# Safe Application of Nanoremediation

Andy Gillett, Judith Nathanail & Paul Nathanail, LQM

**NanoRem Final Conference**

**Nanoremediation for Soil and Groundwater Clean-up - Possibilities and Future Trends**

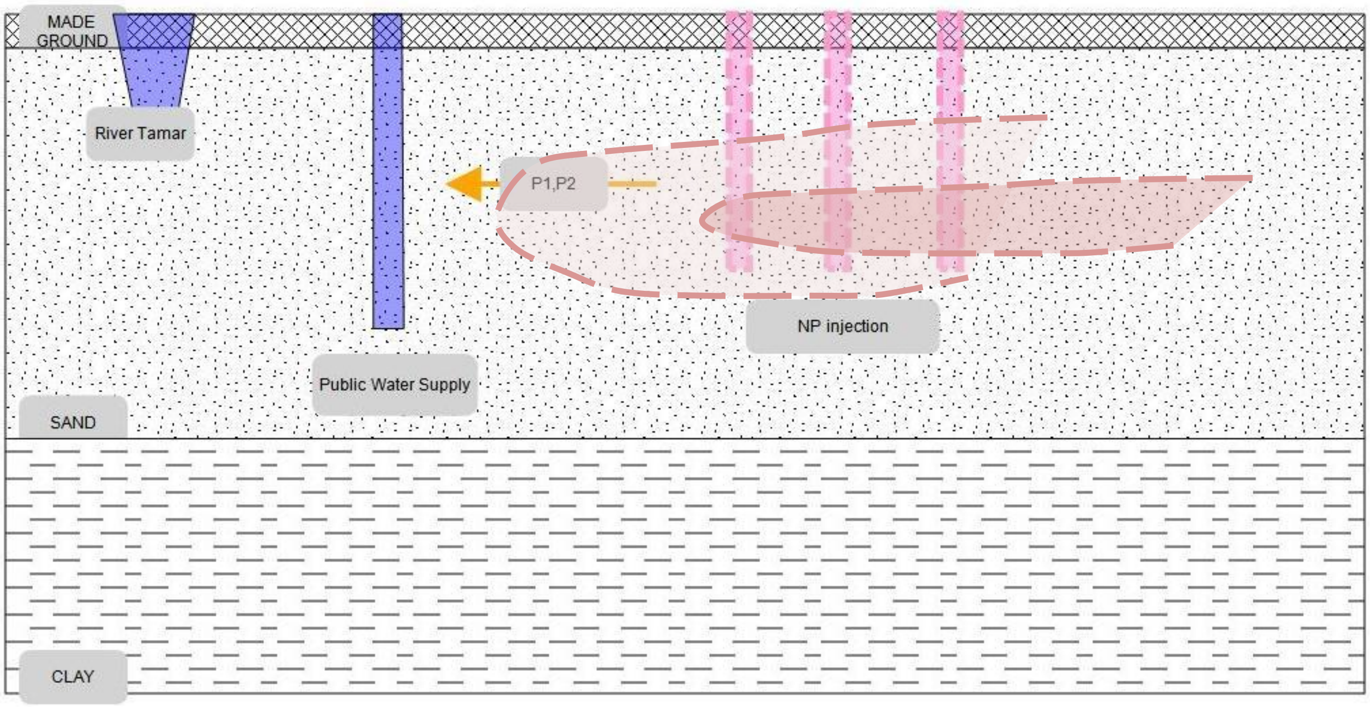
DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V.

Frankfurt am Main, 21st November 2016

# Structure

- **Nano**Technology for contaminated land **Rem**ediation
- Risk assessment
- Conceptual site models
- Toxicity
- Fate
- Transport
- Risk Screening Model
- Possibilities & Future Trends

