Application of Monitored Natural Attenuation for Cleanup of Radionuclides in Groundwater

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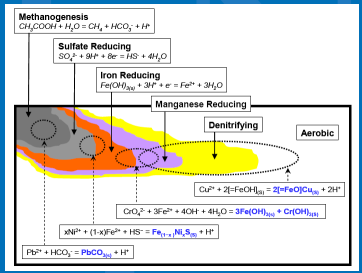

10th SNR
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Albuquerque, NM

Office of Research and Development
Land Remediation and Pollution Control Division, Cincinnati, OH

Outline of Topics

- Preface for OSWER Directive 9200.4-17P
- Background for Hanford 300 Area Uranium Plume
- Technical Evaluation of Factors Influencing Uranium Plume Behavior
- Importance of Technical Issues to other Sites and Contaminants

1

OSWER Directive 9200.4-17P

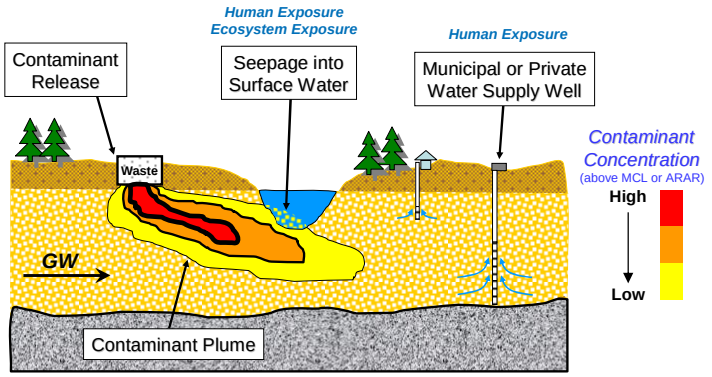
Monitored Natural Attenuation
http://www.epa.gov/swerust1/directiv/d9200417.pdf

- **Stable or shrinking plume** – *CERCLA defines plume dimensions based on concentration/activity criterion; expectation that contaminant migration is arrested.*
- **Source control measures** (*important to limit flux of contaminant being "fed" into the plume*)
- **Identify mechanism(s) of attenuation** (*performance characteristics*)
- **Demonstrate irreversibility of attenuation process** ("sorption") – *recognizes that many inorganic contaminants will persist in subsurface*

USEPA. Common Radionuclides Found at Superfund Sites. EPA 540/R-00-004, Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response, Washington, DC (2002). http://www.epa.gov/superfund/health/contaminants/radiation/pdfs/nuclides.pdf

2

Generalized Site Scenario



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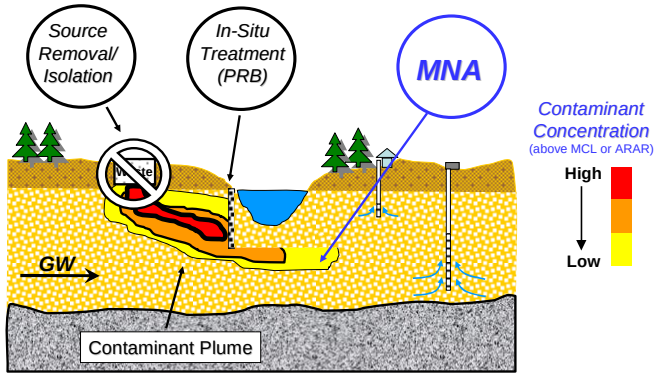
Generalized Site Scenario

