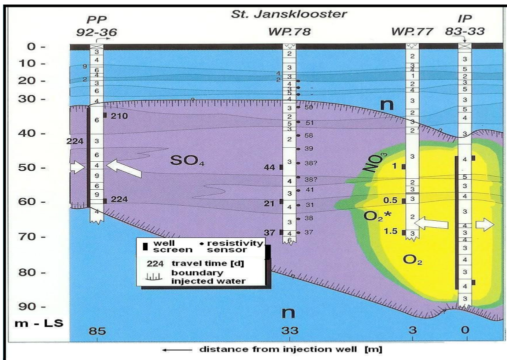

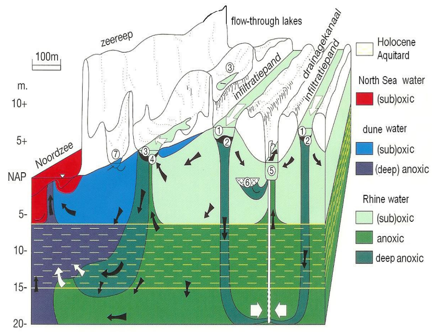

Quality aspects of storing fresh water in brackish aquifers; experiences from Netherlands and Florida

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Deltas in CC Sept. 29- Oct.1, 2010, Rotterdam

Advantages and disadvantages of addressing brackish target aquifers for AR

General advantages of AR	Additional advantages using brackish aquifers
Subsurface storage of water, quality and heat!	Extra subterranean reservoir
Purification	Admixed brackish groundwater less polluted
Damping quality and temp. Fluctuations	Less interference other users of aquifer
Maintain or restore groundwater levels/pressures	Direct reversal of salinization or sea water barrier
Disposal of undesired waters or Reuse of effluents	
Transport of water (aquifer as aquaduct)	
Impede land subsidence	
Reduce storm runoff+erosion, maintain river flows	

General problems of AR	Additional problems in brackish target aquifers
physical clogging of infiltration basins / wells	clogging by clay mobilization
(bio)chemical clogging of recovery systems	
accumulation of pollutants from input	too high recovery --> brackish water
flushing with mobile pollutants (pharma, xenobio)	brackish groundwater exfiltrating elsewhere
leaching of aquifer matrix (pH+redox buffer, CEC)	extra dissolution of CaCO3 and F+ PO4 minerals
mobilization of As, Fe, Mn, Ni, NH4, DOC	mobilization of Na, K, Mg, B, Li, Mo, F, PO4
water losses by lateral outflow or mixing	water losses by vert upflow (buoyancy)
rise of groundwater tables	
interference other users	more corrosion of well materials

Processes accompanying salt (SWI) or fresh water intrusion (FWI) in aquifers without evaporites

Local mixing of fresh and salt groundwater
Direct changes in EC, TDS, osm. press., density, piezometric level
Cation exchange (Na, K, Ca, Mg, Fe, Mn, NH_4, Ba, Li, Rb, Sr)
Precipitation / dissolution of carbonate minerals (cave development)
Formation of dolomite (Mg/Ca >6 mol basis)
Changes in porosity and permeability by:
- Flocculation and deflocculation of clay
- Precipitation (cements) or dissolution (caves) of carbonates
- Dolomitization (generating microporosity)

Desorption of DOC, PO_4, B, F upon FWI
Asorption of B, F upon SWI
Other removal processes: U, SO4 upon SWI

