Impacts of Volatile Organic Compounds from Compost on Ozone Formation

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and Greg Kester, CASA.

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Funding: CASA, CalRecycle, and previously from StopWaste.org, Composting Businesses, and USDA.
My interests and background

• Air quality, and also water quality as well

• All areas of Environmental Chemistry:
  Agriculture, transportation, ecology, clinical, mines…

• Recent VOC-ozone projects -- 7 papers published
  (plus 2 reports.)
  – Insecticide solvents and oil pesticides
  – Dairy and livestock studies: animals, fresh waste, feeds
  – Green scrap compost, biosolids co-composting

• Finding Solutions – practical, cost-effective, sustainable
Field Team and Apparatus for VOC-to-ozone

Spring 2010, studying VOCs from post-composting over-sized material
City of Santa Rosa
Biosolids co-composting Facility – lava rock biofilter
One figure to summarize the main conclusion: compost VOCs are generally weak.
Good ozone vs. bad ozone -- and where does bad ozone come from?

Ozone in the stratosphere (higher than airplanes) is good -- it protects us from the strongest ultraviolet light from the sun.

Ozone at ground level hurts our lungs, and comes from reactions between sunlight and 2 pre-cursors: 

- nitrogen oxides (NO$_x$),
- volatile organic compounds (VOCs)
Estimates are based on the most recent data (2004 – 2006). EPA will not designate areas as nonattainment on these data, but likely on data from 2006 – 2008 or later, which we expect to show improved air quality.

Counties with Monitors Violating the 2008 8-Hour Ozone Standard of 0.075 parts per million (ppm)

(based on 2004-2006 Air Quality Data)

Notes:

1 345 monitored counties violate the 2008 8-hour ozone standard of 0.075 parts per million (ppm).
2 Monitored air quality data can be obtained from the AQS system at http://www.epa.gov/ttn/airs/airsags/
California’s efforts so far:

• Develop an inventory of all VOC and NO\textsubscript{x} sources

• Large reductions in VOCs from urban sources

• Also reductions in VOCs from non-urban sources

• Reductions in NO\textsubscript{x} from cars

• New focus on NO\textsubscript{x} reductions from diesel engines
8-hour average $O_3$, max, South Coast
8-hour average ozone, max, SJV
Complexity of ozone formation

- Diverse mixture of VOCs, some unknown
- Even with multiple measurement techniques, there is no ‘total’ VOC
- Regulations treat all reactive VOCs equally on a pound-for-pound basis
- (Methane and a few others are exempt.)
- However, different VOCs are different molecules – they react differently
- Hence, Ozone Formation Potential
Great variation in formation potential (lbs. ozone per lb. VOC) even among similarly volatile molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Boiling Point, C</th>
<th>MIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>118</td>
<td>0.5</td>
</tr>
<tr>
<td>butyl acetate (n-)</td>
<td>118</td>
<td>0.89</td>
</tr>
<tr>
<td>octane</td>
<td>126</td>
<td>1.11</td>
</tr>
<tr>
<td>butanol (n-)</td>
<td>125</td>
<td>3.34</td>
</tr>
<tr>
<td>octene (1-)</td>
<td>121</td>
<td>3.45</td>
</tr>
<tr>
<td>toluene</td>
<td>111</td>
<td>3.97</td>
</tr>
<tr>
<td>xylene (para,ortho,meta)</td>
<td>139</td>
<td>4.2,7.5,10.6</td>
</tr>
</tbody>
</table>

Also considerable variation within a family of VOCs, e.g. alcohols, etc…

From a regulator: Unfortunately, this may be one issue where the legal system hinders [progress]. We are legally required … the inventory is calculated based on mass not reactivity.
What VOCs come from where?

**Microbial fermentation:**
wood input leads to wood alcohol (low subsequent reactivity)

**Internal combustion engines:**
leads to aromatics and aldehydes (high subsequent reactivity)
Mobile Ozone Chamber Assay (MOChA)

Graduate students Cody Howard and Doniche Derrick.
Mobile Ozone Chamber Assay (MOChA)

Separate lamp unit, with fans to aid temperature control.
Mobile Ozone Chamber Assay (MOChA)
We measure VOCs with multiple techniques. We assess the amount of ozone they actually form (over a few hours), directly at the source. Then match with a photo-chemical model calculation – to assert we have successfully accounted for the overall reactivity.
VOCs found from compost
3-6 Days old windrow

- Alcohols, 85%
- Others, 15%

2-3 Weeks old windrow

- Alcohols, 66%
- Others, 34%

### Comparative Analysis

- **3-6 Days old windrow**
  - Alcohols: 85%
  - Others: 15%
  - Alkenes / Alkynes: 0.9 ± 0.2%
  - Aromatic Hydrocarbons: 0.3 ± 0.1%
  - Ketones: 0.3 ± 0.3%
  - DMDS: < 0.1%
  - Acid / Esters / Others: 6.3 ± 4.3%

- **2-3 Weeks old windrow**
  - Alcohols: 66%
  - Others: 34%
  - Alkenes / Alkynes: 3.3 ± 1.1%
  - Aromatic Hydrocarbons: 1.0 ± 0.8%
  - Ketones: 1.2 ± 1.0%
  - DMDS: 0.1 ± 0.1%
  - Acid / Esters / Others: 14.6 ± 6.0%
From our recently accepted paper in Atmos. Environment.