1 Reduce contaminant flux in subsurface…

2 Use of MNA to remediate dilute portion of plume…



4

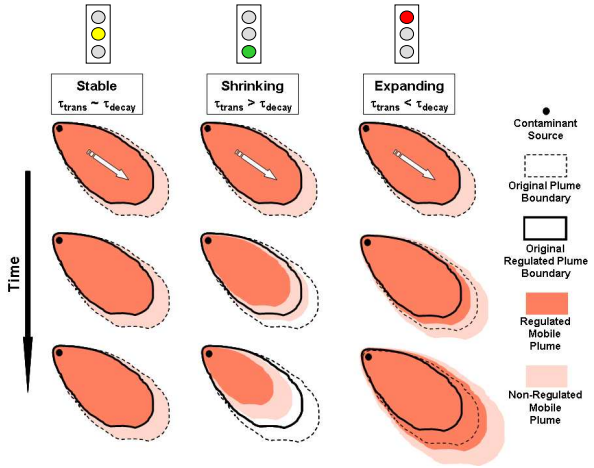
Attenuation Processes

- **Dispersion/dilution?** (May factor into dimensions of "regulated" plume, but not likely sufficient to arrest migration)
- **Transformation** – conversion to something that has different regulatory constraints (e.g., nitrate or perchlorate)
- **Immobilization** – adsorption, coprecipitation, precipitation (majority of the contaminants in the three-volume set, including long-lived radionuclides) ***Note: Immobilization ≠ Retardation***
- **Radioactive Decay** – may be applicable for short-lived radionuclides (e.g., ^{3}H, ^{137}Cs, ^{90}Sr) ***Note: Retardation may benefit this process.***

5

Role of Radioactive Decay

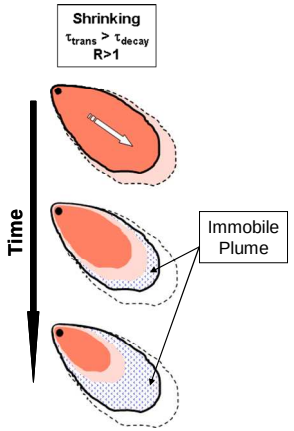
Conservative Chemical Transport



6

Immobilization of Radionuclide

Non-Conservative Chemical Transport

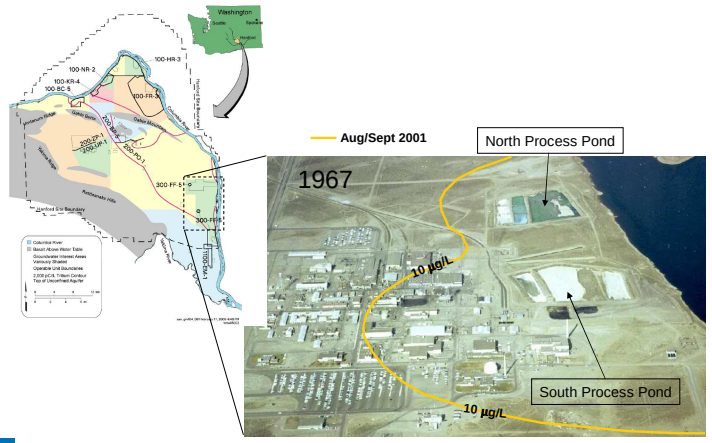


'Immobile' plume represents contaminant mass sorbed onto aquifer solids at any point in time. Future scenarios for evolution of 'immobile' plume:

- Declines in mass & spatial distribution due to radioactive decay
- Remains invariant in mass & spatial distribution
- Evolves to new state that serves as source for development of new dissolved plume caused by:
  - Radioactive decay produces more mobile daughter product(s)
  - Changes in ground-water chemistry cause re-mobilization

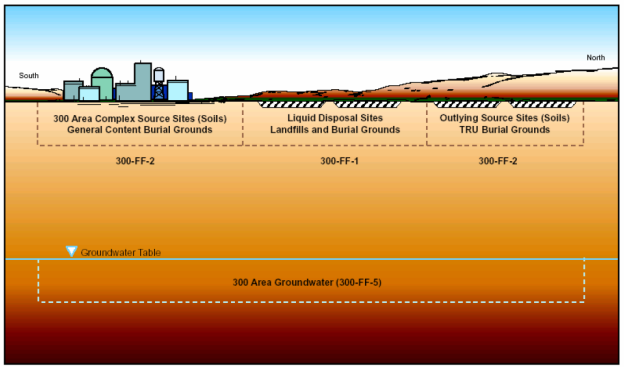
7

Background for Hanford 300 Area



8

Background for Hanford 300 Area



9

http://www.hanford.gov/docs/gpp/library/programdocs-300/300AreaWorkshop0807introA.pdf

Background for Hanford 300 Area

CERCLIS Database (19 March 2009 download)
http://yosemite.epa.gov/r10/nplpad.nsf/epaid/wa2890090077

Site Description

"The site contains approximately 220 facilities and 70 soil waste sites, including solid and liquid waste disposal areas and soil contamination areas. The site also contains 32 miles of contaminated underground piping. The ***disposal areas and plumes of contaminated groundwater*** cover approximately ***1.6 square miles***."