# **Nano**Technology for contaminated land **Rem**ediation



# The stars of the show

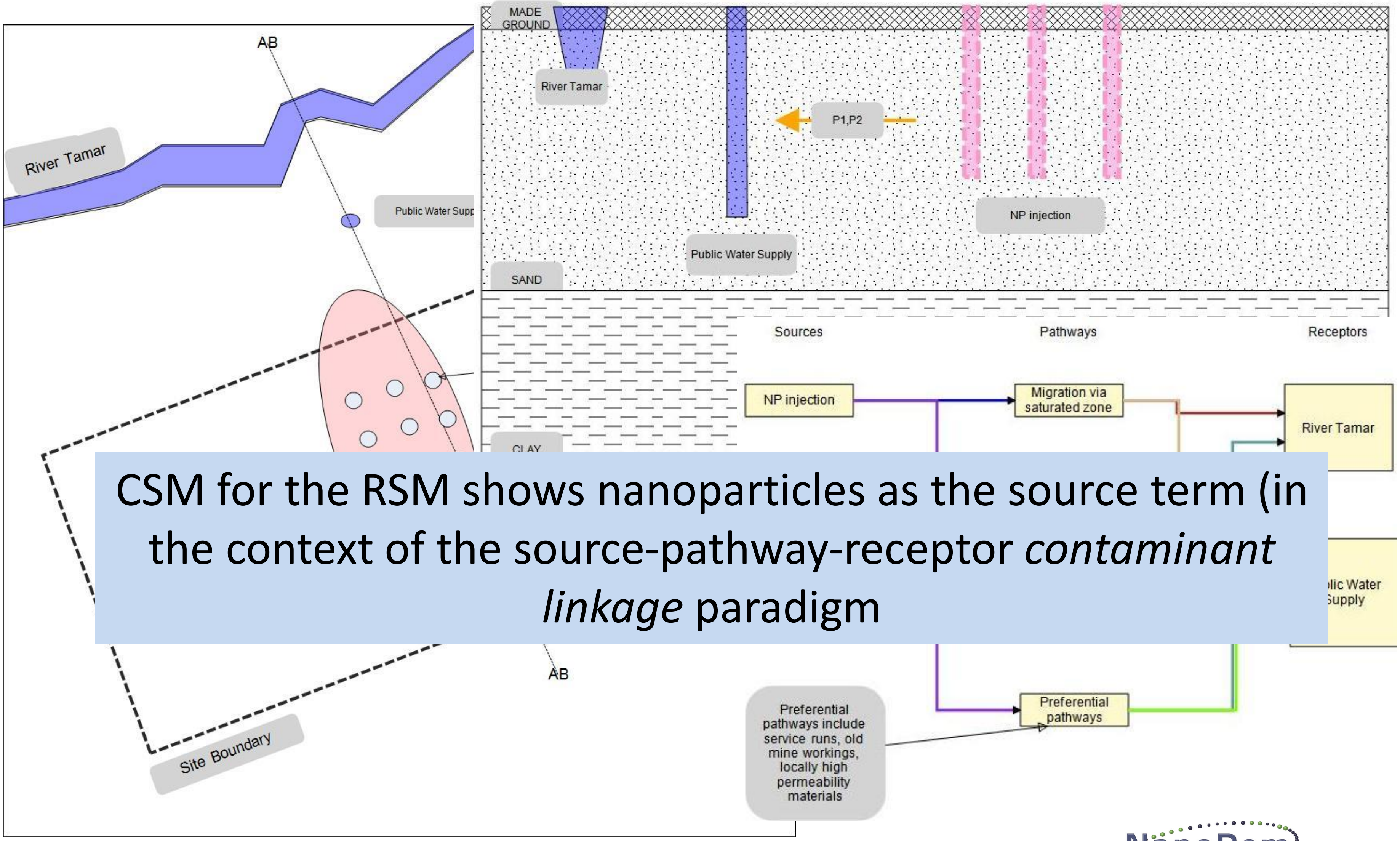
| Nanoparticles | Deployed at: Pilot Site / LSF /LSC |
|---|---|
| nZVI (Nanofer25S) | Spolchemie I, Czech Republic |
| Milled iron nanoparticles | Zurzach, Switzerland |
| Nano Goethite | Spolchemie II, Czech Republic |
| Carbo-Iron | Balassagyarmat, Hungary<br>Neot Hovav, Israel |
| | Nitrastur, Spain |
| Colloidal Fe-zeolites – | Not deployed |
| Fe (VI) salts (ferrates) | Not deployed |
| Non-Fe metals & alloys (Al & Mg) | Not deployed |

# Risk assessment

- used where outcome of an activity is uncertain.
- estimate the level and then evaluate significance of the risk posed by given activity
- includes consideration of exposure (based on fate and transport) and the toxicity of the substance.
- establish the legal context
  - define standard to achieve (Target Concentration)
  - location standard must be achieved (Compliance Point)

