Generalized Guideline for Nanoremediation Application

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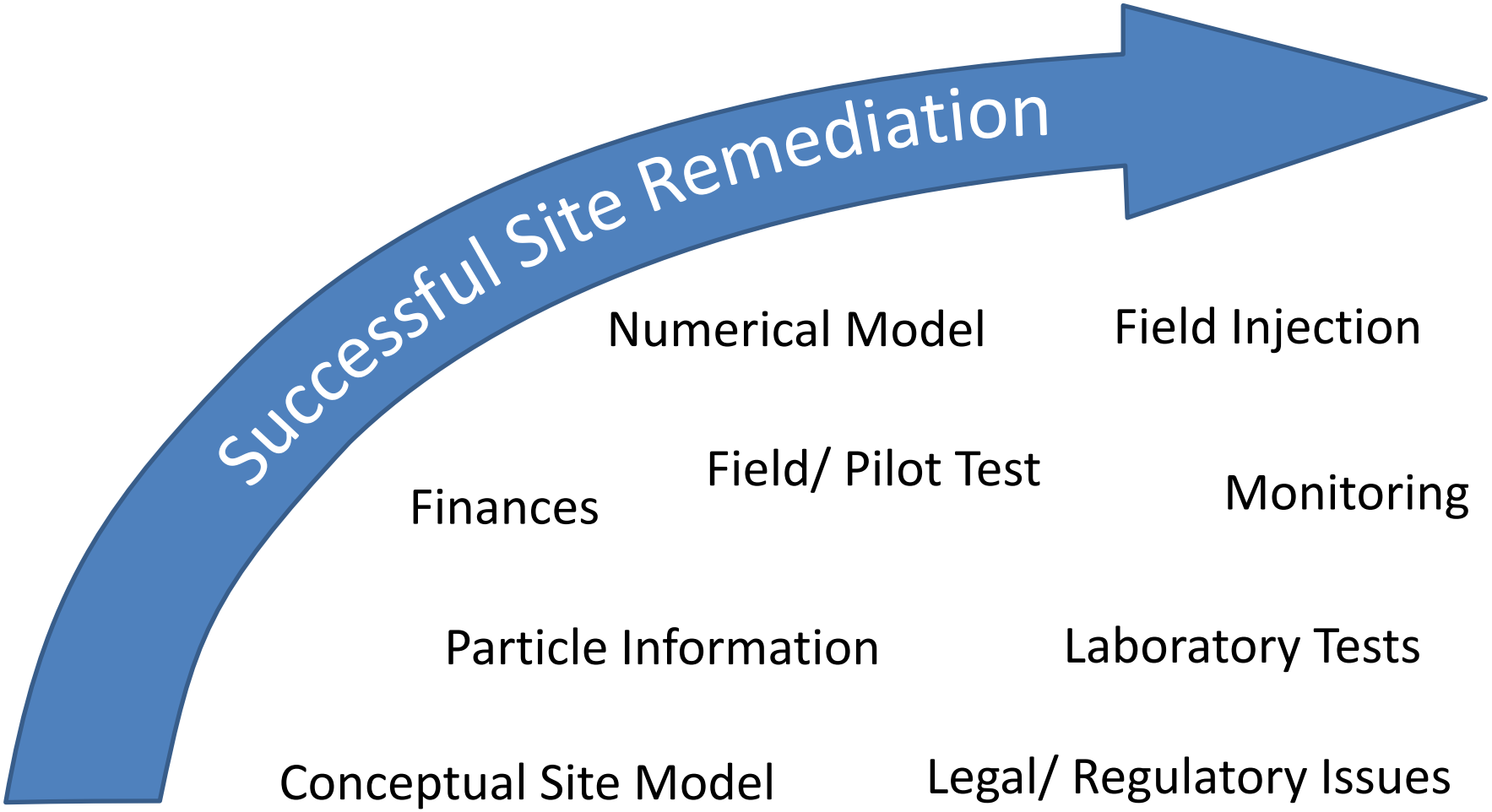
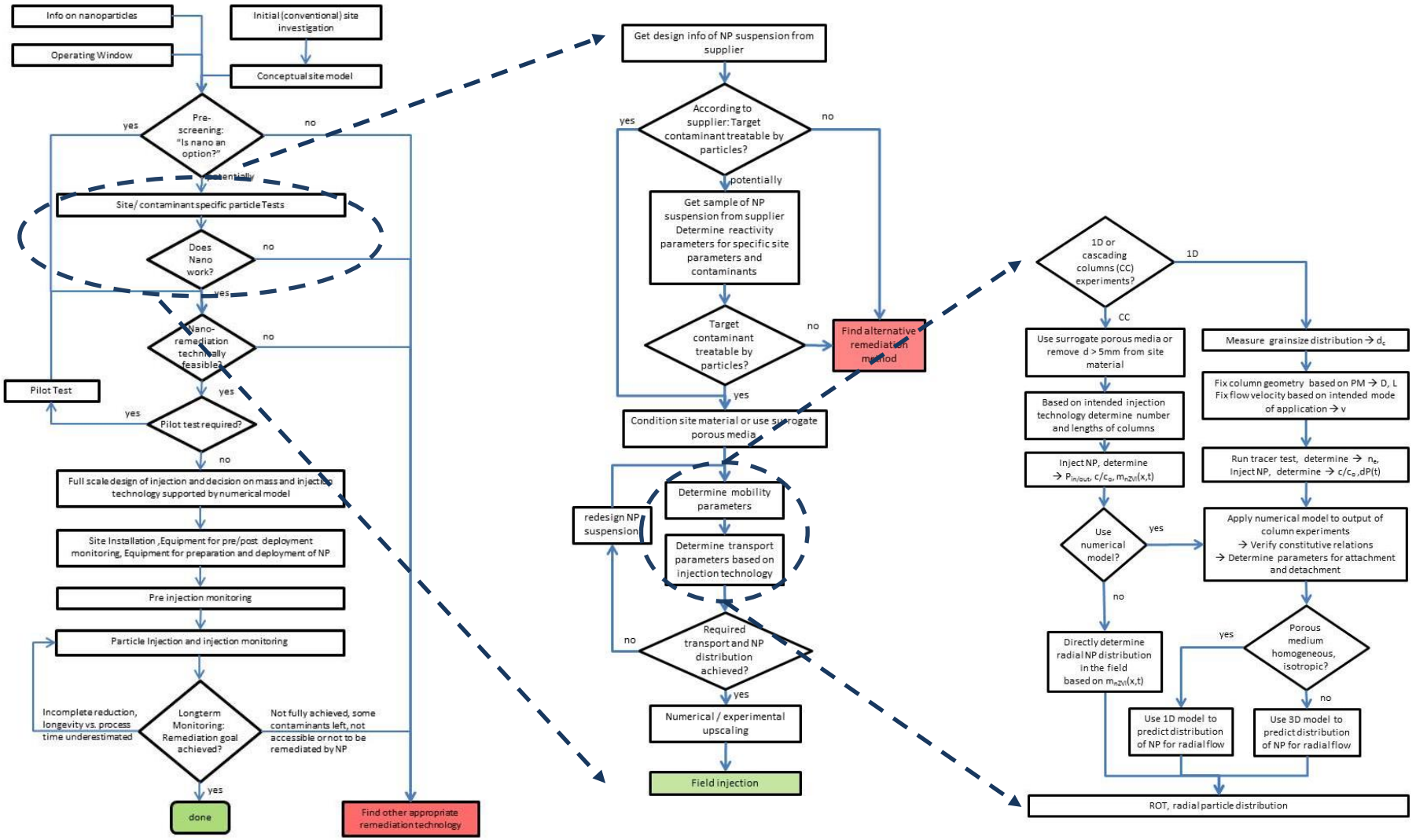
NanoRem Final Conference