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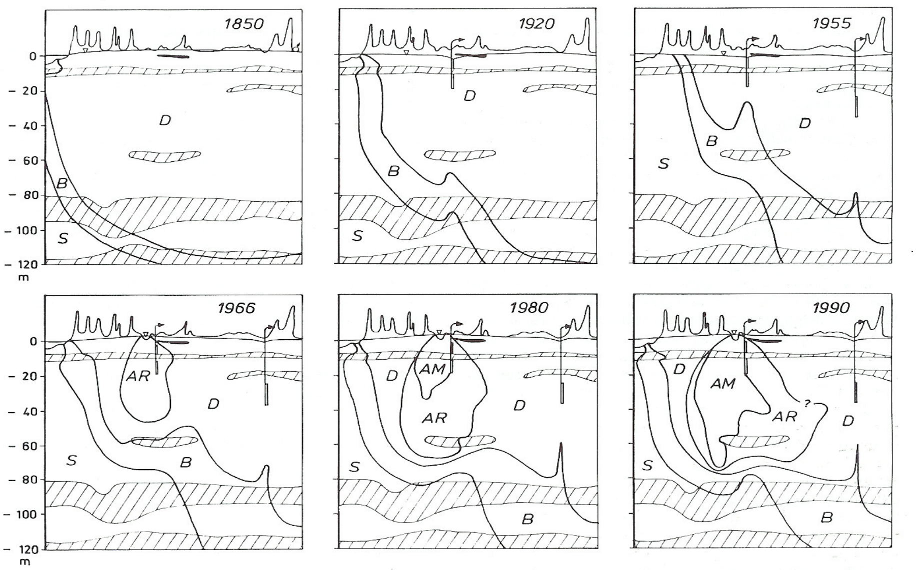
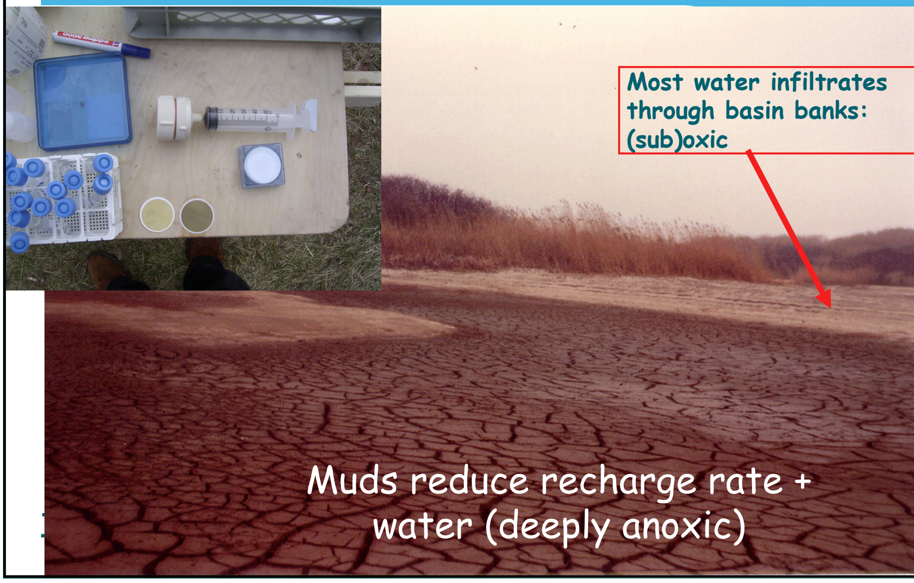
Salizination and MARS north of The Hague (Stuyfzand, 1993 p.97



Clogging of recharge basins and wells. Also neoformation of BOM + $CaCO_3$ precipitation



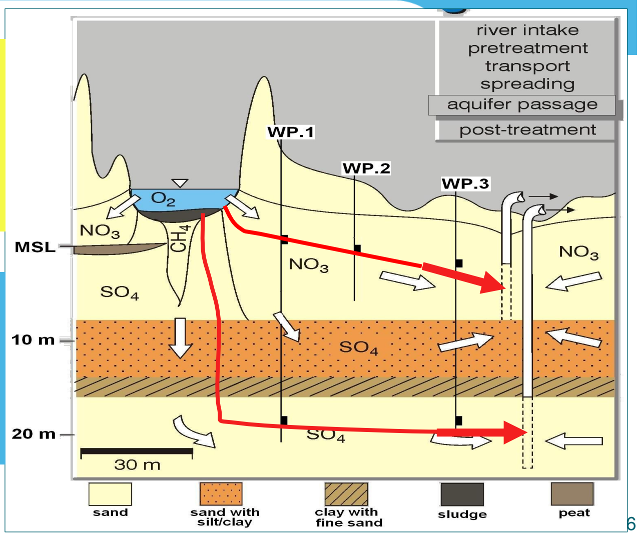
Clogging will lead to (deeply) anoxic conditions → spatial and temporal variations in water quality

