Observations of volatile organic and sulfur compounds in ambient air and health risk assessment near a paper mill in rural Idaho, U. S. A.

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Abstract

The Lewis-Clark Valley is a rural area that includes the cities of Lewiston, Idaho and Clarkston, Washington and the surrounding areas. The largest industry in the Lewis-Clark Valley is a pulp paper mill located in Lewiston which emits particulate matter and odorous sulfur air pollutants. This study analyzed the Lewis-Clark Valley air composition and seasonal, temporal and spatial variations of volatile organic compounds (VOCs) from 2017 to 2018 to determine potential health risks of the paper mill emissions to the surrounding community. Both active and passive air sampling via sorbent tubes were analyzed by thermal desorption - gas chromatography-mass spectrometry (TD-GC-MS). Fifty VOCs including benzene, toluene, chloroform, dimethyl sulfide and dimethyl disulfide were measured in the ambient air of the Lewis-Clark Valley at ten different sites, totaling over 800 samples. In addition, passive sorbent tubes were deployed in 2018 to obtain monthly averages in Lewis-Clark Valley and three urban locations in Idaho and Washington for comparison. United States Environmental Protection Agency (2001) methodology was used to assess cancer risks in the community based on the upper confidence levels of five carcinogens and nine air toxics. The Lewis-Clark Valley had similar levels of benzene to urban areas but had a strong signature of chloroform and sulfides from the paper mill. The cumulative cancer...
risk was $2 \times 10^{-6} - 11 \times 10^{-6}$ mainly due to the compounds chloroform, benzene and carbon tetrachloride. The hazard index of other air toxics was less than one. Overall, these air pollutants were considered low risk to the local population.

**Keywords**

Volatile organic compounds; Sulfur; Paper mill; Gas chromatography; Benzene; Health risk assessment

1. **Introduction**

The Lewis-Clark Valley (LCV)\(^1\) is a rural area with a combined population of over 50,000, located along the Northern Idaho-Eastern Washington border at the confluence of the Snake and Clearwater Rivers. The LCV is at an elevation of 738 feet and has a depth of 2000 feet. It encompasses the cities of Lewiston (46°24′01.4″N 117°00′04.3″W), Clarkston (46°24′58.7″N 117°02′42.7″W), and Asotin (46°20′21.5″N 117°02′53.5″W) and is home to several industries including a large Kraft pulp paper mill (main employer in LCV), engineering and ammunition factories. The paper mill is a primary emitter of local air pollutants and gives the valley its distinctive sulfurous smell that is often noted by residents and visitors. The region is surrounded by agricultural and recreational areas, including Hells Canyon National Recreation Area to the south. The Nez Perce Indian Reservation neighbors the LCV to the east and south. The LCV experiences moderate weather conditions, with hot summers and mild to cold winters. It has also been subject to summer wildfire seasons that have become more frequent in the Northwest in the recent decade.

The paper mill (formerly Potlatch Corporation, now Clearwater Paper Corporation) was built in 1950 and is the only Tier 1 permitted air polluter in the region besides the adjacent Idaho Forest Group (Idaho Department of Environmental Quality, 2020). Air emissions of paper mills typically include particulates, sulfides, thiols, and volatile organic compounds (VOCs) (US Dept of Health and Human Services, 2007; Gavrilescu, 2006). The local

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\(^1\)Abbreviations
- AT averaging time
- CA measured concentration
- CDA Coeur d’Alene
- EC exposure concentration
- ED exposure duration
- EF exposure frequency
- ET exposure time
- HI hazard index
- HQ hazard quotient
- IDEQ Idaho Department of Environmental Quality
- IRIS Integrated Risk Information System
- IUR inhalation unit risk
- LCV Lewis-Clark Valley
- NPT Nez Perce Tribe
- RfC reference concentration
- TRS total reduced sulfur
- UCL upper confidence level
- ACS American Cancer Society
- LCSC Lewis-Clark State College
- US EPA United States Environmental Protection Agency
Idaho Department of Environmental Quality (IDEQ) measures air particulate matter (PM$_{2.5}$) in Lewiston but does not monitor VOCs or sulfur compounds. A few studies regarding the emissions in the LCV have been carried out previously. The Nez Perce Tribe (NPT) conducted a study in 2006–2007 measuring the concentration of various volatile organic compounds (VOCs) including benzene, toluene, ethylbenzene and formaldehyde in the Lewis-Clark Valley (Nez Perce Tribe, 2009). The study found benzene concentration levels to be higher than the national mean and found formaldehyde/acetaldehyde levels to be higher than in surrounding areas (Nez Perce Tribe, 2009). The NPT study also concluded that the ambient air concentration of VOCs studied were similar to that of an urban area (population greater than 50,000). This is likely due to local emissions and the topography of the area. Often in the winter months, temperature inversions develop and keep the particulates and other pollutants in the valley. In 2015, the United States Environmental Protection Agency (US EPA) filed a lawsuit against Clearwater Paper, noting the company’s violations of the Clean Air Act (US EPA, 2015a). Subsequently, the paper mill settled and installed a new digester at the end of 2017. Most recently, a study by the NPT and Washington State University set out to characterize the LCV air during the summers of 2016–2017 in relation to the high formaldehyde previously recorded and these results are forthcoming. Despite these studies, there has not been a study longer than one year during all seasons that measured spatial and temporal variability of VOCs, air toxics and/or hazardous air pollutants (HAP).

Many VOCs are known carcinogens and respiratory exposure to them can pose potential health risks. BTEX (benzene, toluene, ethylbenzene, and xylenes) are associated with oil refineries, gasoline, and vehicular exhaust. Of these, benzene is a carcinogen known to affect the immune system, bone marrow, and the brain (Oak Ridge Reservation Environmental Restoration Program -ORERP; 2006). Toluene is also emitted by paint, printing and adhesive solvents and is known to affect cardiac and nervous systems (ORERP, 2006). Chloroform is a carcinogen and known byproduct of the chlorine bleaching process used by pulp paper mills. It is also produced at hazardous waste sites and sanitary landfills, and it impacts the kidney, liver, cardiac, and nervous systems (ORERP; 2006). The reduced sulfur compounds dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) are emitted during the paper pulping process and may be used in soil fumigants and industrial applications. DMS and DMDS are also naturally occurring in marine and soil environments. These sulfides are known to have respiratory, ocular, and integumentary system impacts (US EPA, 2018a). Studies of odor and health consequences of paper mills include surveying the air and the community for effects which tend to be respiratory and nuisance in nature (Haahtela et al., 1992; Jarvensivu et al., 2000; de Bias et al., 2017).

