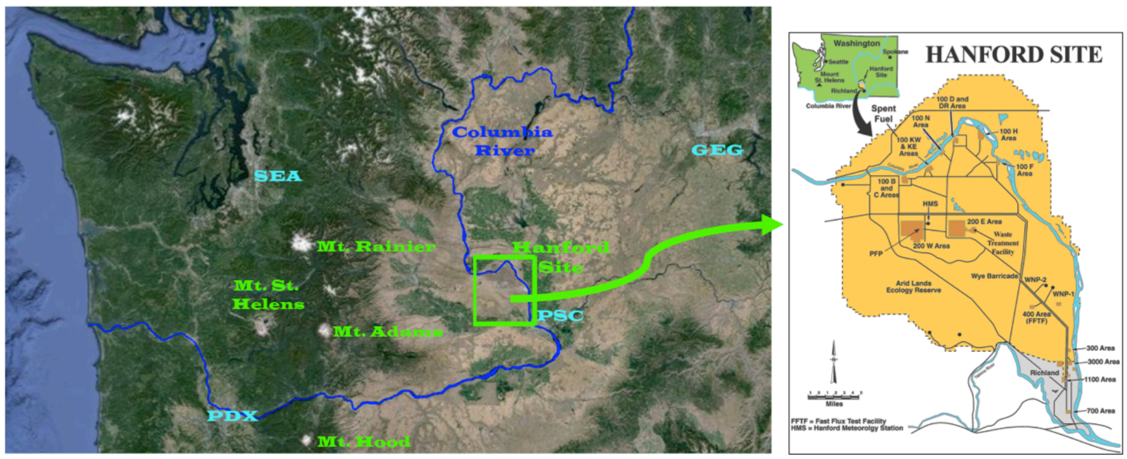
The Hanford Reservation

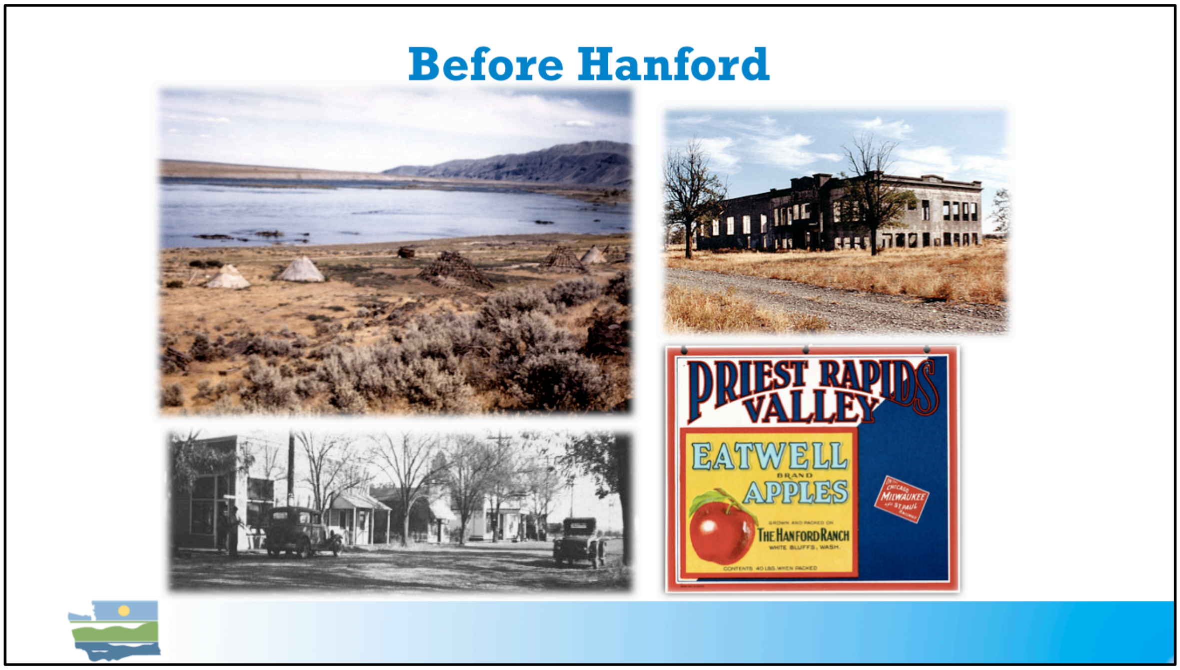
A Veritable History of Chemistry

Jerry Yokel, Lead Chemist
Washington State Department of Ecology
Nuclear Waste Program

Where is Hanford?



