Application of $^{129}$I/I Ratios in Groundwater Studies Conducted at Los Alamos National Laboratory, New Mexico

Patrick Longmire, Ph.D., Michael Dale, Kim Granzow, and Stephen Yanicak

DOE Oversight Bureau, New Mexico Environment Department
1183 Diamond Drive, Suite B, Los Alamos, NM 87544
Application of $^{129}\text{I}/\text{I}$ Ratios in Groundwater Studies Conducted at Los Alamos National Laboratory, New Mexico

- Natural and Anthropogenic Sources of $^{129}\text{I}$odine
- Analytical Methods
- Hydrogeochemical and Hydrological Setting (groundwater mixing) at LANL
- Distribution of $^{129}\text{I}$ and $^{129}\text{I}/\text{I}$ ratios in groundwater
- Summary and Conclusions

Acknowledgment: "This material is based upon work supported by the Department of Energy Office of Environmental Management under Award Number DE-EM0002420."

Disclaimer: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."
Los Alamos National Laboratory, New Mexico

Source: LANL 2007
Natural and Anthropogenic Sources of $^{129}$Iodine

Natural sources of $^{129}$I include cosmic spallation of xenon and fission of uranium occurring in the subsurface.

Fission of uranium releases $^{129}$I to groundwater and the atmosphere from volcanic emissions. Residence times for $^{129}$I in the atmosphere and oceans are two weeks and 40,000 years, respectively.

Anthropogenic $^{129}$I is a fission product of $^{235}$U and $^{239}$Pu processing at nuclear facilities. Isotope ratios of $^{129}$I/I increased in some parts of the world during the 1960’s resulting from atmospheric nuclear testing. Atmospheric $^{129}$I/I ratios ranged from $10^{-7}$ to $10^{-4}$ in the past.
129Iodine and 36Chlorine
Accelerator mass spectrometry

239Plutonium and Tritium
Alpha spectrometry
Electrolytic enrichment and liquid scintillation

Oxyanions
Liquid chromatography/mass spectrometry/mass/spectrometry
Conceptual Model of Groundwater Movement Through the Vadose Zone to the Regional Aquifer, Los Alamos National Laboratory, New Mexico

Source: LANL 2012
Elevated $^{129}$I/I Ratios, $^3$H, and/or Cr(VI) Concentrations In Perched-Intermediate Depth Groundwater Zones

Sources of $^3$H, $^{129}$I, $^{235}$U, $^{239}$Pu, Cr(VI)

Source of $^3$H, $^{129}$I, and $^{239}$Pu

Elevated $^{129}$I/I ratios, $^3$H, and/or Cr(VI)

Groundwater-Flow Paths in Perched Intermediate Depth Groundwater
Elevated $^{129}$I/$^{127}$I Ratios, $^3$H, and Cr(VI) Concentrations In the Regional Aquifer

Sources of Cr(VI), $^3$H, $^{129}$I, and $^{239}$Pu

Major Source of Cr(VI)

Source of $^3$H, $^{129}$I, and $^{239}$Pu

Groundwater-Flow Paths in the Upper Portion of the Regional Aquifer
Residual $^{239}\text{Pu}$ occurs in the alluvium and Bandelier Tuff within Mortandad Canyon. $^{129}\text{I}$ is produced from processing of $^{239}\text{Pu}$.
Eh-pH Diagram for Iodine at 25°C and 1 Bar
(Total dissolved I concentration = 10^{-8} \text{ mol/L. Source: Um et al., 2004})

Perched-Intermediate Depth Groundwater and Regional Aquifer
$^{129}\text{I}/\text{I}$ Ratios in Los Alamos County Supply Wells, New Mexico

Mean $^{129}\text{I}/\text{I} = 101 \times 10^{-15}$ (atom basis)

$1\sigma$ Errors for Measurements
O-1, ±7.66; O-4, ±11.69; PM-1, ±10.95
PM-2, ±11.75; PM-3, ±15.0; PM-4, ±261;
and PM-5, ±134.86

