Changing hydrodynamic conditions and their impacts on contaminant remobilisation in estuaries

Dr Andrew Turner,

Plymouth University

aturner@plymouth.ac.uk

Research interests

- Characterisation of natural solids
- Geochemical association of contaminants with sediments
- Bioaccessibility of contaminants in sediments
- Adsorption of contaminants on sediments

Research interests

- Characterisation of natural solids
- Geochemical association of contaminants with sediments
- Bioaccessibility of contaminants in sediments
- Adsorption of contaminants on sediments

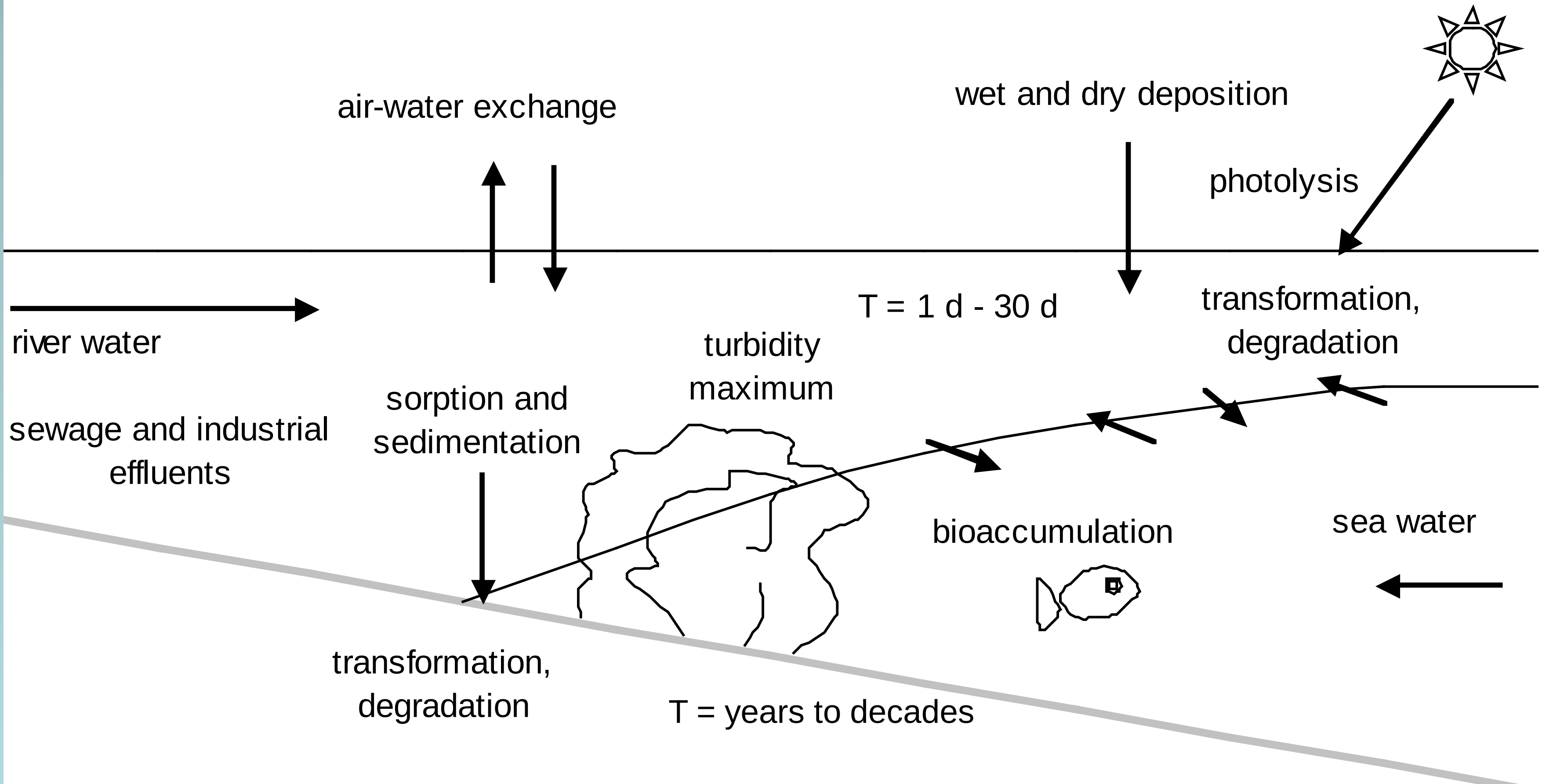
- Trace metals
- Persistent organics
- Platinum metals
- Pharmaceuticals

Impacts of climate change in estuaries

- Geomorphology
- Erosion
- Temperature increase
- Ice melt
- UV radiation
- Primary production
- pH
- Hypoxia
- Salinity