Crucial for pollutants:

- mobility
- (bio)degradation
- toxicity

Zoning:

O_2 = oxic
NO_3 = suboxic
SO_4 = anoxic
CH_4 = deep anoxic



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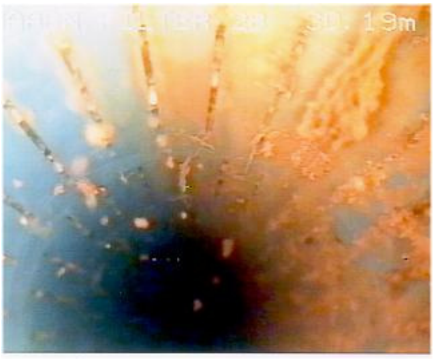
$Fe(OH)_3$ clogging of recovery / pumping wells
Diagnosis by camera inspection + chem analysis



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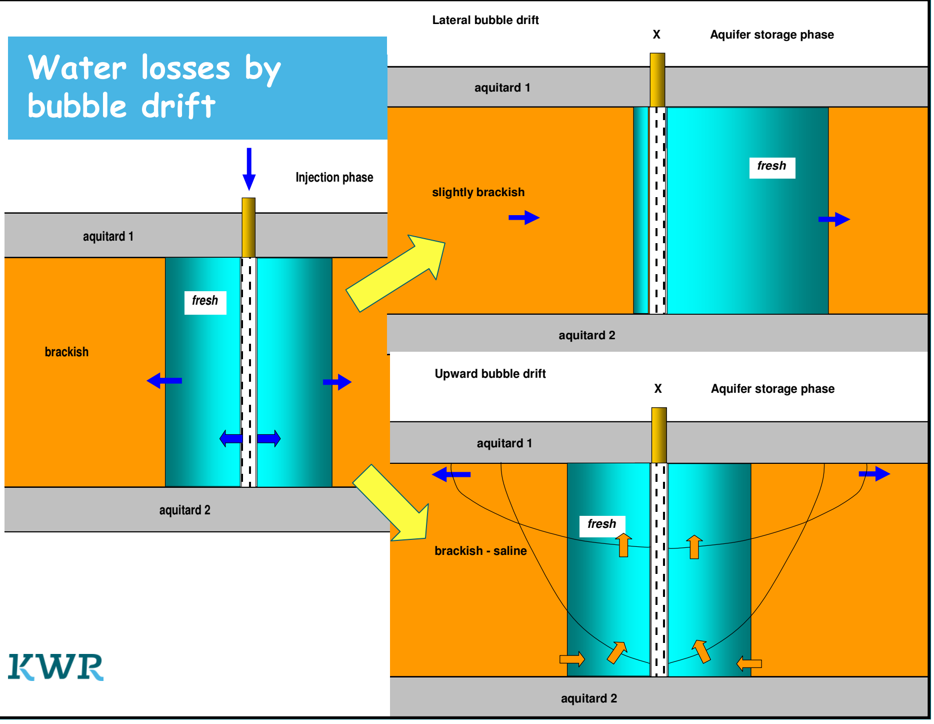
Water losses by bubble drift



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Cation exchange: its duration upon FWI >> SWI

The classical reaction (most text books):

$[Ca]\text{-}EXCH + 2Na^{+} \leftrightarrow [2Na]\text{-}EXCH + Ca^{2+}$

But more realistic is:

$[aCa]\text{-}EXCH + bNa^{+} + cK^{+} + dMg^{2+} \leftrightarrow [bNa,cK,dMg]\text{-}EXCH + aCa^{2+}$

Its duration in aquifers:

$R_{EQ} = t_{EQ} / t_{H2O} = 1 + CEC\ \rho s\ (1 - n) / [n\ \Sigma C]$

Examples:

CEC = 10 meq/kg d.w.; ρs = 2.65 kg/L; n = 0.35

Fresh water intrusion: ΣC = 6 meq/L → R_{EQ} = 9.2

Salt water intrusion: ΣC = 520 meq/L → R_{EQ} = 1.1

Cation exchange triggers various dissolution reactions

Cation exchanger: the main trigger

$[bNa,cK,dMg]\text{-}EXCH + aCa^{2+} \rightarrow [aCa]\text{-}EXCH + bNa^{+} + cK^{+} + dMg^{2+}$

