UNIVERSITEIT GENT

BIOMATH
Department of Applied Mathematics, Biometrics and Process Control

OECD CRITERIA FOR READY BIODEGRADABILITY: ENVIRONMENTAL INTERPRETATION AND STUDY OF ALTERNATIVES

Project of the AISE/CESIO Monitoring and Model validation (M&MV) Task Force

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Outline

- Background
- Database compilation
- Statistical analysis
- Modelling + alternative proposal for 10DW
- Extrapolation to real environment (WWTP, river)
- Conclusions

Background

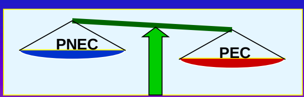
Environmental risk assessment

goal = **estimate** likelihood & extent of adverse **effects** in ecosystems due to exposure to **chemicals**

→ required by EU **chemical legislation**

steps:

– exposure: Predicted **E**nvironmental **C**oncentration **(PEC)**
– effects: Predicted **N**o **E**ffects **C**oncentration **(PNEC)**
– **risk quotient**:



Background (2)

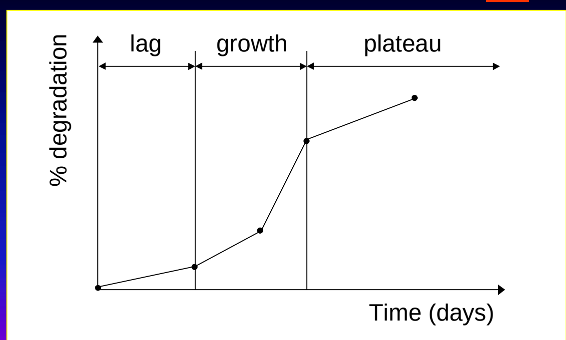
- Ready biodegradability = important feature!!
  – Exposure assessment (PEC), Technical Guidance Document (TGD)
  – Labeling of environmental danger
  – Definition = difficult
- Official OECD guidelines for ready biodegradability
  – “ready test” procedures (301A-F)
  – 10 day window criterion (10DW)

Background (3)

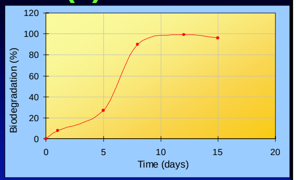
- Official OECD “ready test” procedures (301A-F)
  – Simple batch tests
  – Test setup
    - Inoculum; X< 30 mgSS/l
    - mineral medium
    - test substance; S=2-100 mg/l (depending on test method)
  – duration = 28 days
  – biodegradation characterised through measuring:
    – O_2-consumption (BOD/ThOD) 301C,D,F
    – CO_2-production (CO_2/ThCO_2) 301B
    – DOC-removal 301A,E
  – Typical biodegradation curves (lag, exponential growth, plateau)
  – Number of measurements: “at least 5” (tests with parallel bottles)

Background (4)

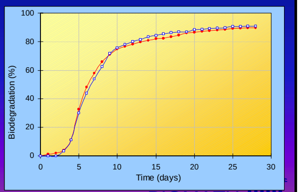
back



Background (5)



Parallel bottles (301A,B,D,E)



O_2-consumption test (301F)

Background (6)

- Comments regarding the test procedures
  - S/X is high compared to WWTP
  - Error introduction: interpolation, parallel bottles
  - Number of measurements = low
  - Repeatability/reliability = low

Background (7)

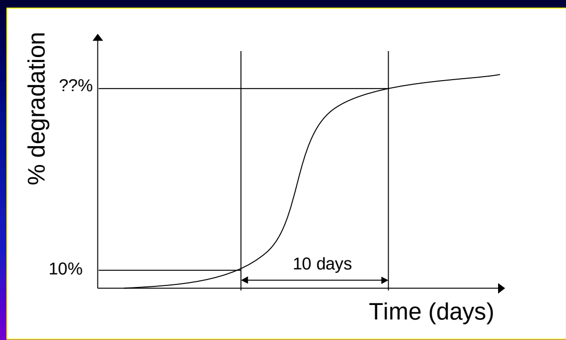
- Current legislation "10 day window approach"
  - lag-phase = when 10% degradation is reached
  - after 10 days → 60% mineralisation (O_2 , CO_2) / 70% removal (DOC) demo
- If not met, more testing required (more costs):
  - inherent biodegradability (more optimal biodegradation conditions)
  - simulation testing, CAS - 303A (closer to reality, "WWTP")
- Degradation rates k (h^{-1}) are assigned