Percent Error: 13 - 36
Atoms \(^{129}\text{I}/\text{g Water in Supply Wells, Los Alamos County, New Mexico}\)

Mean \(\log_{10} \text{atoms } ^{129}\text{I}/\text{g H}_{2}\text{O} = 4.24386 \times (17,533 \text{ atoms } ^{129}\text{I}/\text{g H}_{2}\text{O})\)

1σ Errors for Measurements (\(\log_{10}\))
- O-1, ±2,616 (3.418)
- O-4, ±5,551 (3.744)
- PM-1, ±5,756 (3.760)
- PM-2, ±5,641 (3.751)
- PM-3, ±7,051 (3.848)
- PM-4, ±76,497 (4.884)
- PM-5, ±23,649 (4.374)

Percent Error: 27 - 53
Average $^{129}\text{I}/\text{I}$ Ratios in Selected Monitoring Wells Downgradient From Sources of $^{129}\text{I}$odine, Los Alamos National Laboratory, NM

Mean $^{129}\text{I}/\text{I} = 6,939(e-015)$ (atom basis)

1σ Errors for Measurements
MCOI-5, ±167.07; MCOI-6, ±431.01; R-28, ±316.66; R-42, ±416.62; SCI-1, ±485.72; SCI-2, ±457.67; and R-50(1), ±90.40

Percent Error: 4 – 13, R-50(1) = 24
Atoms $^{129}\text{I}/\text{g Water}$ in Selected Monitoring Wells Downgradient From Sources of $^{129}\text{I}$odine, Los Alamos National Laboratory, NM

Mean $\log_{10} \text{atoms}^{129}\text{I}/\text{g H}_2\text{O} = 6.1400$ (1,380,248 atoms $^{129}\text{I}/\text{g H}_2\text{O}$)

$1\sigma$ Errors for Measurements ($\log_{10}$)
- MCOI-5, ±50,536 (4.704)
- MCOI-6, ±136,924 (5.1365)
- R-28, ±135,445 (5.132)
- R-42, ±85,084 (4.930)
- SCI-1, ±201,882 (5.305)
- SCI-2, ±143,120 (5.156)
- R-50(1), ±27,057 (4.432)

Percent Error: 2 – 14, R-50(1) = 33
$^{129}\text{I}/\text{I}$ Ratios Versus Tritium in Groundwater, Los Alamos National Laboratory, New Mexico

Similar Groundwater-Flow Path(s)

Groundwater Mixing in Regional Aquifer

Tritium (pCi/L)

$^{129}\text{I}/\text{I}(10^{-15})$
$^{129}\text{I}/^{127}\text{I}$ Ratios Versus $^{36}\text{Cl}/\text{Cl}$ Ratios in Groundwater, Los Alamos National Laboratory, New Mexico

Potential Groundwater-Flow Paths From Perched Intermediate Zones to Regional Aquifer

Los Alamos Canyon (former reactor releases of $^{36}\text{Cl}$)

Mixing in Regional Aquifer

LANL Background

$^{129}\text{I}/^{127}\text{I}(10^{-15})$
Summary and Conclusions

• The radioisotope $^{129}$I ($T_{1/2} = 15.7$ Myrs) derived from $^{235}$U and $^{239}$Pu processing at Los Alamos National Laboratory is locally detected in groundwater above background $^{129}$I activities.

• This isotope provides a unique tracer for groundwater investigations conducted at LANL that helps to identify source releases linked to groundwater-flow paths in aquifers.

• Aquifer systems are subject to binary and ternary mixing of natural- and industrial-derived waters containing iodate, chromate, and other chemicals.

• Local background ratios of $^{129}$I/I vary from $54 \times 10^{-15}$ to $220 \times 10^{-15}$ in the regional aquifer (supply wells).
Summary and Conclusions

- Anthropogenic ratios of $^{129}\text{I}/\text{I}$ range from $1,252 \times 10^{-15}$ to $17,367 \times 10^{-15}$ within perched-intermediate depth groundwater in Mortandad Canyon.

