Polychlorinated Biphenyl (PCB) IN Precipitation, Snowpack, Baseflow and Stormwater in the Upper and Middle Rio Grande Watershed with Special Emphasis on Los Alamos National Laboratory

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The data presented was collected by Los Alamos National Laboratory and New Mexico Environment Department Surface Water Quality Bureau and the DOE Oversight Bureau.

The samples were collected within the last 6 years (2005 – 2011).

All data analyzed using EPA Method 1668A.

All data has been blank corrected.
Polychlorinated biphenyls (PCBs) are composed of two benzene rings (12 carbon atoms) forming a biphenyl with 1 to 10 chlorine atoms attached.

209 possible congeners, based on the number and location of chlorine atoms attached to carbon atoms in the benzene rings

PCB homologues are groups of PCB congeners containing the same number of chlorine atoms (1 – 10). Homologue patterns can be used to identify unique mixtures due to different source terms
**PCB Basics**

**Polychlorinated Biphenyls**
- Production began in 1929, banned in 1977
- Between 1930 and 1975 - 1,400 million pounds (635 million kg) produced in US
- in 1976, 95% of all capacitors were filled with PCBs representing 70% of US production
- 5% of all transformers were filled with PCBs representing 30% of US Production (IRAC1979)

**Toxicity**
- PCBs have been shown to cause cancer in animals. PCBs have also been shown to cause a number of serious non-cancer health effects in animals, including effects on the immune system, reproductive system, nervous system, endocrine system and other health effects.
  - probable human carcinogens
- the types of PCBs likely to be bioaccumulated in fish and bound to sediments are the most carcinogenic PCB mixtures (http://www.epa.gov/osw/hazard/tds/pcbs/pubs/effects.htm).

**Aroclors**
- Monsanto brand-name mixtures of PCB congeners (1930-1977)
- Numbering convention (e.g. 1254, 1260)
  - First two digits = Number of carbon atoms in structure (12)
  - Second two digits = Percentage of weight attributable to chlorine (54%, 60%)
Aroclor Common Uses (IARC 1979)

- 1016 - Capacitors
- 1221 - Capacitors, gas-transmission turbines, rubbers, adhesives
- 1232 - Hydraulic fluids, rubbers, adhesives
- 1242 - Transformers, heat transfer, hydraulic l/lubricants (hydraulic fluids, gas-transmission turbines), plasticizers (rubbers, carbonless paper), adhesives
- 1248 - Hydraulic fluids, lubricants, plasticizers, adhesives
- 1254 - Capacitors, transformers, hydraulic/lubricants (vacuum pumps, hydraulic fluids), plasticizers (rubbers and synthetic resins), adhesives, wax extenders, de-dusting agents, inks, cutting oils, pesticide extenders, sealants and caulking compounds
- 1260 - Transformers, hydraulic fluids, synthetic resins, de-dusting agents
- 1268 – Plasticizers (rubbers, synthetic resins), wax extenders
Products that may contain PCBs include:

- Transformers and capacitors
- Other electrical equipment including voltage regulators, switches, reclosers, bushings, and electromagnets
- Oil used in motors and hydraulic systems
- Old electrical devices or appliances containing PCB capacitors
- Fluorescent light ballasts
- Cable insulation
- Thermal insulation material including fiberglass, felt, foam, and cork
- Adhesives and tapes
- Oil-based paint
- Caulking
- Plastics
- Carbonless copy paper
- Floor finish
Normalize total PCB in water by dividing by suspended sediment concentration (SSC) using the equation below:

\[
\text{Total PCB in water (pg/L)}/ \text{SSC (g/L)} = \text{Total PCB in suspended sediments (pg/g)}
\]

This results in a calculated value for total PCB in the suspended sediments.

This value is used to evaluate if you have elevated levels of PCBs in the suspended sediments - indicating a potential source term.

or

The watershed has low or baseline levels of PCB but excessive levels of suspended sediments in stormwater.
Total PCB in Suspended Sediments in Stormwater

<table>
<thead>
<tr>
<th>Location</th>
<th>Mean (ng/g ppb)</th>
<th>Median (ng/g ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Rio Grande (n=43)</td>
<td>0.71</td>
<td>0.15</td>
</tr>
<tr>
<td>Ephemeral Tributaries (n=60)</td>
<td>2.17</td>
<td>0.6</td>
</tr>
<tr>
<td>Urban Runoff LA County (n=49)</td>
<td>63</td>
<td>34</td>
</tr>
<tr>
<td>Rio Grande at Alameda (n=9)</td>
<td>71</td>
<td>73</td>
</tr>
<tr>
<td>LANL Watersheds (n=211)</td>
<td>263</td>
<td>51</td>
</tr>
<tr>
<td>Below LANL SWMUs (n=73)</td>
<td>1,299</td>
<td>57</td>
</tr>
</tbody>
</table>