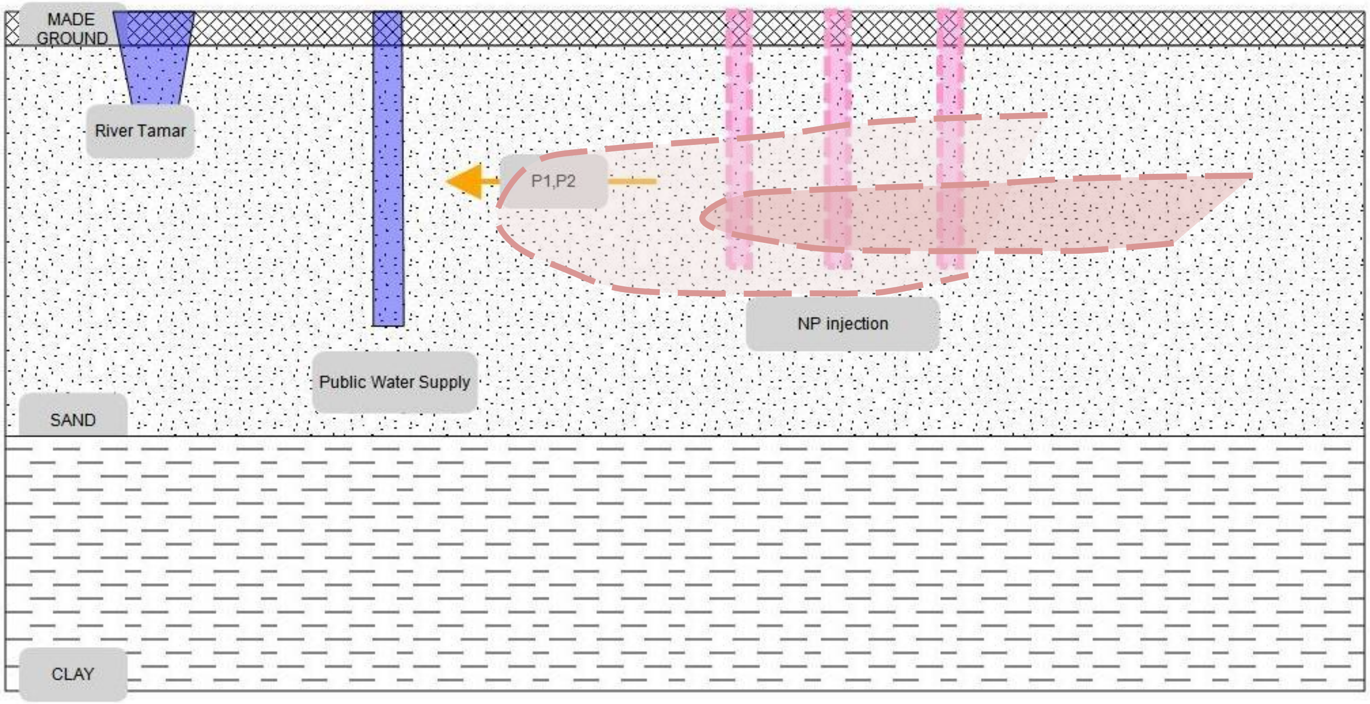
# Visualisation of CSM






CSM for the RSM shows nanoparticles as the source term (in the context of the source-pathway-receptor *contaminant linkage* paradigm

# CSM – Cross Section



# Toxicity

$EC_{50}$ >100 mg/L | $EC_{50}$ <100 mg/L | ND: not determined

| | *P.subcapitata* | *Chlamydomonas sp.* | *D. magna* | *L. variegatus* | *V. fischeri* | *E. coli* | *E. fetida* | *L.multiflorum* | *R. sativus* |
|---|---|---|---|---|---|---|---|---|---|
| | 48 h growth OECD 201 | 48 h photo-synthesis efficiency | 48 h immo-bilization OECD 202 | 96 h mortality | 15 min lumi-nescence ISO 11348-3 | 6 h growth 24 h viability | 48 h mortality OECD 207 | 6 day root elongation OECD 208 | 6 day root elongation OECD 208 |
| NanoFer STAR (NanoIron) | | | | | | | | | |
| Nano-magnetite (UPOL) | | | | | | | | | |
| Milled Fe particles (UVR-FIA) | ND | ND | ND | | | | ND | | |
| Nano-goethite (HMGU) | | | | | | | | | |
| Fe Zeolite (UFZ) | | | | | | | | | |
| Carbo-Iron (UFZ) | | | | | | | | | |
| Bio-nanomagnetite (UMAN) | ND | ND | ND | ND | ND | ND | | ND | ND |