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

How to nano?

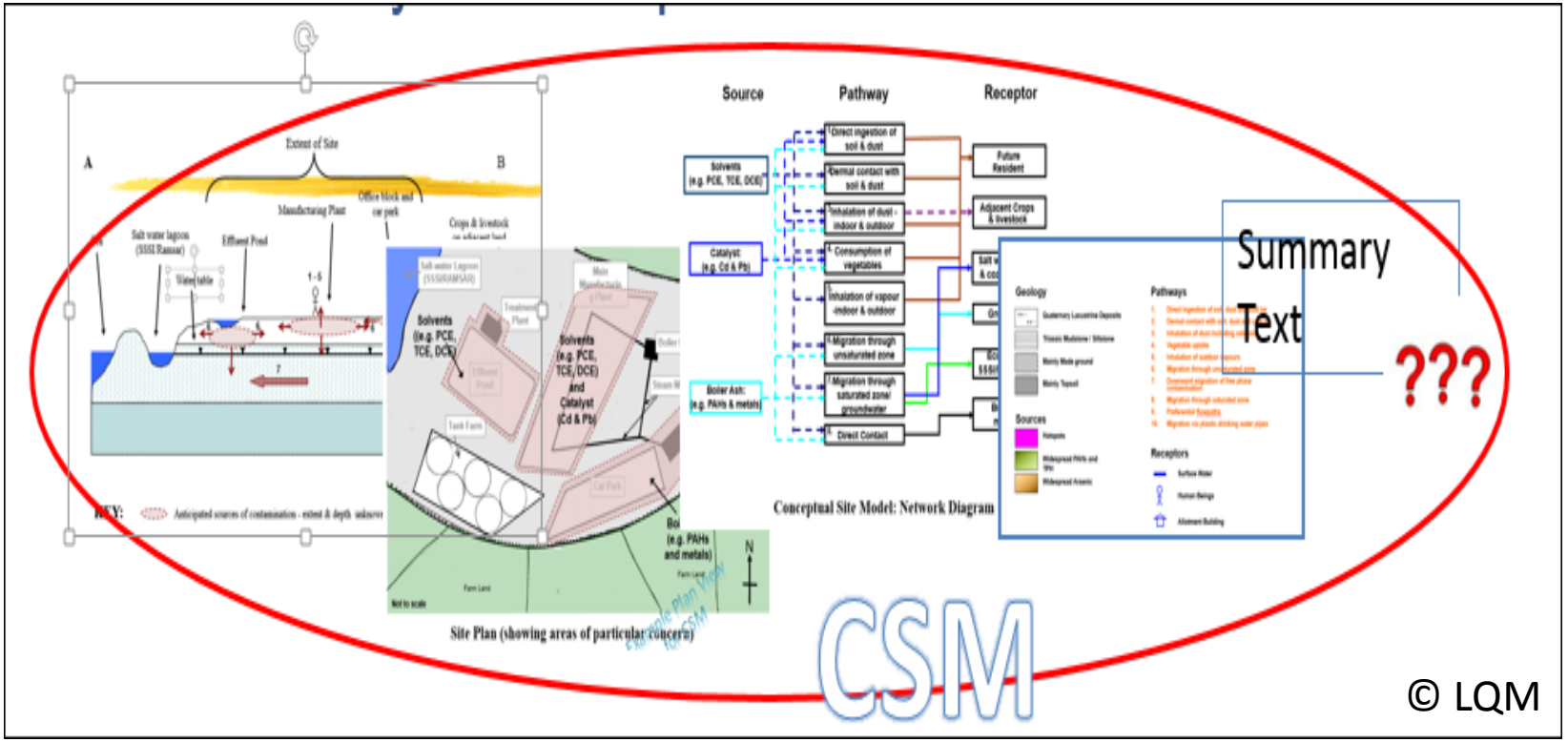

Successful Site Remediation
Numerical Model
Field Injection
Field/ Pilot Test
Finances
Monitoring
Particle Information
Laboratory Tests
Conceptual Site Model
Legal/ Regulatory Issues

