Final Report

Nez Perce National Air Toxics Program

Characterization of Air Toxics Concentrations around a Kraft Pulp and Paper Mill Facility, Lewiston, Idaho

EPA Assistance ID No. XA-97079001-3

Nez Perce Tribe
Environmental Restoration and Waste Management Division
Air Quality Program

September 30, 2009

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Final Report

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The Nez Perce Tribe (NPT) Environmental Restoration and Waste Management (ERWM) Air Quality Program in cooperation with the Idaho Department of Environmental Quality (IDEQ) conducted an air toxics monitoring study in the Lewiston, ID valley and northwestern portion of the Nez Perce Reservation from May 2006-April 2007. The study was funded by a grant from the US Environmental Protection Agency's (EPA) community air toxics program (http://www.epa.gov/air/toxicair/community/).

Purpose of Study

Study objectives were to characterize air toxics concentrations in the Lewiston, Idaho urban area and in nearby areas of the Clearwater River valley including significant parts of the Nez Perce Reservation, to characterize emissions from Clearwater Paper (formerly Potlatch) with a determination of spatial patterns and gradients in air toxics concentrations, evaluate the relative contributions of mill emissions by species to concentrations in the valley, and to characterize air toxics risks, with an emphasis on risks posed by the mill.

The 1863 Nez Perce Reservation is the third largest reservation in EPA Region 10, covering 1200 square miles and portions of five north central Idaho counties: Nez Perce, Latah, Idaho, Clearwater, and Lewis. (Figure 1). These five counties are, generally, what has been defined in a Memorandum of Agreement with EPA, the Nez Perce Tribe, and IDEQ as the Clearwater Airshed. The complex geography of the area (prairies, rolling hills, moderate to deep river valleys, forests, and mountains) contributes to varied microclimatic conditions. At 18,000 people, the population of the Nez Perce Reservation is the second largest reservation population in EPA Region 10. About 2000 tribal members live on or near the Reservation. There is significant anecdotal evidence of high incidences of asthma, allergic rhinitis, and autoimmune diseases for tribal members.

Clearwater Paper is located 1-2 miles outside of the northwestern corner of the Nez Perce Reservation. Approximately 15,500 residents occupy some 6600 households within a 3 mile radius of the Clearwater Paper complex. Emissions from the complex routinely adversely affect air quality (haze and odor) in the cities of Lewiston, Idaho and Clarkston, Washington. These cities have a combined population of 49,300 residents. The outlying communities of Lapwai, Lenore, and Orofino on the 1863 Nez Perce Reservation and Asotin in Washington can also be affected, depending upon meteorological conditions.

The topography of this area is marked by river valleys surrounded by steep hillsides. (Figures 2 and 3). The Lewiston-Clarkston Valley floor (downtown level) is situated at about 740ft elevation while the Lewiston community of the Orchards, south of downtown, is at 1350ft. North of Lewiston across the Clearwater River, the top of the Lewiston Hill and the Palouse Prairie is situated at about 2570ft. The town of Lapwai on the Nez Perce Reservation is located at about 960ft, and the Camas Prairie on the Nez Perce Reservation is located at about 3400ft. Both towns of Lenore (~945ft) and Orofino (~1020ft) are situated along the Clearwater River east of Lewiston.

Peculiar meteorological conditions are often observed in the Clearwater Valley as a result of the complex terrain. In addition to the frequent development of trapping inversions in the valley, especially during the colder months, it is not uncommon to observe wind and pollutant dispersion patterns contrary to the overall mesoscale flow.

There have been some past studies on air toxics in the valley. The motivation for these studies was the finding that the Lewiston-Clarkston area had 12% more total cancers than expected relative to overall Idaho averages. This was based upon data compiled in the Cancer Data Registry of Idaho and the Washington State Cancer Registry.

The first of these studies was completed in 1990 and focused on chloroform concentrations around (then) Potlatch. Maximum downwind concentrations were found to be 2 to 8 ppb. A major modernization was completed after this in 1992 that reduced the use of chlorine dioxide.

A more general year-long hazardous air pollutant (HAPs) study was conducted by IDEQ from July, 1994 through June, 1995. This was a more comprehensive study and included sampling for chloroform, benzene, toluene, ethylbenzene, and xylene on a once every six days schedule at 13 sites plus a background site. The highest annual average chloroform concentration was 0.111 ppb at a site directly across the river from Potlatch. The maximum 24-hour concentration observed was 0.46 ppb at the same site. The annual average chloroform concentration for all sites, excluding background, was 0.07 ppb. The background site concentration was 0.02 ppb. The annual averages for all sites for benzene, toluene, ethylbenzene, and xylene were 0.97, 1.53, 0.30, and 1.27, respectively. The background site concentrations for the same species were 0.19, 0.18, 0.03, and 0.24, respectively.

A third study was conducted in winter and spring of 2003 and, like the first study, focused on emissions from the Potlatch operation. Using the EPA TO-15 sample analysis method and gas chromatograph mass spectrometer (GC/MS) instrument, it identified 21 separate species in ambient samples that are listed in the EPA's Integrated Risk Information System (IRIS) database (internal NPT report). Sampling during this study attempted to define differences in species present between samples taken in and out of the influence of Potlatch plume sources. There appeared to be some significant differences between ambient samples believed to be influenced by the Potlatch sources and those believed to have little or no Potlatch influence. Due to limitations on resources, however, it was not possible to fully characterize these differences or do any notable quantification of concentrations.

Figure 1. Map of the Nez Perce Reservation

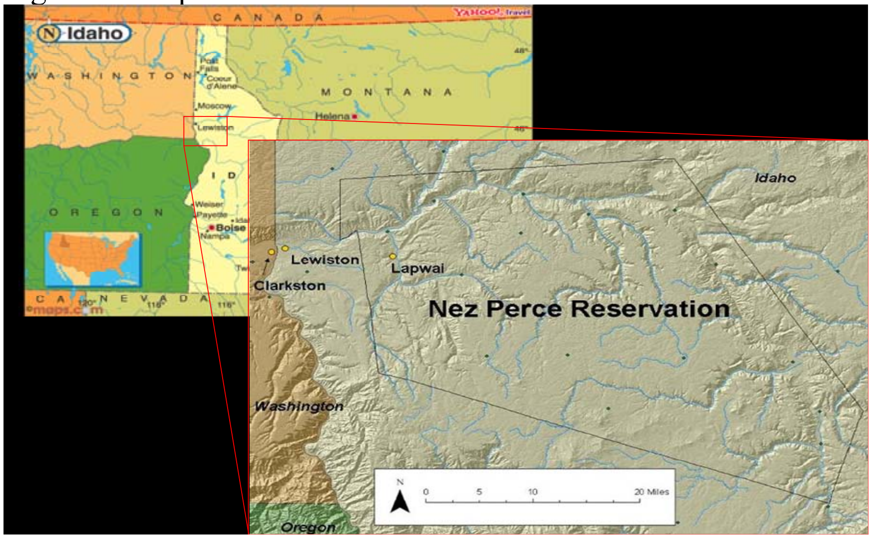


Figure 2. The Lewiston-Clarkston Valley (~740ft elevation). Photo taken looking south from the top of the Lewiston Hill (~2570ft elevation). In the top photo, emissions from Clearwater Paper (middle left), and a low-lying valley inversion can be seen.

Figure 3. The Clearwater River (at ~900ft elevation). Photo taken looking west from the north side of the river near the Spalding Bridge.

Methods

Monitoring and Network Design

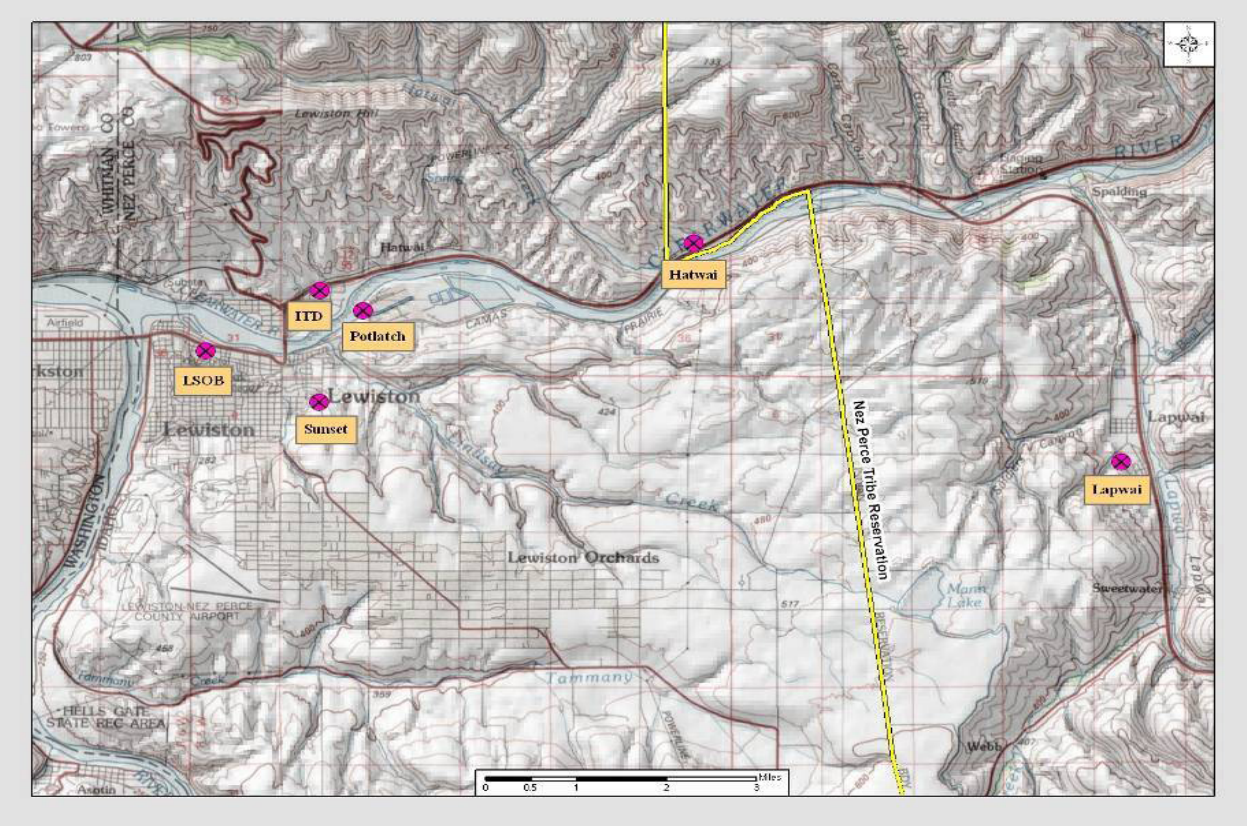
Air samples were collected from five locations to characterize concentrations around the Clearwater Paper pulp and pulp mill. Samples were collected for 24 hours every sixth day on EPA's 1-in-6 day sampling schedule. Concentrations of volatile organic compounds (VOCs), carbonyls (e.g., formaldehyde and acetaldehyde), and particulate metals (e.g., lead and chromium) were measured.

Empirical observations of typical mill plume behavior and associated haze development indicates that the most affected areas lie along the east-west axis of the Clearwater Valley. Depending on meteorological conditions, this can include the area immediately around Clearwater Paper, localities to the west (North Lewiston, downtown Lewiston and surrounding residential areas, and Clarkston), and/or areas to the east (western portions of the Nez Perce Reservation). Areas further to the south in Lewiston and along the axis of the Snake River (e.g. Asotin) are usually much less affected. This information suggested that in order to obtain spatial gradients in air toxics concentrations with respect to the Clearwater Paper facility it was necessary to locate most monitoring activities along the axis of the Clearwater Valley.

A location map showing the Lewiston urban and nearby areas, Clearwater Paper mill facility, and the monitoring sites is shown in Figure 4. The monitoring sites were selected to provide a variety of land use types and spatial resolution. The site descriptions are as follows with the corresponding name used for sample identification:

- Nez Perce Tribe Offices (Background Site) – LAPWAI; Nez Perce Reservation
- The Clearwater River Casino – HATWAI; Located just within the western boundary of the Nez Perce Reservation and frequently affected by plumes from Clearwater Paper. This site also provided the co-located samples for the metals and PM-10 analyses.
- Idaho Transportation Department – ITD; Located near the Clearwater Paper industrial source. This site also provided the co-located samples for VOCs and the carbonyls.
- Idaho DEQ (Lewiston State Office Building) – LSOB; Representative of 'downtown' central Lewiston urban area with commercial and residential mix.
- Idaho Department of Environmental Quality TEOM Site – SUNSET; A residential site in southeast Lewiston near the Clearwater Paper industrial source.

Figure 4. Map of Sampling Locations.



PM10 and metals were sampled using Graseby-Anderson PM10 Hi-Vols provided by IDEQ. VOC and Carbonyl sampling was conducted using ATEC 2200 samplers purchased with EPA grant funds. (Figure 5).

Figure 5. 1-in-6 Day Sampling Equipment

24hr samples; EPA's one in six day sampling schedule; 5/1/2006-4/30/2007

Particulate metals	**Volatile Organic Compounds**	**Carbonyls**
PM10 Hi-Vol. Quartz microfiber filters EPA method IO-3.5	ATEC 2200 sampler canisters EPA method TO-15	ATEC 2200 sampler DNPH cartridges EPA method TO-11A

Arsenic, beryllium, cadmium, chromium, lead, manganese, nickel	Benzene, carbon tetrachloride, chloroform, 1,3-butadiene, 1,2-dichloropropane, methylene chloride, tetrachloroethylene, trichlororethylene, vinyl chloride	Formaldehyde, Acetaldehyde

Samples were taken every six days from each site and picked up by an RJ Lee Group/Center for Laboratory Sciences (RJLG) for evaluation. The methods used for the analysis of the samples are described in the next section.

