Introduction
Mercury (Hg) is a globally transported atmospheric pollutant that can have adverse environmental and human health effects (Carpi and Lindberg, 1997; Schroeder and Munthe, 1998). Its long atmospheric lifetime, 5–12 months (Horowitz et al., 2017), and unique chemical properties allow it to be transported over large distances before being deposited, making it ubiquitous in the environment (Corbitt et al., 2011; Gustin, 2012). Mercury is released into the atmosphere naturally, anthropogenically, or through re-emission of naturally- and anthropogenically-derived Hg (Amos et al., 2013; Gustin et al., 2008). This emission of Hg from surfaces is an important component of the global Hg cycle, as it is what allows Hg to remain in the environment for long periods of time and to be globally distributed (Hintelmann et al., 2002; Schroeder and Munthe, 1998). However, despite its importance in the global Hg cycle, understanding of the drivers of re-emission across spatial and temporal scales is still poor. Terrestrial air-surface exchange of Hg is heavily influenced by substrate properties, atmospheric chemistry, and meteorological factors, which vary across time and sites and make it difficult to adequately assess the key controls (Agnan et al., 2016; Gabriel et al., 2011; Lin et al., 2010; Wang et al., 2006; Zhang et al., 2001).

Seasonal gaseous elemental mercury fluxes at a terrestrial background site in south-eastern Australia
Katrina MacSween, Grant C. Edwards and Paul J. Beggs

Terrestrial air-surface exchange of mercury (Hg) forms an important component of the global Hg cycle, with drivers varying across spatial and temporal scales. These drivers include substrate properties, atmospheric chemistry, and meteorological factors. Vegetation uptake represents the dominant pathway of atmospheric Hg deposition to terrestrial surfaces. This study investigated the drivers of net ecosystem exchange of gaseous elemental mercury (Hg\(_0\)) across multiple seasons in order to gain an understanding of the influence of vegetation and other environmental parameters on the Hg\(_0\) air-surface exchange. Measurements were made continuously using a micrometeorological aerodynamic flux gradient method at a low-vegetated background site in south-eastern Australia, over 14 months. Mean Hg fluxes and atmospheric concentrations across the entire study period were 0.002 ng m\(^{-2}\) h\(^{-1}\) (SD ± 14.23 ng m\(^{-2}\) h\(^{-1}\)) and 0.68 ng m\(^{-3}\) (SD ± 0.22 ng m\(^{-3}\)), respectively. Variability was observed across seasons, with the highest average rate of emissions occurring in austral summer (December, January, February) (0.69 ng m\(^{-2}\) h\(^{-1}\)) and the highest rate of deposition observed in autumn (March, April, May) (–0.50 ng m\(^{-2}\) h\(^{-1}\)). Vegetation uptake dominated Hg flux during the winter and spring when meteorological conditions were cold and light levels were low. This is supported by CO\(_2\) flux data, with a daytime winter mean of 0.80 µmol m\(^{-2}\) h\(^{-1}\) and a spring daytime mean of 1.54 µmol m\(^{-2}\) h\(^{-1}\). Summer Hg fluxes were dominantly emission due to higher solar radiation and temperature. Climatic conditions at Oakdale allowed plant production to occur year-round, however the hot dry conditions observed in the warmer months increased evasion, allowing this site to be a small net source of Hg\(_0\) to the atmosphere.

Keywords: Mercury; Air-surface exchange; Southern Hemisphere; Seasonality

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picture of the Hg biogeochemical cycle (Baya and Van Heyst, 2010; Jiskra et al., 2019; Lee et al., 2000; Obrist et al., 2005; Osterwalder et al., 2017). Few studies have taken place on these time scales, and none have taken place in the Southern Hemisphere where season variability and landmass area are different to the Northern Hemisphere (Edwards and Howard, 2013; Nelson et al., 2012). The Northern Hemisphere has substantially larger landmasses and most of the earth’s forested ecosystems, while the Southern Hemisphere’s smaller landmasses are dominantly comprised of desert and sub-tropical grasslands (Bredenkamp et al., 2002; Jiskra et al., 2018). The larger expanse of ocean in the Southern Hemisphere means that seasonality is heavily influenced by large-scale climate variability that can magnify temperature and rainfall extremes on interannual scales (Bureau of Meteorology, 2020). Further, ultraviolet (UV) radiation in the Southern Hemisphere is approximately 50% greater than the Northern Hemisphere due to earth’s elliptical orbit, more efficient ozone transportation from the equator to higher latitudes and overall less aerosols present in the atmosphere (McKenzie et al., 1996).