Flowchart of Guideline



Prerequisites

- Detailed Site Investigation
- Conceptual Site Model (what we know + what we don't know)



Prerequisites

- Particle List
  - Reaction type
  - Reaction mode
  - Recommended site conditions
  - Stabilizer
  - Application rules
  - Reactivity data for typical target contaminants
  - …

	Reaction types supported by the particles							Reaction mode				Recommendation for site conditions					Stabilizer needed		General rules for use				Possible spin-off applications			Development status		
Particle Type	Oxidation	Reduction	Hydrophobic sorption	Sorption of metals/metalloids	Support of biology treatment	Hydrolysis		Reactive component consumed	Additional reagents needed	Gaseous products formed		Anaerobic	Aerobic	pH << 7	pH ≈ 7	pH > 7	yes	no	Inertization of suspension needed	Dispenser needed			wastewater			Tested at field scale	Ready for up-scaled testing	Research at laboratory scale
Nano iron oxide	X			X	X												X											
Carbo-Iron	(X)	X	X	X	X	(X)		X		X		X			X	X	X		X	X			X			X		
Fe-zeolite BEA 35	X		X						X	X							X											
Fe-zeolite MFI 120	X		X						X	X							X											
Biomagnetite		X		X								X			X			X					X					X
Pd/Biomagnetite		X		X						X		X			X	X		X					X					X
Al, Mg		X						X	(X)	X		X			X	X												X
$BaFeO_4$	X							X		X		X	X	X	X								X					X

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Prerequisites

- Operating Window
  - Requirements/ limitations
  - Process/ Synergies
  - Deployment
  - Operational boundaries
  - Treatable contaminants
  - Hydrogeology
  - Hydrochemistry
  - Additional info

Process Acronym		ReduNP	OxiNP	OxiNP	ReduNP	OxiNP
				Nanogoethite		
		Petr	Petr	UDE, Beate	Carbo-Iron, Katrin/Anett	Trap-Ox Fe-zeolites, Anett
Requirements / Limitations	saturated zone					
	unsaturated zone					
	plume					
	residual					
	pool					
	sorbed					
Process	Main Process	Primarily Reduction Based	Primarily Oxidation Based	Primarily Oxidation Based, anaerobic biodegradation enhanced by ferric oxide nanoparticles.	Primarily reduction based (by Fe(0) component) in combination with adsorption by activated carbon	Primarily adsorption + catalytic oxidation (in combination with hydrogen peroxide)
	Description	enhanced NZVI reduction based process with the use of small size and migrating particles.	anaerobic biodegradation enhanced by oxidic nanoparticles.	Nanogoethite serves as terminal electron aceptor during the degradation of organic contaminants through bacterial oxidation	Composite of Fe(0) and microscale activated carbon (Fe/AC) applied in aqueous suspensions with stabilizers (CMC, humic acid)	Microporous alumosilicate particles loaded with Fe(III) which act as adsorbent and oxidation catalyst
	Tiered approach (nanoremediationas part of a treatment train) recommended?	According to site conditions is recommended nanoremediation as part of treatment train. Generaly the technology is convenient after free phase removal or / and to intermediate area between source and plume.	According to site conditions is recommended nanoremediation as part of treatment train. Generaly the technology is convenient for polishing after source, and high contaminant concentrations removal.	polishing after source removal	> Source zones: contaminant phase or saturated soil should be removed previously by alternative methods (excavation, phase separation...), > Carbo-Iron application is usually followed by subsequent (enhanced) natural attenuation processes after reactive period	Mainly used for formation of a barrier against spreading of plumes which can be regenerated by injection of hydrogen peroxide, can be used as polishing after source removal
	Synergies	Reductive bioremediation	Bioremediation	Bioremediation	> Contaminant retardation in reactive zone due to sorption by AC-component > Bioremediation	sorption by zeolite leads to retardation + collects contaminants which are slowly released from sorbed/trapped state
	risk management	source control/Plume management	plume management	plume management	source control/Plume management	plume management
	Contaminant outcome	Destruction of organic compounds, imobilisation or stabilisation of metals	Destruction	Destruction of organic compounds, imobilisation or stabilisation of metals	Destruction	Destruction

Pre-Screening Tool

- "Simple" Excel based tool
- Combines NP-information, CSM, OW, site specific contaminants, hydro-geo-chemical conditions, injection technology etc. to give