Wind speed, wind direction, temperature and barometric pressure data were gathered from three previously established (not as part of this grant) meteorological stations located at the IDEQ $PM_{2.5}$ monitoring site in southeast Lewiston (SUNSET), the Nez Perce $PM_{2.5}$ tribal monitoring site in Lapwai east of Lewiston (LAPWAI), and at the Clearwater Paper facility. Clearwater Paper provided wind speed, wind direction, and temperature data for the study from their 100 meter meteorological tower on site. Funding from this grant established an additional meteorological tower on the Nez Perce Reservation at Hatwai to measure wind speed, wind direction, and temperature.

In addition to the routine 1-in-6 day measurements, Differential Optical Absorbance Spectrometer (DOAS) monitoring occurred during the last week in June 2006 inside the Clearwater Paper facility complex. (Figure 6). The DOAS is an advanced optical measurement technology that can analyze for formaldehyde. This instrument required a mirror site for reflection of the laser, thus establishing a long path optical absorbance system for chemical measurements.

Figure 6: DOAS

A Proton Transfer Reaction Mass Spectrometer (PTR-MS) mobile laboratory system (Figure 7) was utilized for a few days for establishing a correlation of three independent measurement techniques for formaldehyde concentrations. The PTR-MS instrument was not part of the original proposal but was available at an opportune time for the experiments.

Figure 7. PTR-MS Mobile Lab

<u>Sampling Analysis Methods</u>

The 1-in-6 day sampling analysis, DOAS study and PTR-MS study were conducted by RJLG. Methods are summarized below. Quality assurance procedures can be found in Appendix A, *Air Toxics Monitoring Quality Assurance Project Plan for Characterization of Air Toxics Concentrations around a Kraft Pulp and Paper Mill Facility Located in Lewiston, Idaho*.

Carbonyls Monitoring and Analysis

Two carbonyl compounds, formaldehyde and acetaldehyde were monitored using EPA Compendium Method TO-11a.

PM-10 Monitoring and Analysis

Samples for PM-10 determinations were collected on quartz fiber filters. Details of the sampling and analysis of mass of PM-10 can be found in EPA Method IO-3.5.

Metals Monitoring and Analysis

The protocol for sampling and analysis of the metals can be found in EPA Method IO-3.5. The metals of interest in this study include arsenic, beryllium, cadmium, chromium (total), manganese, nickel, and lead. Aluminum was analyzed as a tracer of crustal contributions. Other metals not included in the proposal but analyzed and included in this report include copper, iron, and zinc.

VOC Monitoring and Analysis

Volatile organic compounds sampling and analysis was performed according to EPA Compendium Method TO-15. The VOCs of interest in this study were benzene, carbon tetrachloride, chloroform, 1,3-butadiene, 1,2-dichloropropane, methylene chloride, tetrachloroethylene, trichloroethylene, and vinyl chloride. This study had also requested the evaluation of VOCs included in the IRIS database, but not listed above, that were identified in one of the earlier studies. These include acetophenone, benzaldehyde, chlorobenzene, cyclohexanone, ethylbenzene, furfural, 1,4-dichlorobenzene, dichlorodifluoromethane, hexane, d-limonene, naphthalene, toluene, trichlorobenzene, 1,1,1-trichloroethane, and trichlorofluoromethane. Of the compounds listed above, acetophenone, benzaldehyde, cylcohexanone, furfural, limonene, and naphthalene were not included in the VOC analysis since there was inadequate time to fully evaluate their storage and recovery from Summa canisters. The final list of VOCs monitored in this study is shown below:

Benzene
1,3-Butadiene
Dichlorodifluoromethane (Freon 12)
Ethylbenzene
m,p-Xylene
o-Xylene
Styrene
Vinyl Chloride (Chloroethene)
Trichlorofluoromethane (Freon 11)
1,1,1-Trichloroethane
Hexane
Dichloromethane
Tetrachloroethylene
Trichloroethylene
1,2-Dichloropropane
Chloroethane
Chloromethane
Carbon Tetrachloride
Chloroform
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene

Formaldehyde Special Study (DOAS)

Formaldehyde was quantified using the DOAS unit which operated for three days during the last week in June 2006. The DOAS technique measures the molecular absorption over a long path. The method is effective for measuring molecules with differential absorption over the measurement wavelength. A full description of the instrument can be found in Mount et al.[1], 2002 and is briefly described here.

The instrument consists of a light source (150 W Xenon lamp) transmitting and receiving optics, spectrograph and computer. Light from the lamp is directed from the lamp to the transmitting telescope and out to a set of retro reflective mirrors, which direct the light beam back to the receiving optics and then into the spectrograph where the light is dispersed and the wavelength region of interest is directed to the detector and recorded by the computer.

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[1] Mount, G.H., Rumburg, B., Havig, J., Lamb, B., Westberg, H., Yonge, D., Johnson, K., Kincaid, R., 2002. Measurement of atmospheric ammonia at a dairy using differential optical absorption spectroscopy in the midultra-violet. Atmospheric Environment, 36, 1799-1810.

The instrument was set up at the northwest corner of the Clearwater Paper waste lagoon on the access road, and the mirrors were located below the road at the southwest corner of the lagoon. The distance from the retro reflector mirrors to the instrument was 1083m for a total measurement path length of 2166m. The light beam path was about 15 feet above the lagoon surface. Based upon the path length, absorption cross section and the instrument sensitivity the detection limit for formaldehyde was 5 ppb.

Emission Tracking with a Mobile Laboratory (PTR-MS)

Ambient VOC measurements close to various emission sources were made with a mobile lab fitted with several different sensors. Instrumentation in the mobile van included a PTR-MS, an Aerodynamic Particle Sizer (APS), a Global Positioning System (GPS), a real-time CO_2 monitor and a sonic anemometer. The PTR-MS measures VOCs that have a proton affinity greater than water. This includes most alkenes, aromatics and organics that contain oxygen, nitrogen and sulfur atoms. The APS sensor is a particle spectrometer that provides the size distribution of particles from 0.5 to 20 micrometers. The GPS tracks the position of the van when in motion, while the sonic anemometer provides wind data to identify plumes or remove periods with wind blowing from behind the van where a gasoline generator was placed to provide AC power for the instruments. The CO_2 instrument provides an indication of combustion plumes and also is used to identify periods of contamination from the onboard generator. All of these instrumentations have fast response capability (~ 1 Hz).

Emissions Inventory

An emissions inventory was used for the modeling work described below conducted by Washington State University's (WSU) Laboratory for Atmospheric Research (LAR). The emissions inventory came from existing and collected data from the AIRPACT-3[2] system.

Modeling

Dispersion modeling was conducted by WSU-LAR using CALMET/CMAQ and CALPUFF. The MM5/SMOKE/CMAQ modeling system was used to investigate the spatial and temporal distributions of air toxics on the Nez Perce Reservation and in the Lewiston, ID – Clarkston, WA urban area for two time periods: August–September, 2006 and December, 2006–January, 2007. Model performance was evaluated using data collected during the one year comprehensive air toxics monitoring program. A related modeling analysis was completed using the CALPUFF dispersion model to simulate selected pollutants emitted from the pulp and paper mill located immediately east of Lewiston, ID. Results from CALPUFF were compared to observations of pollutant concentrations and CMAQ results for selected air toxic pollutants.

Data and Risk Analysis

Risk analysis was conducted by the Idaho Division of Health, Bureau of Community and Environmental Health (BCEH) and the Agency for Toxic Substances and Disease Registry (ATSDR). Data analysis and some additional risk analysis were conducted by Sonoma Technology, Inc. (STI).

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[2] http://lar.wsu.edu/airpact-3/introduction.html

Results

Sample Analysis

The detailed analytical reports of the RJLG sample analyses can be found in Appendix B, *Analytical Report of Air Toxics Analysis of Samples Originating from the Nez Perce Tribe Air Quality Project January 2006 – April 2007.* The data submitted to EPA's Air Quality System database can be found in Appendix C, *Nez Perce Tribe Air Toxics Study Data, Final.*

Formaldehyde Special Study (DOAS)

Results from the analytical report of the RJLG DOAS study are summarized here. During the study period in late June the hourly average values fell between 12 and 27 ppbv. The period of continuous measurements beginning at noon on day 179 and extending to 1600 on day 180 showed increasing formaldehyde concentrations from noon until 0200 the next morning. A sharp 7 ppbv drop in ambient concentration occurred from 0200 to 0300 and the levels then remained relatively constant at about 13 ppbv until 0700. The formaldehyde values increased to about 17 ppbv at the 0800 and 0900 hours and then returned to about 12 ppbv until measurements were discontinued at 1600.

Day 179 (June 28) was very warm with the mid-afternoon temperature exceeding 100 deg. F. The high temperatures and abundant sunlight coupled with low wind speeds likely contributed to stagnation conditions throughout the Clearwater River Valley region. Formaldehyde levels reported at the five valley fixed monitoring stations on June 28 were near summertime maximums. Stations to the east of Clearwater Paper (HATWAI and LAPWAI) recorded 24-hr average formaldehyde levels of 12-13 ppbv. Since winds were from the east the entire time on days 179 and 180, there was good agreement between the upwind fixed station formaldehyde measurements and the minimum levels determined with the DOAS system. Formaldehyde levels recorded at the three sites to the west of Clearwater Paper (ITD, SUNSET & LSOB) on June 28 varied between 14 and 19 ppbv, which again are comparable to the DOAS measurements.

RJLG felt it was unfortunate that winds remained from the east during the entire June sampling period. This precluded the opportunity to detect formaldehyde emissions released by components of Clearwater Paper operations other than the treatment ponds. However, the fact that little if any enhancement in ambient formaldehyde concentration was observed directly over the treatment reservoir implies that the aqueous treatment facility is not a significant source of formaldehyde.

The results of the measurements by this complimentary technique were compared to those obtained by the TO-10a method for formaldehyde. Although the study period was quite short, there was a good correlation of the formaldehyde concentrations by the two analytical methods.

Emission Tracking with a Mobile Laboratory (PTR-MS)

Results from the analytical report of the RJLG PTR-MS study are summarized here. Mobile van sampling was conducted during three days in mid-December, 2005 and four days in June of 2006. The December sampling provided a preliminary survey of VOC emission sources in the Lewiston-Clarkston Valley. A more comprehensive assessment was performed in June that included mobile sampling within the Clearwater Paper facility grounds. Several VOCs were targeted during this second monitoring period which included four compounds/classes that were not evaluated within the scope of the main study. These compounds were methanethiol, dimethyl disulfide, methanol, acetone, and a group of monoterpenes. These compounds were not used in the results of this study.

During both sampling periods, some time was spent in the vicinity of each of the fixed sampling sites. Following the daytime sampling, the van was stationed at the ITD site and measurements were made throughout the night at that site. During the summer period, the van remained stationary at the ITD site during the one in six 24-hr integrated sampling period; June 28, 2006. This allowed a comparison for certain VOC concentrations determined in the 24-hr integrated canisters, the acetaldehyde sampling from the TO-11a methodology, and those measured with the PTR-MS. Additionally, since the PTR-MS provided continuous measurements, a temporal record of concentrations over the 24-hr sampling period was obtained. Table 1 is a summary of the results from the PTR-MS measurements (June 28, 2006, midnight to midnight) and the data obtained from the TO-11a and TO-15 sampling events on the same day. RJLG determined that this mobile, real time monitoring capability underscores the importance and contribution of this type of instrumentation for the analysis of VOCs, particularly those sulfur compounds that are often troublesome by conventional methodologies.

Table 1. Mobile Lab Data. A comparison of results from the 24-hr composite TO-11a and TO-15 sampling with the 24 hour average data from the PTR-MS monitoring at the ITD site on June 28, 2006.

Compound	**PTR-MS 24 Hour Average (ppbv)**	**PTR-MS Standard Deviation (ppbv, 1s)**	**TO-11a (ppbv)**		**TO-15 (ppbv)**	
			ITD 1	**ITD 2**	**ITD 1**	**ITD 2**
Methanol	27	22				
H2S	trace					
Propene	4.4	2.7				
Acetaldehyde	2.8	2.0	6.78	6.91		
Methanethiol	1.5	2.0				
Acetone	4.2	2.9				
Acetic Acid	3.0	2.1				
Dimethylsulfide	1.9	2.3				
Isoprene	0.4	0.5				
Benzene	0.7	1.2			0.33	0.69
Toluene	0.6	1.4			0.24	0.36
Dimethyldisulfide	1.6	1.9				
Styrene	0.1	0.2			0.03	0.01
C2 Benzene	0.5	1.5			0.19	0.19
C3 Benzene	0.3	1.1				
Napthalene	0.1	0.2				
Monoterpene	0.7	1.4				
Pinene	1.2	2.4				

Modeling

Detailed results of the modeling work conducted by WSU-LAR are found in Appendix D, *Final Report: Modeling of Air Toxics from Urban and Industrial Sources within Complex Terrain*.
Results are summarized below.

CMAQ

Air quality modeling was used to simulate temporal and spatial distribution of pollutants and evaluated using the measurement data. The MM5/CMAQ modeling system was run for two months (August and

September) representing the summer period and two months (December and January) representing the winter period to evaluate any seasonal variability.

The MM5/MCIP/SMOKE/CMAQ modeling suite was configured to model air toxics concentrations in an urban area with complex terrain. The modeling configuration included use of a high resolution 1-km grid and the Zangl horizontal dispersion option in MM5. Meteorological and air quality modeling results from MM5 and CMAQ, respectively, were then evaluated and compared to available measurements.