Net ecosystem exchange represents the combined Hg emission, deposition and re-emission processes from both soils and vegetation within an ecosystem, which can vary on diel and seasonal scales (Jiskra et al., 2018; Wang et al., 2016). Emission from terrestrial surfaces is widely believed to be driven by solar radiation, temperature, soil moisture and substrate Hg concentrations (Choi and Holsen, 2009; Gustin et al., 2006; Gustin et al., 1997; Kim et al., 1995; Kim et al., 2012). Vegetation uptake represents the dominant pathway of atmospheric Hg\(^{0}\) deposition to terrestrial surfaces (Jiskra et al., 2018), where Hg is introduced back into the soil substrate by throughfall and litterfall (Wright et al., 2016). Currently it is assumed between 60 and 90% of Hg\(^{0}\) accumulation in the substrate originates from vegetation litterfall (Demers et al., 2013; Obrist et al., 2005; Obrist et al., 2017; Zheng et al., 2016). Surface emissions tend to be highest during warmer months when temperatures and solar radiation are highest, and near zero or negative fluxes occur during cooler months and overnight (Bahlmann et al., 2006; Fritsche et al., 2008; Wang et al., 2006). Strongest Hg\(^{0}\) dry deposition is greatest during the growing season and lower at other times of the year (Jiskra et al., 2019; Obrist et al., 2018).

The positive relationship observed between solar radiation, air temperature, soil temperature and Hg surface emission is believed to be a result of the relationship between the physicochemical properties of Hg\(^{0}\) and the abiotic processes occurring in the substrate (Bahlmann et al., 2006; Choi and Holsen, 2009; Gustin et al., 2002). Solar radiation enhances surface emissions through the reduction of divalent mercury (Hg\(^{2+}\)) to Hg\(^{0}\) within the substrate which is then available for emission (Carpi and Lindberg, 1997; Moore and Carpi, 2005). Higher temperature leads to increased rates of volatilisation of Hg from the substrate due to a reduction in the activation energy required to release Hg from the substrate (Kim et al., 2012). Increasing soil temperatures due to solar irradiation also promotes Hg\(^{0}\) emissions (Wang et al., 2006). The vapour pressure of volatile Hg species is increased with rising soil temperatures which also decreases Hg sorption to the soil and allows greater emission from the substrate (Liang et al., 2014).

The presence of vegetation in the ecosystem adds an extra layer of complexity to the drivers of Hg air-surface exchange. Vegetated ecosystems can represent both a source and a sink for Hg\(^{0}\) over shorter or longer periods, depending on the atmospheric Hg concentration, meteorology, substrates, climate conditions and plant community composition (Agnan et al., 2016; Bash and Miller, 2008; Converse et al., 2010; Lee et al., 2000). Hg is dominantly taken up by vegetation through stomatal respiration, leading to highest accumulation within the leaves (Jiskra et al., 2018; Yuan et al., 2019). Stomatal uptake of Hg by vegetation has been shown to increase during the growing season when photosynthetic productivity is greatest (Laacouri et al., 2013). Concentrations within vegetation remain constant or reduced once plants reach maturity (Erickson et al., 2003; Poissant et al., 2008; Rea et al., 2002). The presence of plants and litter may also impact the soil–air Hg flux by altering air mixing, shading the soil, and influencing soil moisture and temperature (Stamenkovic et al., 2008) and therefore must be accounted for when considering whole ecosystem-level Hg exchange. In a review of global Hg\(^{0}\) flux studies, Agnan et al. (2016) found only 20% of measurements over bare soil in forests and grasslands/shrublands show net deposition. This increased to 48% of measurements in these ecosystems when the presence of vegetation was taken into consideration (Agnan et al., 2016).