→ Indication on potential of nanoremediation

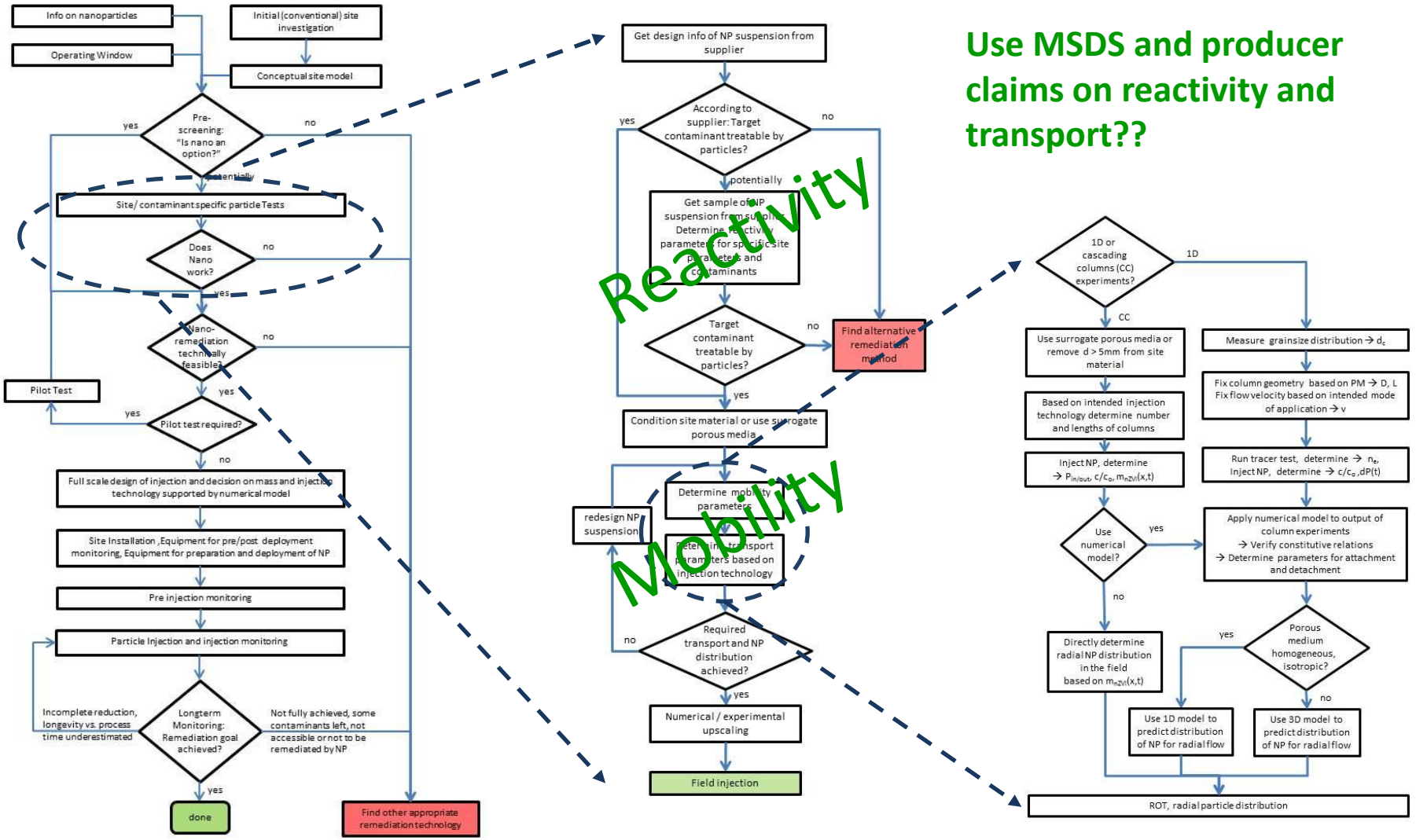
→ List of critical parameters

Prescreening tool

planning tool for applicability of nano-particles at specific sites

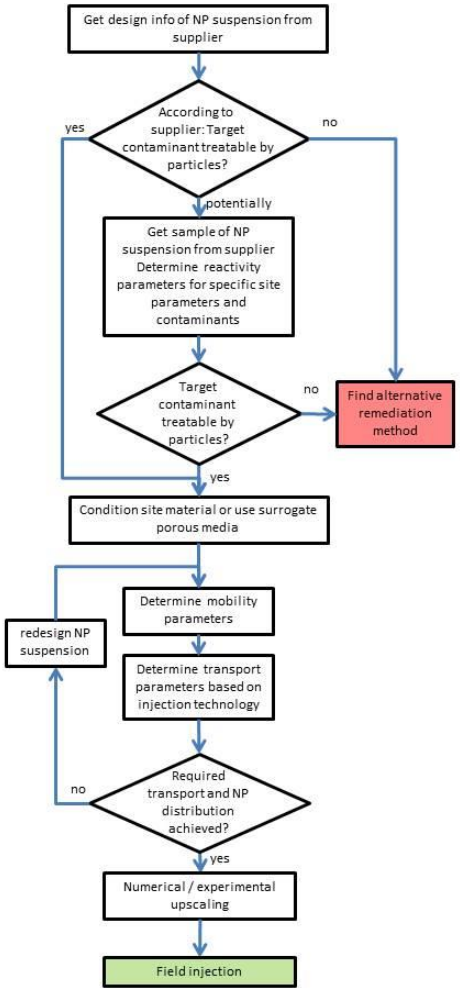
Particle type		Input (drop down or value)	Effect of Condition	
oxidative	reductive		favorable	unfavorable
Condition				
general conditions				
access to site (select)		limited restrictions		
spatial extent of contamination (give m³)		1000		
area affected (give m²)		100		
legal boundary conditions (select)		injection possible		
pilot application possible (select)		Yes		
location of ground water table (m bgl)				
Hydraulic conductivity (kf)		1,0E-05		
expected contaminant mass (kg)		3000		
hydrochemical conditions				
ground water velocity (m/d)		0,1		
	redox potential (mV)	100		
stoichiometry (ration ox/cont)		1		
Background consumption (NOM, factor to stoichiometry)		1		
	m-value mMol/L	10		
	p-value mMol/L	0,1		
	nitrate content in ground water (mg/L)	100		
	sulfate content in ground water (mg/L)	100		
longevity of the particles to be expected (months)		5		
	enhancement of NA (sel.)	Yes		
efficiency of particles (%)		20		
hydrogeolocical conditions				
type particle injection (select)		direct push		
depth of contamination (overburden/pressure needed)		1		
contaminant distribution (select)		blobs		
expected gas production (select)		moderate		
	Sum		17	3
	Result	Looks good, but check yellow parameters		