Statistical comparison of modeled to observed temperature, wind speed, and wind direction were within the typical range seen in previous applications of the MM5 meteorological model. The magnitudes of temperature, wind speed, and wind direction mean biases were equal to or less than 0 K, 0.1 m/s, and 50 degrees, respectively, and mean absolute gross errors were less than 3 K, 2 m/s, and 80 degrees, respectively.

Comparison of the modeled to observed air toxic concentrations (24-hr averages) showed that formaldehyde, acetaldehyde, and benzene were underestimated by as much as a factor of five. Further experiments regarding these three air toxics showed that the modeled concentrations were less sensitive to uncertainties in anthropogenic emissions than to uncertainties in chemical boundary conditions. Concentrations of toluene and ethyl benzene were underestimated most of the time, but the predicted levels were always within a factor of two of the observations. Concentrations of chloroform and the xylene isomers were overestimated most of the time and were within a factor of two for the August-September period.

CMAQ modeling results showed that pollutant spatial distributions depended upon chemistry, pollutant source, and terrain. (Figures 8 and 9). Air toxics with secondary formation, such as formaldehyde, had broad coverage across the model domain, while primary pollutants emitted from a point source tended to remain in the valley because of the terrain. Elevated concentrations of primary mobile pollutants tended to occur along major roadways within the valley. Diurnal patterns of the air toxics were explained by the mixing height and chemical formation rates. Primary pollutant concentrations were lower during the day due to dilution throughout a deeper mixing layer. Formaldehyde and acetaldehyde had much higher concentrations during the August-September period due to higher chemical production rates compared to the December-January period.

Figure 8: Modeled concentration contour maps showing formaldehyde (left) and acetaldehyde (right) partitioned to primary (top) and secondary (middle) for 5:00 pm PST on a typical day.

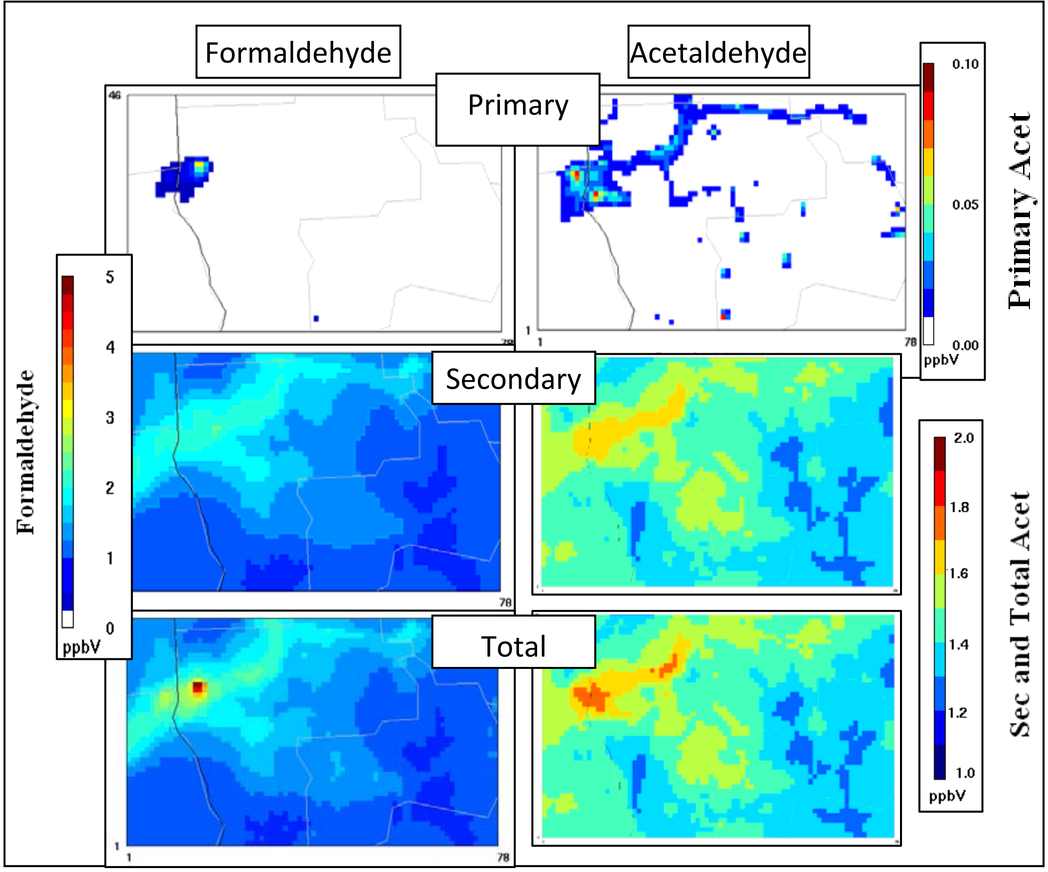
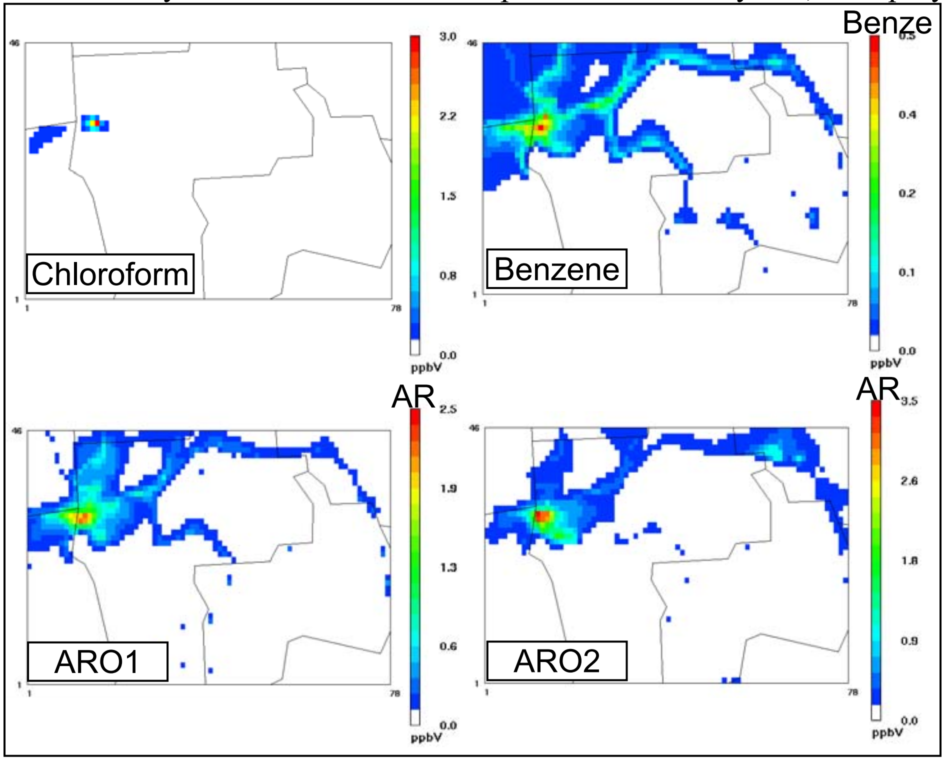


Figure 9. Modeled concentration contour maps showing chloroform, benzene, ARO1, and ARO2 for 5:00 pm PST on a typical day. ARO1 and ARO2 are lumped species that are used to track the rest of the BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds. ARO1 is composed of 70% toluene and 10% ethyl benzene. ARO2 is composed of 22% m-xylene, 22% p-xylene, and 20% o-xylene.



Temperature is an important factor in modeling the evolution of pollutants. In higher temperatures, chemical reactions occur more quickly thus affecting the transformation and destruction of the pollutants. Also, warmer temperatures usually reflect large surface heat fluxes which increase the height of the planetary boundary layer and increase the dilution of pollutants.[3] The results showed, statistically and graphically, MM5 captures the diurnal pattern and monthly means of the observed temperature in the domain.

Wind speed and direction are important factors in the transport of the pollutants. The results showed that patterns in wind speeds were correctly captured by MM5, although variability in wind speed errors were approximately 2 m/s. Winds blowing from the west can carry the pollutants from the paper and pulp mill and the urban area to the Nez Perce Reservation. The results showed that wind direction is captured better for some sites than for others.

Comparison of modeled air toxic concentrations to 24-hour averaged observations showed that formaldehyde, acetaldehyde, and benzene are underestimated for all the simulation months. Further experiments to investigate the causes of underestimations reveal that fires did not explain the factor of three difference between August and September aldehyde observations. However, boundary values for formaldehyde, acetaldehyde, and benzene were seen to have a greater influence on modeled concentrations than their respective emissions. Toluene and ethyl benzene are shown to be underestimated for three months and overestimated for one month. Chloroform and the xylene isomers are shown to be overestimated for most of the time.

Future research should be done to further examine the difference between August and September formaldehyde and acetaldehyde concentrations. An evaluation of formaldehyde and acetaldehyde chemistry, boundary conditions, and emissions is needed. The chemical precursors of formaldehyde and acetaldehyde also need to be evaluated. One possible research opportunity is to run the model for the whole year from May 2006 to April 2007. The full year of model results might show a different correlation between the observations and model results and also seasonal variability of the air toxics.

An investigation into possible additional unknown sources of benzene in the area is needed, and further consideration of potential analytical problems with the benzene measurements is warranted.

Since chloroform is only emitted from an area source and the observation sites are close to that source, the use of a Gaussian-based model, such as CALPUFF, to model chloroform was warranted. WSU-LAR's results from the CALPUFF modeling are summarized below.

CALPUFF

Results from CALPUFF were compared to observations of pollutant concentrations and CMAQ results for selected air toxic pollutants. A CALPUFF simulation of primary industrial emissions in a deep valley provided some valuable information about pollutant dispersion in the chosen domain, but also highlighted some significant inaccuracies of modeling techniques. Tentative evaluations of modeling accuracy could be made by comparing CALPUFF's dispersion predictions to those of CMAQ as well as concentration measurements at corresponding sites and times. Chloroform (CHCL3) was considered the most relevant species for modeling in this case because it is emitted only by the primary industrial operations that motivated this particular study. The CALPUFF model demonstrated its potential for accurate dispersion modeling by predicting CHCL3 concentrations generally within a factor of 2 relative to observations. On average, CALPUFF's CHCL3 predictions were more accurate than those of CMAQ over the summer month that was examined. However, the tendency of CMAQ to overestimate CHCL3 concentrations

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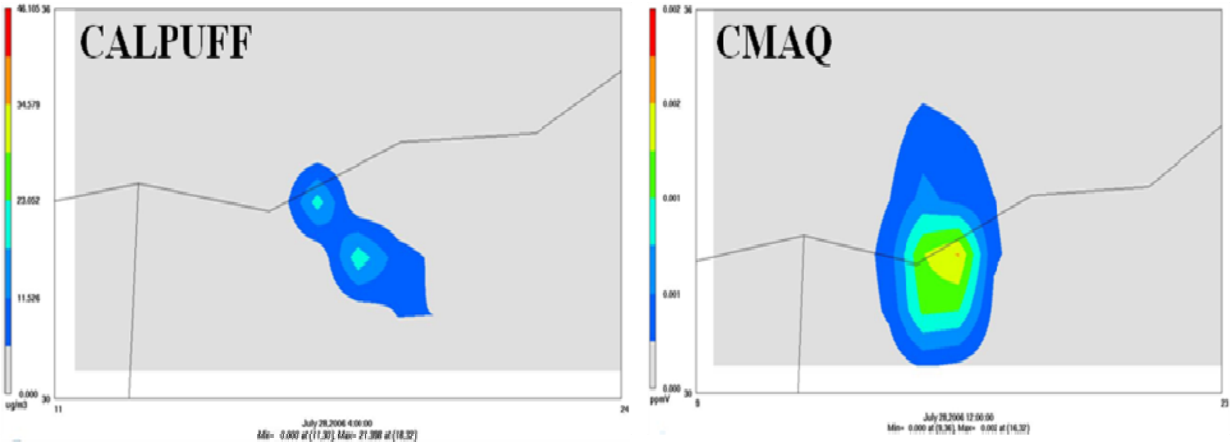
[3] Arya, S. P. (1999), *Air Pollution Meteorology and Dispersion.* Oxford University Press, 157 pp.

combined with CALPUFF's variation of predictions both above and below the observed values make it difficult to actually recognize one model as the more accurate one. The discrepancy between these two models most likely represents the differences in their applied methods of dispersion modeling. (Figure 10).

The pollutants formaldehyde, acetaldehyde, and benzene were also modeled. For these species, which are emitted from industrial and mobile sources and also produced as secondary pollutants, both models severely underestimated the observed concentrations. The similar inaccuracies of CMAQ and CALPUFF predictions for these species may indicate discrepancies in the industrial emission rates, or errors in the models' boundary condition applications, atmospheric chemistry, and/or mobile source emissions. Further research may provide more insight to the causes of the inaccuracies between the dispersion models and measurements.

Figure 10. Model comparison of chloroform dispersion for July 28, 2006, 4:00 AM PST.



Risk Analysis – BCEH/ATSDR

The Idaho Division of Health, Bureau of Community and Environmental Health (BCEH) reviewed the risk presented by air toxics concentrations found from monitoring data results (Appendix E, *Health Consultation: Lewiston Air Toxics Monitoring 2006-2007, Evaluation of Potential Health Effects from Air Toxics, Nez Perce County, Idaho*). Results from the Health Consultation are highlighted below.