In the Columbia Basin, bordered by the Columbia River for 52 miles, Roughly four hours from Seattle, two from Spokane
586 sq. miles; Columbia R. forms eastern boundary for 50 miles



When the army corps of engineers chose this area in 1943, it had three tiny towns – Richland, White Bluffs, and Hanford. The 1200 residents were given 30 days to get off their land for the secret project. Native Americans also used this area for hunting, fishing and root gathering.

Hanford fast facts

- Built during WWII as part of Manhattan Project
- Employed 50,000 at peak of production in 1940s
- Created plutonium for the bomb dropped on Nagasaki
- Operated during Cold War
- Stores 2/3 of total U.S. volume of high-level radioactive waste (56M gal)

- Made about 2/3 nation's plutonium, 1944-1988
- Peak employment: 50,000 during construction
- Current employment: ~10,000

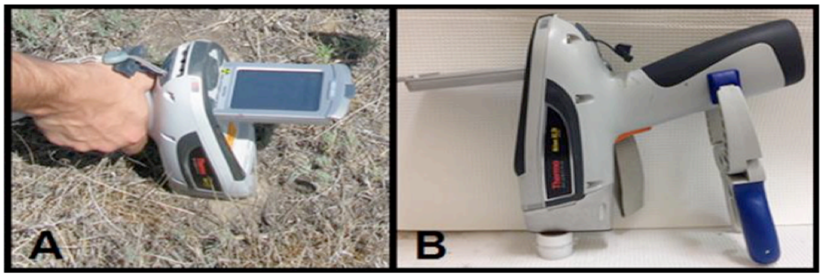
Pre Hanford $PbHAsO_4$ Application 1890 to 1943

5000 acres 14 million kg (30 million lb)

1910 Agriculture chemical application at Hanford townsite, and White Bluff's townsite

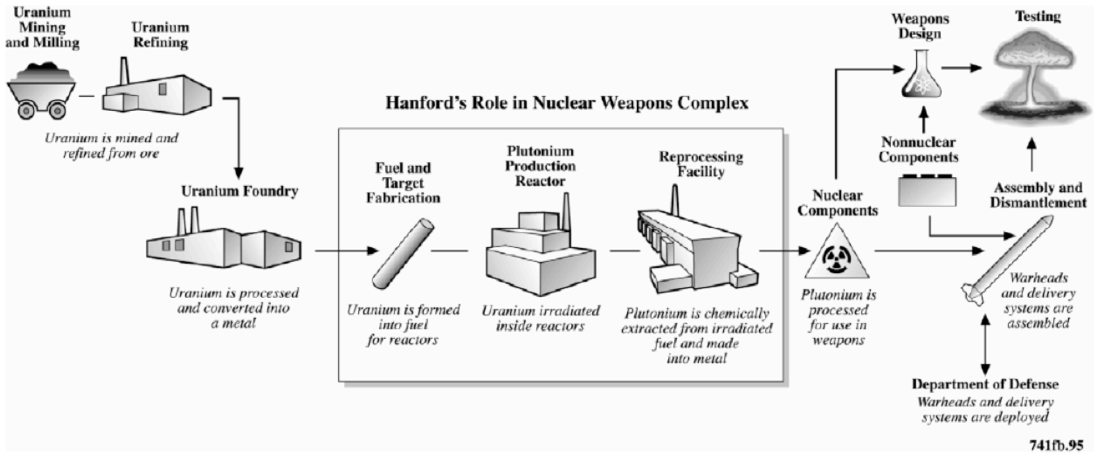
As mentioned, the area had orchards prior to the Manhattan Project.