Figure 3. Average contribution of VOC into the ozone formation according to their reactivity. (Urban VOC average is 3.6 to 3.7, depending on latest model revisions.)
Maximum Incremental Reactivity scale (MIR)
Conclusions

• Compost VOC emissions are dominated by low reactivity compounds

• All VOC sources can have a role in improving air quality – however some may be more important to manage for NO$_x$

• The relative value of VOC reductions is higher in urban areas vs. non-urban

• Future regulations (e.g. state implementation plans) will use reactivity more realistically
Additional Results

The use of a cap of oversized material (from sieving previously finished compost) reduces OFP from VOCs by 25% to 40%.

This could be a cost-effective mitigation, using otherwise un-sold material (which could go to grinder, or to landfill) and which adds compost microbes and aeration when mixed in during turning.

Biosolids co-composting generally shows similar VOCs, with minor differences not significantly affecting ozone formation.
Thank you, and questions?

pggreen @ ucdavis.edu
San Joaquin Valley and Los Angeles Calif. (same scale)
Ozone Cycle and the Dependence on NOx and VOC:

![Diagram of the ozone cycle](image)

Fig. 1. Ozone isopleth diagram showing the hypothetical response of peak 1 h average ozone concentrations within an air basin to changed levels of anthropogenic ROG and NOx emissions. Contour lines are lines of constant ozone concentration (ppb).

Winner, Cass and Harley, Atmos. Env. 1995
NOx show a delayed trend/forecast -- and monitoring data suggests may be slower
Total Reactive Organic Gases (non-exempt VOCs) have actually been quite greatly reduced.
Los Angeles VOC inventory -- and forecast