The levels of contaminants in the air were all below the chronic and acute exposure comparison values (CVs).[4] Three VOCs (carbon tetrachloride, chloroform, and 1,4-dichlorobenzene) and the two carbonyls, acetaldehyde and formaldehyde, were above their cancer CVs. Carbon tetrachloride, acetaldehyde, and formaldehyde were detected above their cancer CVs at all 5 sampling sites. The compound 1,4-dichlorobenzene was detected above its cancer CV at 3 of the 5 sites. The mean level of formaldehyde was found at levels greater than 46 times its cancer CV at all five sites.

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[4] According to the Health Consultation Report, "*Comparison values **are not** thresholds for adverse health effects*. That is, CVs do not represent a level at which a person exposed to a contaminant level above the CV will likely suffer health consequences. This is because CVs are typically set at levels many times lower than the levels at which health effects were observed in experimental animal or human epidemiologic studies. CVs are deemed protective because they include safety or uncertainty factors that account for more sensitive populations, such as young children. Again, if the concentration of a chemical is less than its CV, it is unlikely that exposure would result in adverse health effects, and further evaluation of exposures to that chemical is not necessary. If the concentration of a chemical exceeds a CV, adverse health effects from exposure are not automatically expected, but potential exposures to that chemical from the site should be further evaluated."

No metals with CVs were detected above a CV except for chromium and arsenic compounds which exceeded their cancer CVs at all sampling locations. However, the cancer CV for chromium listed in the table is assuming a ratio of 1 to 6 of chromium VI to chromium III. Chromium VI is a highly toxic form of chromium and is not very common compared to the less toxic chromium III. Only total chromium was measured in this study. Generally, the level of chromium VI in the air is a small percentage of the total chromium. Using the cancer CV for total chromium, the highest average measured was more than 4 times greater than the CV. Assuming that *all* chromium found is chromium VI, the highest average would be 31 times greater than the CV for chromium VI; this is even more unlikely.

Acute and Chronic Risks

By comparing the highest mean levels of each contaminant to its acute and chronic CV value it was found that exposure is not likely to result in any acute or chronic adverse non-cancer health effects. Most of the highest mean values were many times below their chronic CV value, and even further below their acute CV value. Also, no individual 24 hour sample at any of the locations exceeded any of the acute CV values. The only two contaminants that were close to their chronic CVs were acetaldehyde and formaldehyde. The highest mean for acetaldehyde was 3.86 µg/m3 and its chronic CV is 9.4 µg/m3 or 2.4 greater than the highest mean. The highest mean for formaldehyde was 6.19 µg/m3 and the CV is 10.0 µg/m3 or 1.6 times greater than the highest mean.

Cancer Risks

Cancer exposure scenarios generally assume a lifetime exposure to the suspected carcinogen. By looking at the levels of contaminants and comparing those levels to risk-based cancer CVs it is possible to determine a theoretical risk for populations exposed to the current levels of contaminants if exposed over a lifetime (70 years).

The measured average (mean) and median level of a contaminant can be used to calculate how much *extra (excess) risk* of cancer a group of people might have from being exposed to this contaminant in the air for a lifetime. The mean is considered to be the most representative value for these data, though it should be noted that the mean is influenced by high individual maximum values. The median could have been chosen at the best measure, but it was decided to use the mean since high levels appeared to occur for days at a time, and outliers (individual extreme values) did not occur.

The health endpoint considered for all these compounds is increased risk of cancer at specific sites (endpoints) in the body. The most sensitive site is used as the endpoint. For cancer endpoints, the cancer CV is set at the concentration at which it is believed one in a million excess cancers could potentially be attributed to the exposure.

The CVs for cancer risk do not establish a level at which people exposed above the CV are expected to get cancer. Cancer CVs allow health assessors to determine an estimate of the number of unexpected (extra/excess) cancers that might be caused if a group of people were exposed to contaminant levels above the CV every day, 24 hours a day, for an entire lifetime.

The extra cancer calculations are shown in Appendix B of the Health Consultation Report. As shown in Table 3, the highest yearly mean (average) value at a single monitoring site is used in these calculations. The highest yearly mean was derived by taking each monitoring station's data and calculating the mean level for each contaminant. These yearly mean levels were then compared to each other and the highest mean for each contaminant was selected to compare with its CV. It must be noted that using the highest mean value to calculate the extra cancer risk is a conservative approach and will likely overestimate the extra cancer risk since not everyone will be exposed to the highest value for 24 hours a day for a lifetime.

To determine extra cancer risk the following formula was used:

Extra Cancer Risk = C x IUR

C = highest mean concentration of the contaminant IUR = Inhalation Unit Risk (EPA)

When reviewing the extra cancer risk, it is important to know that the methods used to derive the Inhalation Unit Risk values result in upper bound estimates of extra cancers, that is, the true risk is not likely to exceed this value and may be much lower.

- The cancer risk level for this continual exposure to carbon tetrachloride is 9.45 extra cancers per one million people exposed. The cancer endpoint considered is liver cancer.
- The cancer risk level for this continual exposure to chloroform is 7.59 extra cancers per one million people exposed. The cancer endpoint considered is both liver and kidney cancers.
- The cancer risk level for this continual exposure to acetaldehyde is 8.49 extra cancers per one million people exposed. The cancer endpoint considered is upper respiratory tract cancer.
- The cancer risk level for this continual exposure to formaldehyde is 80.5 extra cancers per one million people exposed or 8 extra cancers in 100,000 people. The cancer endpoint considered is upper respiratory tract cancer.
- The cancer risk level for this continual exposure to 1,4-dichlorobenzene is 4.06 extra cancers per one million people exposed. The cancer endpoint considered is liver cancer.
- The cancer risk level for this continual exposure to arsenic is 2.3 extra cancers per one million people exposed. The cancer endpoint considered is skin, lung and bladder cancer.
- The cancer risk level for this continual exposure to total chromium is 10.8 extra cancers per one million people exposed. The cancer endpoint considered is lung cancer. The cancer risk level assuming all chromium was chromium VI is 75.6 extra cancers per one million people exposed: however, it is extremely unlikely that all chromium present in air was chromium VI. Therefore, this theoretical risk calculation is likely to be an overestimate of the extra cancer risk.

The Inhalation Unit Risk is the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 $\mu g/m^3$ in air. This means that, for example, it is possible that for every million people there could be 80.5 extra (unexpected) cases of cancer in people exposed to the highest average of formaldehyde under these circumstances. These extra cases might be attributable to formaldehyde exposure. Formaldehyde was clearly the highest extra risk of all contaminants measured. It is important to note that cancer risk estimates do not provide definitive answers about whether or not a person will get cancer; rather, they are measures of chance (probability).

At first glance, it may seem intuitive to add up the cancer risks for all the contaminants to arrive at a single risk number. However, this is only valid for cancers that occur at the same site in the body. The cancer endpoints listed above for each contaminant are for a specific site in the body. Thus we may add together the following:

- Carbon tetrachloride + chloroform + 1,4-dichlorobenzene = *18.6 extra liver cancers* in 1 million or 1.9 extra cancers per 100,000
- Acetaldehyde + formaldehyde = *89.0 extra upper respiratory tract cancers* in 1 million or 9 extra cancers per 100,000

Thus, the site at greatest risk for developing cancers from lifetime exposure to ambient air in the region is the upper respiratory tract; however, this risk is still considered to be low. Risk was also very slightly elevated for lung and kidney cancers due to total chromium and chloroform individually, as noted above.

Cancer is a common illness, with many different forms that result from a variety of causes; not all are fatal. According to the American Cancer Society, nearly half of all men and one-third of all women in the U.S. population will develop cancer at some point in their lives. Since cancer is very common and the highest risk estimate for the estimated exposure is 9 excess cancers per 100,000 people exposed, it is likely impossible to distinguish these potential excess cases from background levels of cancer in the area.

Since the levels of contaminants in the air were all below the chronic exposure CVs, BCEH concludes that breathing the air in the Lewiston and Clarkston area is not expected to harm health or result in any increase in chronic diseases. Further, although some of the individual contaminants in air were above their cancer CV, none was high enough to increase the cancer risk sufficiently above the background cancer risk level for the community to determine that the effect was significant. In other words, there is not a difference over and above what is expected in an urban population based on statistics for cancer nationwide. Therefore, BCEH concludes that breathing the air in the Lewiston and Clarkston area will not result in an elevated cancer risk to those who live in the Lewiston area and breathe the air for a lifetime.

Since the urban areas of Lewiston have the highest levels of contaminants, it is important that efforts be made to address ways to reduce these levels. Also, though levels of formaldehyde and acetaldehyde within Lewiston city limits were comparable to that found in a recent survey of 10 urban areas across North America, the Lewiston-Clarkston area is much smaller and less populated than the urban areas sampled in the survey and theoretically, should have lower levels. Decreasing the levels of formaldehyde and acetaldehyde would benefit the community and reduce risks throughout the airshed.

Cancer risk in the Lewiston area was previously thought to be elevated based on comparisons with the entire population of Idaho. An additional cancer benchmark comparison of the Lewiston-Clarkston Valley population with a similar population (Coeur d'Alene) was completed by Idaho Cancer Data Registry Epidemiologist Chris Johnson and interpreted by BCEH (Appendix F, *Technical Assistance: Interpretation of Epidemiologic Data, Cancer Rates 1998-2006, Lewiston-Clarkston Zip Codes Compared to Coeur d'Alene Zip Codes*).

BCEH received cancer data analysis of cancer data for Lewiston-Clarkston from the Idaho Cancer Data Registry Epidemiologist Chris Johnson on 4/21/09. The time period of this dataset is 1998-2006. BCEH asked Mr. Johnson to compare cancer rates for Lewiston-Clarkston Zip Codes to those for Coeur d'Alene Zip Codes, and to the state as a whole. Coeur d'Alene was chosen due to its similar size and somewhat similar demographics. The problem with comparing specific communities to state rates in Idaho is that state-wide rates include a disproportionately-lower risk population residing in the eastern half of the state. Rates of risk behavior such as smoking and consumption of alcohol that influence cancer rates are much lower in East Idaho and thus state rates are biased by the contribution of this regional population.

BCEH found there is scant evidence implicating air toxics detected in the 2006-2007 monitoring with an increase in rates of specific cancers known to be associated with the air toxics detected. Higher rates of non exposure-associated cancers found in Lewiston-Clarkston can potentially be explained by differences in health behaviors, occupational exposures, or genetic variability between Lewiston-Clarkston and the rest of the state.

Recommendations

As a result of their analyses, BCEH specifically recommended the following:

- BCEH recommends that the Nez Perce Tribe ERWM Air Quality Program and IDEQ continue air monitoring in Lewiston and surrounding areas. A seasonal monitoring approach that captures daily 24-hour readings during inversions should be attempted since contaminant concentrations may be the highest during these periods.
- BCEH recommends that BCEH work with the Nez Perce Tribe ERWM Air Quality Program and IDEQ to address air pollution in Lewiston and surrounding areas through educational activities.
- BCEH recommends that BCEH work with the Nez Perce Tribe ERWM Air Quality Program and IDEQ to identify the sources of contaminants and work to reduce levels below CVs.
- BCEH recommends that the Idaho Cancer Data Registry review the current cancer incidence data for the Lewiston area and report its findings to BCEH.

Data Analysis - STI

Sonoma Technology, Inc. (STI) performed a series of analyses to provide additional information to address the study objectives (Appendix G, *Lewiston Area Air Toxics Data Analysis, Final Report*). These analyses included data validation, meteorological analysis, spatial gradient analysis, comparisons to national and regional concentrations, and temporal analysis. STI's results are summarized below.

STI determined that concentrations of formaldehyde and acetaldehyde were much higher than expected for an area of Lewiston's size. Formaldehyde was the largest contributor to cancer risk among the pollutants measured and acetaldehyde was a significant contributor. Concentrations of formaldehyde and acetaldehyde were highest in the summer months but did not appear to be related to special events like large wildfires. Secondary production of formaldehyde and acetaldehyde were most likely to be responsible for the seasonal pattern, but it is unclear why concentrations were higher than at other sites in the inland northwest. STI determined that insufficient information was available on local concentrations of anthropogenic and biogenic VOCs to determine why formaldehyde and acetaldehyde concentrations were high.

Of second highest importance, STI determined that analytical laboratory measurements of benzene and 1,3-butadiene concentrations reported in this study did not meet expectations for data quality. The concentrations of benzene were particularly problematic based on both the collocated measurements and comparisons with other pollutants that are typically closely correlated with benzene (e.g., toluene, xylenes).[5] As a result, benzene and 1,3-butadiene concentrations should be considered less reliable for generating risk values, evaluating emissions sources, and assessing spatial gradients in concentrations.

Finally, ambient concentrations of chloroform, tetrachloroethylene, and trichloroethylene were determined to be a result of emissions from Clearwater Paper. The weight-of-evidence consensus from spatial, temporal, and chemical analysis was consistent with Mill emissions. Concentrations of these pollutants were highest at the Idaho Transportation Department site, were emitted from the Mill's chlorine bleaching process, and were high at random times throughout the monitoring period, which is consistent with fugitive (or upset) emissions. Of these pollutants, STI found that chloroform and tetrachloroethylene were small but significant contributors to chronic risk in the Lewiston area.