X-Ray Fluorescence – used for AsPB cleanup



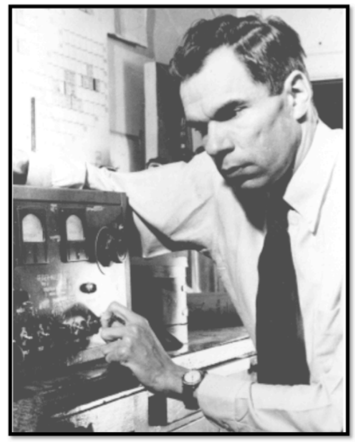
- Data files included sequential sample number, date/time stamp, count duration, and the measured concentrations plus 2σ counting errors for 18 metals (including lead and arsenic). For in situ analysis, a 60 second count time was used.
- How to ensure data is defensible to make remediation cleanup decisions.

Hanford's Major Role



Glenn T. Seaborg: 1912–1999

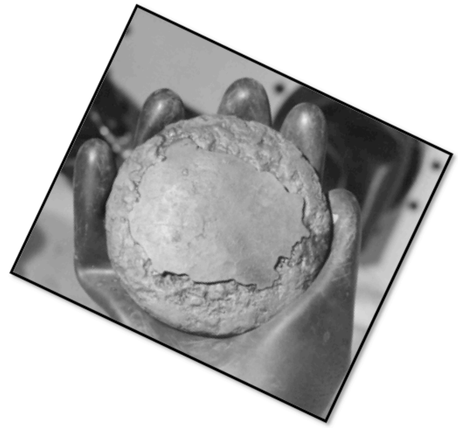
- Plutonium (Element 94): Code name "copper"
- In 1941, it was determined that the newly discovered isotope Plutonium-239 could undergo fission and had potential as a powerful nuclear-energy source.
- Seaborg developed the chemical separation process that would provide plutonium-239 for the Manhattan Project.
- Found that tetravalent, Pu(IV), could be co-precipitated from aqueous solution with insoluble Bismuth Phosphate.



Why Pu and Not U at Hanford?

- U: isotopic enrichment by mass. Gaseous diffusion plants are slow and expensive

- Pu: co-precipitation, solvent extraction, organic phase dissolution, purification separation. Adsorbed on cation exchange resins.



Plutonium puck.

Plutonium Oxidation States – Different Solubilities – Multiple Reactivities - 5f electrons

Molecular behavior of Pu in nitric acid allows for its chemical purification. In 7 molar HNO_3 solution Pu(IV) exists as a complex containing two, four, and six nitrate ligands: $Pu(NO_3)_2{}^{2+}$, $Pu(NO_3)_4$,and $Pu(NO_3)_6{}^{2-}$ (Allen et al. 1996). The hexanitrato anionic species $Pu(NO_3)_6{}^{2-}$ sorbs strongly to an anion exchange column, and anion exchange is used to purify large quantities of plutonium every year. Pu_2O_3 is pyrophoric.

Plutonium is a physicist's dream but an engineer's nightmare. With little provocation, the metal changes its density by as much as 25 percent. It can be as brittle as glass or as malleable as aluminum; it expands when it solidifies—much like water freezing to ice; and its shiny, silvery, freshly machined surface will tarnish in minutes.

It is highly reactive in air and strongly reducing in solution, forming multiple compounds and complexes in the environment and during chemical processing. It transmutes by radioactive decay, causing damage to its crystalline lattice and leaving behind helium, americium, uranium, neptunium, and other impurities. Plutonium damages materials on contact and is therefore difficult to handle, store, or transport.

Why So Many Reactors?

- 8 reactors originally planned on the Columbia River from A to H
- B, D, and F only used for the Manhattan Project – Not enough Pu for a 3rd bomb.
- 1956-1965 9 reactors in use – Cold War politics.
- 1964-1971 shutdown period
- N reactor, dual purpose, operated until 1987 – too close to river

1940 Manhattan Project - Secrecy

Large Chemistry labs to support U and Pu production – gallons of solvents…..gallons of waste…to hell with the environment we are at war.

Hanford: Purex, B plant Bi Po4, U plant (fp-fission products)

B plant and T plants at Hanford were the first to separate Pu from spent fuel using the Bismuth Phosphate process. Pu(IV) could be coprecipitated in aqueous solution with insoluble $BiPO_4$.