There is currently not an established link of cancer risk to VOCs in the LCV. From 2014 to 2018 Idaho Health District 2 (which includes Nez Perce County) had a higher cancer mortality rate, 226 deaths per 100,000 individuals per year in comparison to 175.6 per 100,000 for the rest of the state (Idaho Department of Health and Welfare, 2018). Though the cancer mortality rate may not be significantly different, it is possible this elevated level of cancer mortality can be due in part to exposure to VOCs and/or HAP compounds. Benzene was addressed in the Lewiston area with a conclusion that levels were below the national mean and an overall low risk to the community, with about two extra cancers per...
100,000 (US Dept of Health and Human Services, 2005). The NPT reported that cancer risk and the air quality in the LCV did not show significant differences in cancer rates for individuals living in the valley (NPT, 2009). Upon reviewing the literature on the impacts of pulp paper mills on surrounding communities and workers, low risks were associated with cancers (Soskolne and Sieswerda, 2010); however, many of these compounds are known air toxics and may cause respiratory problems, including asthma and ischemic stroke (Chiu and Yang, 2013). Significantly more cases of mortality (almost double overall) due to lung and bronchus cancers than expected (p = 0.002 for males and p = 0.017 for females) were present in Nez Perce County from 2014 to 2018 (Cancer Data Registry of Idaho, 2018).

Health risk assessments are important for communities to be aware of and can also help local industries make environmental impact decisions. Nationally, the risk for VOCs and HAPs is about $1 \times 10^{-6}$ (1 per million) based on ambient measurements (McCarthy et al., 2009). There was an updated national inventory of HAPs that concluded the total risk of cancers from these substances was $33 \times 10^{-6}$ for all cancers (US EPA, 2014). Differences in risk would be expected in rural and urban areas, but a study in China that looked at VOCs and health risks had about the same cancer risk at urban vs suburban sites of about $2 \times 10^{-6}$ (Zeng et al., 2019).

The purpose of this study was to analyze the ambient short-term and long-term concentrations of VOCs and reduced sulfur compounds in the LCV to determine any increased health risk due to poor local air quality. In addition, seasonality, temporal, and spatial variations were examined for several air toxic and VOC compounds within the LCV. Finally, the LCV air composition and health risk was compared to urban areas including Spokane, Washington-WA, Coeur d’Alene, Idaho-ID and Boise, Idaho-ID.

2. Methods

2.1. Air sampling protocols

Markes International dual sorbent tubes (Tenax®-TA-Sulficarb) were used with Gilian Air Plus and Markes ACTI-VOC low flow air pumps to collect 864 ground-based active samples (2 L volume over 10 min at 200 mL/min flow) in the LCV. Weekly collection occurred at up to 10 locations (Fig. 1A) for samples from February 2017 to December 2018. In addition, 83 total passive or diffusion samples were taken in Idaho (Boise, Coeur d’Alene-CDA, Lewiston) and Washington (Clarkston and Spokane) each month for 2–4 weeks at a time during 2018 (Fig. 1B). Sample sites were chosen to include proximity to the paper mill, distribution around the city centers, background sites, and nearby cities in the region for comparison. Coeur d’Alene, Idaho is similar in size to LCV, and Boise and Spokane are both larger cities with over 200,000 population. Sample site details are shown in Table S1 for reference. Sample collection was based on EPA method 325 using Markes EPA-325 sorbent tubes (Markes International, 2009; US EPA, 2015b; 2019). Tenax®TA sorbent tubes were also used for this purpose, to determine long-term exposure to air toxics. Depictions of the sampling set up are shown in Figure S1.

Prior to sampling, sorbent tubes were blanked using the thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) method detailed below. Field blanks for...
active samples were transported to the sampling site, uncapped, briefly attached to the pump and recapped without running the pump. Field blanks for passive samples were also transported to the site but were left capped and hung side by side with the actual sample tube for the entire duration. Upon return to the laboratory, samples were purged with ultra-high purity (UHP) N₂ gas for 5 min at a flow rate of 100 mL/min to reduce water vapor. Samples were then placed in a desiccator for short term storage or wrapped in foil and refrigerated for up to a week until analyzed via TD-GC-MS.

In addition to air sampling above, there is a PM₂.₅ monitor at one of our sampling sites (Site 8, Sunset Park) that is hosted by the (IDEQ). This data is publicly available after archival, and can be obtained via US EPA website (US EPA, 2020a). This data was used in comparison and to elucidate fire episodes and winter inversions.

2.2. TD-GC-MS

The following method is adapted from EPA TO-17 method (US EPA, 1999). Samples were desorbed using a thermal desorption unit (Markes Unity 2) for 5 min at 50 °C and 10 min at 200 °C, with UHP He carrier gas at a flow rate of 25 mL/min. A sulfur cold trap was heated from 30 °C to 250 °C at a rate of 40 °C/s and maintained for 10 min during split-less injection into a gas chromatograph-mass spectrometer (Agilent 7820A GC, Agilent 5977E MSD). An Agilent DB-624 UI, 60 m × 320 μm x 1.8 μm gas chromatograph column was used for compound separation, with oven temperature programming consisting of 40 °C for 2 min, 10 °C/min ramp to 195 °C, and 12.5 min hold at final temperature for a total run time of 30 min. UHP He gas was used as carrier gas at a flow-rate of 1.5 mL/min. The mass spectrometer detector (MSD) was operated in scan mode with trace ion detection and an applied EM voltage of 1441 V, ion source temperature of 230 °C and quadrupole temperature of 150 °C. The MSD ran at a scan speed of 1562 amu/s, 45.00 and 280.00 amu range, with a solvent delay of 3.25 min. Mass ions lower than 45.00 amu were omitted due to strong residual signal from carbon dioxide collected in the tubes.