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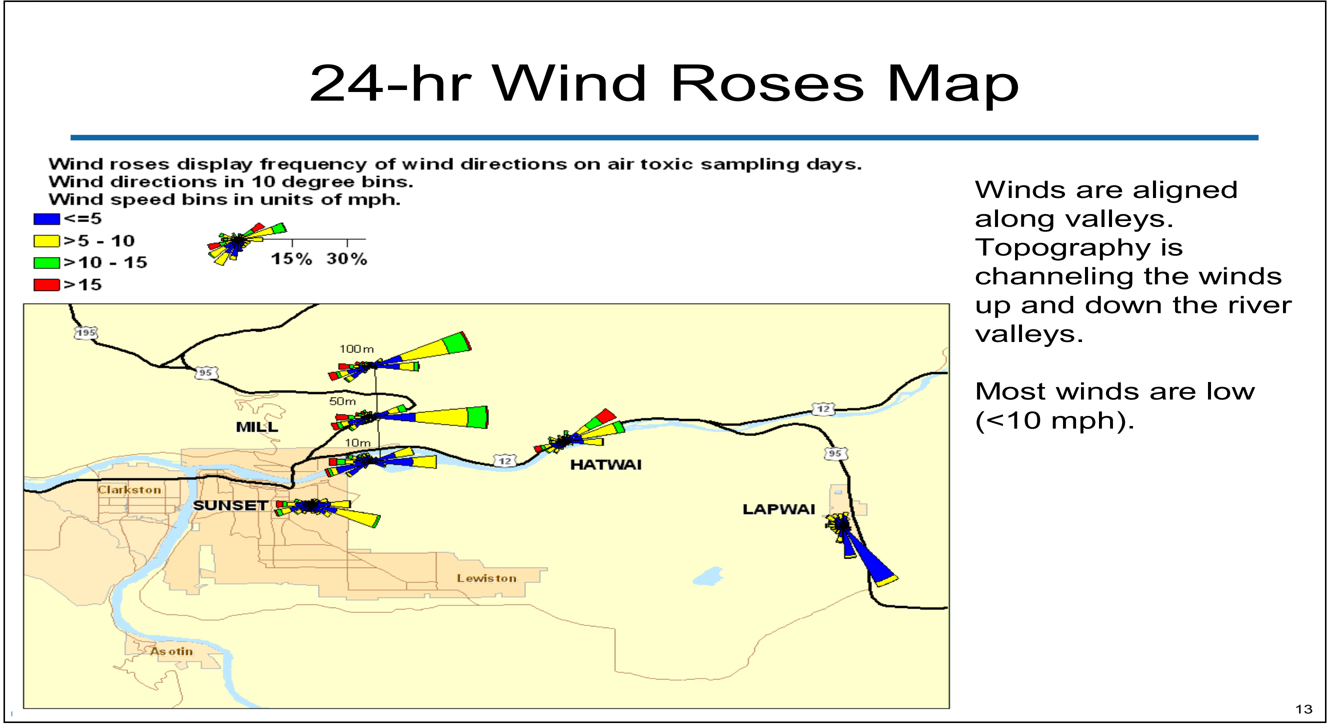
[5] STI found that given the good correlation of other pollutants taken from the same canisters, the measurement process was not the principal issue. Rather, STI could state with confidence that some step in the analytical process was causing problems with the benzene concentration analysis. Of the other pollutants examined, 1,3-butadiene was inadequately correlated, and STI felt that may be partially explained by data at or below the method detection limit (MDL).

Wind Rose Maps

STI generated wind rose maps to illustrate the predominant wind patterns during the air toxics monitoring sampling period. Wind roses indicate the direction and speed of winds. The wind arcs point in the direction from which the wind originates. Four sites collected meteorological data during the special study: Lapwai, Hatwai, Sunset, and a wind tower on the Clearwater Paper property. The wind tower collected meteorological data at three heights, 10 m, 50 m, and 100 m above the ground. Meteorological data were collected at 10 m above the ground at the Lapwai, Hatwai, and Sunset sites.

STI evaluated the wind data. 24-hour results showed that winds are aligned along valleys with the topography channeling the winds up and down the river valleys and most winds being below 10mph (Figure 11). Daytime winds are predominately from the west along the Snake River and from the north in Lapwai, with wind speeds more likely to be high in the daytime (Figure 12). Nighttime winds are from the east (south for Lapwai) with wind speeds low. Overall, winds flow upslope during the day and downslope during the night in a classis diurnal drainage flow (Figure 13).

Figure 11. 24-hr Wind Roses



24-hr Wind Roses Map

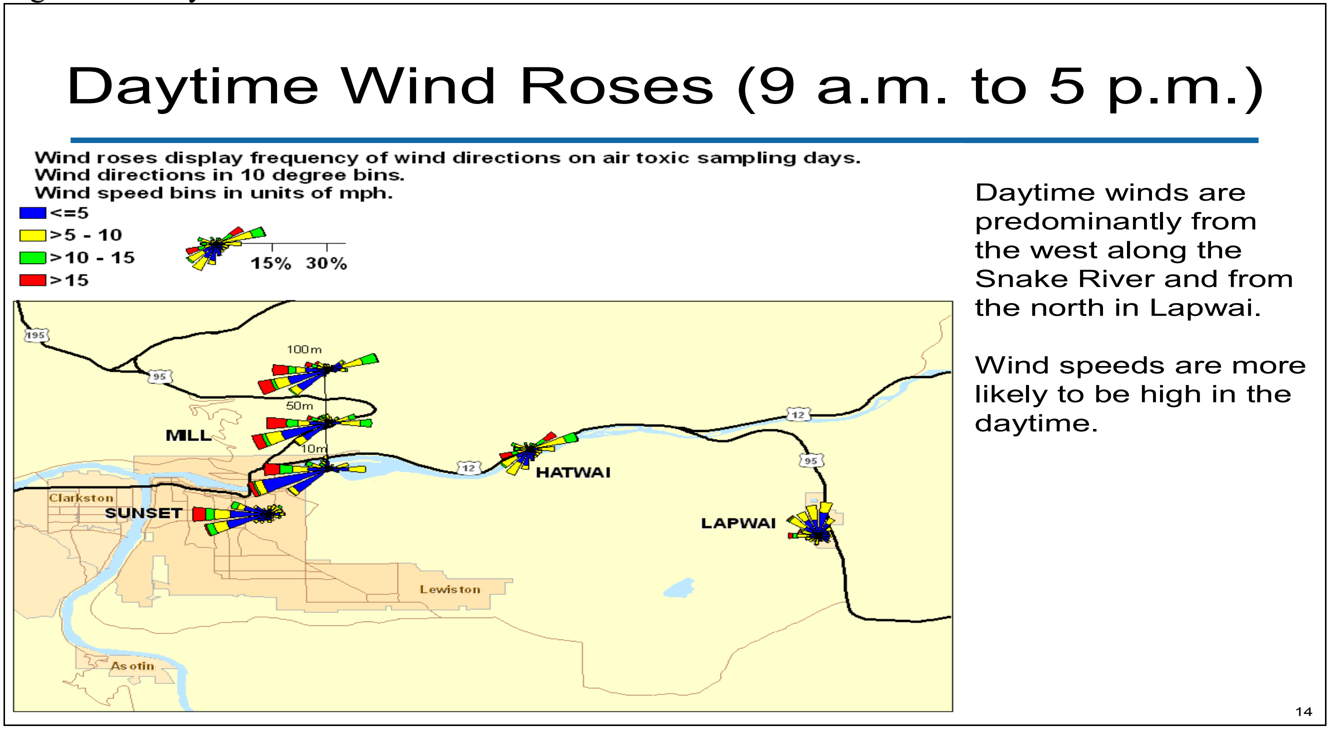
Wind roses display frequency of wind directions on air toxic sampling days.
Wind directions in 10 degree bins.
Wind speed bins in units of mph.

🟦 <=5
🟨 >5 - 10
🟩 >10 - 15
🟥 >15

Winds are aligned along valleys. Topography is channeling the winds up and down the river valleys.

Most winds are low (<10 mph).

Figure 12. Daytime Wind Roses



Daytime Wind Roses (9 a.m. to 5 p.m.)

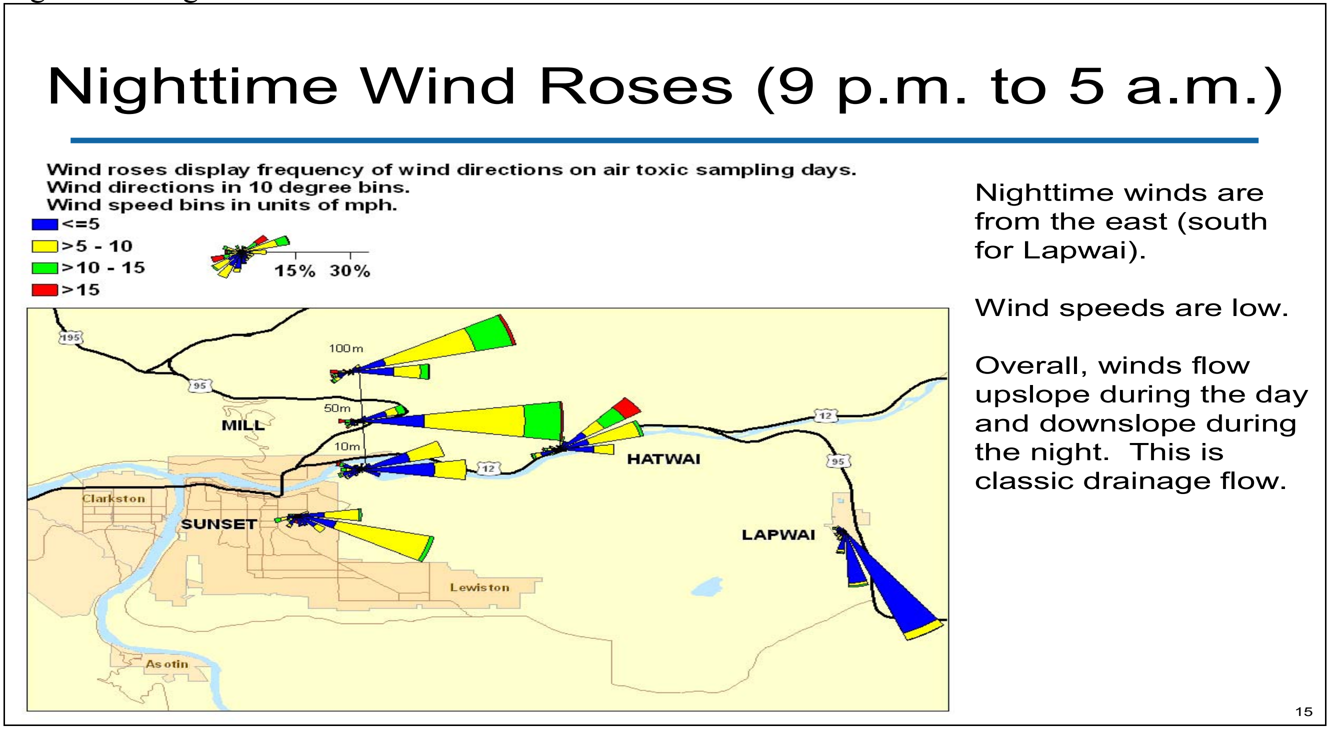
Wind roses display frequency of wind directions on air toxic sampling days.
Wind directions in 10 degree bins.
Wind speed bins in units of mph.

- 🟦 <=5
- 🟨 >5 - 10
- 🟩 >10 - 15
- 🟥 >15

Daytime winds are predominantly from the west along the Snake River and from the north in Lapwai.

Wind speeds are more likely to be high in the daytime.

Figure 13. Nighttime Wind Roses



Nighttime Wind Roses (9 p.m. to 5 a.m.)

Wind roses display frequency of wind directions on air toxic sampling days.
Wind directions in 10 degree bins.
Wind speed bins in units of mph.

- 🟦 <=5
- 🟨 >5 - 10
- 🟩 >10 - 15
- 🟥 >15

Nighttime winds are from the east (south for Lapwai).

Wind speeds are low.

Overall, winds flow upslope during the day and downslope during the night. This is classic drainage flow.

Spatial Fingerprint Maps

Examining the relative concentrations of chemicals monitored at different sites can reveal characteristic relationships that "fingerprint" an emissions source. For example, motor vehicles often produce characteristic emissions of benzene, toluene, xylenes, and ethylbenzene. The concentrations in the atmosphere of these pollutants can reveal the influence of motor vehicle emissions. In contrast, a pulp and paper mill would be expected to have a very different chemical emissions signature. According to the

Toxics Release Inventory, Clearwater Paper emitted formaldehyde, acetaldehyde, lead, manganese, and some chlorinated byproducts in 2006.[6] Other chemical compounds emitted by the Mill were not monitored in this study.

To display widely varying concentration ranges for different pollutants on the same figure, STI employed a normalization scheme. Annual means were generated for each pollutant at each site. For pollutants with collocated measurements, the mean concentration of both monitors was taken. After generating annual means at each site for each pollutant, the Lewiston area mean concentration was created by taking the average of all five sites for each pollutant. This area average was then used to normalize each pollutant's concentrations. The concentrations of each pollutant at each site were divided by the area average to generate a siteratio centered on a value of 1. The natural logarithm was then applied to this site ratio to center the values on zero and remove the positive bias in ratios for high concentrations. The results are displayed in Figures 14 through 16.

Figure 14 shows the gradients in pollutant concentrations for hydrocarbon and carbonyl compounds in the Lewiston area. Bars above the line indicate higher than average site concentrations, while those below the line indicate concentrations that are below the average. For the hydrocarbons, concentrations of most of the species are highest at the LSOB site. Concentrations are about average at ITD and Sunset and are usually well below the Lewiston average in Hatwai and Lapwai. Overall, the gradient in concentrations goes from high in the west to low in the east. This observation fits with STIs earlier predictions from the wind directions that concentrations of the primarily emitted hydrocarbons would be higher at the western sites as a result of low nighttime winds blowing from the east.