This study investigated the drivers of net ecosystem Hg exchange across multiple seasons in order to gain an understanding of the influence of vegetation and environmental parameters on Hg air-surface exchange across seasonal time scales. Measurements were made continuously using a micrometeorological aerodynamic flux gradient method at a low-vegetated background site in south-eastern Australia, over a 14 month period. South-eastern Australia’s climate is primarily classified as temperate or subtropical, experiencing warm to hot summers and cool winters, with an annual average maximum temperature of 25°C and annual average minimum temperature of 13°C (Bureau of Meteorology, 2020). As Australia’s climate is milder than typically observed in the Northern Hemisphere, we hypothesise that the drivers of Hg air-surface exchange may behave differently to those elsewhere.

**Methods**

**Site description**

This study took place at Oakdale, New South Wales, Australia; a rural area on the far south-west edge of the Sydney basin (lat. 34° 03’ 11” S, long. 150° 29’ 50” E, altitude 457 m). Measurements were undertaken from 3 April 2017 to 21 June 2018 (445 days), within an agricultural grazing paddock. Soils for the region were classified as sandy clay loam. No known major point sources of Hg were identified within the region. Vegetation cover consisted of low grass, less than 2 cm, with sparse low shrubs edged by tall eucalyptus trees. However, these were out of the measurement fetch. At the start of the study the vegetation coverage was patchy, and the
greatest coverage occurred during spring (SI, Figure S1). The paddock was also regularly grazed by cattle or cut, keeping canopy height low over the duration of the field campaign.

**Substrate samples**
Substrate samples were collected 3 times over the duration of the study: at the beginning, mid-way point and end of the study. Samples were collected at 5 locations within the main fetch of the flux tower. Surface vegetation, along with soils at depths of 0 to 2 cm and 5 to 10 cm were sampled using clean equipment and stored in double sealed plastic bags. Vegetation and soil samples were dried at 105°C for 24 h before analysis (Mudroch and Bourbonniere, 1994). Hojdova et al. (2015) estimated that between 5 and 8% of Hg was lost from the sample when dried in an oven at this temperature over 3 days. Samples were only dried for 24 hours to limit the potential amount of Hg lost in the drying process. Soil samples were then sieved into >250 µm, 63 µm to 250 µm (sand), and <63 µm (silt/clay) size fractions.

Total mercury (THg) contents of soil and vegetation samples were determined in triplicate using a DMA-80 direct mercury analyser (Milestone Inc., Shelton, CT, USA) and US EPA Method 7473, with an instrument detection limit of 0.0015 ng of Hg. Instrument precision was verified to within 5% using 5 repetitions of 100 µL of a 100 ppb Hg standard. Calibrations were checked using National Institute of Standards and Technology (NIST) traceable Standard Reference Material (SRM, NIST 1575a and 2709a). Mean blank concentration measured between each triplicate sample was 0.04 ng g⁻¹ (SD ± 0.02, n = 120). Soil organic carbon (SOC) was determined according to the loss on ignition method described by Nelson and Sommers (1996).

**Aerodynamic flux gradient method**
Hg\(^\text{g}\) fluxes were determined using a micrometeorological aerodynamic flux gradient method and assumptions outlined in Edwards et al. (2005). Hg\(^\text{g}\) flux was calculated according to Equation 1:

$$F = -K \frac{\Delta C}{\Delta z} \ln\left(\frac{z_d - z}{z_d - z_1}\right) - \Psi_{z2} + \Psi_{z1} \quad \text{(Equation 1)}$$

where \(F\) is the Hg\(^\text{g}\) flux (ng m\(^{-2}\) s\(^{-1}\)), \(K\) is the eddy diffusivity (m\(^2\) s\(^{-1}\)), \(C\) is the Hg\(^\text{g}\) concentration at height \(z\) (\(z_d = 0.44\) m and \(z_2 = 1.24\) m), \(u^*\) is the friction velocity (m s\(^{-1}\)), \(K\) is the von Kármán constant (0.40), \(d\) is the zero-plane displacement height (m), and \(\Psi\) is the integrated universal similarity functions as given by Businger et al. (1971) for the two measurement heights (\(z_i\) and \(z_j\)). By convention, a positive flux is upward (emission) and a negative flux is downward (deposition).