Cleanup Progress

"Early Actions: In 1992, DOE conducted two early actions: 1) excavated and removed 14,000 cubic yards of uranium-contaminated soil and sediment from wastewater disposal trenches, and 2) removed barrels containing uranium-contaminated solvents from one landfill."

"Long-Term Actions: …[*substantial control of surface contaminant sources*]…The selected ***remedy for contaminated groundwater in the 300 Area is monitored natural attenuation, but this interim remedy is in the process of being reevaluated due to performance issues***."

10

Background for Hanford 300 Area

EPA/ROD/R10-96/143, 07/17/1996
(*Directive 9200.4-17P published 1999*)

"This ROD addresses actual or threatened releases from the wastes sites in the 300-FF-1 Operable Unit and the ***groundwater in the 300-FF-5 Operable Unit***."

"The selected remedy for 300-FF-5 is an ***interim remedial action*** that involves imposing restrictions on the use of the groundwater until such time as health-based criteria are met for uranium, trichloroethene, and 1,2-Dichloroethene."

"The selected interim remedy includes:
- ***Continued monitoring of groundwater that is contaminated above health-based levels to ensure that concentrations continue to decrease***;
- Institutional controls to ensure that groundwater use is restricted to prevent unacceptable exposures to groundwater contamination…"

11

Background for Hanford 300 Area

Conceptual Model Supporting Interim GW Action

- Most of the U mass is in the 1st few feet of sediments in the liquid waste disposal sites
- Remove this source and the U concentrations will attenuate to < DWS.
- Expedited Response Action in 1991 removed contaminated soil from trenches with dramatic U concentration decreases.
- The RI/FS Report (May 1995) suggested that the plume would attenuate to meet the drinking water standard in 3 to 10 years from late 1993.

http://www.hanford.gov/docs/gpp/library/programdocs-300/300AreaWorkshop0807introA.pdf

DOE/RL-2006-20 Revision 1
The Second CERCLA Five-Year Review Report for the Hanford Site

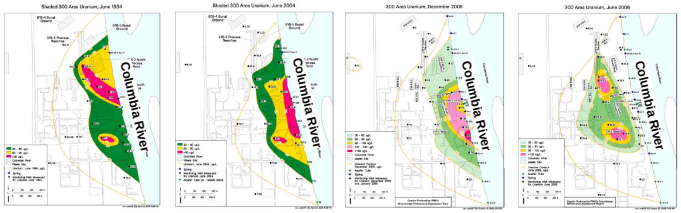
"Remediation of the uranium plume in the 300 Area groundwater through natural attenuation with monitoring ***has not achieved the remedial action objectives in the ten-year time frame*** envisioned when the ROD for interim action for groundwater was established."

12

Background for Hanford 300 Area

- Uranium concentrations and plume dimensions have been sustained beyond expectations
- Spatial distribution of plume mass is dynamic in time

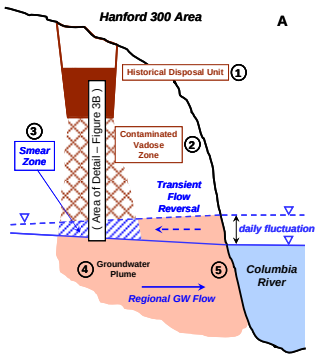
June 1994 **June 2004** **December 2005** **June 2006**



13

Current Conceptual Site Model

Hanford 300 Area uranium plume provides an opportunity for retrospective analysis (EPA/600/R-08/114)



1. Contaminated surface soils (source removal)
2. Dispersed residual contamination in vadose solids
3. Zone impacted by water table fluctuations (GW-SW interactions)
4. Plume in continuously saturated zone
5. Transition zone between GW & SW (includes sediments)

14

Contaminant Source Term

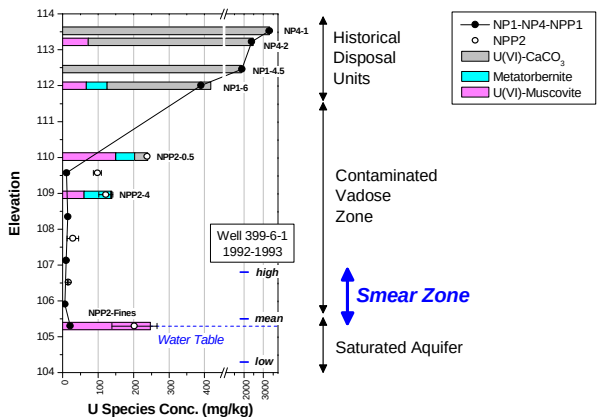
From PNNL-15121 Summary:

- "***Both precipitated and adsorbed U(VI) exists*** in the sediments."
- "An average of 37.5% of the residual, sorbed uranium appears accessible to dissolution/desorption…" "Adsorbed U(VI) predominates in sediments with total uranium <25 mg/kg."
- "The vadose zone sediments beneath both SPP and NPP will ***remain as potential source terms*** to maintain groundwater U(VI) concentrations at or above the drinking water standard."
- "Increasing groundwater levels at high river stage will solubilize sorbed U(VI) from the capillary fringe and lower vadose zone."

http://ifchanford.pnl.gov/pdfs/15121.pdf

15

Contaminant Source Term

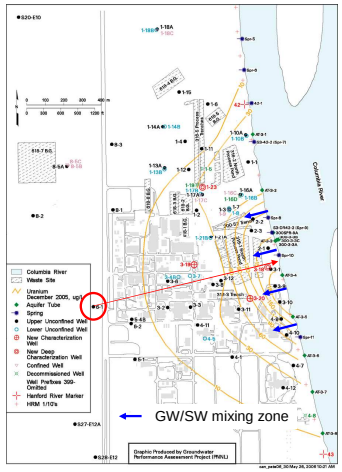


16

Hydrologic Factors Influencing U(VI) Transport

Pitfalls in original characterization effort supporting model development:

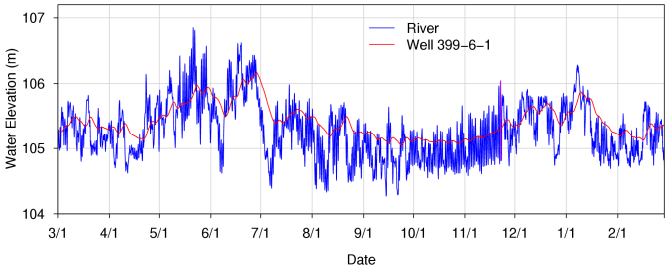
- Assumed no continuing source to saturated aquifer (surface soils removal action)
- Development of U partition coefficient (Kd) that did not account for influence of SW on variable GW chemistry (alkalinity)
- *Transport modeled using mean hydraulic gradients vs. transient states influenced by Columbia River stage*



17

Hydrologic Factors Influencing U(VI) Transport

- Well 399-6-1 is ~900 meters inland from Columbia River
- Year-long monitoring record from March 1992 to February 1993



Waichler, S. R. and S. B. Yabusaki. Flow and Transport in the Hanford 300 Area Vadose Zone-Aquifer-River System. PNNL-15125, Pacific Northwest National Laboratory, Richland, WA (2005). http://www.hanford.gov/docs/gpp/library/programdocs-300/PNNL-15125.pdf

Yabusaki, S. B., Y. Fang, and S. R. Waichler (2008), Building conceptual models of field-scale uranium reactive transport in a dynamic vadose zone-aquifer-river system, Water Resour. Res., 44, W12403, doi:10.1029/2007WR006617.

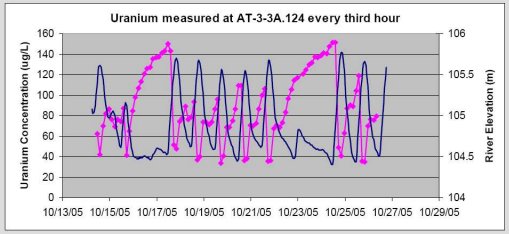
18

Hydrologic Factors Influencing U(VI) Transport

GW/SW Transition Zone

"…variations in concentrations are a function of dilution rather than any chemistry effects caused by the difference in water chemistry between groundwater and river water."