In contrast to the clear gradient in spatial concentrations among most of the hydrocarbons, the chlorinated hydrocarbons show a more complicated set of spatial patterns that is more pollutant-specific (Figure 15). Concentrations of chlorobenzene were high at the Lapwai site but were not detected in any significant amount at other sites. The main sources of chlorobenzene are industrial chemical processing and its use in herbicides, pesticides, and degreasing.[7] Local concentrations may be a result of herbicide or pesticide use near the Lapwai site. Concentrations of chloroform and tetrachloroethylene were highest at the ITD site, which is consistent with nighttime emissions from the Mill meandering across the river. Finally, there were slightly higher concentrations of dichlorobenzenes and dichloromethane at the LSOB site. These pollutants are solvents with a variety of uses: insecticide/fumigant; germicide/disinfectant; solvent for tars, oils, asphalts, and paints; paint stripping; degreasing; aerosol spray propellant for automotive spray products, etc.[8,9]

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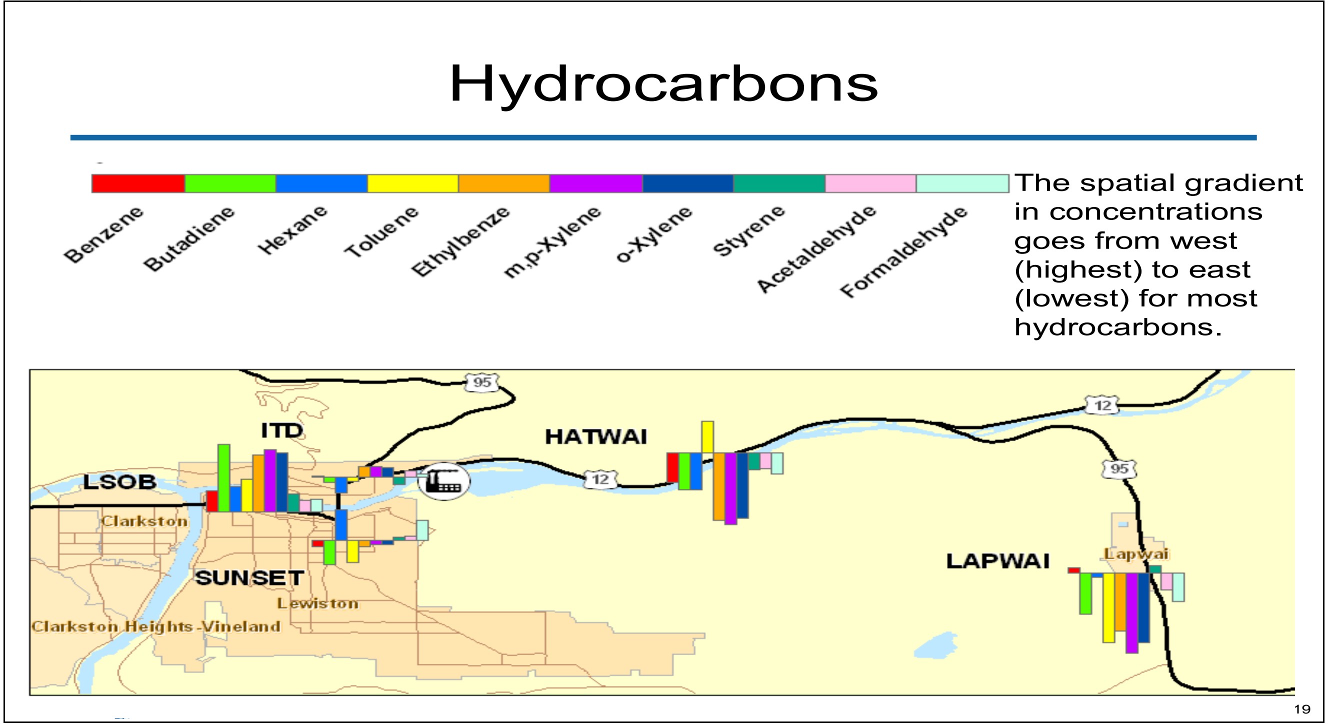
[6] U.S. Environmental Protection Agency (2008) Toxics Release Inventory (TRI) program. Available on the Internet at <http://www.epa.gov/tri>.

[7] http://www.epa.gov/ttn/atw/hlthef/chlorobe.html.

[8] http://www.speclab.com/compound/c95501.htm, http://www.epa.gov/ogwdw000/pdfs/factsheets/voc/tech/o-dichlo.pdf, http://www.speclab.com/compound/c541731.htm, http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s062dich.pdf, http://www.epa.gov/ttn/atw/hlthef/dich-ben.html, http://www.epa.gov/ogwdw/contaminants/basicinformation/dichloromethane.html#two, http://www.epa.gov/ttn/atw/hlthef/methylen.html#ref1.

[9] According to the Sonoma Tech Report (Appendix G of this report to EPA), dichloromethane is sometimes used as a de-icing agent.

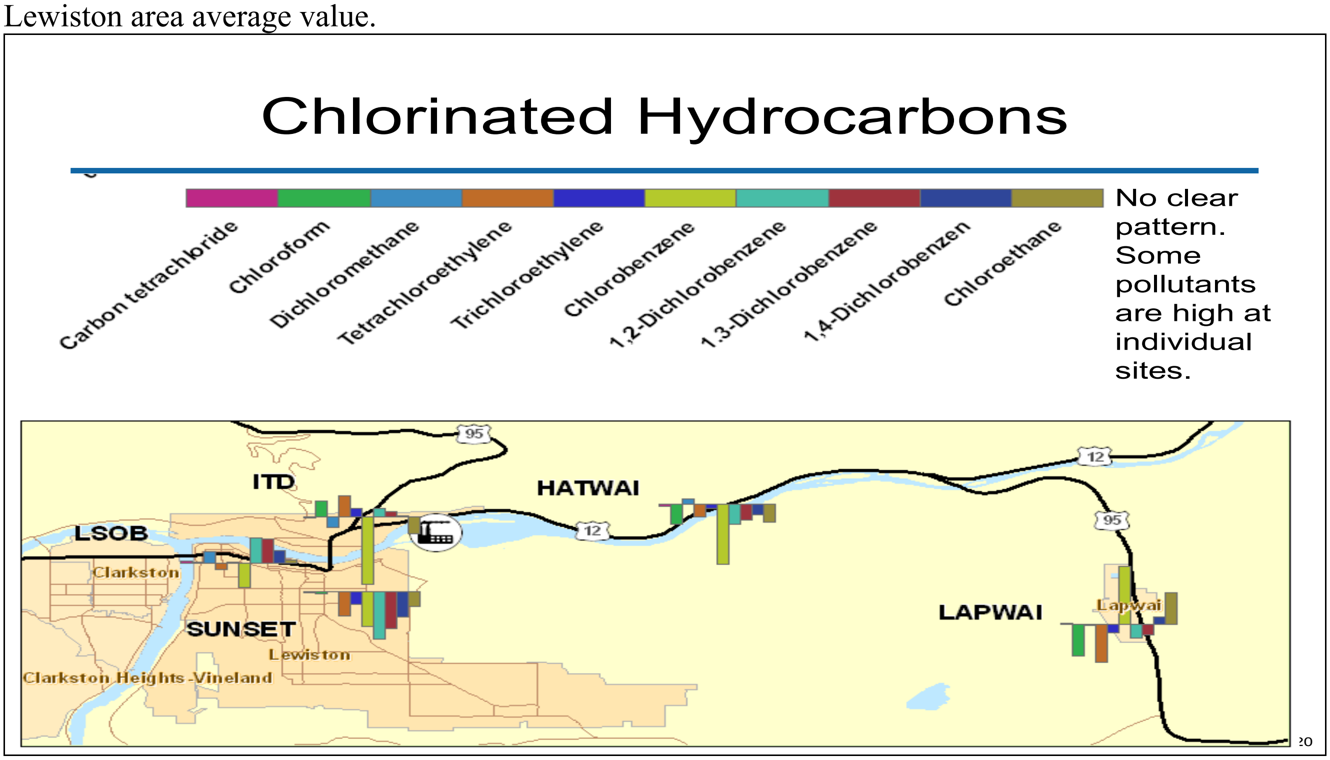
Figure 14. Fingerprint map of annual mean concentrations of hydrocarbons relative to the Lewiston area average value.



Hydrocarbons

The spatial gradient in concentrations goes from west (highest) to east (lowest) for most hydrocarbons.

Figure 15. Fingerprint map of annual mean concentrations of chlorinated hydrocarbons relative to the Lewiston area average value.

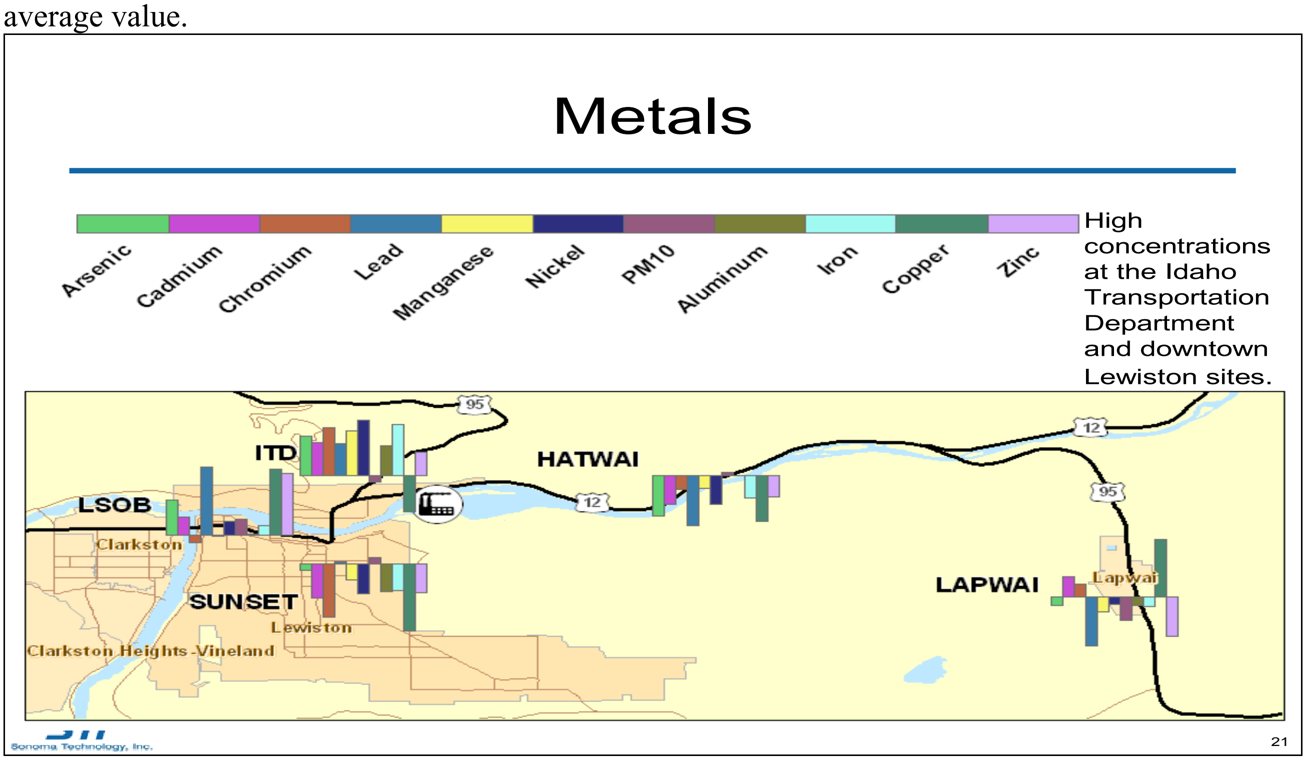


Chlorinated Hydrocarbons

No clear pattern. Some pollutants are high at individual sites.

The PM10 metals were highest overall at the ITD site (Figure 16). All metals except copper were elevated at the ITD site. Sources could include the port, brake linings, road dust, and the mill. The LSOB site reported high concentrations of lead, zinc, and copper which, according to STI, may be consistent with incinerator activity.[10] Most of the other PM10 metals were only slightly high at LSOB site. Copper concentrations were particularly high at the Lapwai site, which may be a result of a single house-fire event. Overall, most metals concentrations were lower at the Sunset, Hatwai, and Lapwai sites.

Figure 16. Fingerprint map of annual mean concentrations of PM10 metals relative to the Lewiston area average value.



High concentrations at the Idaho Transportation Department and downtown Lewiston sites.

STI found that the overall impression from the fingerprint map analysis was of a predominant set of high concentrations at the ITD and LSOB sites relative to Sunset, Hatwai, and Lapwai. These observations were consistent with emissions from the Mill and Lewiston area moving west. The implication is that concentrations of most of the pollutants examined would be higher at the westernmost sites during the nighttime than during the daytime. Even concentrations of those pollutants STI expected to be higher during the daytime (i.e., formaldehyde and acetaldehyde) were not highest at the eastern sites (i.e., daytime downwind flow to the east).

National and Regional Comparisons

In addition to understanding the local spatial gradients of concentrations, it is important to understand how the pollutant concentrations compare to concentrations in nearby areas and at the national level. The Nez Perce County population of 38,000 people in 2005 is relatively low compared to other areas that have comparable toxics measurements (Figure 17). Nez Perce County would be in the 6th percentile of population for national counties with toxic hydrocarbon measurements. Similarly, Nez Perce County is in the 26th percentile of population for counties with toxic metals measurements (all sizes). If one assumes that population is a good proxy for pollution emissions, and assumes that upwind transport of pollutants is minimal given the relative isolation of the Lewiston metropolitan area, then one might predict low concentrations of most VOCs and metals relative to other U.S. counties with air toxics measurements.