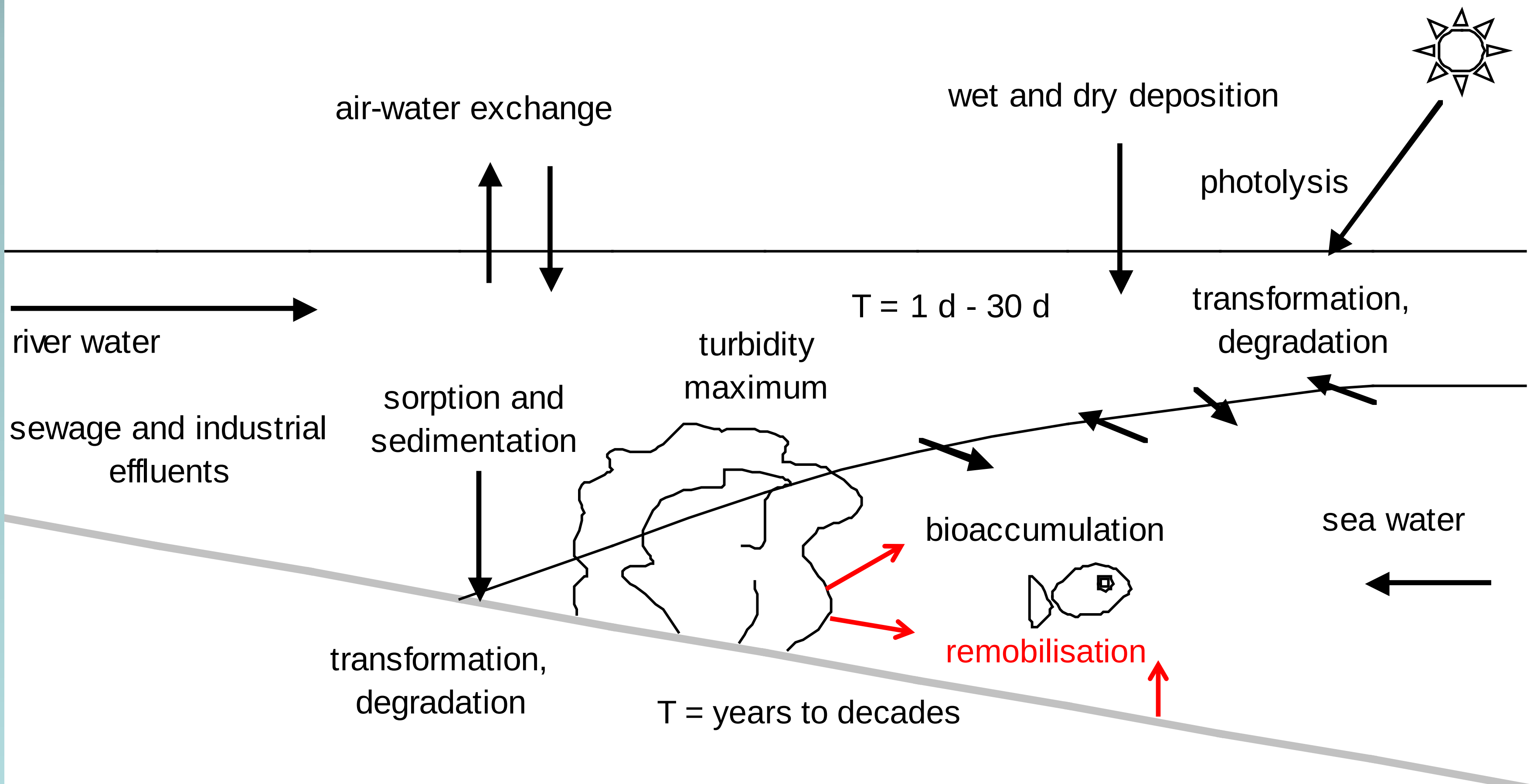
- Contaminant-hydrodynamic interactions

Behaviour of contaminants in an estuary

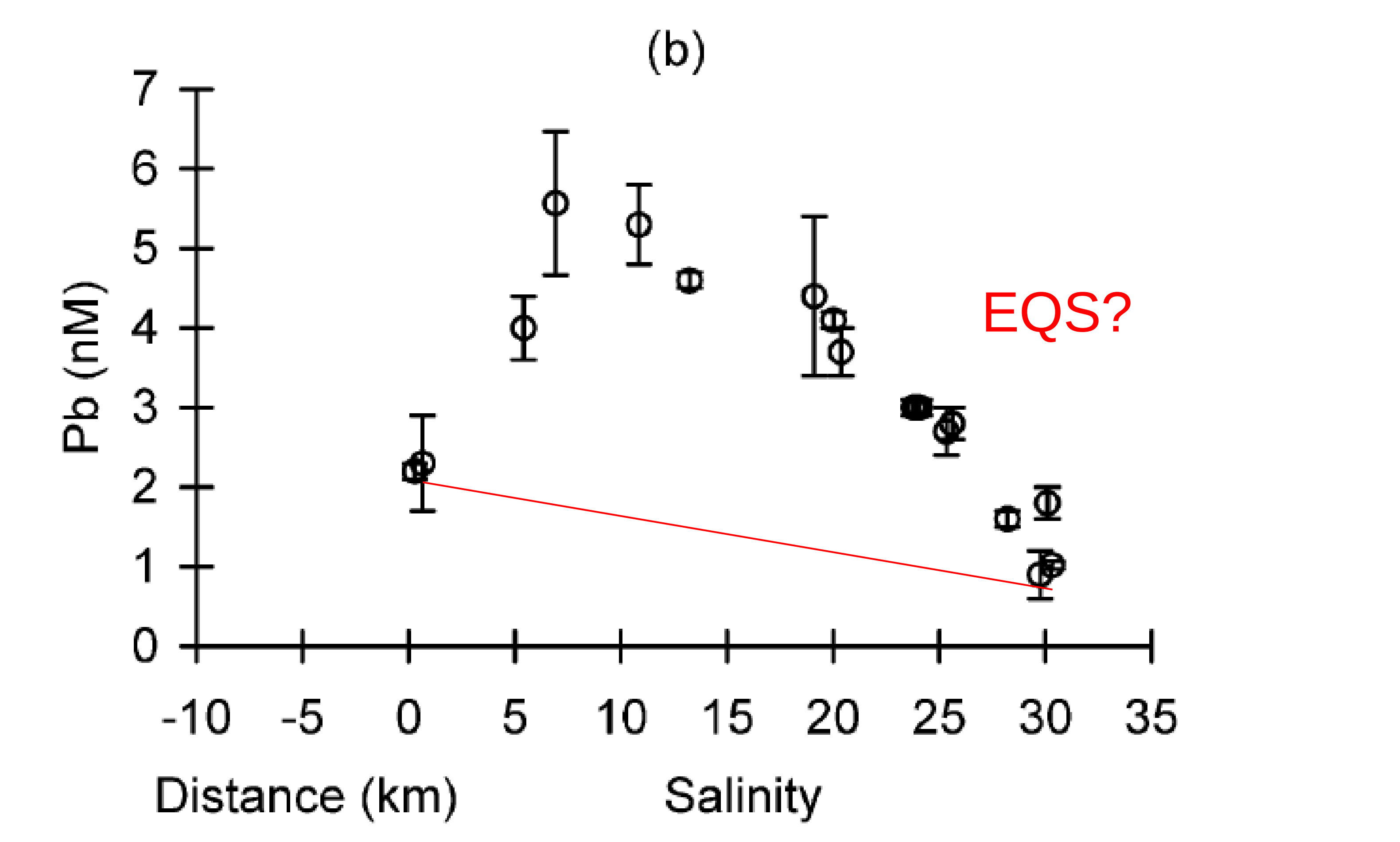


(i) Estuarine hydrodynamics
(ii) Contaminant sources
(iii) Contaminant behaviour

Behaviour of contaminants in an estuary



(i) Estuarine hydrodynamics
(ii) Contaminant sources
(iii) Contaminant behaviour



Remobilisation of lead in the Mersey estuary
(Martino et al., 2002)

Effects of changing hydrodynamics on sediment processes

(i) River flow (abrupt, continuous) RF

Increased sediment load/input

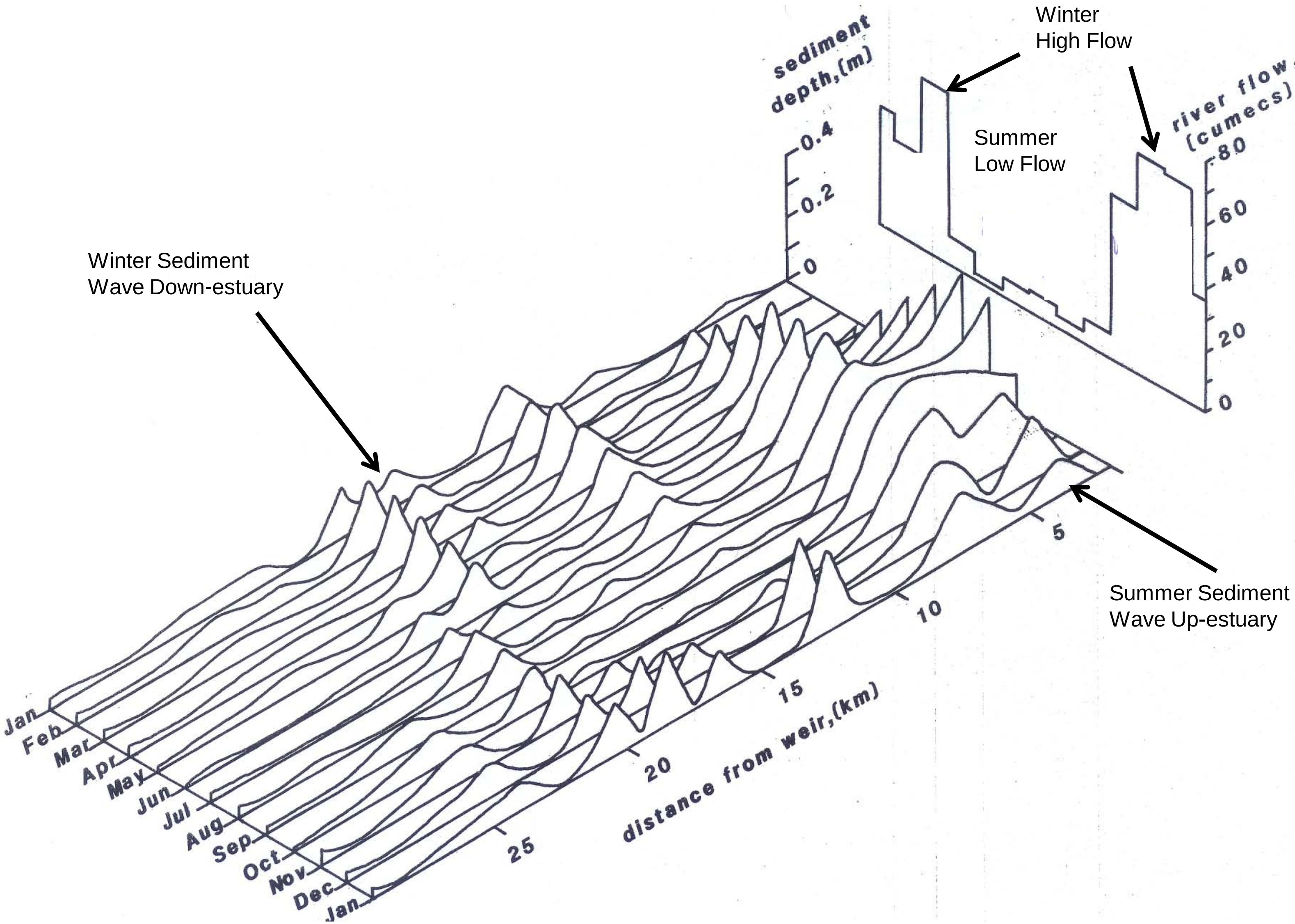
Increased energy – more local resuspension, export