- High frequency water sampling for uranium in October 2005
- River elevation shown in blue, uranium concentration shown in red



Source: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-16805.pdf

19

Modeling Uranium Transport

1993 Numerical Model

Modeling Assumptions in Phase I Remedial Investigation (1994)
- 3-D saturated unconfined aquifer; **vadose zone not modeled**
  - Spatially distributed hydraulic conductivity (4 hydrofacies types)
  - Flow field driven by monthly changes in river stage fluctuations
  - Uranium mobility controlled by constant K_d
  - Natural flushing predicted to largely decrease U to < 20 ug/L by 2018 (end of institutional controls)

Prediction Update for U < 20 ug/L in RI/FS (1995)
- "Refinement" of Phase I RI estimate: **3 to 10 years** from late 1993 to meet standard
- Analytical model assumptions
  - Steady-state saturated flow
  - Constant hydraulic conductivity: 1830 m/day
  - Constant hydraulic gradient: $5x10^{-4}$
  - 500 m travel distance from process trenches to Columbia River
  - Uranium mobility controlled by "best estimate" constant Kd ~ 1 to 2 mL/g
- No interaction between aquifer and river
- No interaction between aquifer and vadose zone

http://www.hanford.gov/docs/gpp/library/programdocs-300/300AreaWorkshop0807introA.pdf

Modeling Uranium Transport

Both hydrology and chemistry matter…

- "…rising and falling river stage provides a ***hydrologic mechanism to mobilize U(VI) from the vadose zone*** and transport it to groundwater." **PNNL-15121**
- "U(VI) forms neutral and ***anionic aqueous-carbonate complexes*** in Hanford Site pore and groundwaters that ***suppress adsorption, enhance U(VI)-precipitate solubility, and lower retardation factors***." **PNNL-17031**
- "U(VI) Kd values for Hanford sediments show significant variability (0 to >100 mL/g). The primary factors affecting Kd are a) ***sediment texture***, as a control on reactive-surface area and adsorption-site concentration, b) ***clay and silt fraction mineralogy***, as a control on adsorption-site strength, and c) ***pH and dissolved inorganic carbon***, as a control on U(VI) aqueous speciation." **PNNL-17031**

http://ifchanford.pnl.gov/pdfs/15121.pdf
http://ifchanford.pnl.gov/pdfs/chg_final_rpt_17031.pdf

Role of Models in Site Characterization

A model is not a substitute for adequate site characterization!

- First step is development of a technically sound CSM (***SOURCE*** to receptor) – revised based on site data
- Next step is developing water transport model that adequately captures spatial heterogeneity and time-dependent variability
- Next step is to incorporate chemical reactions that capture all important factors for radionuclide speciation (aqueous & solid)
- Need to confirm that chemical reaction database is current and accurate for contaminant and important major element chemistry

USEPA. Documenting Ground-Water Modeling at Sites Contaminated with Radioactive Substances, EPA/540/R-96/003, Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response, Washington DC (1996). (http://www.epa.gov/rpdweb00/docs/cleanup/540-r-96-003.pdf)

Reminder…

Q: How does MNA differ from an engineered remedy?

1) Engineered remedy is designed from the "ground up" to achieve a specific removal process, e.g., reactive media in a permeable reactive barrier (PRB)
2) Natural Attenuation is due to some process *to be evaluated* to understand performance characteristics
   - Need to identify reactive media and system hydraulic characteristics
   - Need to understand factors under which reactive media are functioning
   - Need to determine performance criteria relative to site-specific GW conditions

The Burden of Proof

- Mass of contaminant that is currently moving and anticipated to move through the subsurface
- Identification of process causing attenuation – radioactive decay and/or immobilization
- Determination of capacity within aquifer to attenuate contaminant
- Determination of stability of immobilized contaminant to resist re-mobilization
- Identification of monitoring parameters that can be used to track continued performance (*hydrology & chemistry*)

24

Questions?

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25

Development of EPA Technical Resource Documents for MNA

- What is covered in the EPA three-volume set on MNA for inorganic contaminants in ground water?
  - Volume 1 – Immobilization and transformation processes along with methodological approach for site characterization
  - Volume 2 – Contaminant-specific discussions of attenuation processes and characterization approaches for "metals" (As, Cd, ClO_4, Cr, Cu, Ni, NO_3, Pb, Se)
  - Volume 3 – Discussion of radioactive decay as a factor in plume development and characterization requirements; contaminant-specific discussions of attenuation processes and characterization approaches for radionuclides (Am-Pu, Cs, ^3H, I, Ra, Rn, Sr, Tc, Th, U)

26