2.3. Quality control

Analytical standards were prepared and analyzed from liquid solutions of 48 VOCs (AccuStandard M-502-PAK 60 compound 0.2 mg/mL) and two sulfur compounds (Acros Organics 99% Dimethyl disulfide, Alfa Aesar 99+% Dimethyl sulfide) diluted to 100 ppmv in HPLC grade methanol. These standard solutions were injected onto a sorbent tube using Markes calibration solution loading rig with UHP N₂ at a rate of 100 mL/min for 5 min. The tubes were then capped, wrapped in aluminum foil, and stored for 1–7 days in a refrigerator until analyzed. To calculate the mass of compound injected in the case of liquid solutions, the densities of the sulfides were used (DMS = 0.846 g/mL and DMDS = 1.06 g/mL). Calibration curves with masses ranging from 0.40 to 60.0 ng resulted in R² values of 0.98–0.99 (Table S2).

Percent recovery checks were prepared and analyzed (10–20 ng) with excellent recovery close to 100%. When compounds were outside of the 80–120% range, the calibration process was repeated. Precision based on paired samples was on average 90% with a range of 85–95%. The method limit of detection (LOD) ranged from 0.01 to 0.12 μg/m³ depending
on the compound. The LOD was based on seven low level (0.1 ng) spiked sorbent tube analysis and calculated by standard deviation multiplied by three, divided by the typical air volume of 2 L (3s/2).

Table S2 gives a full list of compounds, showing the compound information, retention times, quantification ions used in MSD, limit of detection and representative linearity of calibration during the sampling period. An example chromatogram of a standard (10 ng VOC), active sample from Mill Rd (Site 6) and blank are shown in Figure S2. The sulfides are shown in the sample (peaks 4 and 20) as they were calibrated separately from the VOC standard. Representative calibration curves for benzene, toluene, DMS, and DMDS are shown in Figure S3.

2.4. Data analysis

Masshunter Chemstation data analysis software (Agilent) was used to process raw GC-MS data and quantify the compounds present in the sample. Each individual peak was manually inspected for positive identification (using 3–4 mass qualifiers and retention time) as well as accurate peak area integration (manual integration when necessary). Calibration curves of peak area versus mass (ng) injected were used to determine the mass in each sample.

Active sample concentrations were calculated by subtracting the average mass of blanks (n = 12) from the reported mass values for the samples, then dividing by the sample volume in L, giving ng/L or μg/m³ (Equation (1)). These can be converted to ppbv by multiplying by RT/(P × MW) if necessary or for comparison, where R is the ideal gas law constant 0.08206 L atm/(mole K), MW is molecular weight (g/mole), T is measured temperature (K) and P is measured atmospheric pressure (atm) during sampling. For 298 K and 1 atm this multiplier equals 24.45/MW. The preferred unit is μg/m³ as that was directly measured. Passive sample concentrations were calculated by using the mass values divided by a corresponding uptake rate and the time of sampling in minutes (Equation (2)). Uptake rates used are found in Table S.3. Equation (3) converts the concentration from volume mixing ratio (ppbv) to mass concentration (μg/m³).

Concentrations (C) of analytes were calculated as follows:

**Active Samples:**

\[
C( \mu g / m^3) = (m_{sample} - m_{blank}) / V \tag{1}
\]

Where C = ambient concentration in μg/m³, m is the mass of chemical in ng, V is the volume of the sample in L, and 1 ng/L = 1 μg/m³.

**Passive samples:**

\[
C(\text{ppbv}) = (m_{sample} - m_{blank}) \times 1000 / (U \times t \times (T/298)^{1/2}) \tag{2}
\]

\[
C( \mu g / m^3) = C(\text{ppbv}) \times MW/24.45 \tag{3}
\]
Where C is the ambient concentration in ppbv or μg/m³, U is the uptake rate of chemical on a specific sorbent in (ng ppmv⁻¹ min⁻¹), t is the sampling time in minutes - typically between 20,000–43,000 min (14–30 days), T is the average temperature in Kelvin units during the sampling time period, 1000 converts 1 ppmv to ppbv, MW is the molecular weight of the compound (g/mole), and 24.45 is the molar volume of an ideal gas at 1 atm and 298 K.

Equation (2) temperature dependence was adopted from U.S. Environmental Protection Agency (2018b).

2.5. Health risk assessment

The effect of exposure to VOCs can be determined by the use of toxicological and risk models. An accepted procedure, commonly used in human health risk assessments under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Superfund, uses the maximum exposure concentration times a risk or hazard factor for selected chemicals (US EPA, 2001; 2009). The inhalation unit risk (IUR) factors and risk categories are available through Integrated Risk Information System, IRIS (US EPA, 2020b). US EPA ProUCL 5.1 software (US EPA, 2016) was used to address non-detects in the data set and also determine general statistics and upper confidence limits (95 UCL) of select species at specified sampling locations.

The following equations were used in calculating risk (US EPA, 2009)

\[
\text{Risk} = \text{EC} \times \text{IUR}
\]  

(4)

Where EC is the exposure concentration in μg/m³, calculated by Equation (5), and IUR is the inhalation unit risk in (μg/m³)⁻¹, or the lifetime risk for an individual exposed to.

1 μg/m³ of developing cancer.

\[
\text{EC} = \frac{\text{CA} \times \text{ET} \times \text{EF} \times \text{ED}}{\text{AT}}
\]  

(5)

Where:

CA is the measured concentration in μg/m³, which was taken as the UCL or the upper confidence limit (95%) of the chemical,

ET is the exposure time (hrs/day), or 24 h/day (residential)

EF is the exposure frequency (days/year), or 350/year (residential)

ED is the exposure duration (years), or 26 years (residential)

AT is the averaging time (hrs) = 70 years × 365 days/year × 24 h/day = 6 \times 10^5 h (expected lifetime)

For non-carcinogens, a hazard quotient (HQ) can be calculated based on the inhalation chronic reference concentration (RfC) in (μg/m³):
Specifically, the HQ will be used to assess the non-carcinogenic effects from compounds like benzene and toluene. An HQ greater than one indicates that estimated exposure dose may not be protective of non-carcinogenic health effects. If the HQ is less than one, then non-carcinogenic health effects should not occur. The hazard index (HI) is the sum of HQs of each compound.