- Anthropogenic ratios of $^{129}\text{I}/\text{I}$ range from $2,690 \times 10^{-15}$ to $11,688 \times 10^{-15}$ within the regional aquifer in Mortandad Canyon (centroid of chromium plume).

- Variability in $^{129}\text{I}/\text{I} \times 10^{-15}$ ratios and concentrations of anthropogenic iodate is controlled by non-uniform source releases of this isotope and iodate over time and non-uniform mixing (ternary) of groundwater in different aquifers.
Supplemental Slides
Plume Map of Total Dissolved Chromium and Elevated Above Background $^{129}$I/I Ratios within the Regional Aquifer, Los Alamos National Laboratory

Sources of $^{239}$Pu Processing

Treated TA-21 Effluent Discharge ($^3$H, $^{239}$Pu, and $^{129}$I)

Treated TA-35/50/55 Effluent Discharge ($^3$H, $^{239}$Pu, and $^{129}$I)

Elevated $^{129}$I/I Ratios in Groundwater
### Iodine Yield, Percent Per Fission

([http://www-nds.iaea.org/sgnucdat/c3.htm](http://www-nds.iaea.org/sgnucdat/c3.htm))

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Thermal</th>
<th>Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{232}$Th</td>
<td>not fissile</td>
<td>0.431 ± 0.089</td>
</tr>
<tr>
<td>$^{233}$U</td>
<td>1.63 ± 0.26</td>
<td>1.73 ± 0.24</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>0.706 ± 0.032</td>
<td>1.03 ± 0.26</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>not fissile</td>
<td>0.622 ± 0.034</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>1.407 ± 0.086</td>
<td>1.31 ± 0.13</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>1.428 ± 0.36</td>
<td>1.67 ± 0.36</td>
</tr>
</tbody>
</table>
$^{129}\text{I}/\text{I}$ Ratios in Upper Portion of the Regional Aquifer, Los Alamos National Laboratory, New Mexico

Mean $^{129}\text{I}/\text{I} = 75 \times 10^{-15}$ (atom basis)

1σ Errors for Measurements:
- R-24, ±26.80
- R-34, ±8.09
- R-35b, ±7.85
- R-36, ±8.82
- R-47, ±4.82
- and R-9, ±12.42
Atoms $^{129}$I/g Water in the Upper Portion of the Regional Aquifer, Los Alamos National Laboratory, New Mexico

Mean $\log_{10}$ atoms $^{129}$I/g H$_2$O = 4.0327 (10,782 atoms $^{129}$I/g H$_2$O)

$1\sigma$ Errors for Measurements ($\log_{10}$)
R-24, ±13,730 (4.138); R-34, ±3,809 (3.581);
R-35b, ± 2,916 (3.465); R-36, ±11,780 (4.071);
R-47, ±1,846 (3.266); and R-9, ±4,064 (3.609)
$^{129}\text{I}/\text{I}$ Ratios in Selected Monitoring Wells Near or in Los Alamos Canyon, Los Alamos National Laboratory, New Mexico

Mean $^{129}\text{I}/\text{I} = 200(\text{e-015})$ (atom basis)

1σ Errors for Measurements
LAOI-3.2, ±35.05; LAOI-3.2a, ±111.57; TA-53i, ±27.35; and R-6i, ±67.17;
Atoms $^{129}$I/g Water in Selected Monitoring Wells Near or in Los Alamos Canyon, Los Alamos National Laboratory, New Mexico

Mean $\log_{10}$ atoms $^{129}$I/g H$_2$O = 4.6065 (40,411 atoms $^{129}$I/g H$_2$O)

1σ Errors for Measurements ($\log_{10}$)
LAOI-3.2, ±10,422 (4.018); LAOI-3.2a, ±32,993 (4.518); TA-53i, ±8422 (3.925); and R-6i, ±19,644 (4.293)