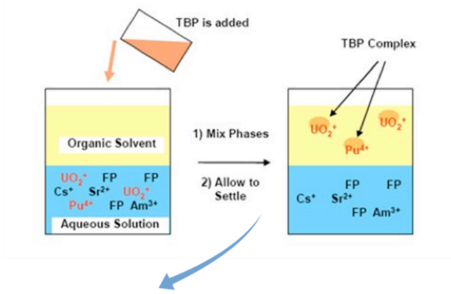
Disadvantages: 9(1) inability to recover U (2) large volume of wastes and process chemicals used (3) batch process (4) no air filters

Redox process at S plant. Solvent extraction using hexone, methyl isobutyl ketone, which is immiscible in water. Will extract Uranyl nitrate and Plutonyl nitrate.

Advantage over $BiPO_4$:(1) operate continuously (2) recover U and Pu
Disadvantages: (1) volatility and flammability (2) nonvolatile reagent added to waste

Remember during this time only Geiger counters were used. Pressure and Temperature meters.
Lots of hands on.
Technology and Safety were advancing.

PUREX (Plutonium Uranium Redox Extraction)



Fuel dissolved in Nitric Acid

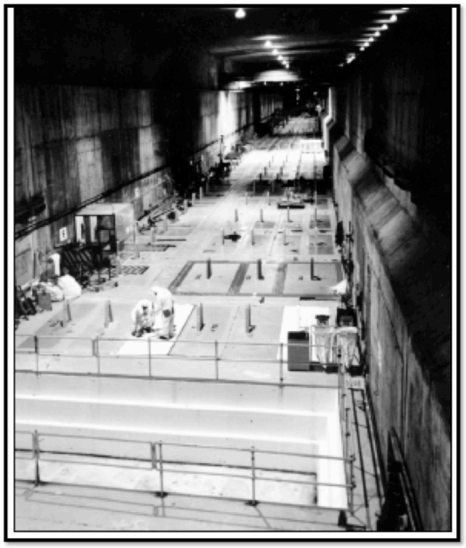
- Organic soluble Uranium and Plutonium phase.
- Plutonium plus ferrous sulphamate – Pu +3 aqueous oxidation state.
- Advantages: 1)Lower waste volumes 2)TBP less volatile than Hexone 3) Lower operating costs
- Disadvantages: 10 million gallons of water discharged each day 1956-1990.

Reprocessing Plant

Five plants were built for chemically reprocessing irradiated spent fuel and recovering plutonium.

The PUREX Plant was the largest. It's about 304 meters (1000 feet) long, 18 meters (60 feet) wide, and 30 meters (100 feet) tall.

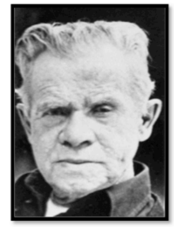
PUREX



40 percent of its height is underground.

5 foot concrete walls for shielding.

We don't know so let's be conservative.



Harold McCluskey

- Working in Pu Reclamation Facility.
- Cation exchange column degradation over 4 month period.
- 4 months standing idle due to union strike.
- Harold was recovering Americium with 7 molar nitric acid.
- Organic resin column degradation plus nitrate = TNT explosive
- Atomic Man - Exposed to 500 times the occupational standard for Americium.

Federal and state regulations that changed how the chemistry was looked at

- **United States Atomic Energy Commission (AEC)**
- **United States Environmental Protection Agency (EPA)**
- **Resource Conservation and Recovery Act (RCRA)**
- **Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)**
- **Washington State Model Toxics Control Act, (MTCA usually mis-pronounced Motca)**
  - **Chapter 70.105D RCW**

AEC was an agency of the United States government established after World War II by Congress to foster and control the peacetime development of atomic science and technology.

EPA created for the purpose of protecting human health and the environment by writing and enforcing regulations based on laws passed by Congress. The EPA was proposed by President Richard Nixon and began operation on December 2, 1970, after Nixon signed an executive order.

Resource Conservation and Recovery Act (**RCRA**), enacted in 1976, is the principal federal law in the United States governing the disposal of solid waste and hazardous waste.

