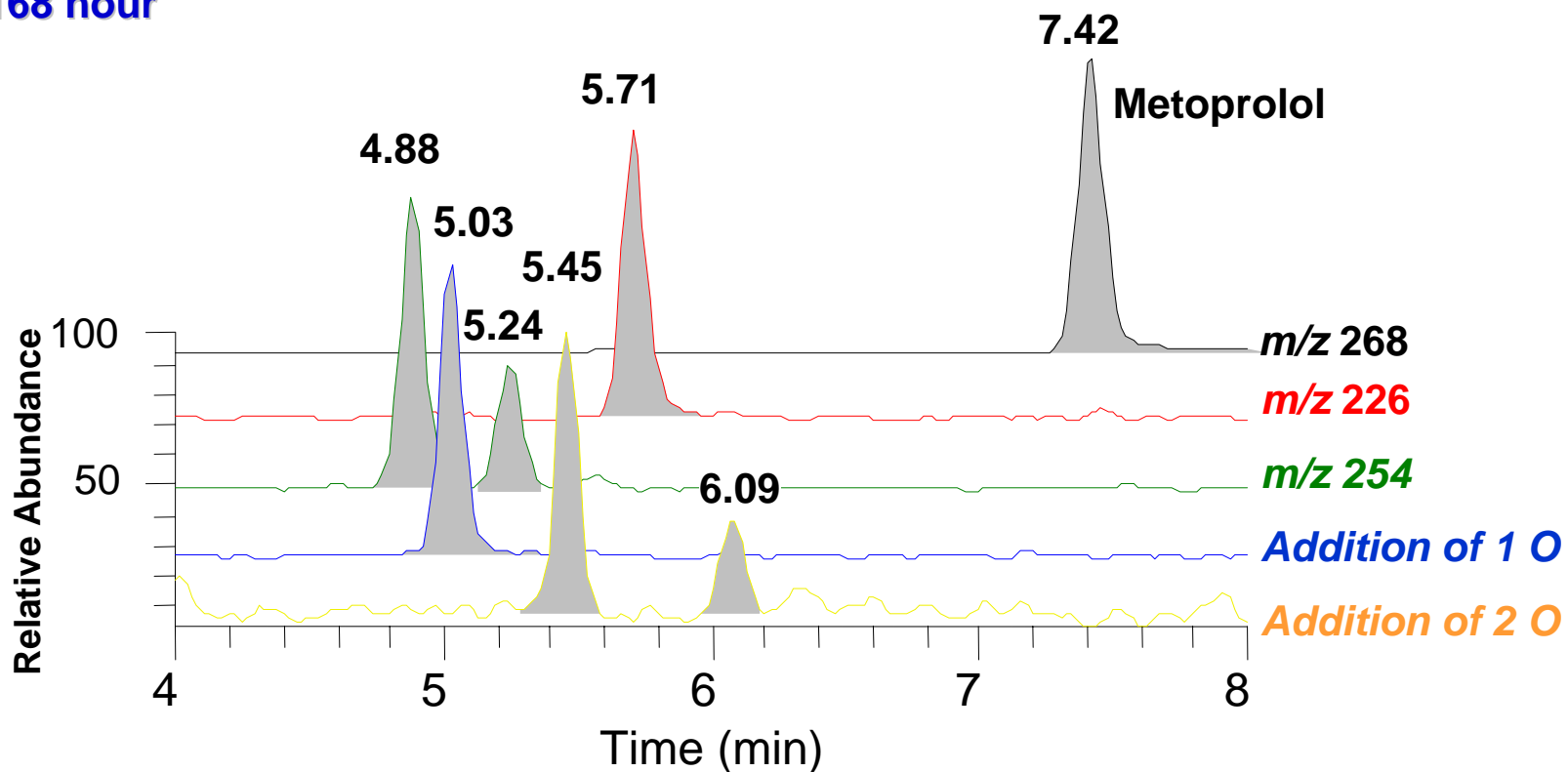


Liu & Williams 2007 *Environ. Sci. Technol.*, 41, 803-810



# Transformation Products from Metoprolol in River Water

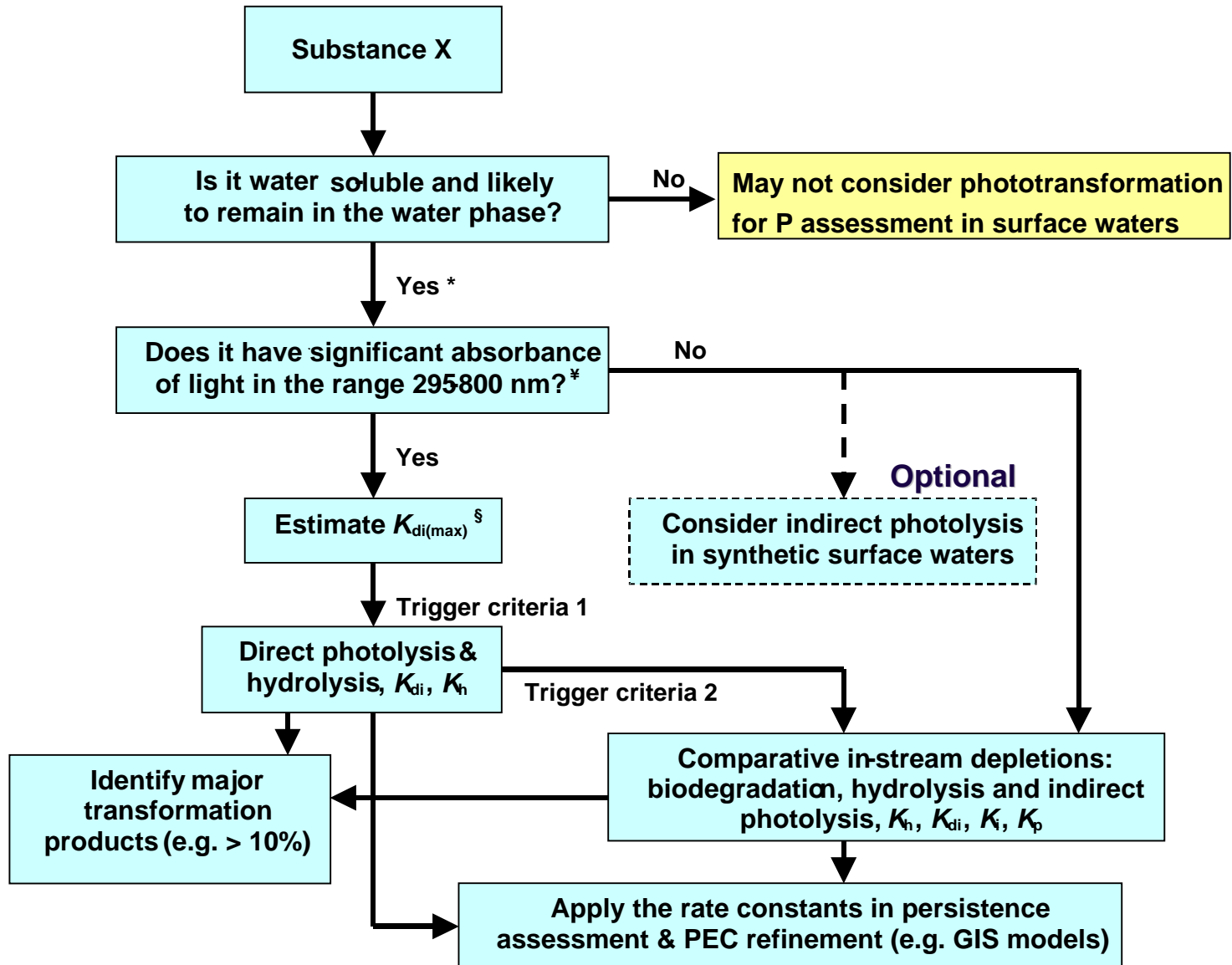
168 hour



Liu et al. 2009 *Photochem. Photobiol. Sci.* DOI:10.1039/b817890a



# Integrated Persistence & ERA of Chemicals in Surface Waters



# Summary: Use for Persistence Assessment Under REACH

- Integrated approach for simultaneous measurements of multi-kinetics
  - Not only photolysis, but also other photo-induced reactions (indirect phototransformation, hydrolysis and biodegradation)
  - Cost effective comparing to measuring kinetics separately
  - Environmental relevance
- Measured kinetics / half-life can be used for P assessment
  - $P_{\text{persistent marine}}$ : if  $t_{1/2} > 40$  days in surface water (> 60 days for marine)
- Can generate information of major transformation products if needed, e.g. > 10%
  - REACH includes assessment of transformation products



# Summary: Use for Environmental Risk Assessment Under REACH

- Can be related to natural environmental conditions for local and regional ERA
- Can apply river catchment models, such as GREAT-ER & PhATE™ for PEC refinement
  - Using environmentally relevant depletion processes, e.g.  $k_p$ ,  $k_h$  and  $k_b$
- Better temporal and spatial resolution for site specific assessment



# Conclusions

- An integrated framework with guidance on when and how to use it for what substances
  - Case-by-case assessment and substance specificity
  - Environmental relevance
- Overall transformation half-lives can be used for both persistence assessment and PEC refinement
  - Extrapolation to field considered variation of surface waters, e.g. light intensity / penetration, suspended solids & turbidity
- Further research may be needed to test the framework with more substances in surface waters
  - New ECETOC Taskforce on abiotic processes  
<http://www.ecetoc.org/task-forces>
  - Can develop QSAR approach when more data are available



# Acknowledgement



[www.brixham-lab.com](http://www.brixham-lab.com)