Seaward shift of turbidity maximum

Decrease in (water) residence time

Exposure to lower salinities

Bale et al., 1985



Effects of changing hydrodynamics on sediment processes

(ii) Sea level rise SLR

Inundation

Tidal asymmetry

Landward shift of turbidity maximum

Reduction in bottom shear

Increase in (water) residence time

Exposure to higher salinities

Contaminant (trace metal) remobilisation through RF

Driver for remobilisation

Equilibrium partitioning:

$$C_\mathrm{w} \leftrightarrow C_\mathrm{s}$$

remobilisation

C_s = concentration on sediment, μg kg^{-1}

C_w = concentration in water, μg L^{-1}

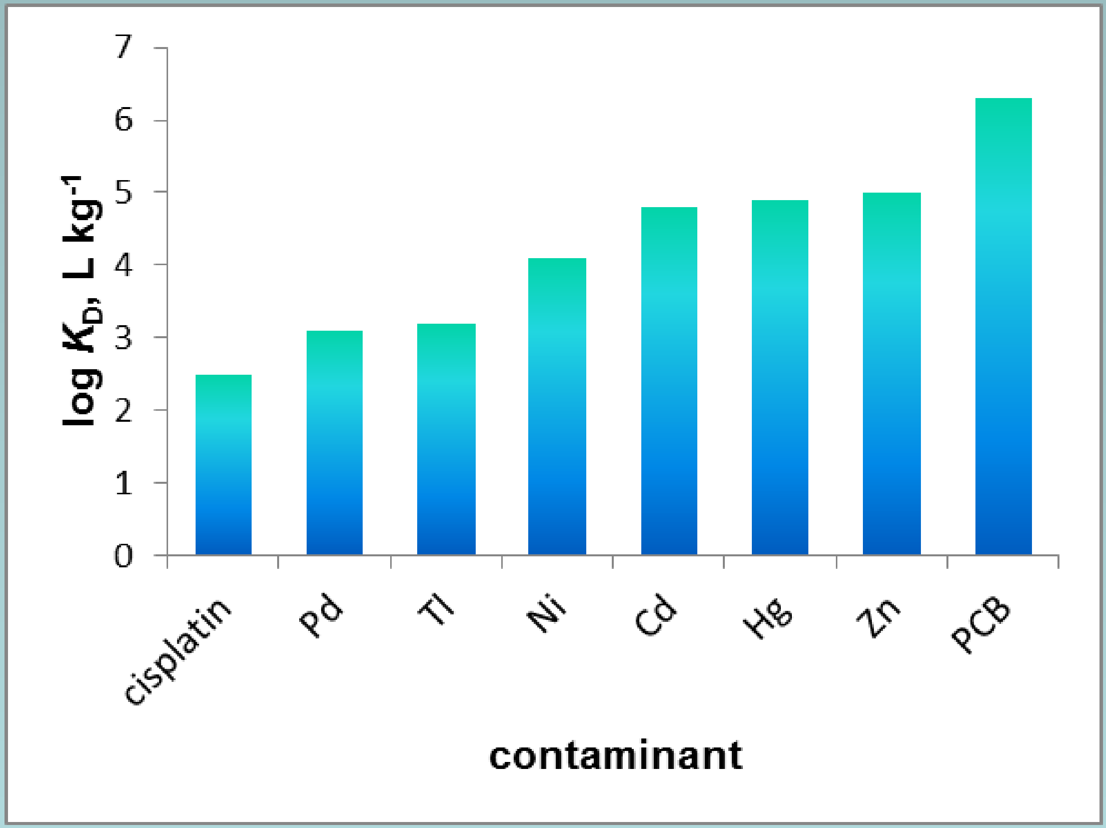
Sediment-water partition coefficient, K_D:

$$K_\mathrm{D} = \frac{[C_\mathrm{s}]}{[C_\mathrm{w}]}$$

K_D in L kg^{-1}

Indicative K_D values in the River Plym, UK

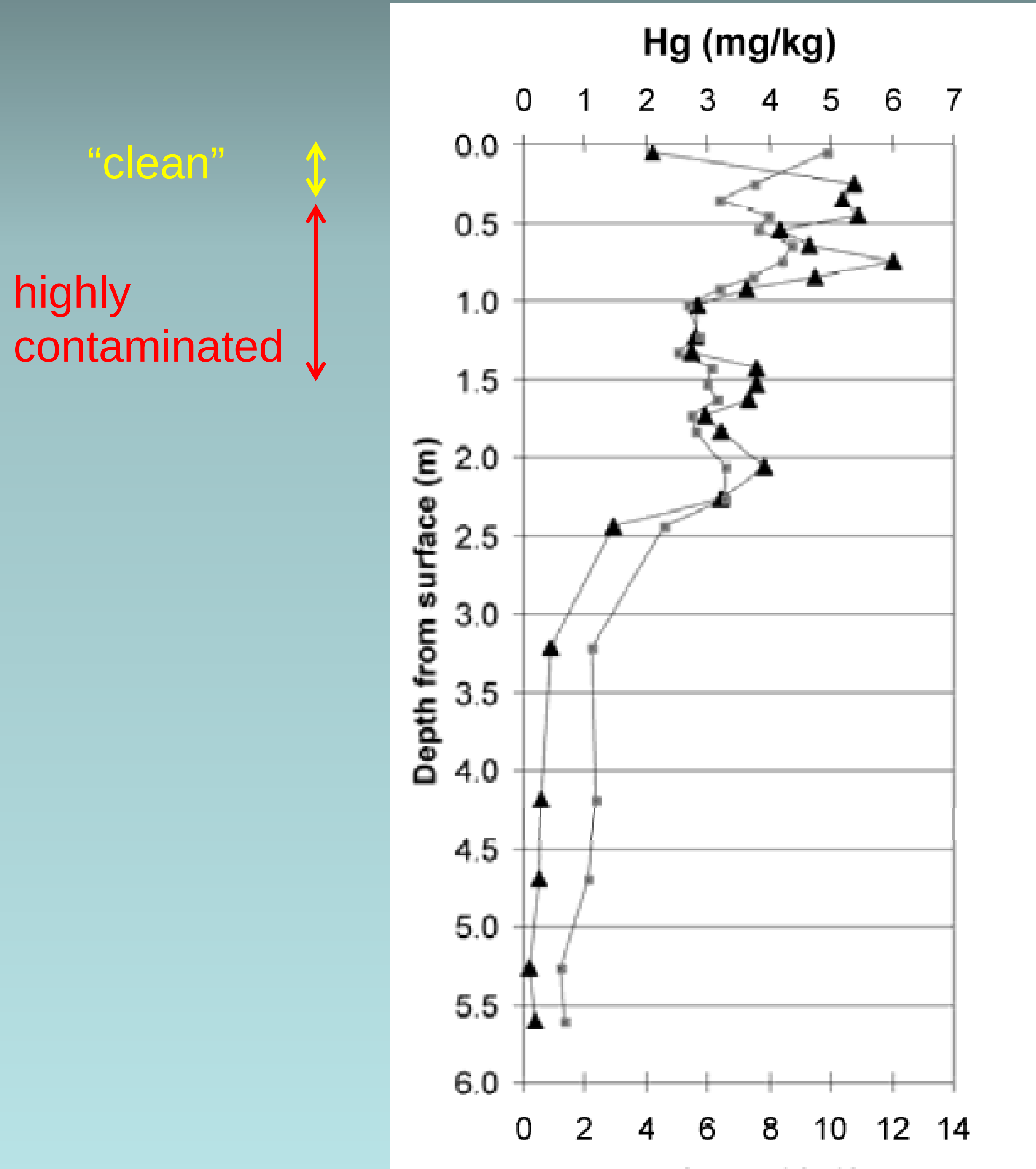
$$K_D = \frac{[C_s]}{[C_w]}$$



Increasing association with sediment

Historical accumulation of contaminants over decades/centuries

Mercury, Mersey estuary (Vane et al., 2009)