Comprehensive Environmental Response, Compensation, and Liability Act (**CERCLA**), a 1980 law commonly known as Superfund, authorizes EPA to respond to releases, or threatened releases, of hazardous substances that may endanger public health, welfare, or the environment.

The Washington State Model Toxics Control Act, Chapter 70.105D RCW ("MTCA" or the

Washington State - MTCA 1989

- MTCA is the state counterpart to CERCLA
  - one of the biggest differences between the two is that MTCA treats petroleum as a regulated hazardous substance.
  - significant because petroleum products are the only substances of concern at many contaminated sites such as gas stations, and properties with old heating fuel tanks.
- The Washington State Model Toxics Control Act, Chapter 70.105D RCW ("MTCA" or the "Act") creates a comprehensive regulatory scheme to identify, investigate, and clean up contaminated properties that are, or may be, a threat to human health or the environment. The cost of cleaning up such properties can be extraordinarily high.

Washington State - MTCA 1989

- MTCA was approved by voter initiative in 1988 and adopted by the legislature in 1989
  - it raises funds to clean up contaminated sites
  - prevents the creation of future hazardous waste sites.
- Since the adoption of MTCA, private parties that are potentially liable under the Act have funded most of the cleanups conducted in Washington.
- MTCA's liability reach is so extensive that nearly any person with any connection to a contaminated property is potentially liable for the entire cost of the cleanup. Understanding and controlling that risk is essential.

Another difference is that MTCA allows potentially liable persons to recover attorneys' fees and expenses spent litigating liability and damages with other potentially liable persons. CERCLA does not allow recovery of such attorneys' fees or expenses.

For these reasons, most cost recovery actions in Washington are brought under MTCA rather than CERCLA.

MTCA Cleanup Levels and Risk Calculation (CLARC) Web Site

Chemical Name	CAS #	Ground Water Method A (µg/L)	Ground Water Method B Non cancer (µg/L)	Ground Water Method B Cancer (µg/L)	Ground Water Maximum Contaminant Level Goal (µg/L)	Ground Water Maximum Contaminant Level (µg/L)	Ground Water WA Maximum Contaminant Level (µg/L)	RfDo Oral Reference Dose (mg/kg-day)	Source	CPFo Oral Cancer Potency Factor (kg-day/mg)	Source
acenaphthene	83-32-9		9.60E+02					6.00E-02	I		
acenaphthylene	208-96-8										
acephate	30560-19-1		6.40E+01	1.01E+01				4.00E-03	I	8.70E-03	I
acetaldehyde	75-07-0										
acetochlor	34256-82-1		3.20E+02					2.00E-02	I		
acetone	67-64-1		7.20E+03					9.00E-01	I		
acetone cyanohydrin	75-86-5										
acetonitrile	75-05-8										
acetophenone	98-86-2		8.00E+02					1.00E-01	I		
acifluorfen, sodium	62476-59-9		1.04E+02					1.30E-02	I		
acrolein	107-02-8		4.00E+00					5.00E-04	I		
acrylamide	79-06-1		1.60E+01	8.75E-02	0.00E+00	1.00E+03		2.00E-03	I	5.00E-01	I
acrylic acid	79-10-7		4.00E+03					5.00E-01	I		
acrylonitrile	107-13-1		3.20E+02	8.10E-02				4.00E-02	A	5.40E-01	I
alachlor	15972-60-8		1.60E+02	1.56E+00	0.00E+00	2.00E+00	2.00E+00	1.00E-02	I	5.60E-02	C
alar	1596-84-5		2.40E+03	4.86E+00				1.50E-01	I	1.80E-02	C
aldicarb	116-06-3		1.60E+01					1.00E-03	I		
aldicarb sulfone	1646-88-4		1.60E+01					1.00E-03	I		
aldrin	309-00-2		2.40E-01	2.57E-03				3.00E-05	I	1.70E+01	I

PCB Congener EPA SW-846 Method 1668

Concentration:
1-2000 ng/kg

Precision:
Not Applicable.