Site Specific Particle Tests

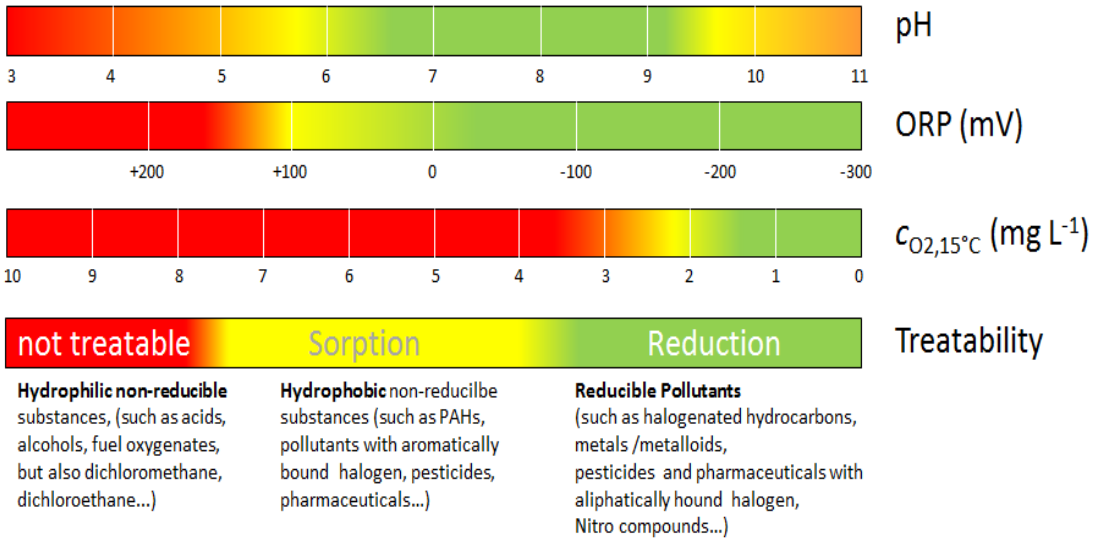


Use MSDS and producer claims on reactivity and transport??

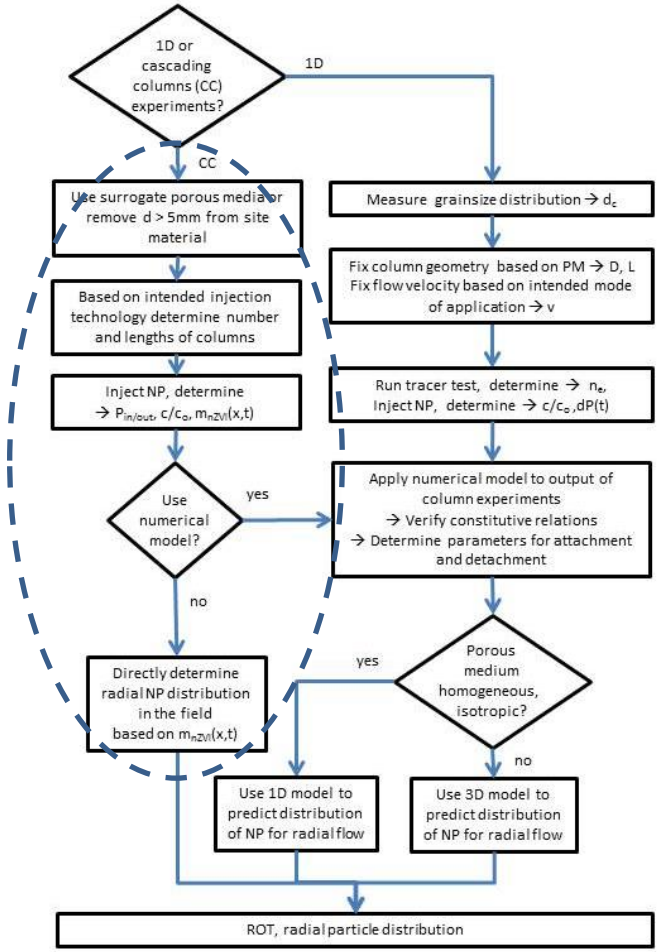
Site Specific Reactivity Tests



- For specific site conditions and/or specific contaminants
  - Batch tests for yes/no decisions
  - Column tests for mass balance and longevity