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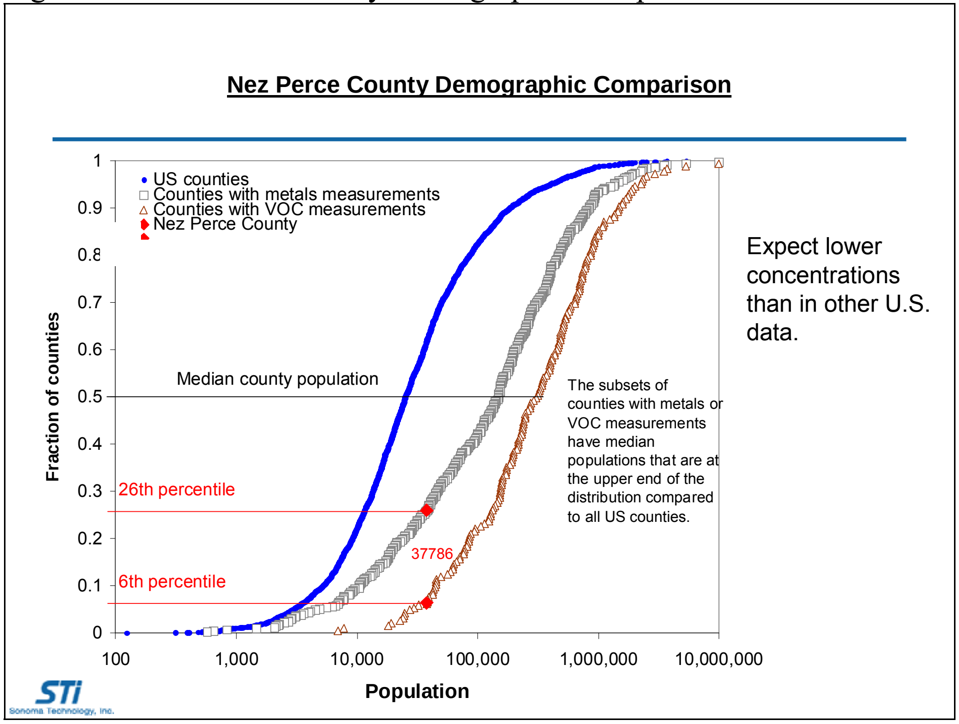
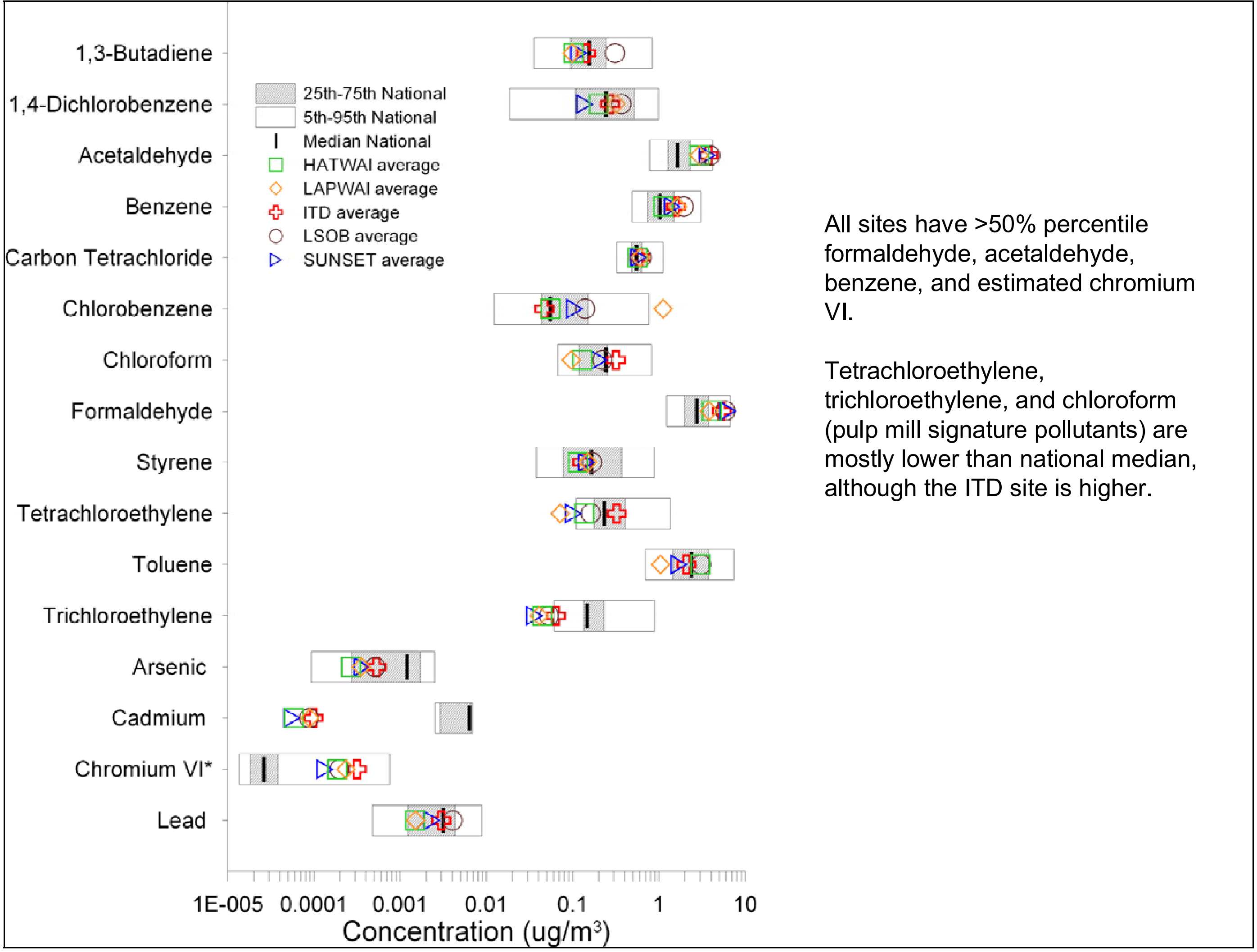
[10] According to IDEQ, there is an animal incinerator less than two miles to the south/southwest and one less than two miles to the northeast. Furthermore, there is human crematory within 2 miles to the south. There is also an ammunition manufacturer at 3 separate locations to the south and southeast that according to the TRI release copper and lead. It is unknown at this time if other incinerators exist in the immediate area surrounding the LSOB site.

Figure 17. Nez Perce County Demographic Comparison.



That was not the case, however. Figure 18 shows a comparison of national distribution of annual mean concentrations from 2003-2005 with the annual mean concentrations at Lewiston area monitoring sites. Across all Lewiston area sites, formaldehyde and acetaldehyde were always between the 75th and 95th percentile of annual mean concentrations observed. The estimated hexavalent chromium concentrations (generated by multiplying total chromium concentrations by 0.34) were also always above the 75th percentile. The Lapwai site is the only Lewiston area site with a pollutant—chlorobenzene—above the 95th percentile concentration nationally. Concentrations of chlorobenzene at other sites were not elevated relative to national levels. A few other pollutants were observed at concentrations above the 50th percentile. These pollutants include benzene, 1,3-butadiene, toluene, chloroform, tetrachloroethylene, and 1,4-dichlorobenzene. Note that benzene and 1,3-butadiene concentrations were not reliably measured. Unfavorable topography may be a major reason for high concentrations. The river valley may trap emissions locally, especially under low-wind nighttime conditions.

Figure 18. Comparison of national distribution of annual mean concentrations from 2003-2005 with the annual mean concentrations at Lewiston area monitoring sites.

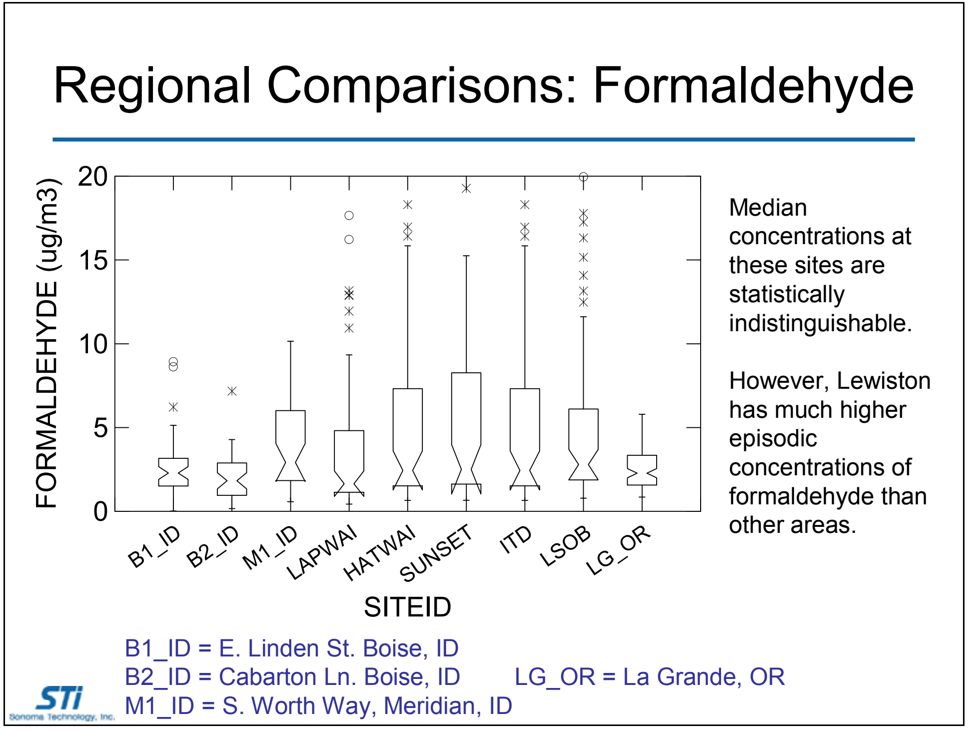


All sites have >50% percentile formaldehyde, acetaldehyde, benzene, and estimated chromium VI.

Tetrachloroethylene, trichloroethylene, and chloroform (pulp mill signature pollutants) are mostly lower than national median, although the ITD site is higher.

Because concentrations of some of the key pollutants measured were higher than expected, a regional comparison of concentrations was performed. Available monitoring data from 2006 and 2007 from eastern Oregon, eastern Washington, and the Boise area were downloaded from the EPA's Air Quality System (AQS). Median formaldehyde concentrations were statistically indistinguishable across most of the sites at a value of about 2 to 3 μg/m^3. (Figure 19). However, the upper distribution of concentrations in Lewiston was higher than that at other regional sites. Moreover, the very high episodic concentrations of formaldehyde were much higher at each of the Lewiston sites than at any of the other inland northwest sites. The much higher concentrations at the upper end of the distribution results in high annual mean concentrations of formaldehyde. Acetaldehyde plot values were comparable to the formaldehyde values, with very similar median acetaldehyde concentrations across the inland northwest but very high episodic concentrations at the Lewiston area sites (Figure 20). According to STI, the regional comparison implications are that high concentrations are likely locally derived and do not appear to be transported in, and more than half of the concentrations for key risk drivers such as formaldehyde and potentially benzene and 1,3-butadiene, are likely to be locally derived.

Figure 19. Notched box whisker plot of formaldehyde concentrations (ug/m3) at Lewiston area sites; three Boise, ID sites; and the La Grande, OR, site.



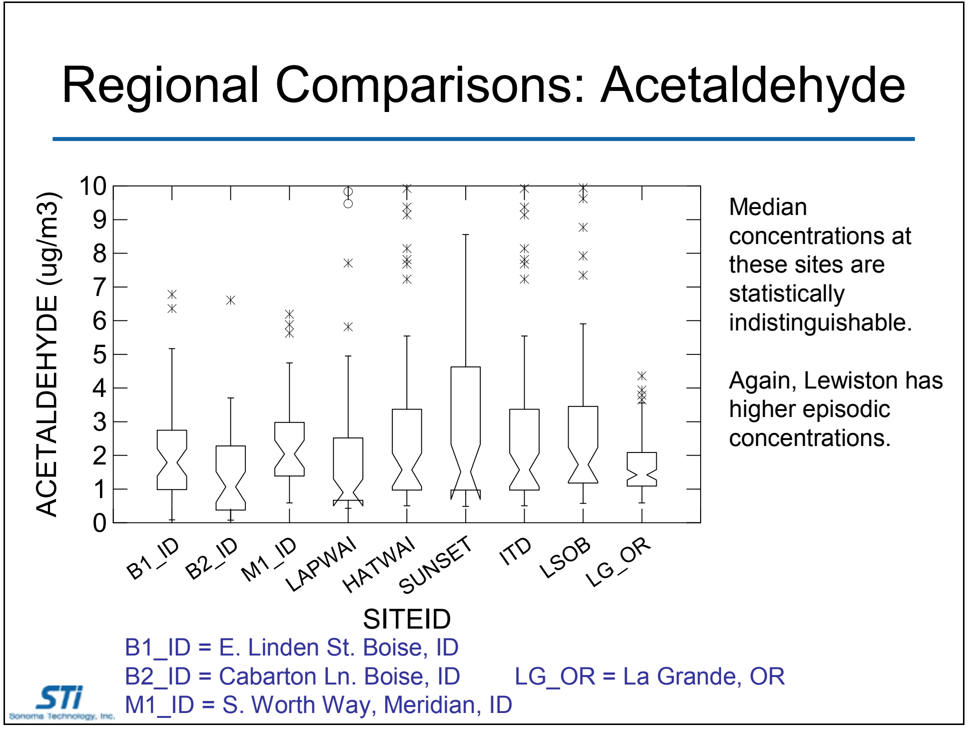
Regional Comparisons: Formaldehyde

Median concentrations at these sites are statistically indistinguishable.