Calcite dissolution due to Ca-sequestration by exchange

$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^{-}$

fluoro-apatite dissolution due to Ca-sequestration by exchange

$Ca_5(PO_4)_3F + 6CO_2 + 6H_2O \rightarrow 5Ca^{2+} + 3H_2PO_4^{-} + F^{-} + 6HCO_3^{-}$

Gibbsite dissolution if pH > ca. 8.5

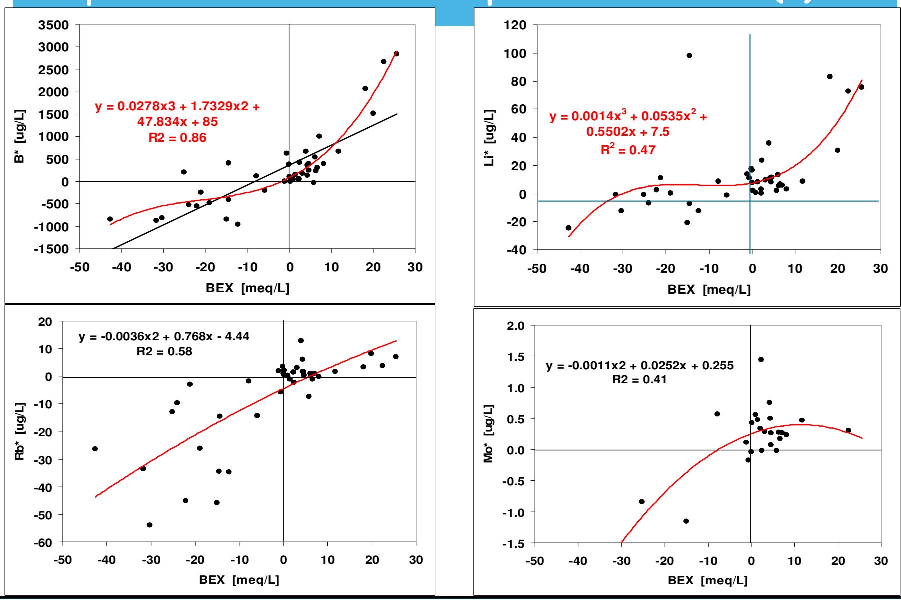
$Al(OH)_3 + OH^{-} \rightarrow Al(OH)_4^{-}$

Results in concentration increases for:

Na, K, Mg, HCO3, PO4, F, OH (pH up), (Al)

Results in change from CaHCO3 in NaHCO3 or MgHCO3 type

B, Li, Rb +Mo, corrected for marine contribution via Cl, are pos. linked to BEX: desorption due to FWI (+)



Correcting individual ions for contribution of sea salt → losses or gains by hydrogeochemical reactions

$$X^* = X - \alpha_X Cl^-$$

$$\text{with: } \alpha_X = X/Cl \text{ in SMOW}$$

Major constituent	factor mg/L	factor mol/L	Trace constituent	factor mg/L	factor mol/L
Na^+	0.5564	0.8581	B	$2.3\ 10^{-4}$	$7.541\ 10^{-4}$
K^+	0.0206	0.0187	Br^-	$3.48\ 10^{-3}$	$1.543\ 10^{-3}$
Ca^{2+}	0.0213	0.0188	F^-	$7.19\ 10^{-5}$	$1.341\ 10^{-4}$
Mg^{2+}	0.0668	0.0974	Li^+	$9.34\ 10^{-6}$	$4.773\ 10^{-5}$
SO_4^{2-}	0.1401	0.0517	Mo	$5.17\ 10^{-7}$	$1.913\ 10^{-7}$
TotH (Ca^{2+} + Mg^{2+})		0.1162	Rb^+	$6.06\ 10^{-6}$	$2.513\ 10^{-6}$
BEX = Na*+K*+Mg*	meq/L	1.0716	Sr^{2+}	$4.21\ 10^{-4}$	$1.702\ 10^{-4}$

Example:

Na = 50, Cl = 100 mg/L → Na* = 50 – 56 = -6 mg/L

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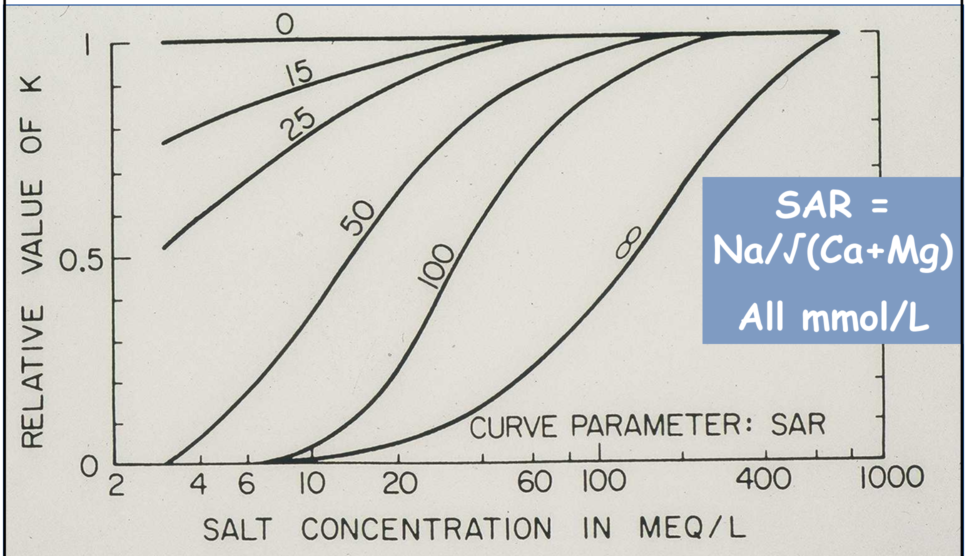

Figure 3.5 Effect of SAR and salt concentration of soil solution on hydraulic conduct sandy loam. (*Redrawn from McNeal, 1968.*)

Slide obtained from Herman Bouwer

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Arsenic mobilizing processes in general
During AR especially # 2+5+6+7

No.	Mobilizing process	Trigger	Freq
1	Desorption by decreasing AEC	Ripening of iron(hydr)oxides (Fe^{2+} flushing, Time, Temp increase); Increase of pH and Temp; Clay+peat compaction?	C
2	Anion exchange	Flushing with higher conc of PO_4, H_4SiO_4, HCO_3, DOC, SO_4, F, I; Changes in selectivity of sorbent	CC
3	Dissolution of minerals containing As traces (like glauconite?, apatite, vivianite, siderite, struvite)	Flushing of (deeply) anoxic system with lower pH and lower conc of PO_4, Fe^{2+}, CO_3, etc.	C
4	Dissolution of As-minerals (like As_2S_3)	Flushing of (deep) anoxic system with higher conc of CO_3^{2-} which raises solubility by complexes as $As(CO_3)_2^-$, $As(CO_3)(OH)_2^-$, $AsCO_3^+$	RR
5	Oxidation of Fe-sulphide minerals	Moderate or no input of O_2 and high input of NO_3 with Fe^{2+} (partly) escaping from oxidation; Lowering of groundwater table	CC
6	Reduction of H_3AsO_4 to H_3AsO_3	High input of CH_4, H_2, labile DOC; High input of H_2S but Fe^{2+} low; Contact with SOM; Inundation or rise of groundwater table; Raised Fe^{2+} input	CC
7	Reductive dissolution of iron(hydr)oxides and manganese oxides		