3. Results/discussion

3.1. Active (grab) sampling results

Spatial, seasonal, and temporal variability were examined in grab sample data (n = 864) taken from 2017 to 2018 in the LCV. General statistics are shown in Table 1 for both 2017 and 2018 for compounds in order of decreasing mean 2018 value. There were several compounds that were often or always under the detection limit, and those with non-detect frequency higher than 90% for 2018 or with mean values close to zero were omitted from Table 1. ProUCL 5.1 (EPA, 2016) software was used to estimate the non-detect values for calculating statistics such as mean and standard deviation. Either a normal, log-normal, or Chebyshev fit were used by ProUCL 5.1 to calculate statistics and upper confidence levels (UCL) at 95% confidence level. The mean and standard deviation values shown in Table 1 are calculated after Kaplan-Meier (KM) substitution of non-detect values (EPA, 2016).

The main components that were detected in the ambient air included DMS, DMDS, toluene, benzene, xylenes (m,p), ethylbenzene, chloroform, dichlorodifluoromethane (CFC-12) and trichloro-fluoromethane (CFC-11). This is consistent with major emissions of traffic and paper mill. The values for CFC-12 were not reported due to calibrations with the liquid solution resulting in positive bias (about double). A later analysis after this study showed that the gas standard for CFC-12 was much more reliable. However, CFC-11 was in the range of reported literature for North America showing an average of 1.1 μg/m³ or about 200 pptv (Montzka et al., 2018).

3.2. Spatial variation

To visualize the 2017–2018 data spatially, the 2-year averages for various compounds were plotted in a Fig. 2. Based on the hot spots (red) and distribution of contours in each graph, the major sources of the compounds can be elucidated. For example, the paper mill and/or the compost sites were the apparent source of DMS, DMDS and chloroform, according to these spatial plots (Fig 2). This spatial pattern was not the same for benzene or toluene. Instead, these compounds were shifted west towards the city centers, and thus attributed to auto traffic. Methylene chloride had a similar pattern, reflective of industrial processes.

The distribution of the compounds is also consistent with the diurnal west/east wind patterns of the LCV, which are shown in Figure S4. These wind roses were generated using Cli-MATE, Midwestern Regional Climate Center, 2019 and show the wind direction and frequencies based on the times of the day during 2018. Most LCV active sampling
took place between 6 and 21 hr of the day, during which the winds are easterly (morning) or westerly (midday). The concentration gradients are shown to be mainly west to east, consistent with wind transport from the sources in these general directions.

3.3. Seasonal variation

Active samples were categorized by seasons where winter included the months of January through March, spring included April through June, summer included July through September, and fall included October through December. The true seasonal changes were at the latter half of the cut off months, but for simplicity the groupings included the whole month. Average meteorological data during 2017–2018 are given in Table S.4 for reference to general conditions in LCV.

Concentrations of aromatics including benzene, toluene and xylene in active samples during the different seasons of 2017–2018 are plotted in Fig. 3A. Toluene values were highest in this group, followed by xylenes (m,p) and benzene. Ethylbenzene was not shown but was much smaller than the other aromatics. For each of the three compounds there was a spike in concentrations in the summer of 2017 that is likely due to wildfire emissions, since 2017 had a significant amount of wildfire smoke. The effects of wildfire on the LCV will be discussed in a future publication. The lower seasonal trend was in spring (both years), and in general 2018 was less variable than 2017 for the aromatics.

In Fig. 3B DMS and DMDS concentrations for grab samples are plotted by season. DMS was the dominant sulfide in all seasons except for the winter months and fall 2017. DMS was highest in the summer months, especially in 2017, potentially due to wildfire emissions during that season (Meinardi et al., 2003). DMDS was often not detected during the year due to its short lifetime compared to DMS. These two compounds are byproducts of paper pulp processing, and were expected to exhibit the same seasonal pattern, but they did not. Near the paper mill, DMDS was observed over 100 μg/m$^3$ (∼26 ppbv) on occasion. These outliers may skew the mean but were not shown in Fig. 3 in order to keep the scale reasonable.

Fig. 3C shows active/grab sampling concentrations for the halocarbons chloroform, methylene chloride, tetrachloroethylene and carbon tetrachloride in the LCV by season. These species are carcinogenic, and some may be byproducts of paper bleaching (chloroform) or other industrial processes and solvents. Chloroform concentrations spiked in the summer of 2017, decreased in the fall of 2017, then increased over 2018. Methylene chloride concentrations spiked in the summer of 2017 as well, generally increased in spring and summer and had lower concentrations in the fall. Lower tetrachloroethylene (TCE) concentrations were observed than chloroform and methylene chloride and TCE did not show strong seasonal trends for 2017 or 2018. Carbon tetrachloride was only measured in spring 2018 and on and showed wide variation within a season.

3.4. Temporal variation

LCV grab samples were collected at various times of the day, with a focus in the morning, afternoon, and early evening. The widest range of temporal samples was taken at the Lewis-Clark State College (LCSC) site 7. Samples were grouped into hour of the day in which the sampling was begun. Fig. 4 plots the temporal variations of benzene, chloroform,
and DMS grab sample concentrations at LCSC (site 7). Fig. 4A shows the concentration values of benzene were fairly consistent throughout the day though slightly higher in the morning at the LCSC site, ranging from 0 to 4 μg/m$^3$, and some outliers between 6 and 12 μg/m$^3$. The trend in Fig. 4B shows that chloroform concentrations peak in the morning and taper off with a slight increase at the end of the day. Possible causes of this trend are industrial emissions and/or the morning boundary layer in the LCV. It is possible that there are nighttime emissions that are trapped overnight in the valley and begin to mix in the morning hours with the boundary layer dissipating. Fig. 4C shows a similar trend of higher DMS concentration values in the morning hours of the day with lower concentrations in the evenings and night hours. The highest observed concentration of DMS was within the 8–9 am hour of the day, up to 60 μg/m$^3$. This trend fits with the observational trend of odorous smelling air in the morning hours of the day. There is a sampling bias with a majority of the samples being morning hours, with no samples taken between hours 24:00–6:00 due to logistics. An ongoing study in this laboratory using a Total Reduced Sulfur (TRS) analyzer showed that there are TRS concentration spikes in the mornings and late evenings. The percent of DMS in the TRS was not determined for the current study, but this diurnal trend is consistent with that shown in Fig. 4C. Currently, samples show that DMS and DMDS make up about 30% of TRS, making them a good marker for the paper mill emissions.