Hg\(^\text{g}\) gradients were calculated using air samples collected alternating between two heights (\(z_i = 0.44\) m and \(z_j = 1.24\) m) and quantified using a Tekran 2537B (Tekran Instruments, Knoxville, TN, USA). The detection limit is stated as 0.1 ng m\(^{-3}\) by the manufacturer. The Tekran instrument is presumed to only analyse for Hg\(^\text{g}\), as low speciated Hg concentrations are assumed to be lost in the filters and unheated sample lines (Huang et al., 2013; Lindberg et al., 2002). Sample air was drawn from the sample inlets through a 0.2 µm polytetrafluoroethylene (PTFE) filter by a PTFE pump at 10 L min\(^{-1}\). The 2537B sub-sampled from this flow through an additional 0.2 µm PTFE filter. Switching of sampling between the intakes took place every 10 minutes (2 × 2537B samples) and was achieved using a PTFE solenoid valve controlled by LabVIEW software. Internal calibration of the 2537B occurred every 23 hours throughout the study using the internal mercury permeation source. Permeation sources were verified at the beginning and end of the study, as well as part-way through when the Tekran was removed for routine maintenance using manual mercury vapour injection to 2% resolution of the permeation source. Permeation source verification consisted of 5 injections to each trap of Hg\(^g\) at a concentration of 7 pg µL\(^{-1}\) and 4 pg µL\(^{-1}\) to a relative deviation of ±5%. Thirty-minute running means of the Tekran measurements were used to calculate flux gradient.

Half hour running means were used when calculating Hg flux to reduce variability. The initial mean flux gradient was first averaged over a 90 minute period (five 10 min samples at one height and four 10 min samples at the other height). After the first gradient was constructed, a running mean was then calculated at 30 minute intervals. Density corrections due to water vapour and heat outlined by Webb et al. (1980) were applied to each averaging period. Quality assurance methods were applied to the micrometeorological data based on the constraints of Monin-Obukhov similarity theory. This included filtering for low wind speeds (<0.5 m/s), to allow for sufficient fetch. Highly stable and unstable conditions (stability parameter, \(z/L\) (Monin-Obukhov length), less than −5 or greater than 5), were also removed since micrometeorological methods are most suitable for slightly stable to slightly unstable conditions (Wagner-Riddle et al., 1997). Hg intakes were run side by side for a period of 6 days at the start of the study period (not included in the overall dataset) to determine the minimum resolvable gradient and flux detection limit, as defined by the assumptions outlined by equation 8 of Edwards et al. (2005). Minimum resolvable gradient was 0.02 ng m\(^{-3}\), with a flux detection limit of 1.8 ng m\(^{-2}\) h\(^{-1}\). 34% of Hg flux values fell below the theoretical gradient resolution of 1.8 ng m\(^{-2}\) h\(^{-1}\) as defined by equation 8 of Edwards et al. (2005). These values were not removed from the data analysis to avoid any artificial increase in observed means.

**Eddy covariance measurements**
Eddy covariance flux measurements of sensible and latent heat, carbon dioxide (CO\(_2\)), water vapour and momentum (required for Hg flux gradient) were taken at a height of 3.12 m using a CSAT-3 sonic anemometer (Campbell Scientific, Logan, UT, USA) and Li-7200 closed-path, infrared gas analyser (Li-Cor Biosciences, Lincoln, NE, USA). CO\(_2\) flux measurements were also conducted to look at the relationship between Hg flux and vegetation uptake. Li-Cor samples were collected at 10 Hz using a SmartFlux System (version 1.10). The Li-Cor 7200 was replaced part
way through the study period with an open-path 7500 Analyzer due to hardware malfunction.