$EC_{50}$ is defined as an effect concentration at which an effect of 50% is observed

# Fate

| Nanoparticle | Aspects of fate relevant to risk assessment studied | Findings |
|---|---|---|
| Nanofer 25S | Particle oxidation and Fe speciation in groundwater from Spolchemie I, | Fast degradation in presence of oxygen, likely to react with electron acceptors other than contaminant. |
| Nanofer STAR (activated) | Long term anaerobic corrosion and Fe speciation (Spolchemie I, contaminated with chlorinated hydro-carbons) | Transformation products are iron minerals commonly found in sediment and soils i.e. Fe oxides, Fe hydroxides and Fe carbonates. |
| Milled ZVI | None (fate experiments addressed: Reactivity) | N/A |
| Carbo Iron (field relevant conditions) | Contaminant sorption after long term aging | Sorption ability not expected to be significantly reduced. |
| Fe zeolites (field relevant conditions) | Alteration of elemental composition, BET specific surface area, catalytic activity and MTBE adsorption after long-term aging in presence of NOM | Changes in zeolite composition are mainly due to uptake of divalent cations from the hard water. |

# Fate

| Nanoparticle | Aspects of fate relevant to risk assessment studied | Findings |
|---|---|---|
| **BNM/ Pd-BNM** | None (fate experiments addressed: Removal of Cr (VI) and Reactivity) | N/A |
| **Nano Goethite** | Changes in Fe content & speciation of particles exposed for 1 year to BTEX (Spolchemie II)<br>NB Mobility unlikely, since Nano-Goethite loses its stabilizing humic acid coating during transport. | $Fe_{tot}$ content decreased; Mostly Fe(III) measured<br>Fe-speciation showed nG resistant to chemical changes after 1 year.<br>Mineral composition constant, but size & crystallinity of nano-needle increased. |
| **Mg/Al particles** | None (poor long term reactivity, no further fate experiments reported. | N/A |

# Fate

- In general, NPs increase in size, decrease in reactivity and undergo chemical transformations to minerals common in the subsurface
- Mobility enhancing coatings may be lost
- However, there is insufficient detail to formally include changes in the nature of the particles as part of a risk model.
- The model therefore (conservatively) assumes that particles maintain their reactivity/toxicity.

# **Table 3:** Nanoparticle Transport Distances Recorded from Large Containers and Flume

| Container | Particle | Maximum distance (m) | Notes |
|---|---|---|---|
| LSF | ZVI - NANOFER STAR | 1.5 | Most particles were transported more than 0.3m; a small amount reached 1.44m |
| LSC | Iron-oxides Goethite | 2.5 | 1.7 m Transport during injection; no further transport detected after injection at higher levels; however maximum 2.6m further transport was observed after injection at base level |
| LSF | Carbo Iron | 0.8 | Particle distribution was not uniform<br>Solid particles came out of the outlets, 3.5m from injection point but analysis shows Fe(0) content greatly diminished |

# Transport

- The issue is not too much transport but too little
- Efforts focus on increasing transport not controlling it
- NB Dissolved phase plumes:
  - Hydrocarbons ca 100 - 400m
  - Chlorinated solvents ca 1-2km
  - Anions ca 20km?