Remobilisation from resuspended “old” sediment

Increase in C_s

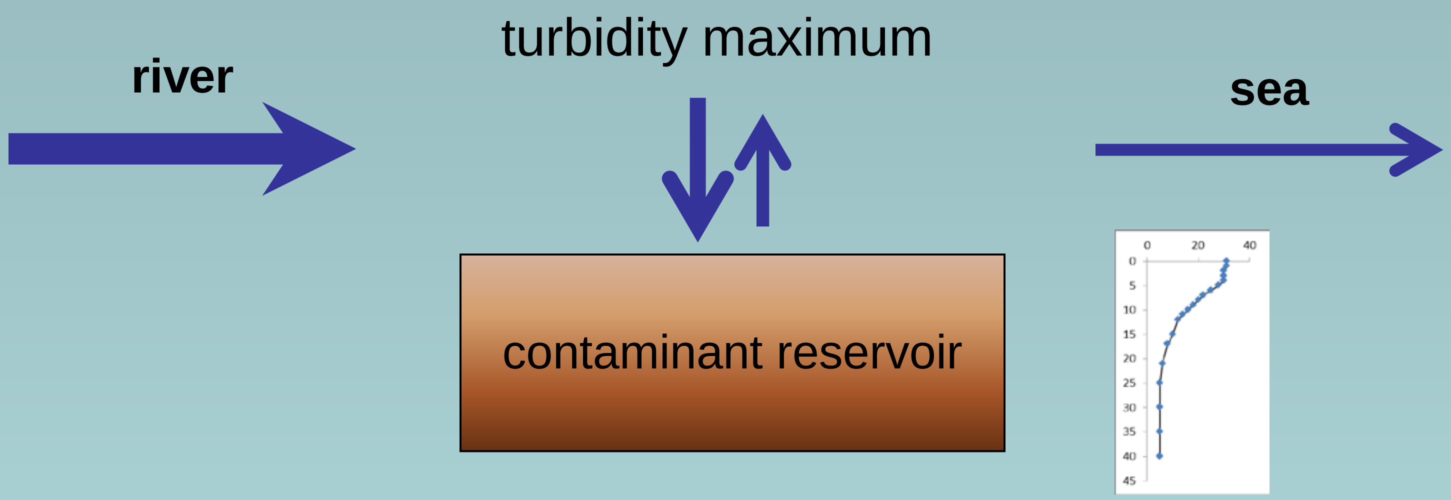
$$K_\mathrm{D} = \frac{[C_\mathrm{s}]}{[C_\mathrm{w}]}$$

Injection from pore waters (equilibrium/oxidation-reduction)

$$K_\mathrm{D}* = \frac{C_\mathrm{s}}{C_\mathrm{pw}}$$

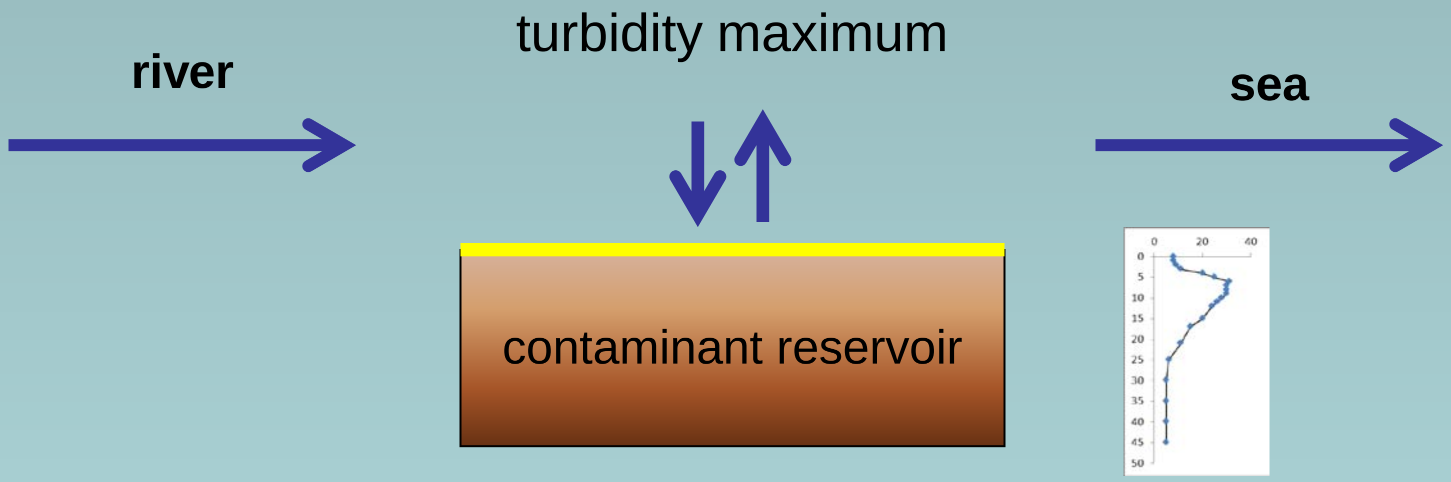
$$K_\mathrm{D} \bullet K_\mathrm{D}*$$

Fluxes and storage of contaminants in estuaries - historical



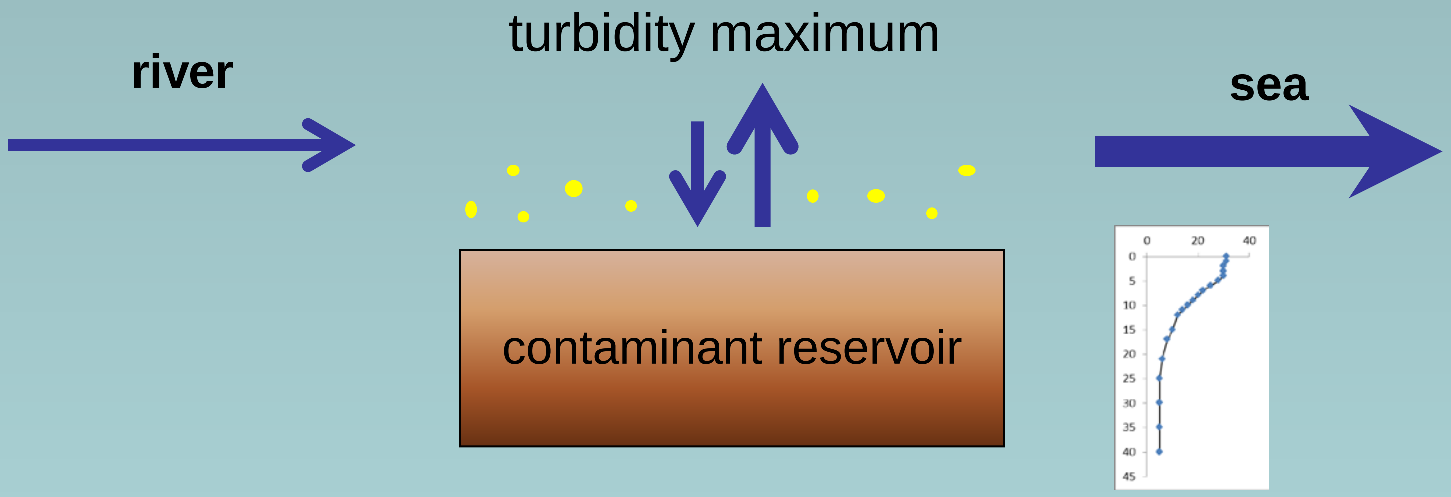
T = years to centuries

Fluxes and storage of contaminants in estuaries - present



T = years to decades

Fluxes and storage of contaminants in estuaries – RF



T = years to decades

Degree of mobilisation:

- Magnitude of K_D
- Extent of sediment resuspension
- Change in C_s (ΔC_s)
- Pore water concentration

Offset by:

- Re-precipitation/re-adsorption
- Reversibility of adsorption
- Reaction kinetics

Trace metal contaminant remobilisation through SLR

Driver for remobilisation

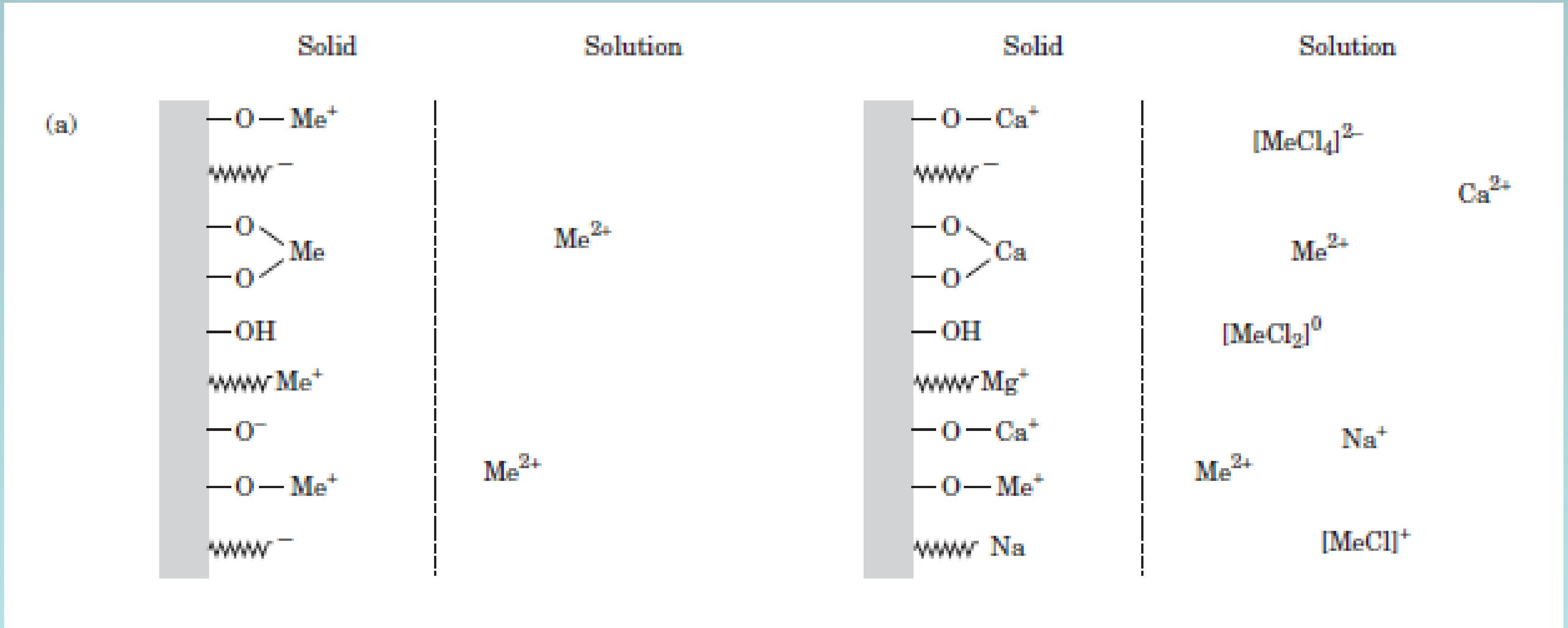
Salinity-induced desorption

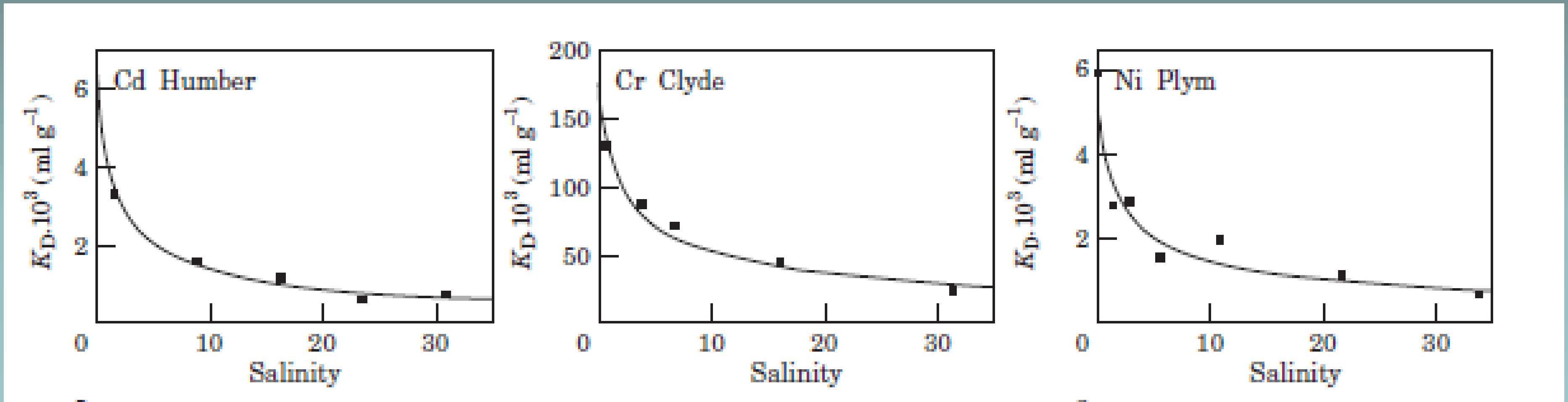
$$K_D = \frac{[C_s]}{[C_w]}$$

Decrease in K_D

river

saline

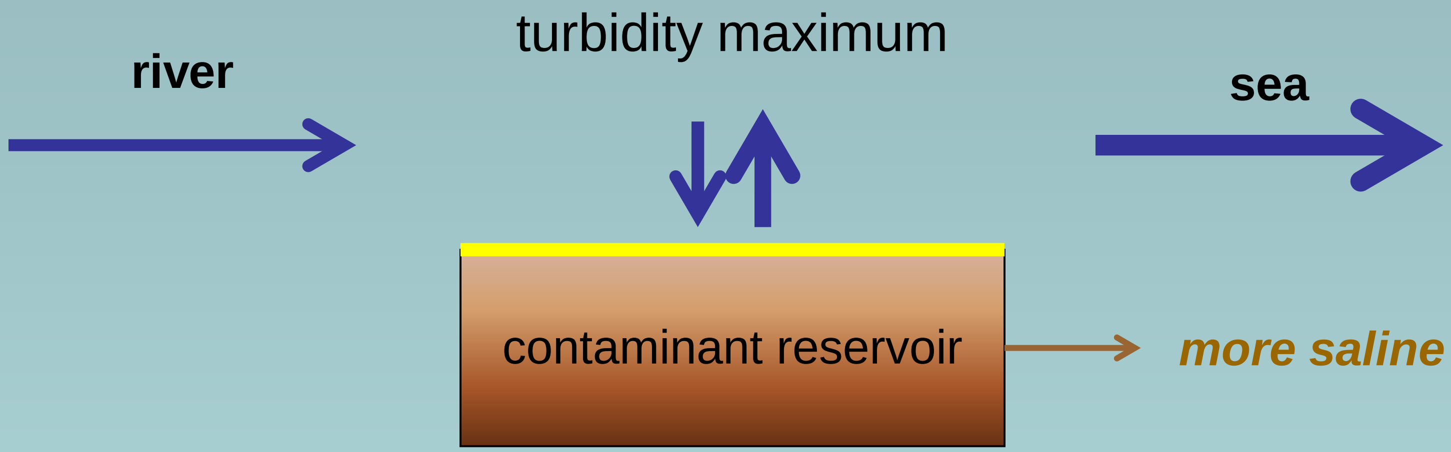




(Turner and Millward, 2002)