Site Specific Mobility Tests

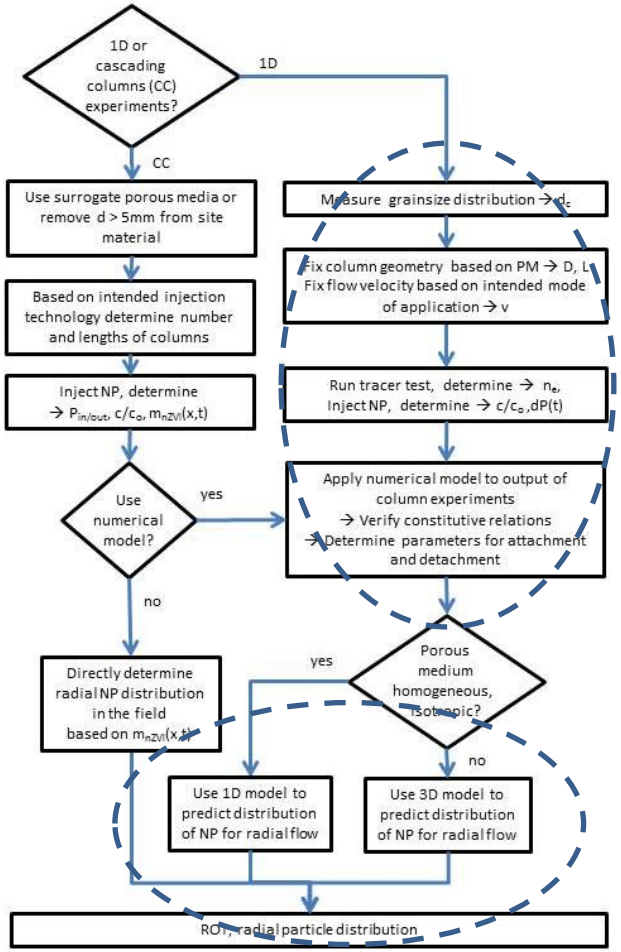


Goal:

- homogeneous particle distribution in reactive zone
- Safe NP deposit → Renegades?

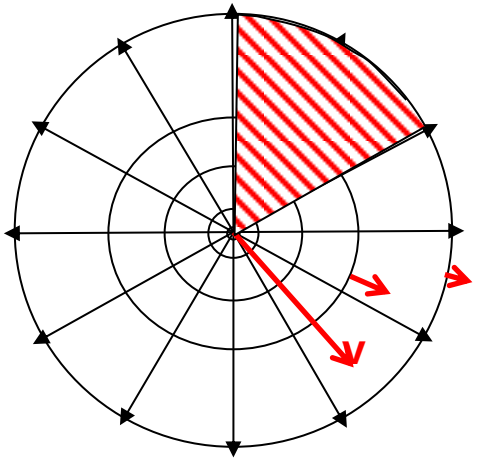
- Cascading column experiments
  - Experimental reproduction of radial flow field (hyperbolically decreasing v)
  - High resolution in time and space
    - Direct indication of **travel distance and of homogeneity of NP distribution**
    - Input for numerical model to predict **particle placement in radial flow field**

Site Specific Mobility Tests



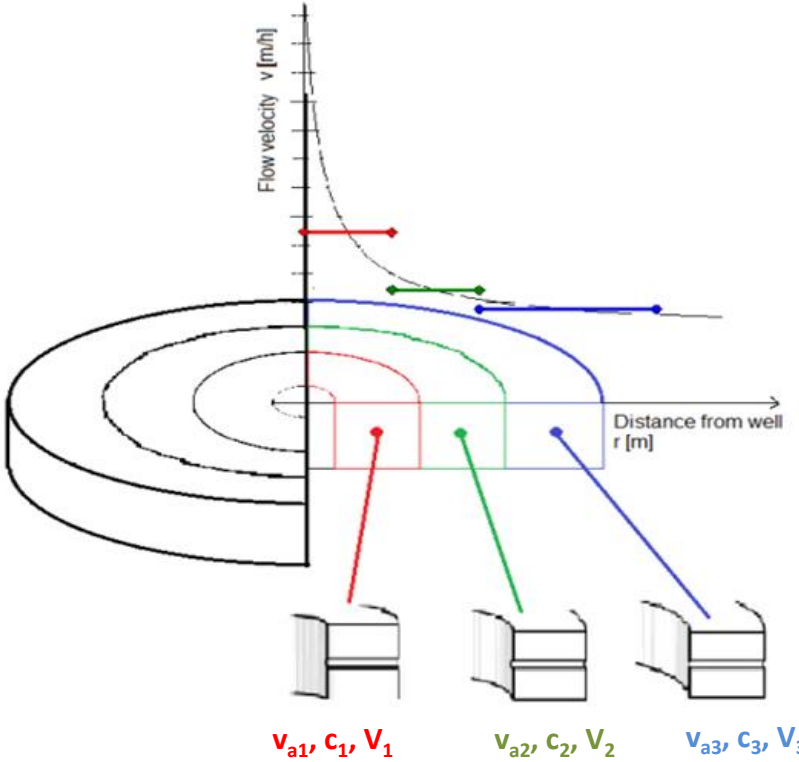
- Small column experiments based on filtration theory
  - Particle breakthrough and particle deposition
    - calculate attachment efficiency, particle deposition rate coefficient → Prediction of travel distance for **base flow → Renegades**
    - Input for numerical model → use MNMs or MNM3D to predict **particle placement in radial flow field**