Detection:
Method 1668A was validated and preliminary data were collected in a single laboratory. Estimated Method Detection Limits (EMDLs) and Estimated Minimum Levels (EMLs) were determined with common laboratory interferences present. Those provided are the EMDLs for solid/semi-solid samples; additional data are provided in the method. Without interferences, EMDLs and EMLs will be, respectively, 5 and 10 pg/L for aqueous samples, 0.5 and 1.0 ng/kg for soil, tissue, and mixed-phase samples, and EMLs for extracts will be 0.5 pg/uL.

Revision Number:
Revision A, December 1999

Instrument used for this test:
HRGC/HRMS

Sampling and Analysis Changed from Industrial to Human and Ecological risk

- EPA Contract Laboratory Program 1980 to analyze "superfund samples" in a broad based manner. Setup to analyze quickly for enforcement.
- ASTM D6956-03 "Standard Guide for Demonstrating and Assessing Whether a Chemical Analytical Measurement System Provides Analytical Results Consistent with Their Intended Use"
- EPA "Guidance for the Data Quality Objectives Process" QA/ G-4

From secrecy to legally defensible results

- EPA came out with guidance on defensible methods, defensible sampling, project planning, accreditations, verification and validation.
- Statistical defensibility.
- Technical requirements for labs producing Hanford data.

Personnel
- ✓ Uncertainty
- ✓ Instrument calibration
- ✓ QC procedures
- ✓ Record retention
- ✓ Test methods and validation
- ✓ Standards traceability
- ✓ Control charting
- ✓ Detection and quantitation levels
- ✓ Corrective action

Teaching people about Hanford is important

Perception

Reality

Because of environmental protections, improvements in chemical testing , and defensible results, we can be sure the river is safe for recreation and all uses.

And we can devise ways to clean soil or ensure it is removed from areas where it might further contaminate groundwater.

From field to classroom

Cleanup will continue for another 40 years. It is important to engage students.
Describe student projects at CBC

Table 3.1.1: **Nitrate Summary Statistics: 2012 – C Tank Farm**

Nitrate				
	Northeast	Northwest	Southwest	Southeast
Sample Size	13	7	22	8
Mean (ppm)	38.8	14.37	40.20	81.95
Standard Deviation (ppm)	4.62	4.41	9.85	17.19
Range (ppm)	13.8	10	29.4	50.3
Minimum Usual Value (ppm)	29.56	5.55	20.5	47.57
Maximum Usual Value (ppm)	48.04	23.19	59.90	116.33

Based upon the information given in table 3.1.1 the maximum usual value for the nitrate concentration in the SE sector is 116.33 ppm. One data value has been flagged for further investigation which belongs to well 299-E27-14. On September 7, 2012 a nitrate concentration level of 118.0 ppm was recorded in the southeastern sector, which is above the maximum usual value stated above. Calculations used to find the typical nitrate concentrations beneath the C Tank Farm in 2012 can be found in appendix B.

I think you guys have the key to answering the main question which was what is the nitrate to technetium-99 ratio at E27-23 and at E27-7.