### 3.5. Correlations and concentration ratios

To discover relationships between compounds and sources in LCV, correlation plots were made. Some examples appear in Fig. 5. The entire two year data set was used to look for patterns, and because of the variability, few strong correlations resulted, but some were observed. Specifically, ethylbenzene and xylene were strongly correlated ($R^2 = 0.99$), benzene and toluene were somewhat correlated ($R^2 = 0.74$) at Site 7 (LCSC). East of the paper mill at Site 3 (Casino) chloroform and DMS has a moderate correlation ($R^2 = 0.83$).

Benzene to toluene ratios (B/T) have been used to estimate vehicular sources. A value of less than 1 is indicative of vehicular exhaust as the source, where a decrease in this value is correlated with proximity to the source (Gelencsér et al., 1997; Zalel et al., 2008). In the LCV data set, these ratios were investigated and are tabulated in Table 2. In each case, the ratio at a site is related to the atmospheric lifetimes of the pair. Benzene has a lifetime ($\tau$) of about 9.4 days and is less reactive than toluene which has a $\tau \sim 1.9$ days with respect to hydroxyl radicals (Bretón et al., 2017; Ragothaman and Anderson, 2017). As the compounds get farther from the source, they will decay at different rates, thus increasing the (B/T) ratio as the air mass is farther from the source. The ratios seen in Sites 4–8 LCV are indicative of a slightly aged vehicular sources, as they are close to one, while the other sites are farther away from the city centers. These ratios are slightly higher than others reported such as 0.45 (Kerchich et al., 2011).

Likewise, DMS/DMDS ratios were calculated at each site (Table 2). DMS has a lifetime of a day or less (Lenschow et al., 1999) and is less reactive than DMDS which has a $\tau \sim 0.3–3$ hr (Hearn et al., 1990). Other investigations of sulfur compounds near paper mills reveal that when the DMS/DMDS mixing ratio is greater than one it is indicative of proximity to the source (de Bias et al., 2017). The ratios observed in LCV were very high, meaning
very close to the source. Sites 1 and 9 (Lewiston Hill and Lapwai) were farthest from the paper mill (6) and were lowest ratios. Although the paper mill is the apparent source of these compounds, the highest ratios were often at adjacent sites. This is likely because the emissions are at much higher elevations of the smokestacks, and the samples were taken on the ground level. Wind transport and diffusion will affect the emission plume and may be slightly downwind of the source.

### 3.6. Passive sampling results

Passive sampling had some advantages over grab sampling since it was used to determine exposure concentrations of a few important compounds over a longer time period. One disadvantage was that it did not have concentration/time resolution within the sampling time frame. The active sampling can make up for that detail as discussed in the previous section. In addition, only three compounds were chosen for passive sampling (benzene, toluene and xylene) due to limited availability of uptake rates on the sorbents used for 2 and 4 week periods (Markes International, 2015). The concentrations of the passive samples were converted from ppbv to μg/m$^3$ using MW/24.45 to be consistent with the grab sampling. The long-term averages generally are smaller than the short-term grab sample concentrations. Both values were used in ProUCL 5.1 to calculate UCLs for 2018, compared to grab samples to calculate risk of LCV in next section (3.7).

Yearly averaged long-term data (1 sample per month at each location) were plotted in Fig. 6 using box and whisker plots for benzene, toluene, and xylene in 2018. Elevated levels of each compound are observed in the urban areas (Boise, Spokane) compared to the less populated areas (LCV and CDA). However, LCV was not statistically different from the other areas with respect to these compounds at the 95% confidence level. Toluene levels were dominant compared to m,p-xylene and benzene. BTEX (benzene, toluene, ethylbenzene and xylenes) are associated with vehicular exhaust and it is likely that the differences in rural and urban areas are from traffic emissions. The benzene/toluene ratios were close to one or less in the LCV and the other urban areas, suggesting that gasoline exhaust indeed was a likely source of BTEX there (Table 2). There also may have been an industrial emission contribution. For reference, concentrations of benzene in the LCV were slightly higher than comparable rural areas in Canada (You et al., 2008) but lower than suburban areas in China (Zeng et al., 2019), which ranged from 0.1 to 0.2 μg/m$^3$ to 1.5 μg/m$^3$, respectively.

Fig. 7A shows the monthly concentrations of benzene, toluene, and xylene for the 2018 long-term (passive) data in the LCV. The benzene levels decreased from winter to spring and then had some variability for the rest of the year, with the highest concentrations in August and November. This may be due to summer wildfires as shown in the PM$_{2.5}$ data in Fig. 7B, and more frequent inversions in the colder months. Toluene and xylene concentration values were variable but increased in the fall. From January to May the long-term samples were collected using the Carbopack™-X sorbent, whereas Tenax®TA tubes were used from May through December. Differences between the spring-summer months and fall-winter months may be affected by this change, although both sorbent types effectively sample BTEX compounds. (Markes Int., 2015) The PM$_{2.5}$ also increases in the Fall of 2018, which is a
sign of local temperature inversions, not wildfires. The inversions likely caused the VOCs to also increase in the later months of the year.

### 3.7. Evaluation of health risk

The human health risk from exposure to VOCs in the LCV was determined using active grab samples and passive samples, both representing long term exposures. Five carcinogens were assessed from the active samples in LCV: benzene, carbon tetrachloride, tetrachloroethylene, chloroform, and methylene chloride (Table 3). Benzene risk was also assessed from passive samples at both LCV and the three other sites, representing 2–4 week averaging times throughout 2018 (Table 3).