However, Lewiston has much higher episodic concentrations of formaldehyde than other areas.

B1_ID = E. Linden St. Boise, ID
B2_ID = Cabarton Ln. Boise, ID
M1_ID = S. Worth Way, Meridian, ID
LG_OR = La Grande, OR

Figure 20: Notched box whisker plot of Acetaldehyde concentrations at Lewiston area sites; three Boise, ID sites; and the La Grande, OR, site.



Regional Comparisons: Acetaldehyde

Median concentrations at these sites are statistically indistinguishable.

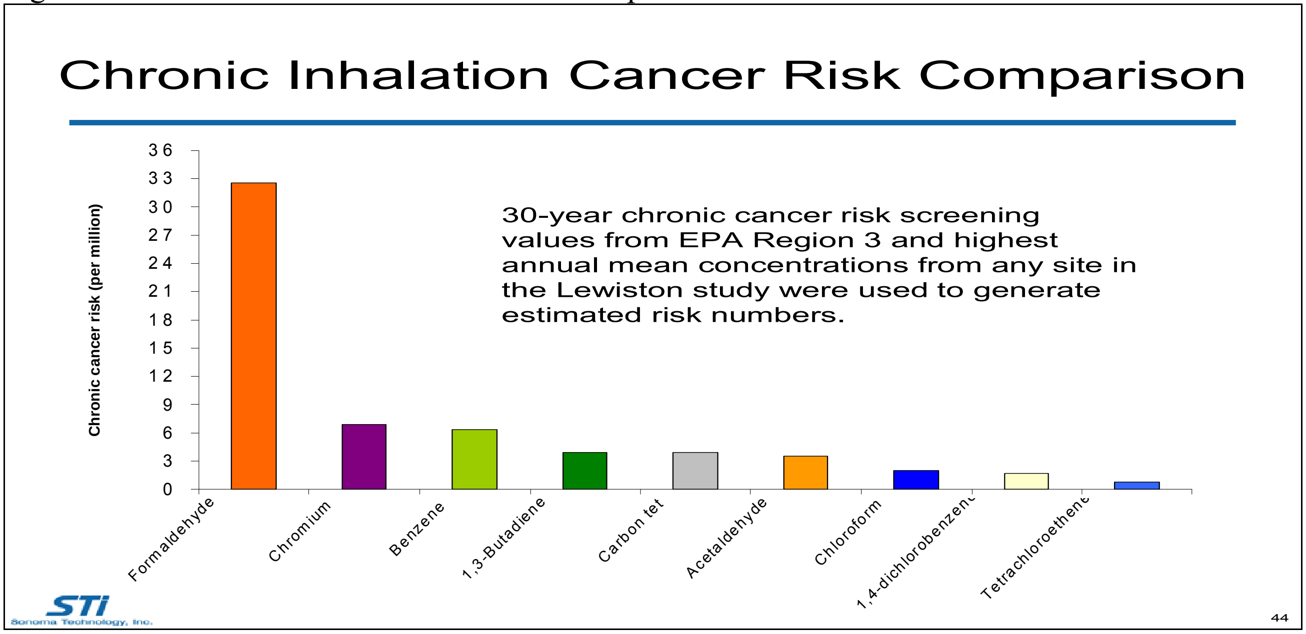
Again, Lewiston has higher episodic concentrations.

B1_ID = E. Linden St. Boise, ID
B2_ID = Cabarton Ln. Boise, ID
M1_ID = S. Worth Way, Meridian, ID
LG_OR = La Grande, OR

Comparing Chronic Risk Values among Pollutants

STI's analysis determined that overall, the chronic cancer risk from formaldehyde is larger than the sum of risk for all other pollutants combined. (Figure 21). Formaldehyde risk is far greater than other species and is the only pollutant with a risk exceeding 10 per million. From a policy perspective, reducing formaldehyde concentrations would provide the most reduction in health risk. The risk from chromium is next, and assumes that the toxic form of chromium (hexavalent chromium) is approximately 16% of the total chromium measured. Benzene and 1,3-butadiene have the next highest values and are primarily emitted from mobile sources. However, the accuracy of these annual mean concentrations is in question based on the collocated analysis. Carbon tetrachloride is next and is a background pollutant that, although it is no longer emitted in the United States, has a very long residence time in the atmosphere. Concentrations of carbon tetrachloride are declining at a rate of approximately 1% per year.[11] Acetaldehyde correlates very well with formaldehyde but is not as toxic to the respiratory system. Chloroform and tetrachloroethylene are both likely emitted from the Mill, but present considerably lower risk contributions than other pollutants on the list.

Figure 21. Chronic Inhalation Cancer Risk Comparison



30-year chronic cancer risk screening values from EPA Region 3 and highest annual mean concentrations from any site in the Lewiston study were used to generate estimated risk numbers.

Given formaldehyde's prominence among cancer risk pollutants, additional analyses were performed to determine the likely cause of the high concentrations of formaldehyde. A time series was plotted to determine the seasonal pattern of concentrations. Figure 22 plots individual concentrations of formaldehyde measured during the year at each site along with a five-site average and standard deviation. Concentrations are clearly highest in the summer months, with particularly high concentrations in July when solar radiation is at its peak. High summer concentrations are consistent with formaldehyde seasonal patterns observed nationally and are responsible for the relatively high annual mean concentrations. Concentrations in May, June, July, and August often exceeded 10 ppb at one or more sites and almost always exceeded 10 ppb at all sites in July. This seasonal pattern is consistent with high summertime emissions or secondary photochemical production. The most likely sources of summertime emissions are secondary production of reactive VOCs such as biogenic emissions (e.g., isoprene and terpenes), fires, or some local primary emissions. This seasonal pattern could be consistent with

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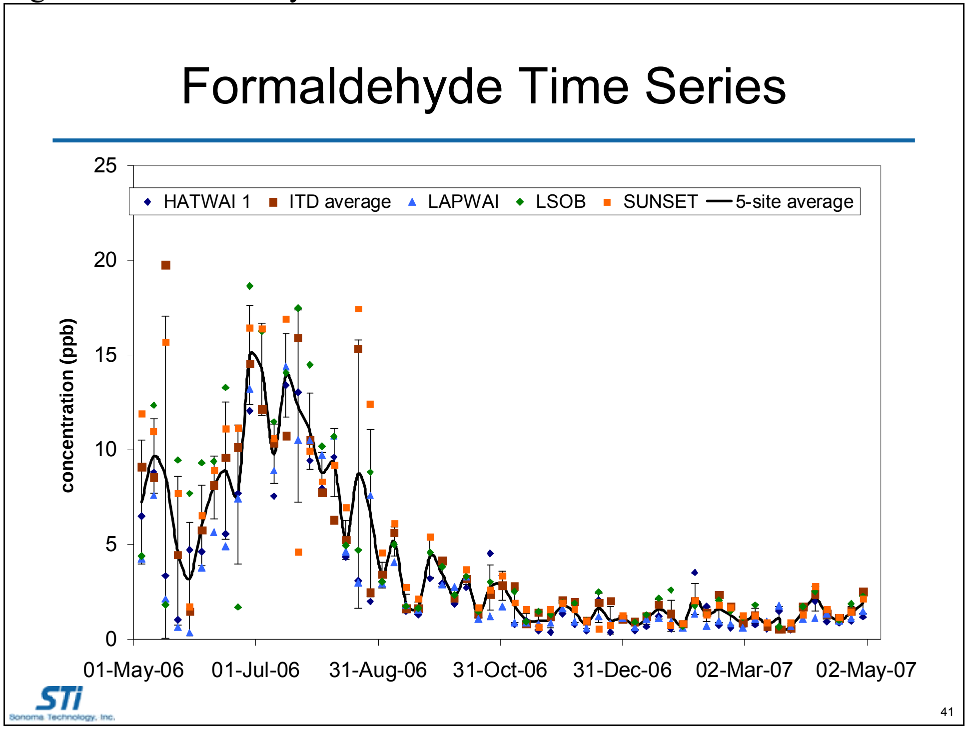
[11] Montzka S.A., Butler J.H., Elkins J.W., Thompson T.M., Clarke A.D., and Lock L.T. (1999) Present and future trends in the atmospheric burden of ozone-depleting halogens. *Nature* **398**, 690-694.

secondary production arising from high VOC concentrations emitted locally that only produce large amounts of formaldehyde during the warm summer months with high solar radiation.

Figure 22. Formaldehyde Time Series



Normally, STI would consider the seasonal pattern seen in Figure 22 a simple example of high secondary production, but the episodically high concentrations in the Lewiston area are far higher than those in Boise or La Grande as shown in Figure 19. Total VOC emissions are very unlikely to be higher in Lewiston than in the Boise area, and biogenic secondary production is unlikely to be responsible for higher concentrations than those in La Grande or Boise. Some combination of high secondary production, topographically trapped concentrations, and high VOC concentrations from anthropogenic and/or biogenic sources may be the most likely cause. Diurnal measurements of formaldehyde, acetaldehyde, and key precursor species like isoprene, terpenes, toluene, benzene, pentane, and total nonmethane organic compounds (TNMOC) would be very valuable in understanding the cause of locally high formaldehyde and acetaldehyde concentrations.

Conclusions

As a result of this monitoring study, STI determined that a few key issues emerged that should be considered by the Nez Perce Tribe and Lewiston area residents. Most importantly, concentrations of formaldehyde and acetaldehyde are much higher than expected for an area of Lewiston's size. Because formaldehyde is the largest contributor to cancer risk among the pollutants measured and acetaldehyde is a significant contributor, this result is significant. Concentrations of formaldehyde and acetaldehyde were highest in the summer months but do not appear to be related to special events like large wildfires. Secondary production of formaldehyde and acetaldehyde are most likely to be responsible for the seasonal pattern, but it is unclear why concentrations are higher in the Lewiston area than at other sites in the inland northwest. Insufficient information is available about local concentrations of anthropogenic and biogenic VOC concentrations to determine why formaldehyde and acetaldehyde are high. The Mill may be indirectly responsible for some of the high formaldehyde and acetaldehyde concentrations, but this hypothesis cannot be tested with the available monitoring data.

Of second importance, analytical laboratory measurement issues with the benzene and 1,3-butadiene concentrations reported in this study call into question the reliability of the laboratory results. The concentrations of benzene were particularly problematic based on both the collocated measurements and comparisons with other pollutants that are typically closely correlated with benzene (e.g., toluene, xylenes). As a result, benzene and 1,3-butadiene concentration data should be considered less reliable for generating risk values, evaluating emissions sources, and assessing spatial gradients in concentrations.

Of the pollutants examined, only three met initial criteria for consensus with respect to spatial, temporal, and chemical characteristics for Mill emissions. Concentrations of chloroform, tetrachloroethylene, and trichloroethylene were all highest at the ITD site, were emitted from the Mill's chlorine bleaching process, and were essentially randomly high, a pattern that is consistent with fugitive (or upset) emissions. Of these pollutants, chloroform and tetrachloroethylene are small but significant contributors to chronic risk in the Lewiston area. It is also possible that the Mill contributes substantially to formaldehyde and acetaldehyde concentrations indirectly through VOC emissions of both anthropogenic and biogenic photochemical precursors. However, this conclusion is not possible to validate with the available monitoring data. If the Mill contributes substantially to formaldehyde and acetaldehyde concentrations, the relative health impact from the Mill's emissions would be much larger than those of the chlorinated hydrocarbon emissions alone.

Recommendations

STI determined that, overall, concentrations of formaldehyde (and acetaldehyde) are high enough, and of sufficient concern for health risk, to be worthy of additional study. While the chronic cancer risk from these pollutants is not high enough to be considered an urgent danger, the concentrations are sufficiently out of the ordinary to be very interesting. A number of potential actions can be taken to examine the high concentrations. The current monitoring study has shown that concentrations are high in the summer and are much higher than those seen at other monitoring sites in the inland northwest. However, the origin of the high concentrations cannot be specifically identified, given the presumably lower or similar emissions characteristic of other nearby sites such as those in Boise or eastern Oregon. Further examination of the existing meteorological data may be useful for comparing average summer-day wind speeds at each of the monitoring sites to average non-summer day wind speeds to assess the valley's ventilation on high concentration days (i.e. are hot summer days stagnant enough to account for locally high concentrations?).

Setting up a single, long-term air toxics monitoring site in the Lewiston area should be considered. The sampling expertise acquired during the monitoring study would help improve data collection efficiency. Additionally, it may be interesting to use a more highly time-resolved measurement system such as an Aethalometer™ to investigate local meteorological impacts on the concentrations and test whether the topography is, in fact, trapping emissions in the local area as a result of inversion layers over the Clearwater Valley. Assessing inversion layer days and trying to correlate them with days when concentrations of primary and secondary pollutants are high may yield additional insight into the sources of high concentrations.

Another special study should be considered to focus on the causes of high local formaldehyde and acetaldehyde concentrations, potentially based on the Photochemical Assessment Monitoring Stations (PAMS) monitoring protocol. Because formaldehyde is the largest problem and highest in the summer months, a three-month monitoring program with diurnal measurements of 3-hr or 1-hr duration may be sufficient to identify the cause of the high local concentrations. Specifically, four to six measurements a day at one or two sites would be sufficient to characterize diurnal patterns in formaldehyde and acetaldehyde concentrations. Additionally, canisters measuring hydrocarbon precursors like pentane, isoprene, toluene, and TNMOC could be used to isolate the potential sources of precursors. The expected diurnal patterns of formaldehyde from direct emissions, indirect local production, and transported formaldehyde would be identifiable and distinguishable with this monitoring setup. However, this kind of sampling program is relatively expensive.