$K_D = K_D^0(S+1)^{-b}$

Fluxes and storage of contaminants in estuaries - SLR



T = years to decades

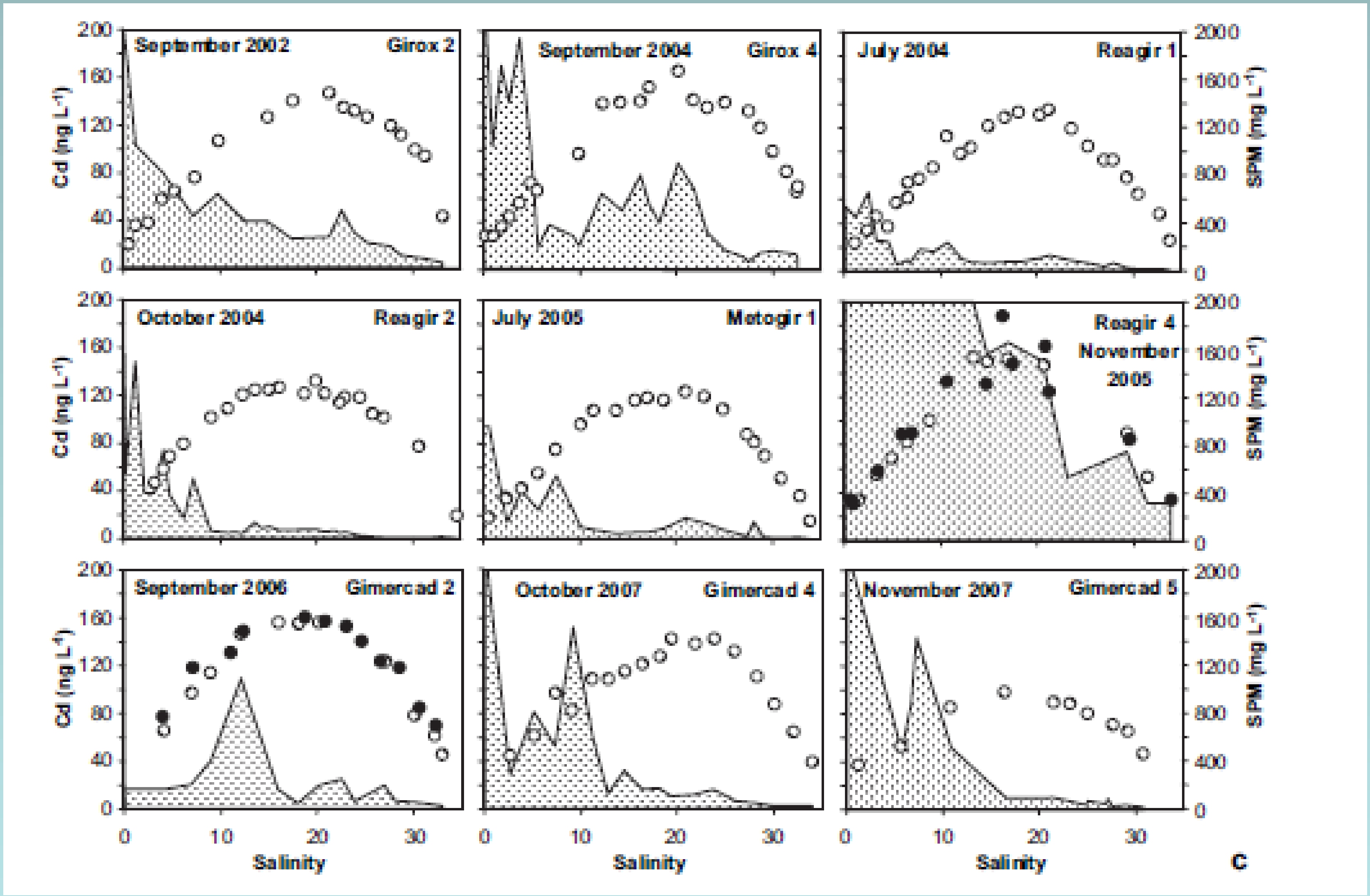
Degree of mobilisation:

- Sensitivity of K_{D} to salinity (magnitude of b)
- Extent of sediment exposure
- Change in S (ΔS)

Offset by:

- Reversibility of adsorption
- Desorption kinetics

Dissolved Cd in the Gironde estuary (Darlin et al., 2009)



Dissolved Cd in the Penze estuary (Waeles et al., 2005)