# Qualitative Pre Deployment Risk Assessment Protocol

## (Nathanail et al 2016)

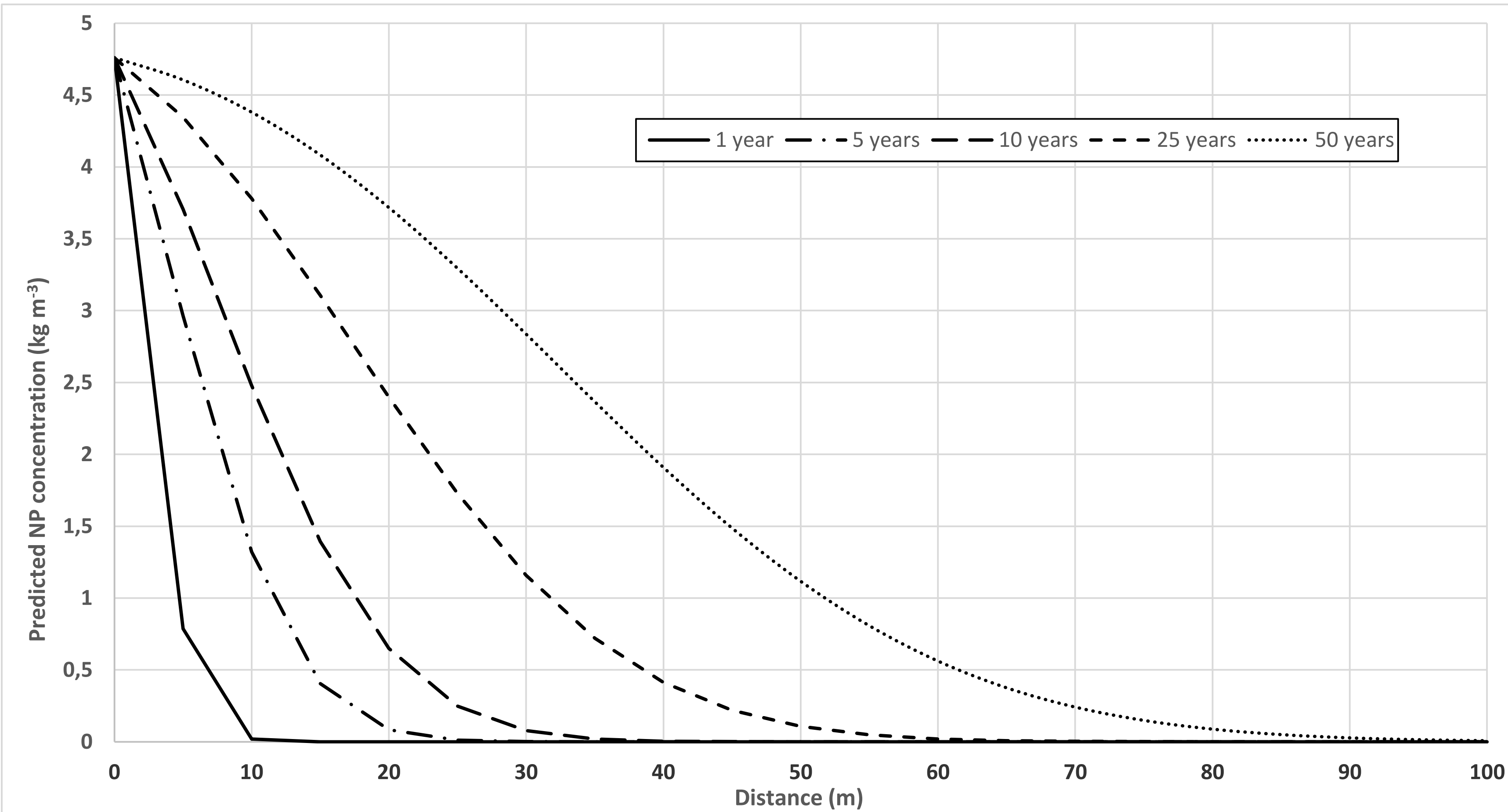
- Its probably not a risk if:
  - There are no receptors of concern (so why remediate?)
  - Hydraulic containment is already in place.
  - There is already a down gradient PRB or other attenuation/mitigation mechanism in place.
  - Chemicals injected for competitor technologies (ISCO/ISCR )would travel further.
  - Injection point >100m from receptor & no karstic flow.
  - contaminant plume extends down gradient >100m.
  - Injection pressure is less than fracking pressure.
  - Tracer tests show surface water unreached/ no daylighting
  - Facilitated transport, inc. colloid transport, insignificant (low TDS).