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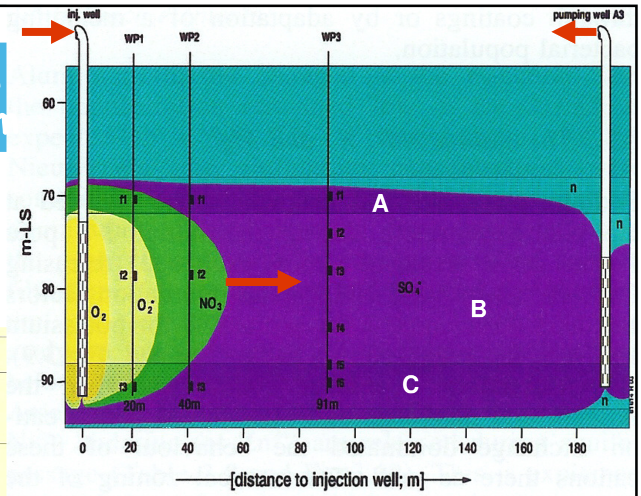
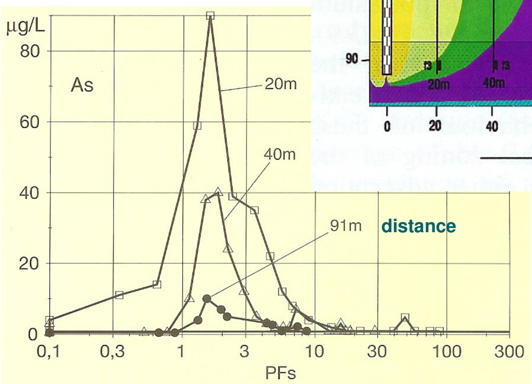
As mobilization in ASTR system

From layer C with very reactive FeS_2





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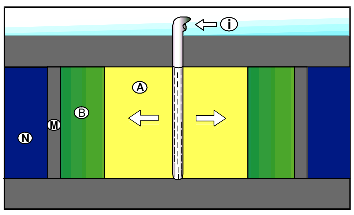
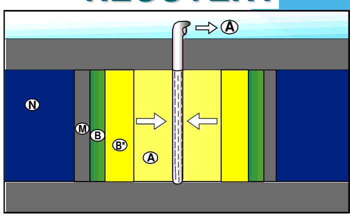
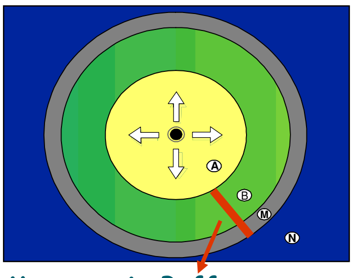
Typical zoning in ASR bubbles