The cumulative risk of inhalation exposure to these compounds in the LCV (active sampling) is 11 extra cancers per million people using Equation (5). The main compound contributing to this risk is chloroform, of the five selected compounds. The hazard index is 0.67 for the major compounds detected, which is less than 1, indicating a low risk of non-cancer events.

Passive sampling may be more indicative of the overall concentrations (CA) and thus the exposure concentration (EC) compared to the active sampling since passive sampling represents a long term average concentration of the 2–4 week period. The results from these passive concentrations are in Table 3. The calculated LCV risk using passive sampling was lower than the method using the active sampling, at 2 extra cancers per one million people (compared to 12 in a million). Overall, LCV risk was lowest (with regards to benzene) compared to the city sites, where Spokane, WA had the highest risk of $2.5 \times 10^{-6}$, or about 3 extra cancers per million people. This was somewhat expected since there is more traffic and industry in these cities, and the source of benzene in LCV is not likely from the paper mill. Toluene's hazard quotient was the highest in LCV compared to the other sites (Table 3), but not significantly so. Both toluene and xylene have a low overall hazard quotient, indicating low risk of non-cancer events.

According to the National Air Toxics Assessment of 2014, the national cancer background risk for cancer is 3 per million and total risk for all factors is 32 per million, while Nez Perce County is 3 per million background risk, with total risk of 25 per million (US EPA, 2014). Therefore, this study is consistent with a low risk of extra cancers. Considering LCV is a rural area, the risk is quite similar to the urban centers nearby.

ProUCL 5.1 uses non-detects and detected data to extrapolate UCL values for each site to calculate cancer risk. For LCV, the highest UCL site was used in calculations. In addition, the IUR, RfC and exposure time (ET) values have uncertainties associated with them, sometimes by a factor of 10 (US EPA., 2009, 2020). Although there is a small cancer risk associated with these values there are many other factors that put the population at risk of cancer. The American Cancer Society (ACS) recognizes many factors that can cause cancer such as genetics, smoking and tobacco, diet and physical activity, solar and other radiation exposure, and viruses and other infections (ACS, 2020). This study addressed the risk associated with the air toxic compounds measured during a two-year period and has some limitations. Not all compounds that are toxic were measured in this study. The risk
calculated here is from a fraction but not all pollutants. Hydrogen sulfide and sulfur dioxide were not measured due to the sampling method not trapping them. These may have other ill effects. This was not a lifetime study but extrapolated from the two-year values. The risk shown here is also representative, not indicative of personal risk necessarily.

4. Conclusion
The major VOC pollutants in the LCV come from the emissions of local industries, based on spatial plots. The sulfides (DMS and DMDS) and chloroform are emitted from the paper mill and it is evident that benzene emissions come from automobile traffic and/or factories. The seasonal variation of the VOCs show concentration spikes for benzene, toluene, xylene, and DMS in the summer months. This seasonal variation observed is likely due to wildfire emissions, especially for the summer of 2017 when there was a significant fire season. There were also November spikes as well. Seasonal variations of chlorinated VOCs like chloroform, showed similar trends for 2017 and 2018. The temporal variation of VOCs showed diurnal patterns for DMS and chloroform rising in the morning hours, which can be attributed to paper mill emissions and diurnal inversions. Passive samples in larger cities such as Spokane and Boise exhibited higher concentration values for benzene, toluene, and xylenes, likely due to traffic/industrial emissions. However, the concentrations of these compounds in the LCV were not statistically different from the urban areas.

The calculated health risks for the carcinogens measured in this study were considered low risk to the LCV population. The cumulative calculated risk was between 2 and 11 extra cancers per million people using the 95% UCL for active and passive sampling, respectively. This is lower than the national average (US EPA, 2014), but is still higher than the background levels. The risk of benzene exposure for LCV was similar to that of Boise, ID, and only slightly lower than CDA and Spokane. In addition, the risk of non-carcinogenic effects was considered low, as the hazard index was less than 1 for all areas observed. Thus, exposure to levels of VOCs in the LCV does not pose a significantly elevated health risk to the community. This study focused on a rural area that has significant industrial emissions, as well as potential risk levels for VOC exposure.

Supplementary Material
Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. A): Map of the Lewis-Clark Valley (LCV) showing locations of both active (grab) sampling sites (1–10) including the pulp paper mill (6), and passive (longterm) sampling sites (L1–L4) during the 2017–2018 period. The city boundaries are indicated by solid gray lines and the Nez Perce Reservation is indicated by dashed gray lines. Also indicated are the city centers of Clarkston and Lewiston, the Nez Perce County Regional Airport and Clearwater Compost, just south of the paper mill (1). B) Map of the Northwest United States.
Indicated are the locations of Lewiston, ID and other long-term passive sampling sites (Spokane, WA, Coeur d'Alene, ID and Boise, ID) utilized in 2018.
Fig. 2.
Surface contour plots generated from two year averages in LCV: DMS, DMDS, Chloroform, Benzene, Methylene Chloride and Toluene. The color bar is in units of μg/m³ and reflects the observed means at each of the ten sampling sites.
Fig. 3.
Seasonal box and whisker plot of VOCs and sulfur compounds in LCV A) aromatics - benzene, toluene and m,p-xylene B) sulfides - DMS and DMDS, C) halocarbons - chloroform, methylene chloride, tetrachloroethylene, and carbon tetrachloride (SP18-FA18 only) at the LCV sites. (W = Jan–March; SP = April–June; S = July–Sept; FA= Oct–Dec).
Fig. 4.
Temporal variation of select compounds at LCSC during 2017–2018 A) Benzene B) Chloroform C) DMS at LCSC (Site 7) for 2017–2018 period. Grab samples were binned into the hour of sampling. Error bars are based on 10% precision of duplicates.
Fig. 5.
Select VOC correlation plots from 2017 to 2018 samples in LCV A) Chloroform vs DMS at site 3 B) Benzene vs Toluene at site 7 C) Xylene (m,p) vs Ethylbenzene at site 7. Strong correlations exist at sites close to the paper mill (Casino-Site 3) and close to the city centers (LCSC – Site 7). Chloroform and DMS were correlated when close to the paper mill, while BTEX were correlated between the city centers of Lewiston and Clarkston.
Fig. 6.
Box and whisker plots for 2018 passive monthly samples at four Northwestern locations. Outliers are excluded.
Fig. 7.
A) Monthly variation in long term (passive) concentrations at the LCV sites (L1-4) during 2018. Error bars represent one standard deviation. B) IDEQ PM$_{2.5}$ data for 2018 obtained from US EPA (2020a) at Site 8.
Overall statistics from active sampling, method limit of detection (LOD), % non-detects (ND), KM mean (standard deviation) and range during 2017–2018 sampling. All concentrations are in μg/m$^3$ units.