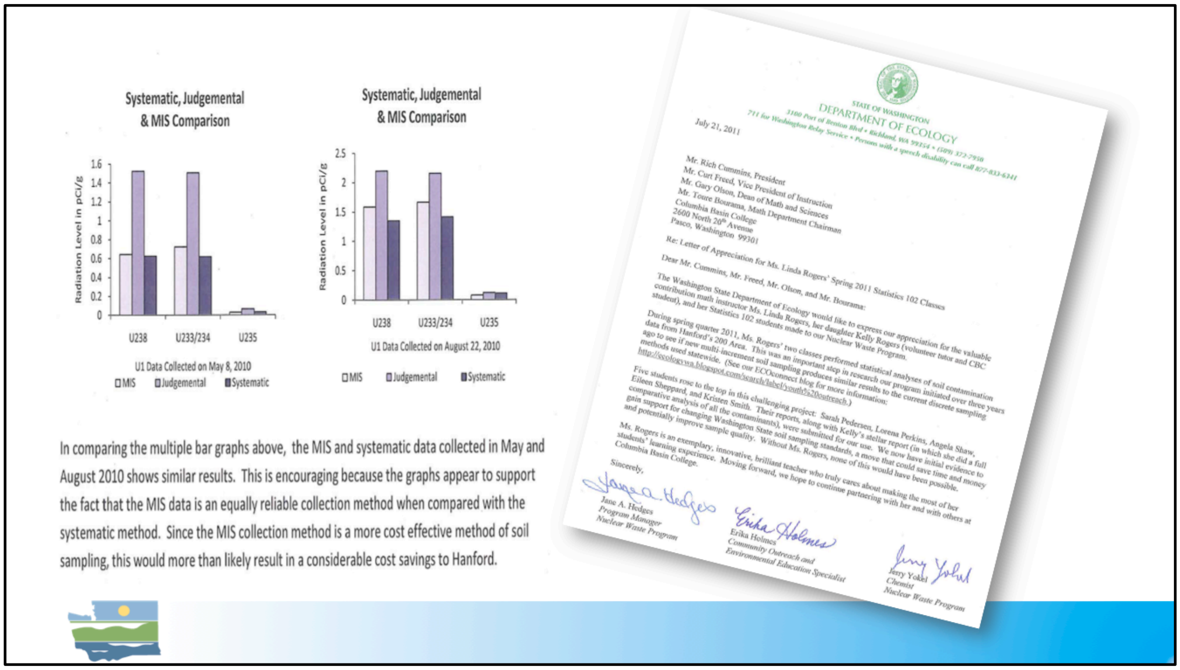
I didn't really think we would have solved this question so fast; but nitrate-sulfate ratio is the key!!!

...You have discovered the sulfate and nitrate concentrations in one area of C farm have a straight line correlation

From this ratio we should be able to find an associated waste type or certainly eliminate many waste types as possible candidates.

Columbia Basin College statistics classes;

One class examined groundwater contamination at the C-Tank Farm.



STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
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711 for Washington Relay Service • Persons with a speech disability can call 877-833-6341

July 21, 2011

Mr. Rich Cummins, President
Mr. Curt Freed, Vice President of Instruction
Mr. Gary Olson, Dean of Math and Sciences
Mr. Toure Bourama, Math Department Chairman
Columbia Basin College
2600 North 20th Avenue
Pasco, Washington 99301

Re: Letter of Appreciation for Ms. Linda Rogers' Spring 2011 Statistics 102 Classes

Dear Mr. Cummins, Mr. Freed, Mr. Olson, and Mr. Bourama:

The Washington State Department of Ecology would like to express our appreciation for the valuable contribution math instructor Ms. Linda Rogers, her daughter Kelly Rogers (volunteer tutor and CBC student), and her Statistics 102 students made to our Nuclear Waste Program.

During spring quarter 2011, Ms. Rogers' two classes performed statistical analyses of soil contamination data from Hanford's 200 Area. This was an important step in research our program initiated over three years ago to see if new multi-increment soil sampling produces similar results to the current discrete sampling methods used statewide. (See our ECOconnect blog for more information: http://ecologywa.blogspot.com/search/label/youth%20outreach.)

Five students rose to the top in this challenging project: Sarah Pedersen, Lorena Perkins, Angela Shaw, Eileen Sheppard, and Kristen Smith. Their reports, along with Kelly's stellar report (in which she did a full comparative analysis of all the contaminants), were submitted for our use. We now have initial evidence to gain support for changing Washington State soil sampling standards, a move that could save time and money and potentially improve sample quality. Without Ms. Rogers, none of this would have been possible.

Ms. Rogers is an exemplary, innovative, brilliant teacher who truly cares about making the most of her students' learning experience. Moving forward, we hope to continue partnering with her and with others at Columbia Basin College.

Sincerely,

Jane A. Hedges
Program Manager
Nuclear Waste Program

Erika Holmes
Community Outreach and Environmental Education Specialist

Jerry Yokel
Chemist
Nuclear Waste Program

Sampling technique proved statistically valid and Did we change the rule?