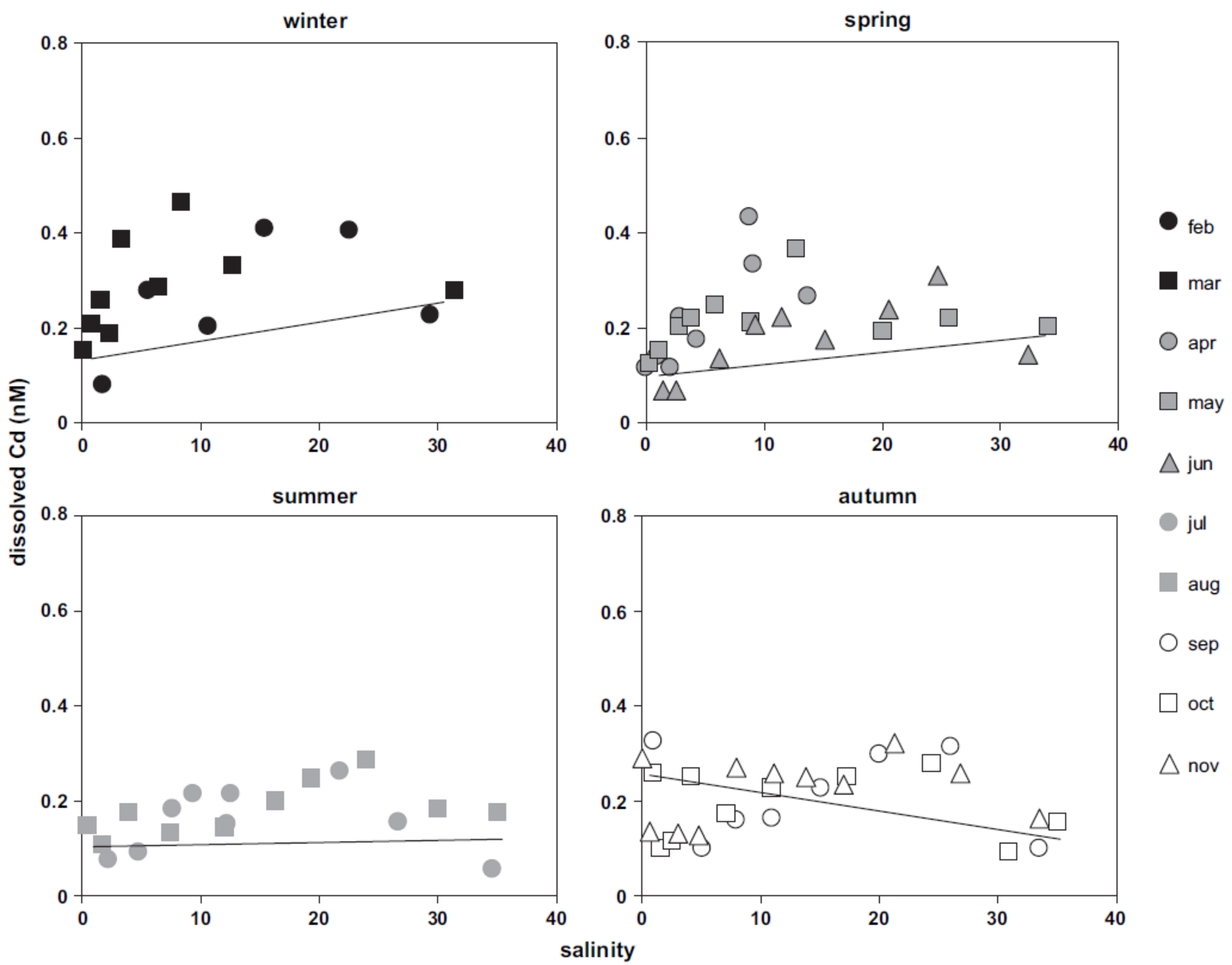
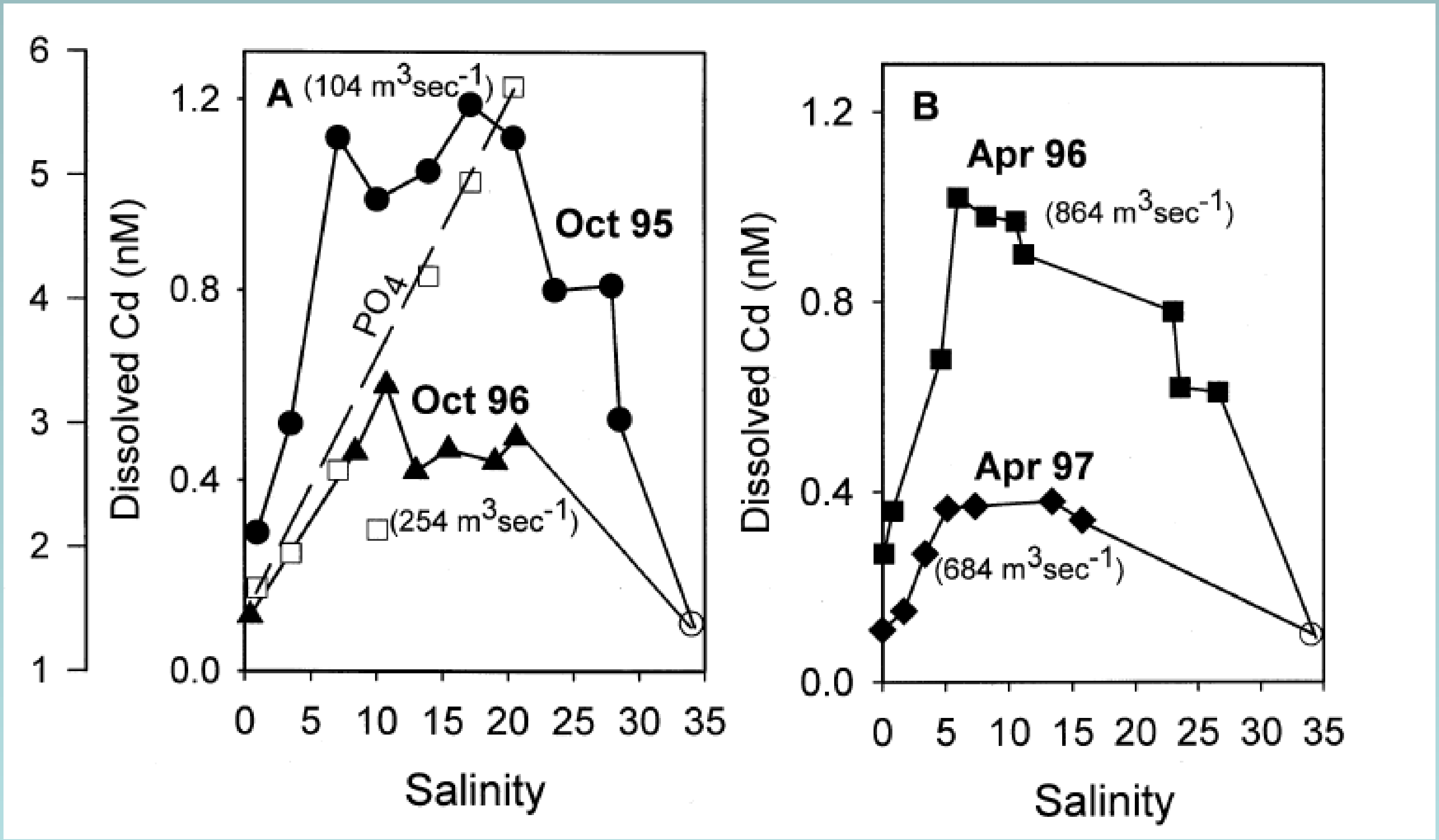


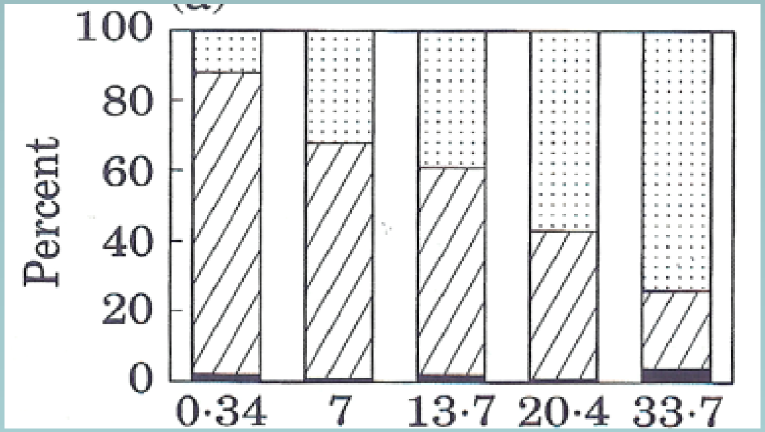
Fig. 4. Dissolved cadmium salinity distribution.

Dissolved Cd in San Francisco Bay (Yang & Sanudo-Wilhelmy, 1998)



Ready remobilisation of Cd

Adsorption highly reversible



Turner and Millward (1994)

$[b] > 1$

Pharmaceutical remobilisation through RF

Cytotoxic anticancer drugs

Hospital and municipal wastes

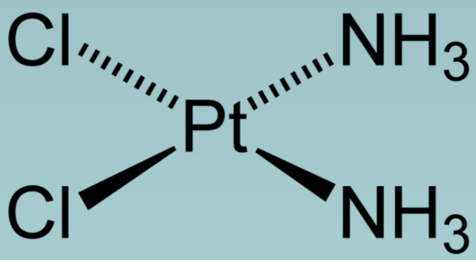
Non-selective:

“potentially all eukaryotic organisms are at risk”

(Johnson et al. 2008; J. Hydrology 348, 167)