Post-processing and quality control of eddy covariance fluxes was undertaken using Li-Cor EddyPro® software (version 6.2.0). Eddy covariance fluxes were flagged according to the quality control conditions outlined by Foken et al. (2004). Fluxes given a 2 flag were removed from further analysis. Webb, Pearman and Leuning density corrections were applied to account for temperature and moisture changes between intake and measurement point as outlined by Webb et al. (1980). Sonic anemometer tilt and angle of attack corrections were applied using a double rotation method to align the x-axis to the current mean prevailing wind, as outlined by Wilczak et al. (2001) and Van der Molen et al. (2004). 77% of the data obtained over the study period remained after these quality assurance measures were applied to the dataset. Mean study footprint for 90% of measurements was 208 m. The footprint during unstable conditions was 150 m while 85% of flux measurements took place. The stable condition mean footprint was 568 m, accounting for 9.1% of measurements, and neutral mean footprint was 221 m with 7.2% of measurements.

**Environmental variables**
The four components of net radiation, long-wave incoming (LW↓) and outgoing (LW↑), and short-wave incoming (SW↓) and outgoing (SW↑), were measured at 3.12 m using a Net Radiometer (Apogee Instruments SN-500). Air temperature was obtained using a CSAT-3 sonic anemometer and relative humidity was measured using Li-Cor 7200. Soil temperature was measured using five t-type thermocouples at depths of 2, 5, 10, 20 and 30 cm. Soil Volumetric Water Content (VWC) was measured at three depths (5, 15, and 30 cm), using a CS616 water content reflectometer (Campbell Scientific Inc.) for 5 cm measurements and MP306 Moisture Probes at 15 cm and 30 cm. Soil heat flux was measured at two depths (5 cm and 15 cm) using HP015C Self-Calibrating Heat Flux Sensors (Campbell Scientific Inc.). All radiation and substrate variables were logged using a CR3000 Campbell Scientific data logger, averaged over 30 minutes at 60 Hz.

**Data analysis**
Statistical analysis was undertaken in numerous forms to assess the potential relationships between Hg fluxes and environmental parameters and to determine significance of variance between Hg fluxes across multiple time scales. All statistical analysis and correlations were undertaken using MATLAB® software. Variables were chosen based on those previously shown to influence Hg fluxes in the literature. Analysis was performed across the entire study period and then for each season (autumn 2017 and 2018 were grouped together). Fluxes were also separated into positive fluxes (Hg⁺ emission) and negative fluxes (dry Hg⁺ deposition) to identify how environmental variables influenced emission and deposition trends.

Two-way t-tests were used to determine if seasonal and diel Hg flux trends were statistically different from each other. Null hypothesis was rejected if the difference between means was found to have a significance less than 5% (p-value < 0.05), unless stated otherwise. T-scores are used to determine how different the t-test was from the mean, with the greater the t-score the greater the statistical difference from the mean. Spearman correlations were performed to determine relationships between Hg fluxes and individual environmental variables. Correlations were deemed to be statistically significant if p-values were <0.01.

Diel composites were calculated by first binning each measurement made in the same half-hour period over 24 hours within each season. Basic statistical values (mean, maximum, minimum, median, 25% quartile (lower) and 75% quartile (upper)) were then calculated for each half-hour binned period to provide a 24hr time series. Cumulative Hg fluxes were calculated by continuously adding the previous half-hour value to current value over the entire study duration. Gaps within the data were forced to zero to preserve the cumulative calculations.