| Compound                  | LOD  | 2017 % ND | 2017 Mean ± SD | 2017 Range   | 2018 % NDs | 2018 Mean ± SD | 2018 Range   |
|----------------------------|------|-----------|----------------|--------------|------------|----------------|--------------|
| Dimethyl sulfide           | 0.04 | 50.2%     | 1.54 ± 5.05    | 0.01–54.99   | 25.8%      | 1.44 ± 3.23    | 0.01–29.72   |
| Toluene                    | 0.02 | 0.3%      | 1.77 ± 3.80    | 0.03–41.95   | 0.4%       | 1.16 ± 1.79    | 0.03–24.42   |
| Trichloromonofluoromethane | 0.02 | 3.0%      | 0.86 ± 0.56    | 0.06–4.73    | 1.1%       | 1.10 ± 0.45    | 0.09–2.40    |
| Xylenes (m,p)              | 0.04 | 1.8%      | 0.79 ± 1.14    | 0.03–11.46   | 0.2%       | 0.78 ± 0.84    | 0.05–9.16    |
| Benzene                    | 0.03 | 1.2%      | 1.46 ± 8.03    | 0.02–120.70  | 64.8%      | 0.62 ± 2.64    | 0.01–35.89   |
| Disulfide, dimethyl        | 0.02 | 9.3%      | 0.15 ± 0.19    | 0.02–1.55    | 2.8%       | 0.26 ± 0.34    | 0.03–3.33    |
| Chloroform                 | 0.02 | 4.8%      | 0.23 ± 0.35    | 0.02–2.55    | 5.8%       | 0.20 ± 0.65    | 0.02–13.18   |
| Ethylbenzene               | 0.02 | 12.6%     | 0.15 ± 0.18    | 0.03–3.22    | 4.3%       | 0.19 ± 0.22    | 0.03–3.79    |
| Methylen chloride          | 0.03 | 37.8%     | 0.18 ± 0.30    | 0.02–2.57    | 7.9%       | 0.19 ± 0.26    | 0.02–2.24    |
| p-Cymene                   | 0.02 | 64.9%     | 1.46 ± 8.03    | 0.02–120.70  | 64.8%      | 0.62 ± 2.64    | 0.01–35.89   |
| Carbon Tetrachloride       | 0.02 | N/A       | N/A            | N/A          | 56.5%      | 0.18 ± 0.22    | 0.11–0.75    |
| Benzene, 1,2,4 trimethyl   | 0.12 | 79.3%     | 0.13 ± 0.42    | 0.12–14.6    | 84.4%      | 0.11 ± 0.48    | 0.12–8.81    |
| Tetrachloroethylene        | 0.01 | 23.7%     | 0.08 ± 0.17    | 0.01–1.85    | 17.1%      | 0.08 ± 0.13    | 0.02–1.39    |
| Naphthalene                | 0.01 | 66.1%     | 0.08 ± 0.16    | 0.03–1.17    | 47.7%      | 0.07 ± 0.12    | 0.02–1.75    |
| Mesitylene                 | 0.03 | 36.6%     | 0.09 ± 0.15    | 0.03–1.15    | 51.8%      | 0.06 ± 0.16    | 0.03–2.77    |
| Benzene, propyl-           | 0.03 | 52.0%     | 0.06 ± 0.11    | 0.03–0.73    | 55.9%      | 0.04 ± 0.09    | 0.03–1.53    |
| Benzene, 1,3 dichloro      | 0.02 | 72.4%     | 0.02 ± 0.06    | 0.02–0.56    | 50.1%      | 0.03 ± 0.05    | 0.02–0.33    |
| Styrene                    | 0.02 | 95.8%     | 0.00 ± 0.04    | 0.02–0.55    | 71.2%      | 0.02 ± 0.06    | 0.02–0.72    |
| Benzene, (1-methylethyl)   | 0.02 | 88.3%     | 0.01 ± 0.05    | 0.02–0.70    | 91.2%      | 0.01 ± 0.03    | 0.02–0.39    |
| Benzene, 1,2,3-trichloro   | 0.02 | 81.1%     | 0.01 ± 0.03    | 0.02–0.25    | 89.6%      | 0.01 ± 0.03    | 0.02–0.35    |
| Benzene, butyl-            | 0.02 | 71.5%     | 0.02 ± 0.05    | 0.02–0.56    | 86.3%      | 0.01 ± 0.02    | 0.02–0.38    |
| Benzene, 1,2,4-trichloro   | 0.02 | 79.6%     | 0.01 ± 0.03    | 0.02–0.26    | 89.1%      | 0.01 ± 0.02    | 0.02–0.21    |

$^a$approximated LOD.
Table 2

Average ratios for benzene/toluene (ppbv/ppbv) and DMS/DMDS (ppbv/ppbv) at each sampling site. These values were based on the ratios of individual active samples in the 2017–2018 period (A) or ratios of monthly passive samples during 2018 (P). Location types are listed including background/rural (B), city center (C), paper mill (M), or other city location (O) for comparison.