Readily biodegradable	1
Readily biodegradable, failing 10DW	0.3
Inherently biodegradable	0.1
Not biodegradable	0

next

Background (8)

back



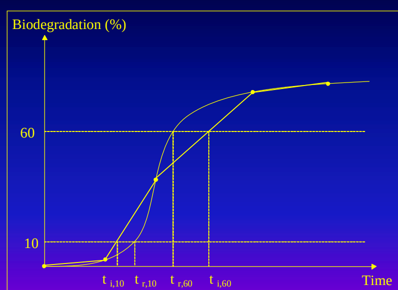
Background (9)

- Comments regarding the 10DW approach
  - Lag: 1st over 10% / linear interpolation / reality demo
  - Scientific background ?
  - Problematic substances
    - mixtures (e.g. surfactants) → biphasic degradation curves
    - 10DW not applicable
- Goal of project
  - Look for an alternative for the 10DW
  - Approach:
    - Data collection
    - Statistical analysis
    - Modelling
    - Extrapolation to real world

next

Lag-phase determination

back



Database compilation

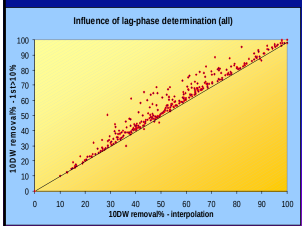
- collection of raw data (different chemicals) of:
  - ready biodegradability tests
  - CAS data
  - monitoring data (real life data from river and WWTP)
- Unique database containing raw data of over 800 chemicals

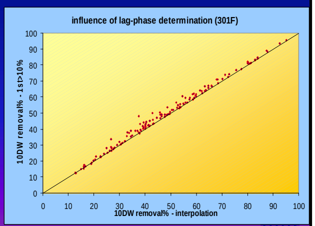
Statistics - Within Test (1)

- Mean degradation levels:
  - large standard deviations → scatter
  - 10DW mineralisation level = in critical zone (50-60%)
  - plateau is not reached after 10DW

Statistics - Within Test (2)

- Lag-phase determination
  - 1st > 10% higher mineralisation levels
  - interpolation = widely applied (too conservative bad reflection of reality)
  - Solution = increase measuring points (e.g. 301F)



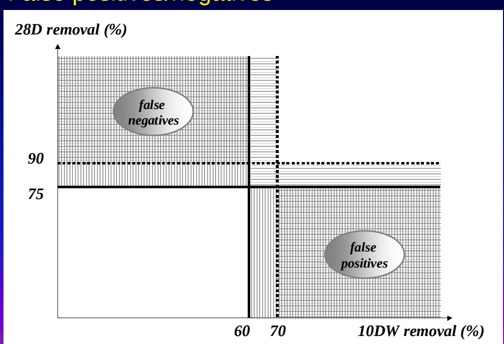


Statistics - Within Test (3)

- Correlation between 10DW-28d
  - Plateau not reached after 10DW !!!
  - Failing 10DW
    → 15.9% over 75% (O_2/CO_2, 28d)
    13.9% over 90% (DOC,28d)
  - Passing 10DW
    → 14.5% under 75% (O_2/CO_2, 28d)
    10.3% under 90% (DOC,28d)
  - 10DW-criterion = often (25-30%) erroneous decision

Statistics - Within Test (3)

- False positives/negatives



Modelling - Non-mechanistic (1)

- Models:
  - first order with lag

$$\begin{cases} t \leq lag \Rightarrow y = 0 \\ t > lag \Rightarrow y = A*(1-e^{-k_1*(t-lag)}) \end{cases}$$

  - Gompertz with lag $y = A * e^{-e^{-k_g (t-lag)}}$
  - Chapman $y = A*(1-e^{-k_c*t})^{-\frac{1}{n}}$

Modeling - Non-mechanistic (2)

- modelfits: good/bad

  bad fits ⟶ { model structure (biphasic) / practical identifiability (data quality)

  ⟶ Median used to characterize distribution of rate parameter (less sensitive for outliers)

- Model comparison
  - none of models superior based on statistical F-test
- For simplicity
  - first order model used to propose alternative

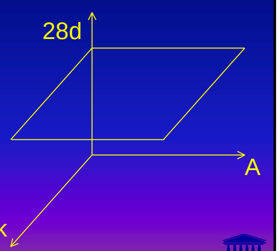
Modeling - Non-mechanistic (3)

- Alternative for 10DW
  - ***One parameter*** vs mineralisation levels (10DW/28d)
    - poor correlation caused by “outliers” (e.g. high k / low A)
    - correlation for parameter A much better than for parameter k