Experimental Upscaling

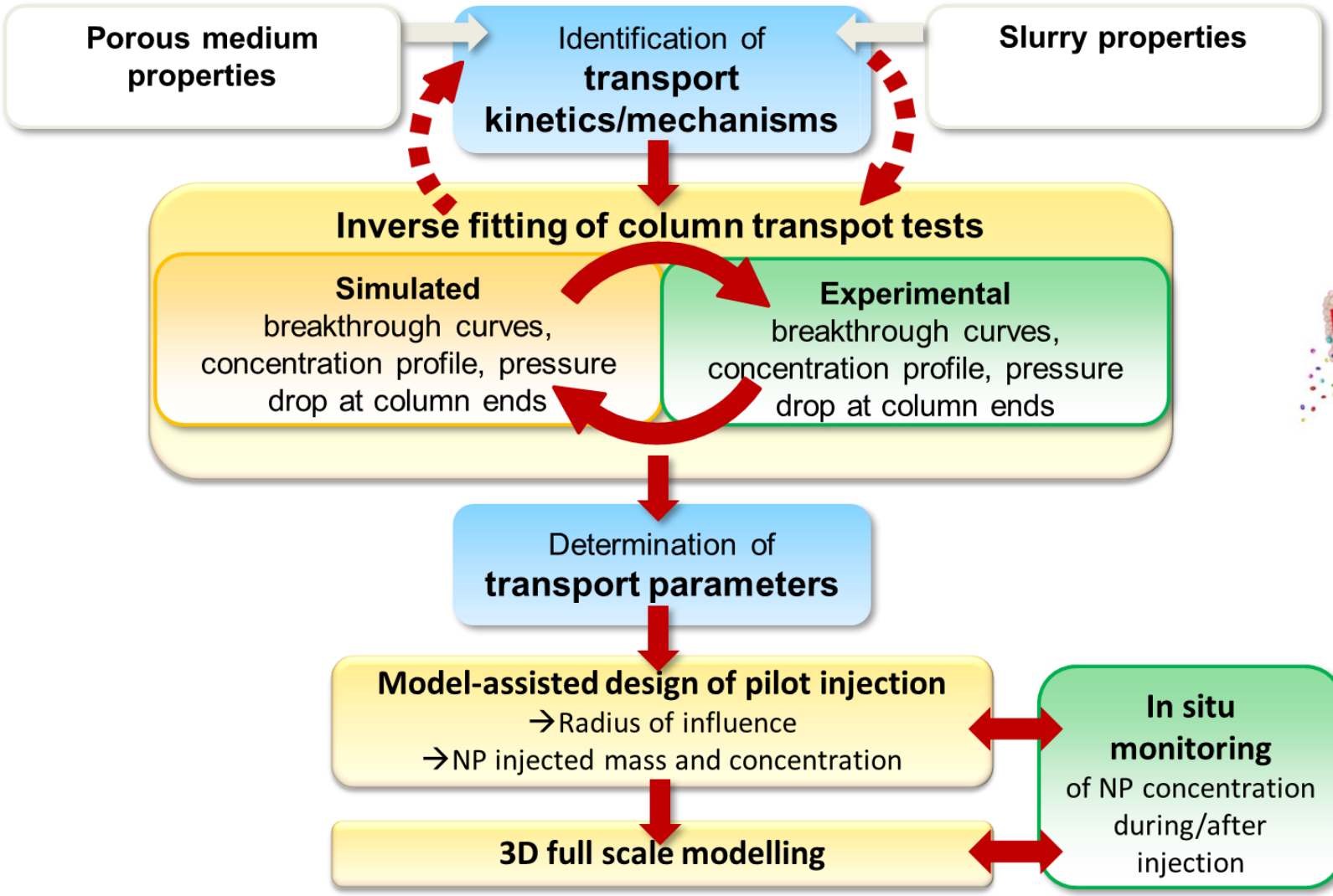


1D

2D



Model Assisted Upscaling



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Pilot Tests

- Selection of nanomaterial, evaluation of efficiency and longevity
- Particle distribution (ROT) → distance of application wells
- Effects on aquifer properties
- Reactivity and reaction kinetics, formation of intermediate products
- Verification of application method and performance of proposed equipment
- Cost estimation for a full scale remediation

Full Scale Design

- Based on monitoring, site specific particle tests, numerical model, remediation goal and pilot test decide on
  - NP to be used (pure / modified / composite / …)
  - Composition of slurry (NP concentration, surfactants, additives, stabilizers, …)
  - Injection technology (direct push injection, well infiltration, …) and well spacing
  - Target NP concentration in subsurface and total NP mass to be injected
  - Injection monitoring
  - Health and safety measures

Site Installation and NP Deployment

- Drilling/DP equipment
  - Installing of wells prior to injection, use packers to focus injection
  - Use direct push technology
- Preparation of slurry
  - Dispersers, vessels, inert gases, dosing equipment, injecition pumps, water supply, …
- Deployment of slurry
  - Injection pumps, packers, direct push rods,
- Monitoring
- Health and safety

Monitoring

- Pre-Injection Monitoring
  - Qualitative and quantitative delineation of contamination
  - Characterization of hydrochemical milieu
  - Determination of aquifer properties

    → direct push / depth oriented soil and water sampling

- Monitoring during NP injection
  - Particle transport and distribution

    → direct measurement via susceptibility sensors or water samples

    → indirect measurement via temperature or tracers

    (caution: ROI is not necessarily equal to ROT)

Monitoring

- Monitoring during system recovery phase
  - Determination of natural flow conditions
  - Confirmation of NP distribution (renegades?)

    → **Monitoring of head (water table)**

    → **Evaluation of soil samples**

- Long term monitoring
  - Determination of success

    → **Analysis of water samples for daughter products, metabolites and end products of reaction**

    → **Analysis of soil samples**

    → **Final data analysis**

Long Term Performance "Success?"

- Reduction of concentration
  - Based on ground water samples
  - Point type information
  - High spatial and temporal uncertainty
  - No information on inventory or emission
- Reduction of emission
  - Based on ground water samples
  - Integrative approach necessary (e.g. pumping test)
  - High certainty, but only snapshot ("rebound effect")
  - No (little) information on inventory
- Reduction of inventory
  - Based on soil samples
  - Only point type information possible
  - high uncertainty due to heterogeneity
  - Comparison before – after uncertain
  - No (little) information on emission

Regulatory Issues

- Description of technology
  - General mode of operation
  - Site installations
  - NP deployment / injection technology to be applied
  - Necessity of pilot test
  - Detailed description of monitoring system

- Description of suspension
  - Particles
  - Additives
  - Stabilizers

Regulatory Issues

- Description of chemical processes
  - Applicability to given contaminants
  - Reaction kinetics, degradation products