| Site # | Location Type | Sampling Type | Location Name         | Benzene/Toluene ppbv/ppbv | DMS/DMDS ppbv/ppbv |
|--------|---------------|---------------|-----------------------|---------------------------|-------------------|
| 1      | B             | A             | Lewiston Hill         | 2.19                      | 2.34              |
| 2      | B             | A             | Spiral Highway        | 1.57                      | 23.99             |
| 3      | B             | A             | Clearwater Casino     | 1.71                      | 19.37             |
| 4      | C             | A             | Port of Clarkston     | 1.02                      | 17.93             |
| 5      | C             | A             | Clearwater Park       | 1.12                      | 36.43             |
| 6      | M             | A             | Clearwater Paper Mill | 1.01                      | 16.47             |
| 7      | C             | A             | Lewis-Clark State College | 0.87                      | 22.70             |
| 8      | C             | A             | Sunset Park           | 1.00                      | 48.89             |
| 9      | B             | A             | Lapwai City Park      | 1.28                      | 11.13             |
| 10     | B             | A             | Warner Avenue         | 1.62                      | 23.12             |
| L2     | C             | P             | Lewiston, ID          | 0.97                      | N/A               |
| L3     | O             | P             | Spokane, WA           | 0.97                      | N/A               |
| L6     | O             | P             | Couer d’Alene, ID     | 0.67                      | N/A               |
| L7     | O             | P             | Boise, ID             | 0.63                      | N/A               |
Table 3

Cancer risk factors for five carcinogens and Hazard Quotients for non-carcinogenic effects in the LCV using site specific UCLs from active sampling during 2017–2018. Also included are cancer risk factors and hazard quotients calculated from UCLs at passive sampling sites at LCV and other sites in the Northwest during 2018.

| Active Sampling | Compound     | Site | n  | CA (μg/m³) | EC (μg/m³) | IUR* (μg/m³)⁻¹ | Cancer Risk | RfC* (μg/m³) | HQ |
|-----------------|--------------|------|----|------------|------------|----------------|-------------|-------------|----|
|                 | Benzene      | 8    | 92 | 1.35       | 0.48       | 7.80E-06       | 3.8E-06     | 30          | 1.6E-02 |
|                 | Carbon Tetrachloride | 5    | 35 | 0.42       | 0.15       | 6.00E-06       | 9.0E-07     | 100         | 1.5E-03 |
|                 | Chloroform   | 6    | 67 | 0.80       | 0.28       | 2.30E-05       | 6.5E-06     | 98          | 2.9E-03 |
|                 | Methylene Chloride | 8    | 92 | 0.33       | 0.12       | 1.00E-08       | 1.2E-09     | 600         | 1.9E-04 |
|                 | Tetrachloroethylene | 5    | 64 | 0.19       | 0.07       | 2.60E-07       | 1.8E-08     | 40          | 1.7E-03 |
|                 | Toluene      | 4    | 54 | 3.44       | 1.23       | N/A            | N/A         | 5000        | 2.5E-04 |
|                 | Ethylbenzene | 7    | 292| 0.85      | 0.30        | N/A            | N/A         | 100         | 3.0E-03 |
|                 | Xylene, m,p- | 7    | 292| 3.17      | 1.13        | N/A            | N/A         | 10          | 1.1E-01 |
|                 | Styrene      | 4    | 54 | 0.13       | 0.04       | N/A            | N/A         | 100         | 4.5E-04 |
|                 | Benzene, propyl- | 8    | 97 | 0.16       | 0.06       | N/A            | N/A         | 100         | 5.5E-04 |
|                 | Mesitylene   | 4    | 54 | 0.27       | 0.10       | N/A            | N/A         | 6.0         | 1.6E-02 |
|                 | Benzene,1,2,4-trimethyl | 7    | 292| 0.60       | 0.21       | N/A            | N/A         | 6.0         | 3.5E-02 |
|                 | Benzene,1,2,4-trichloro- | 1    | 51 | 0.03       | 0.01       | N/A            | N/A         | 0.2         | 4.6E-02 |
|                 | Naphthalene  | 10   | 50 | 0.34       | 0.12       | N/A            | N/A         | 0.3         | 4.0E-01 |
|                 | Cumulative Cancer Risk |   |    |           |            |                | 1.1E-05     |            |    |
|                 | Hazard Index  |   |    |            |            |                | 5.4E-01     |            |    |

| Passive Sampling | Compound  | City | Site | n  | CA (μg/m³) | EC (μg/m³) | IUR* (μg/m³)⁻¹ | Cancer Risk | RfC* (μg/m³) | HQ |
|------------------|-----------|------|------|----|------------|------------|----------------|-------------|-------------|----|
|                  | Benzene   | LCV  | L2   | 16 | 0.71       | 0.25       | 7.80E-06       | 2.0E-06     | 30          | 8.4E-03 |
|                  |          | Spokane | L5  | 14 | 0.92       | 0.33       | 2.5E-06       | 1.1E-02     |             |    |
|                  |          | CDA   | L6   | 11 | 0.85       | 0.30       | 2.4E-06       | 1.0E-02     |             |    |
|                  |          | Boise | L7   | 12 | 0.74       | 0.26       | 2.1E-06       | 8.8E-03     |             |    |
|                  | Toluene   | LCV  | L2   | 16 | 2.38       | 0.85       | N/A            | N/A         | 5000        | 1.7E-04 |
|                  |          | Spokane | L5  | 14 | 1.77       | 0.63       | N/A            | N/A         | 1.3E-04     |    |

*Note: CA and EC represent the measured concentrations for active and passive sampling, respectively. IUR is the Inhalation Unit Risk. RfC is the Reference Concentration, and HQ is the Hazard Quotient.*
| Compound         | Site | n | CA (μg/m³) | EC (μg/m³) | IUR (μg/m³)⁻¹ | Cancer Risk | RfC (μg/m³) | HQ      |
|------------------|------|---|------------|------------|---------------|-------------|-------------|---------|
| CDA              | L6   | 11| 1.33       | 0.47       | N/A           | N/A         | 9.5E-05     |         |
| Boise            | L7   | 12| 2.15       | 0.77       | N/A           | N/A         | 1.5E-04     |         |
| Xylene, (m,p)    | LCV  | 9 | 1.87       | 0.67       | N/A           | N/A         | 6.7E-03     | 100     |
| Spokane          | L5   | 14| 1.88       | 0.67       | N/A           | N/A         | 6.7E-03     |         |
| CDA              | L6   | 11| 1.35       | 0.48       | N/A           | N/A         | 5E-03       |         |
| Boise            | L7   | 12| 2.11       | 0.75       | N/A           | N/A         | 7.9E-03     |         |

*Integrated Risk Information System (IRIS) values (US EPA, 2020b).*