# Risk Screening Model (RSM)

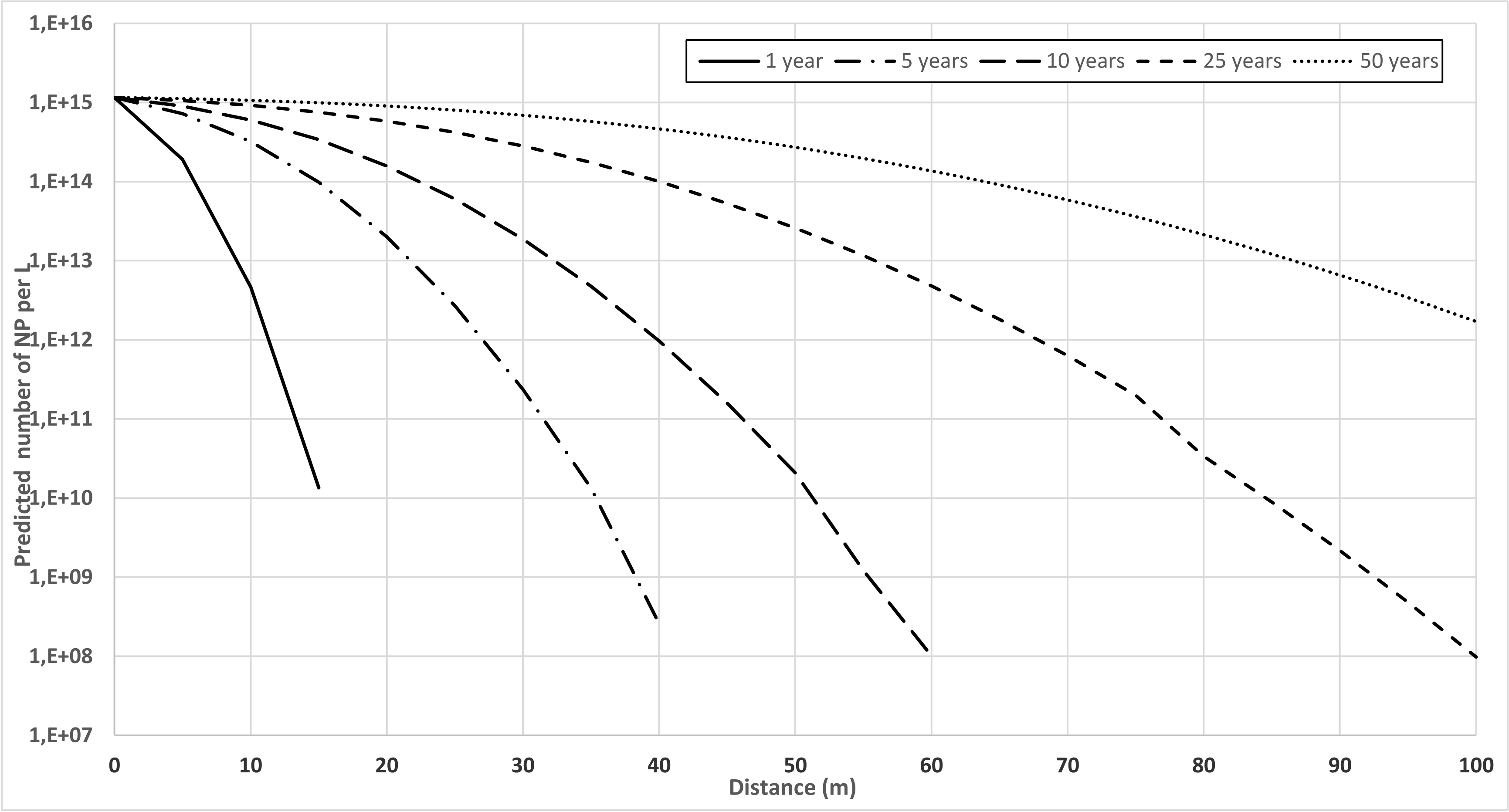
- The aim of the RSM is to evaluate the risks to identified receptors from renegade *NanoRem nanoparticles* applied to a site for groundwater remediation.
- Based on Environment Agency Remedial Targets Methodology MS Excel™ spreadsheets
- Key input is $k_{att}$ & $k_{det}$ coefficients