⟶ { A = good representation of ultimate mineralisation degree / A should be used in new alternative criterium

Modeling - Non-mechanistic (4)

- Alternative for 10DW
  - ***Combinations of parameters*** vs mineralisation levels (10DW/28d) creating 3D-plots
    - using:
      - A as X-value
      - k as Y-value
      - 10DW, 28d as Z-value



Modeling - Non-mechanistic (5)

- clear differentiation when using logarithmic scale for k

  ⟶ 3D-partitioning technique (see figure)

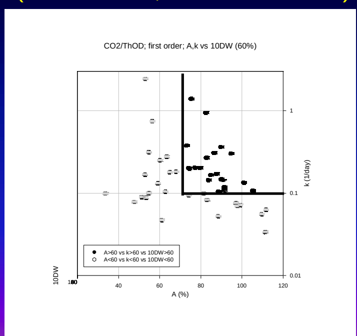
- Proposal (first order)

CO_2,O_2	
10DW > 60%	A > 70%, k < 0.1 d^{-1}
28d > 75%	A > 75%, k < 0.1 d^{-1}
DOC	
10DW > 70%	A > 60%, k < 0.2 d^{-1}
28d > 90%	A > 80%, k < 0.3 d^{-1}

next

Modeling - Non-mechanistic (6)

- Example (First order A, k vs. 10DW 60%)



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Modeling - Mechanistic (1)

- Models:
  - Single Monod
  - Double Monod
- General
  - Good fits for both models
  - choice between models ⟶ heuristically
  - Double Monod also fitted biphasic degradation curves
  - Mean μ_{max} for: { Single Monod is 0.12 d^{-1} / Double Monod is 1.2 d^{-1}

Modeling - Mechanistic (2)

- Model comparison
  - mechanistic vs. non-mechanistic
    - mechanistic → better fitting performance (lower SSE)
    - no superior model due to low number of measurements
- Correlation between kinetics and mineralisation
  - lack of suitable data (301F)

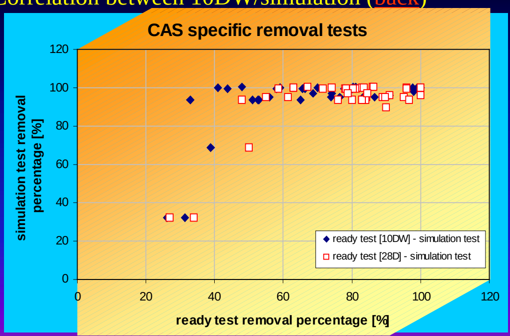
Extrapolation – Simulation (CAS)

- Poor correlation between 10DW/simulation (CAS) (fig)
  - passing 10DW → high removal
  - failing 10DW → not always low removal
  - more data needed
- Poor correlation between kinetics/simulation data from CAS-test (***one parameter***)
- Correlation between kinetics/simulation data from CAS-test (***two parameters - 3D partitioning***) (fig)

→ partitioning is not clear

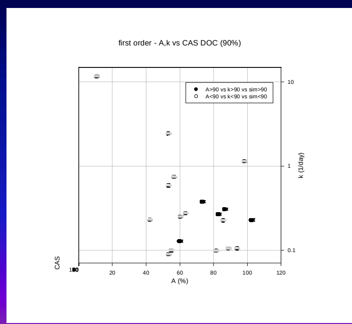
Extrapolation - Simulation

- Correlation between 10DW/simulation (back)



Extrapolation - Simulation

- Correlation between kinetics/simulation data from CAS-test (***two parameters - 3D-partitioning***)



Conclusions (1)

- Statistics
  - 10DW
    - not realistic - not reliable (wrong decisions in 25-30% of the cases)
    - certainly not applicable for mixtures
    - more measuring points (301F) required

Conclusions (2)

- Modelling
  - No superior model - first order used for simplicity
  - bad correlation using only one parameter
  - new criterion proposed using 2 parameters - 3D partitioning technique
  - more measuring points (301F) required

Conclusions (3)

- Extrapolation
  - 10DW not representative for real environment
  - Correlation with combined parameter criterion not as good
  - more data needed to give more power to conclusions

Final Conclusion

- Legislation has no real scientific backbone
- Test methods
  - are not representative for reality
  - Not always reliable
- High discrepancy between use of modelling in:

Wastewater Treatment Engineering ↔ Risk Assessment and Regulation

- Modelling knowledge should be used in regulation !!