Outliers > 90th 90th Percentile
Outliers < 10th 10th Percentile
Median
Mean (Red Dot)
<table>
<thead>
<tr>
<th></th>
<th>Aroclor</th>
<th>1016</th>
<th>1242</th>
<th>1248</th>
<th>1254</th>
<th>1260</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-CBs</td>
<td></td>
<td>2</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Di-CBs</td>
<td></td>
<td>19</td>
<td>13</td>
<td>1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Tri-CBs</td>
<td></td>
<td>57</td>
<td>45</td>
<td>21</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td>Tetra-CBs</td>
<td></td>
<td>22</td>
<td>31</td>
<td>49</td>
<td>15</td>
<td>—</td>
</tr>
<tr>
<td>Penta-CBs</td>
<td></td>
<td>—</td>
<td>10</td>
<td>27</td>
<td>53</td>
<td>12</td>
</tr>
<tr>
<td>Hexa-CBs</td>
<td></td>
<td>—</td>
<td>—</td>
<td>2</td>
<td>26</td>
<td>42</td>
</tr>
<tr>
<td>Hepta-CBs</td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4</td>
<td>38</td>
</tr>
<tr>
<td>Octa-CBs</td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>7</td>
</tr>
<tr>
<td>Nona-CBs</td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
</tr>
<tr>
<td>Deca-CB</td>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

- Columns may not total 100% due to rounding; "—" signifies less than 1%.
- Lot-to-lot variability exists but has not been quantified.
- Impurities include chlorinated dibenzofurans and naphthalenes; see World Health Organization (WHO) (1993) for sample concentrations.
- Sources: Adapted from Silberhorn et al. (1990), ATSDR (1995).
Typical Homologue Distribution for Some Aroclors

Percent (%)

Mono-CBs | Di-CBs | Tri-CBs | Tetra-CBs | Penta-CBs | Hexa-CBs | Hepta-CBs | Octa-CBs | Nona-CBs | Deca-CB

1016 | 1242 | 1248 | 1254 | 1260
Rainfall demonstrates a bimodal distribution with peaks in the Di-CL and Te-CL homologue groups while snowpack demonstrates a shift toward higher chlorinated PCBs

Volatilization of lower chlorinated congeners in snowpack? Increased dust loading on snowpack – source of higher chlorinated congeners?
Upper Rio Grande and Chama River stormwater exhibits a bimodal homologue distribution with peaks in the Tri-CL and Hx-CL homologue groups.
Ephemeral tributary stormwater (red) does not have the same bimodal pattern as Rio Grande stormwater and there is a slight shift towards larger levels of higher chlorinated congeners.
Los Alamos County urban runoff (purple) displays smaller levels of the lower chlorinated congeners and a shift towards higher chlorinated congeners.
Rio Grande above Alameda stormwater (teal) shows a continued reduction of lower chlorinated congeners and the highest levels of Hx-CL and Hp-CL congeners.
Middle Los Alamos Canyon (black) homologue pattern is similar to what we see in the Rio Grande above Alameda
Aroclor 1254 was used as a cutting oil which was discharged into a septic tank which drained into small ephemeral drainage in Los Alamos Canyon.

LA-SMA-2 is the monitoring point for that drainage and the homologue pattern is unique to that drainage.
Summary

Baseline flows in the upper Rio Grande and tributaries, snowpack and precipitation are nearly always below the Human Health criteria.

Upper Rio Grande and ephemeral tributary stormwater often exceed the Human Health criteria and occasionally exceed the Wildlife Habitat criteria.

Los Alamos County urban runoff, Rio Grande above Alameda and LANL watersheds nearly always exceed the Human Health criteria and usually exceed the Wildlife Habitat criteria.

Stormwater below LANL SWMUs nearly always exceeds the Wildlife Habitat criteria and exceeds the Aquatic Life Acute criteria in twenty-five percent of the samples collected.

Normalizing total PCB in water data to SSC can be used to evaluate between baseline levels of PCBs and those impacted by potentially contaminated sources.