# Risk Screening Model (RSM) for applying the NanoRem nanoparticles to groundwater remediation

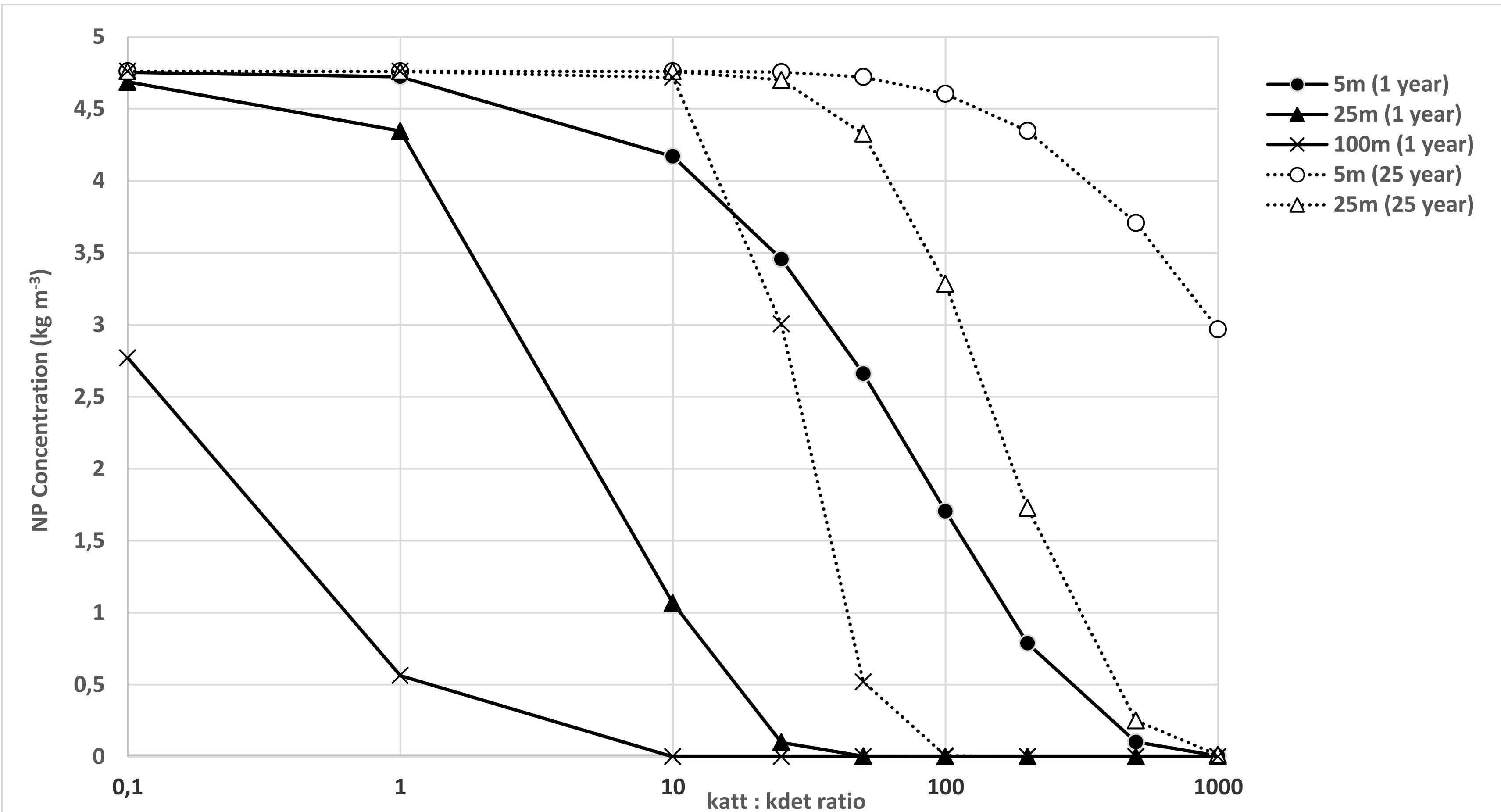
# Travel distances over time



# NP Attenuation over time



# $K_{att}/k_{det}$


5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
NP Concentration (kg m-3)
0,1
1
10
100
1000
katt : kdet ratio
5m (1 year)
25m (1 year)
100m (1 year)
5m (25 year)
25m (25 year)

# Possibilities & Future Trends

- The RSM will help practitioners provide to regulators site specific evidence of the (extremely low) risks of deploying NPs for groundwater remediation
- The RSM and the earlier qualitiative protocol demonstrate that in a wide range of conditions NanoRem particles are extremely unlikely to escape polluted groundwater
- The UK government requested moratorium on deploying NPs for environmental remediation looks increasingly ripe for lifting

# Thank you for your attention

This project received funding from the European Union Seventh Framework Programme (FP7 / 2007-2013) under Grant Agreement No. 309517.



Paul Nathanail
Land Quality Management Ltd, University of Nottingham Innovation Park
Triumph Road, Nottingham NG7 2TU. UK

paul@lqm.co.uk

website: www.lqm.co.uk