<table>
<thead>
<tr>
<th>Rankings</th>
<th>Source Category</th>
<th>Summer 2005</th>
<th>% of Total</th>
<th>Summer 2010</th>
<th>% of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LIGHT DUTY PASSENGER CARS</td>
<td>237.15</td>
<td>30.5%</td>
<td>142.82</td>
<td>23.5%</td>
</tr>
<tr>
<td>2</td>
<td>CONSUMER PRODUCTS</td>
<td>99.68</td>
<td>12.8%</td>
<td>102.57</td>
<td>16.9%</td>
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<tr>
<td>3</td>
<td>RECREATIONAL BOATS</td>
<td>65.56</td>
<td>8.4%</td>
<td>57</td>
<td>9.4%</td>
</tr>
<tr>
<td>4</td>
<td>OFF-ROAD EQUIPMENT (LAWN AND GARDEN)</td>
<td>54.93</td>
<td>7.1%</td>
<td>45.27</td>
<td>7.5%</td>
</tr>
<tr>
<td>5</td>
<td>ARCHITECTURAL COATINGS (PAINTS AND THINNERS)</td>
<td>44.58</td>
<td>5.7%</td>
<td>31.89</td>
<td>5.3%</td>
</tr>
<tr>
<td>6</td>
<td>PETROLEUM MARKETING (GASOLINE EVAPORATIVE LOSSES)</td>
<td>27.13</td>
<td>3.5%</td>
<td>26.96</td>
<td>4.4%</td>
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<tr>
<td>7</td>
<td>OFF-ROAD EQUIPMENT (OTHER)</td>
<td>29.69</td>
<td>3.8%</td>
<td>20.4</td>
<td>3.4%</td>
</tr>
<tr>
<td>8</td>
<td>COATINGS (PAINTS AND THINNERS - NON ARCHITECTURAL)</td>
<td>22.77</td>
<td>2.9%</td>
<td>20.39</td>
<td>3.4%</td>
</tr>
<tr>
<td>9</td>
<td>HEAVY DUTY GAS TRUCKS</td>
<td>29.63</td>
<td>3.8%</td>
<td>16.09</td>
<td>2.7%</td>
</tr>
<tr>
<td>10</td>
<td>OFF-ROAD EQUIPMENT (CONSTRUCTION AND MINING)</td>
<td>20.84</td>
<td>2.7%</td>
<td>15.54</td>
<td>2.6%</td>
</tr>
<tr>
<td>11</td>
<td>HEAVY DUTY DIESEL TRUCKS</td>
<td>15.7</td>
<td>2%</td>
<td>13.12</td>
<td>2.2%</td>
</tr>
<tr>
<td>12</td>
<td>GAS CANS</td>
<td>22.21</td>
<td>2.9%</td>
<td>13.09</td>
<td>2.2%</td>
</tr>
<tr>
<td>13</td>
<td>MOTORCYCLES</td>
<td>14.99</td>
<td>1.9%</td>
<td>12.19</td>
<td>2%</td>
</tr>
<tr>
<td>14</td>
<td>DEGREASING</td>
<td>9.09</td>
<td>1.2%</td>
<td>10.2</td>
<td>1.7%</td>
</tr>
<tr>
<td>15</td>
<td>CHEMICAL (PROCESS AND STORAGE LOSSES)</td>
<td>8.85</td>
<td>1.1%</td>
<td>9.67</td>
<td>1.6%</td>
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<tr>
<td>16</td>
<td>OFF-ROAD RECREATIONAL VEHICLES</td>
<td>9.08</td>
<td>1.2%</td>
<td>9.16</td>
<td>1.5%</td>
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<tr>
<td>17</td>
<td>AIRCRAFT*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
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<tr>
<td>18</td>
<td>PRINTING</td>
<td>6.54</td>
<td>0.8%</td>
<td>6.86</td>
<td>1.1%</td>
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<tr>
<td>19</td>
<td>OTHER (WASTE DISPOSAL)</td>
<td>7.45</td>
<td>1%</td>
<td>6.68</td>
<td>1.1%</td>
</tr>
<tr>
<td>20</td>
<td>ADHESIVES AND SEALANTS</td>
<td>3.15</td>
<td>0.4%</td>
<td>3.84</td>
<td>0.6%</td>
</tr>
<tr>
<td>21</td>
<td>PETROLEUM REFINING (EVAPORATIVE LOSSES)</td>
<td>3.1</td>
<td>0.4%</td>
<td>3.07</td>
<td>0.5%</td>
</tr>
<tr>
<td>22</td>
<td>FOOD AND AGRICULTURE (CROP PROCESSING AND WINERIES)</td>
<td>2.61</td>
<td>0.3%</td>
<td>2.7</td>
<td>0.4%</td>
</tr>
<tr>
<td>23</td>
<td>TRAINS</td>
<td>2.55</td>
<td>0.3%</td>
<td>2.45</td>
<td>0.4%</td>
</tr>
<tr>
<td>24</td>
<td>LIVESTOCK WASTE (LAYERS)</td>
<td>2.36</td>
<td>0.3%</td>
<td>2.36</td>
<td>0.4%</td>
</tr>
<tr>
<td>25</td>
<td>PESTICIDES</td>
<td>2.45</td>
<td>0.3%</td>
<td>2.09</td>
<td>0.3%</td>
</tr>
<tr>
<td>-</td>
<td>All other Sources</td>
<td>35.51</td>
<td>4.6%</td>
<td>30.42</td>
<td>5%</td>
</tr>
<tr>
<td>-</td>
<td>Total</td>
<td>777.59</td>
<td>100%</td>
<td>606.82</td>
<td>100%</td>
</tr>
</tbody>
</table>

Note: Natural Sources not included

Data Source: 2007 Almanac published by the California Air Resources Board.
The San Joaquin Valley is different from Los Angeles.

State has authority over stationary sources, not transportation.
San Joaquin Valley NOx emissions inventory, summer season

2005

- Heavy Duty Diesel Trucks: 40.5%
- Farm Equipment (Tractors): 9.9%
- Light Duty Passenger Cars: 10.2%
- Manufacturing and Industrial (Boilers, IC Engines): 14.6%
- Off-Road Equipment (Construction and Mining): 6.1%
- Off-Road Equipment (Other): 5.7%
- Agricultural Irrigation Pumps: 5.6%
- Trains: 3.7%
- Other: 3.8%
Ground-level ozone improving, but slowly.

Graph titled: Days Exceeding Ozone Standard -- San Joaquin Valley.

The graph shows trends in the number of days exceeding ozone standards from 1975 to 2010 for both State 8hr and Federal 8hr categories. The graph includes a polynomial trend line for the State 8hr category, indicated by "Poly. (State 8hr)."

Key points:
- The graph indicates a general decrease in the number of days exceeding ozone standards over time.
- The polynomial trend line suggests a more gradual decrease compared to the fluctuating data points.
- The correlation coefficient $R^2 = 0.21$ with $p < 0.01$ suggests a significant but moderate relationship between the variables.

The data points show variability with peaks and troughs, indicating periods of improvement and regression in ozone levels.