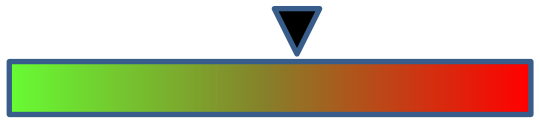
- Risk / Risk Management
  - to ecology
  - to humans
  - Options for risk mitigation
  - Stakeholder involvement

Regulatory Issues

- Alternative Technologies
  - Technical aspects
  - Combination with other technologies / treatment trains

- Financial aspects

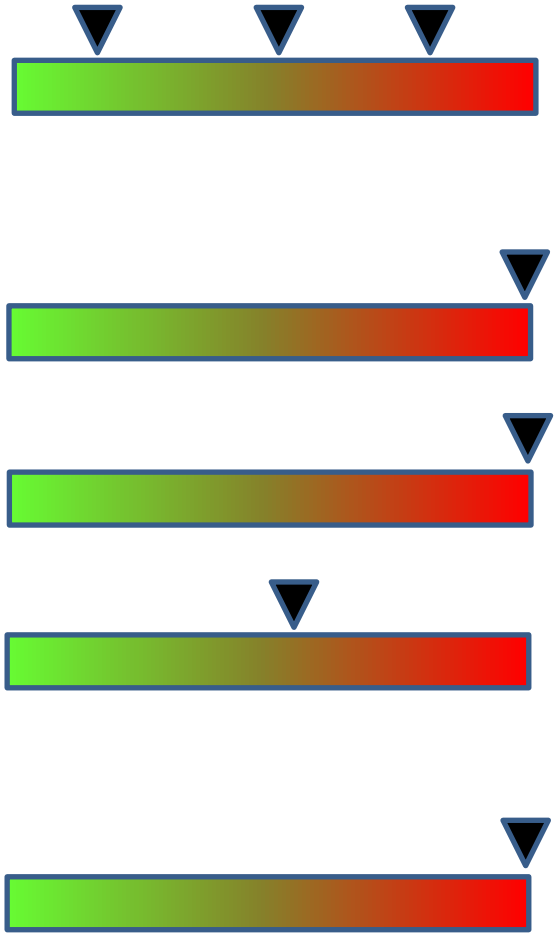
- Long Term Risk
  - Stability of NP in subsurface
  - Change of land use (zoning) due to nanoremediation?
  - Stakeholder involvement



- Best Practice
  - Well documented sites with comparable NP application

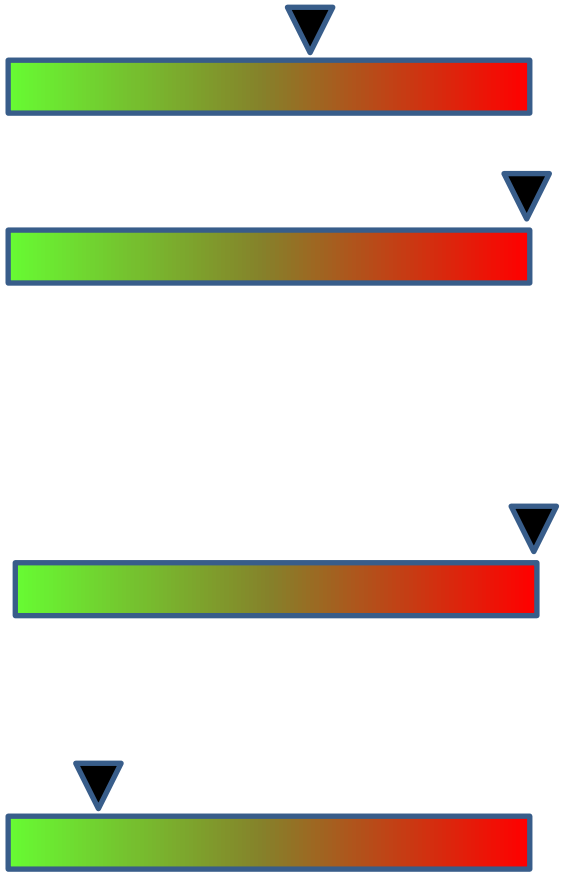
Financial Issues / Cost Drivers

- Regulatory Aspects
  - Injection permit, monitoring, reporting
- Remediation Goal
- Time Horizon / Time Limitations
- Site Installation and Mobilization of Equipment
- Additional Site Investigation



Financial Issues / Cost Drivers

- Cost for NP and Suspension
- Hydrogeological Conditions
  - Injection system and operation
  - Aquifer pre-treatment
- Geometry, Inventory and Accessibility of Contaminants
- Miscellaneous
  - Shipping costs, customs
  - Compensation of land owners



Examples of Nanoremediation

Site	Country	Site Primary Investigator	Target Cont.	NP-Type	Reaction Principle	Aquifer
Solvay	CH	Solvay	CHC	FerMEG12 (milled nZVI)	Reduction	porous / unconfined
Spolchemie 1	CZ	Aquatest	CHC	NANOFER 25S / NANOFER STAR	Reduction	porous / unconfined
Spolchemie 2	CZ	Aquatest	BTEX	Nano-Goethite (Iron-Oxide)	Oxidation / microbial enhancement	porous / unconfined
Neot Hovav	IS	Negev, BGU	TCE, cis-DCE, toluene	Carbo-Iron®	Adsorption / Reduction	fractured
Balassagyarmat	HU	Golder	PCE, TCE, DCE	Carbo-Iron®	Adsorption / Reduction	porous / unconfined
Nitrastur	ES	Tecnalia	As, Pb, Zn, Cu, Ba, Cd	NANOFER STAR	Reduction	porous / unconfined

→ see CLAI:RE NanoRem Bulletin for details

Thank you for your attention

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 309517

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