Chemists at Ecology 23 Total

Job Title	Per Name	Org Partial	Work Loc Abbrev NM	Mail Stop	Desk Phone	per email ad
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CHEMIST 2	Powers, Kelsey	EAP	ECY ManLab		(360) 871-8824	kpow461@ecy.
CHEMIST 2	Wood, Rebecca B	EAP	ECY ManLab		(360) 871-8811	rewo461@ecy.
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CHEMIST 3	Iwenofu, Samuel	HWTR	ECY HQ	47600	(360) 407-6346	siwe461@ecy.
CHEMIST 3	Jones, Meredith J	EAP	ECY ManLab		(360) 871-8833	mosb461@ecy
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CHEMIST 4	Ginder, Kamilee	EAP	ECY LabAccred		(360) 871-8841	kgin461@ecy.w
CHEMIST 4	Huntamer, Dickey	EAP	ECY ManLab		(360) 871-8809	dihu461@ecy.w
CHEMIST 4	Kammin, Bill	EAP	ECY HQ	47600	(360) 407-6964	wkam461@ecy
CHEMIST 4	Momohara, Dean	EAP	ECY ManLab		(360) 871-8808	dmom461@ecy
CHEMIST 4	Rue, Alan	EAP	ECY LabAccred		(360) 871-8844	arue461@ecy.
CHEMIST 4	Smith-Jackson, Noe'l	NWP	ECY RCL		(509) 372-7926	nsmi461@ecy.
CHEMIST 4	Stone, Alex B	HWTR	ECY HQ	47600	(360) 407-6758	alst461@ecy.w
CHEMIST 4	Weakland, John A	EAP	ECY ManLab		(360) 871-8820	jwea461@ecy.
CHEMIST 4	Yokel, Jerry W	NWP	ECY RCL		(509) 372-7937	jyok461@ecy.w

Will your students be part of the future Hanford Workforce?

References

- Benedict,M., Pigford,T.H., Levi,H.W. (1981) Nuclear Chemical Engineering McGraw-Hill Book Company
- The U.S. Department of Energy (1996) DOE/EM-0266 Closing the Circle on the Splitting of the Atom Office of Environmental Management
- U.S. Department of Energy (1997, January) DOE/EM-319 Linking Legacies Office of Environmental Management
- ASTM D6956-03 "Standard Guide for Demonstrating and Assessing Whether a Chemical Analytical Measurement System Provides Analytical Results Consistent with Their Intended Use" (2003)

Questions?

Hanford Learning.org

- HanfordLearning.org was founded to create nonpartisan, high-quality educational materials and facilitate experiential learning about Hanford for Washington students. We are funded by a Public Participation Grant through the Washington State Department of Ecology.
- We provide free educational support to Washington educators:
- Classroom presentations about Hanford
- Tailor-made lesson plans and activities
- Online curricula
- **Email: info@hanfordlearning.org**
  Phone: +1(509)416-6552
  Mailing Address: P.O. Box 4724, West Richland, WA 99353

Department of Energy OpenNet System

- https://www.osti.gov/opennet/index.jsp

- The OpenNet database provides easy, timely access to over 485,000 bibliographic references and 140,000 recently declassified documents, including information declassified in response to Freedom of Information Act requests. In addition to these documents, OpenNet references older document collections from several DOE sources.

The Manhattan Project https://www.osti.gov/opennet/manhattan_resources.jsp

- *The Manhattan Project: An Interactive History*
The intent of this website history is to provide an informative, easy to read and navigate, comprehensive overview of the Manhattan Project. Five main topical areas–Events, People, Places, Processes, and Science–are further divided into sub-sections, each with an introductory page and as many as a dozen or more sub-pages.
- *Manhattan District History*
General Leslie Groves, head of the Manhattan Engineer District, in late 1944 commissioned a multi-volume history of the Manhattan Project called the *Manhattan District History*. The classified history was "intended to describe, in simple terms, easily understood by the average reader, just what the Manhattan District did, and how, when, and where." The volumes record the Manhattan Project's activities and achievements in research, design, construction, operation, and administration, assembling a vast amount of information in a systematic, readily available form. The *Manhattan District History* contains extensive annotations, statistical tables, charts, engineering drawings, maps, and photographs. Only a handful of copies of the history were prepared.

The PNNL Hanford Online Environmental Information Exchange (PHOENIX) was launched to improve public access to public data and to enhance decision making processes at the Hanford Site by providing query, analysis, visualization, and extraction tools for basic Hanford Site characterization information in an intuitive map-based environment.