Platinum-based anticancer drugs:

cisplatin, carboplatin, oxaliplatin

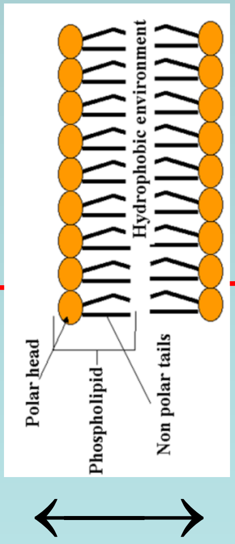


plasma

$[Cl^-]$ = 100 mM, or 3.7 g L^{-1}

$PtCl_2(NH_3)_2$

stable

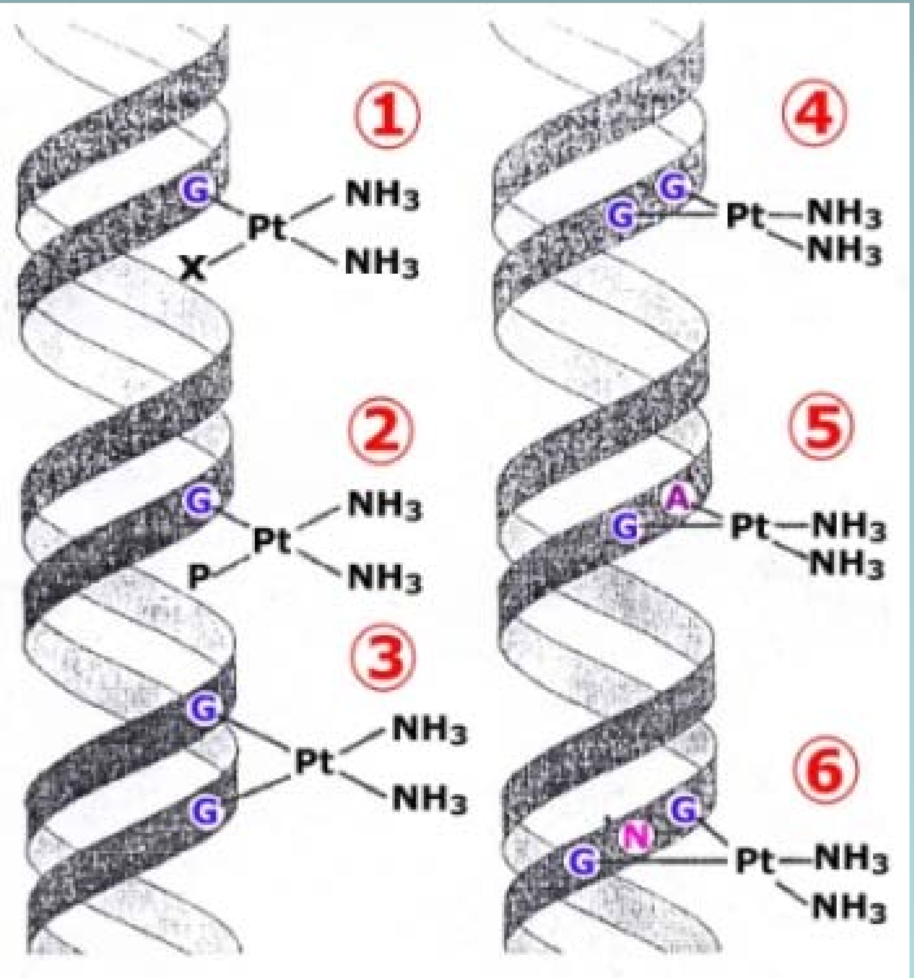


intracellular

$[Cl^-]$ = 4 mM, or 150 mg L^{-1}

$PtCl(OH_2)(NH_3)_2^+ + Cl^-$

reactive



①
G
Pt
NH3
NH3
X
②
G
Pt
NH3
NH3
P
③
G
G
Pt
NH3
NH3
④
G
G
Pt
NH3
NH3
⑤
A
G
Pt
NH3
NH3
⑥
G
N
G
Pt
NH3
NH3

(i) River flow (abrupt, continuous) RF

Increased sediment load/input

Increased energy – more local resuspension, export

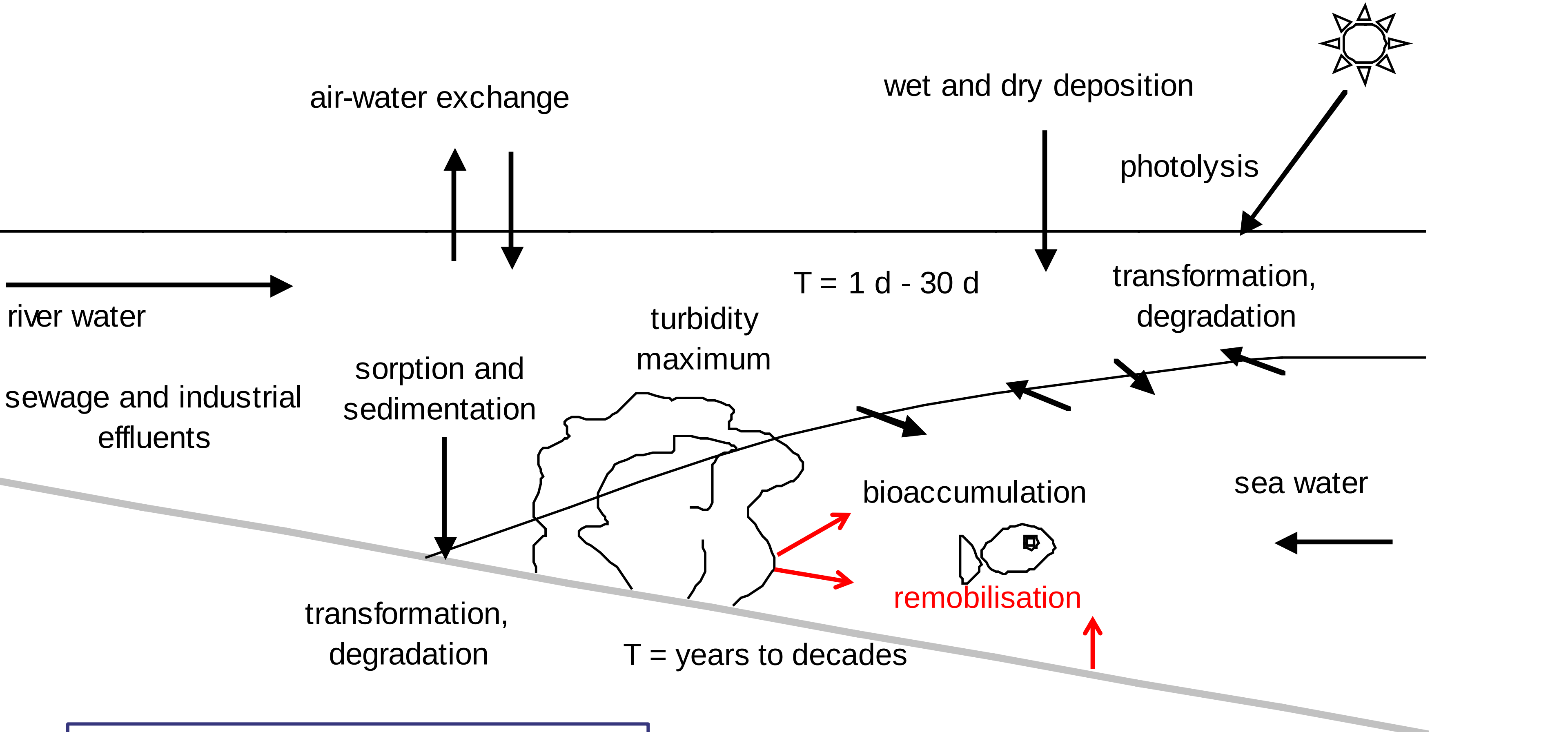
Seaward shift of turbidity maximum

Decrease in (water) residence time

Exposure to lower salinities

Behaviour of contaminants in an estuary

$PtCl(OH_2)(NH_3)_2^+ \longleftrightarrow PtCl_2(NH_3)_2$



(i) Estuarine hydrodynamics
(ii) Contaminant sources
(iii) Contaminant behaviour

Conclusions

Remobilisation dependent on:

- **Estuary and susceptibility (RF versus SLR)**
- **History of use and contamination**
- **Contaminant chemistry (K_D, redox, reversibility, kinetics)**

Conclusions

Additional considerations:

- **Change in reaction variables (temperature, pH, oxygen)**
- **Change in abundance and diversity of invertebrates (bio-mobilisation)**