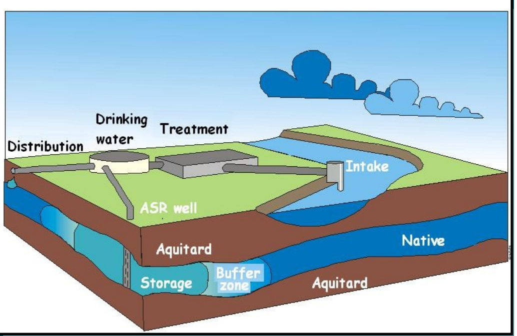
STORAGE & ***RECOVERY***



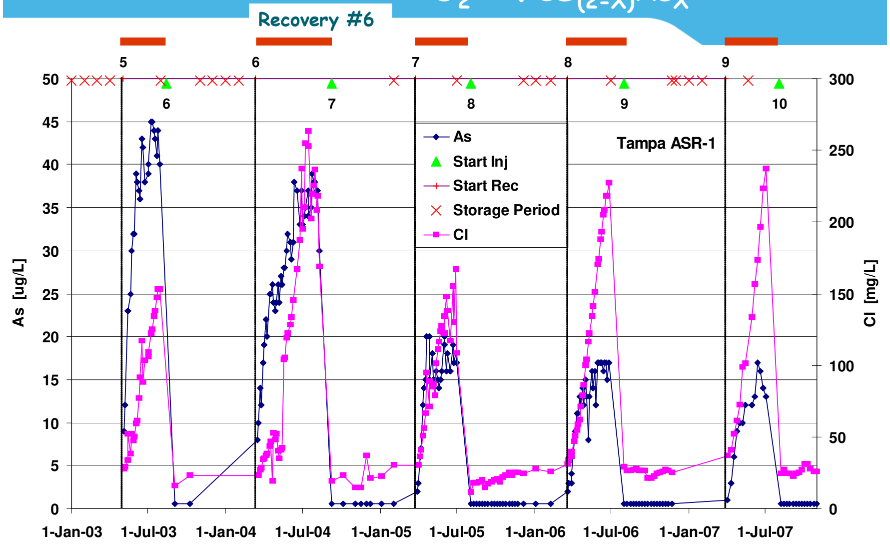




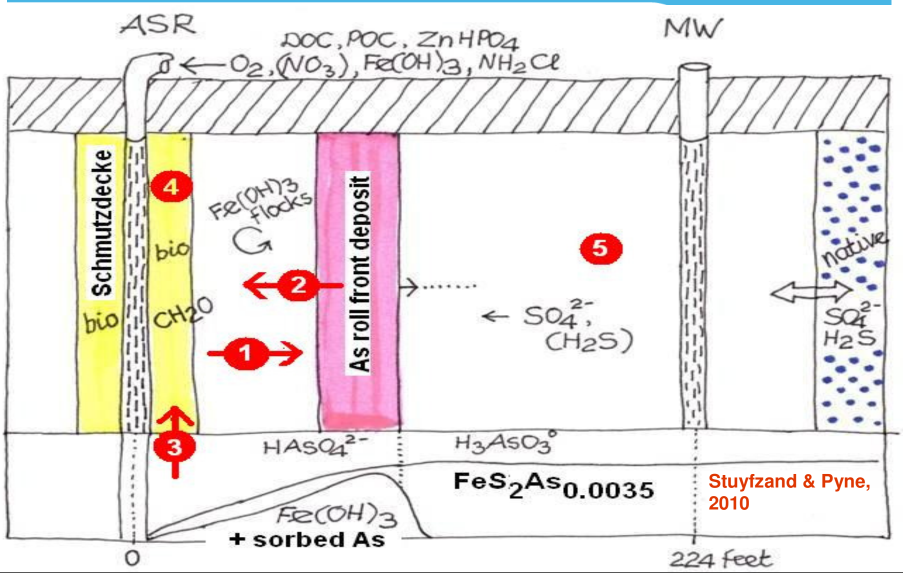
B+M = anoxic Buffer zone



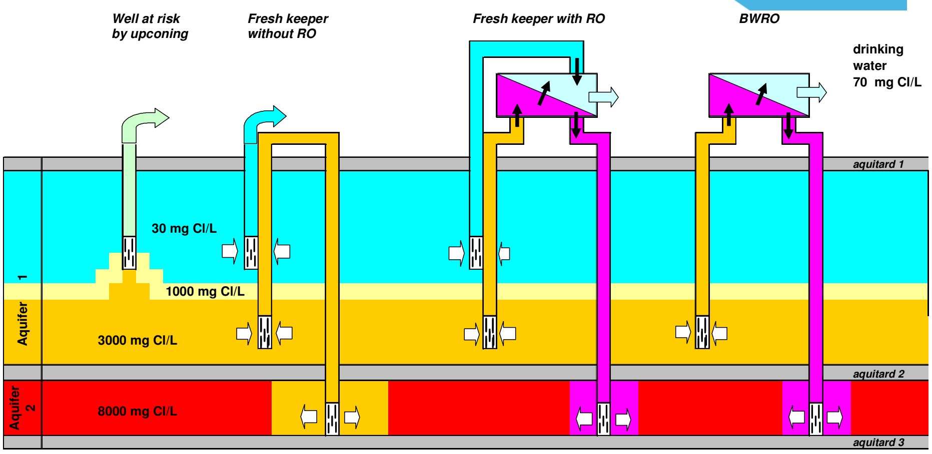
Arsenic mobilization in Florida ASR systems: $O_2 + FeS_{(2-X)}As_X$



Conceptual model of As peaking during ASR backpumping with zonation of processes (im)mobilizing As in Florida.



The aquifer for waste disposal: MC from brackish groundwater RO (BWRO)



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Some conclusions

When addressing brackish aquifers, take care of:

- Clay migration: by selecting low SAR infiltrate and aquifer with low clay content (+dominant clay type being kaolinite)
- Removal of TSS by pretreatment + sel intake
- Well management to prevent ageing of clogging
- Measures to reduce WRI in ASR applications (As, Mn): reduce input of oxidants (As), keep pH > 7.5 (Mn)

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