PCB homologue signatures can be used to differentiate between different source terms.
Total PCB in Stormwater in Los Alamos County

Aquatic Life acute Criteria 2,000,000 pg/L

WH Criteria 14,000 pg/L

Human Health Criteria 640 pg/L

LA County Yard - Pre D & D (n=20)
LA County Yard Post D & D (n=9)
Timber Ridge (n=14)
South Fork Acid Canyon (n=22)
DP Canyon (n=11)
Walnut, Kwage, Graduation, N-Fork Pueblo (n=8)

Outliers > 90th
90th Percentile
75th Percentile
Mean (Red Dot)
Median
25th Percentile
10th Percentile
Outliers < 10th

<table>
<thead>
<tr>
<th>Location</th>
<th>Mean</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA County Yard - Pre D &amp; D (n=20)</td>
<td>3,673,782</td>
<td>1,410,000</td>
</tr>
<tr>
<td>LA County Yard Post D &amp; D (n=9)</td>
<td>110,400</td>
<td>59,000</td>
</tr>
<tr>
<td>Timber Ridge (n=14)</td>
<td>58,830</td>
<td>34,100</td>
</tr>
<tr>
<td>South Fork Acid Canyon (n=22)</td>
<td>24,887</td>
<td>8,410</td>
</tr>
<tr>
<td>DP Canyon (n=11)</td>
<td>48,729</td>
<td>36,100</td>
</tr>
<tr>
<td>Walnut, Kwage, Graduation, N-Fork Pueblo (n=8)</td>
<td>24,230</td>
<td>3,040</td>
</tr>
</tbody>
</table>
Total PCB in Suspended Sediment in Los Alamos County Stormwater Runoff

Mean           1,192             160                   79                 75                   48                     17
Median           348             90                   59  21      47              8

Outliers > 90th
90th Percentile
75th Percentile
Mean (Red Dot)
Median
25th Percentile
10th Percentile
Outliers < 10th

LA County Yard Pre D & D (n=14)
LA County Yard Post D & D (n=6)
Timber Ridge (n=12)
South Fork Acid Canyon (n=19)
DP Canyon (n=8)
Walnut, Kwage, Graduation, North Fork Pueblo Canyons(n=8)

Mean 1,192 160 79 75 48 17
Median 348 90 59 21 47 8
PCB Homologue Distribution in Stormwater in DP Canyon

Percent of Total PCB (%)

Mono-Cl
Di-Cl
Tri-Cl
TE-Cl
Pe-Cl
Hx-Cl
Hp-Cl
Oc-Cl
No-Cl

E038 (DP above TA-21)  
(n=11)
PCB Homologue Distribution in Stormwater in DP, S. Fork Acid, N. Fork Pueblo, Walnut, and Kwage Canyons

Percent of Total PCB (%)
PCB Homologue Distribution in Typical LA Urban Runoff (n=40)
South Fork Acid, DP, Graduation, Kwage, Walnut, North Fork Pueblo Canyons
PCB Homologue Distribution in Typical Los Alamos County Urban Runoff vs Upper Rio grande Ephemeral Tributary Stormwater

Percent of Total PCB (%)
PCB Homologue Distribution
Typical LA Urban Runoff vs Las Alamos County Yard Runoff

Percent of Total PCB (%)
PCB Homologue Distribution
Typical LA Urban Runoff vs Timber Ridge Runoff

- Mo-CB
- Di-CB
- Tri-CB
- Te-CB
- Pe-CB
- Hx-CB
- Hp-CB
- Oc-CB
- No-CB
- De-CB

Typical LA Urban Runoff (n=40)
Timber Ridge drainage (n=14)
PCB Homologue Distribution
Timber Ridge Drainage vs LA-SMA-2 Stormwater

Percent of Total PCB (%)
Concentrations of PCBs in stormwater runoff from Los Alamos County urban areas are nearly always greater than the New Mexico Human Health water quality criteria.

Concentrations of PCBs in stormwater runoff from Los Alamos County urban areas are usually greater than the New Mexico Wildlife Habitat water quality criteria.

Average concentrations of PCB in Los Alamos County urban runoff (0.034ug/L; n=55) are 2.4 times the New Mexico Wildlife Habitat water quality criteria (0.014 ug/L). Median value was 0.017 ug/L.

Average concentration of PCB in suspended sediments in Los Alamos County urban runoff is 61 ng/g (ppb); (n=47). Median value was 34 ng/g (ppb).

Using an average concentration of 61 ng/g in suspended sediments, the suspended sediment concentration would have to be reduced to 230 mg/L to meet the WH Habitat Criteria.

Recent work at the Los Alamos County Yard (future Trinity development site) has reduced the average PCB concentrations in stormwater by over 33 times and the average levels in suspended sediment by 7.5 times.
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