**Results and Discussion**

**Site Characteristics**
Total soil Hg concentration at Oakdale had a mean value of 69 ng g⁻¹ (standard deviation (SD) ± 22 ng g⁻¹) over the duration of the study, classifying it as a background site. Soil Hg concentration varied little with depth with a mean Hg concentration of 67 ng g⁻¹ (SD ± 20 ng g⁻¹) and 73 ng g⁻¹ (SD ± 23 ng g⁻¹), at a depth of 0–2 cm and 5–10 cm, respectively. Surface vegetation Hg concentration averaged 82 ng g⁻¹ (SD ± 5 ng g⁻¹). Substrate and vegetation Hg concentrations were found to not vary significantly over the duration of the study. Vegetation at this site was dominated by low-lying grasses, with surface coverage varying over the study duration. It was therefore assumed that trends in Hg fluxes would follow those typically seen at vegetated background sites. Vegetation coverage was approximately 50% at the beginning of the study, exposing more bare soil, and greatest during spring when increased rainfall allowed for almost 100% vegetation coverage. Vegetation then started to die back during the hot and dry conditions of summer leading to approximately 75% vegetation coverage (Figure S1).

**Mercury fluxes**
Mercury exchange fluxes exhibited highly variable bidirectional exchange over the study duration. Mean exchange was near zero, 0.002 ng m⁻² h⁻¹ (SD ± 14.23 ng m⁻² h⁻¹), with a daytime mean flux of 0.31 ng m⁻² h⁻¹ (SD ± 11.94 ng m⁻² h⁻¹), and a nighttime mean of −0.22 ng m⁻² h⁻¹ (SD ± 11.34 ng m⁻² h⁻¹) (Table 1). Variability in Hg fluxes was also observed across seasons with the highest average net emissions occurring in austral summer (December, January, February) (0.69 ng m⁻² h⁻¹) and highest average net deposition observed in austral winter (June, July, August), 2017 (−0.50 ng m⁻² h⁻¹). Winter 2018 (June 1 to June 21, 2018) presented with a higher average deposition rate of −0.95 ng m⁻² h⁻¹, however, only 21 days were recorded before the measurement period ended.

Despite the net exchange Hg fluxes observed at Oakdale being low, they were still within range of those observed for grasslands globally. Recent reviews of Hg flux studies
suggest a median between 0.4 and 0.6 ng m$^{-2}$ h$^{-1}$ and a range between −18.7 and 41.5 ng m$^{-2}$ h$^{-1}$ (Agnan et al., 2016; Zhu et al., 2016). Obrist et al. (2005) found under controlled prairie grassland conditions, that during the cooler months daily net exchange was low or experienced net deposition while net emission was exhibited during the warmer months, peaking at 16 ng m$^{-2}$ h$^{-1}$. Seasonal Hg flux measurements made over a cornfield were highest in spring (19.5 ng m$^{-2}$ h$^{-1}$) while corn was growing, and lowest in autumn (−0.1 ng m$^{-2}$ h$^{-1}$) when the field was bare and snow covered (Baya and Van Heyst, 2010). Converse et al. (2010), at a high elevation meadow, observed deposition during spring (−4.8 ng m$^{-2}$ h$^{-1}$), emission during summer and winter (2.5 ng m$^{-2}$ h$^{-1}$ and 4.1 ng m$^{-2}$ h$^{-1}$, respectively) and near zero flux in autumn.

Micrometeorological Hg flux measurements undertaken in sub-alpine south-eastern Australia (Nimmo Plain) during summer had an average Hg flux of 0.2 ng m$^{-2}$ h$^{-1}$ (SD ± 14.5 ng m$^{-2}$ h$^{-1}$) (Howard and Edwards, 2018), comparable to the summer fluxes observed at Oakdale (0.67 ng m$^{-2}$ h$^{-1}$, SD ± 7.76 ng m$^{-2}$ h$^{-1}$). Flux chamber measurements at a background site (Pulganbar, north-eastern New South Wales) observed average fluxes of 0.17 ng m$^{-2}$ h$^{-1}$ (SD ± 0.09 ng m$^{-2}$ h$^{-1}$) in both April and June (Edwards and Howard, 2013), whereas Oakdale experienced net deposition during this time. Differences between these sites may be driven by the differences in site characteristics. Both Nimmo Plain and Oakdale were dominated by similar surface vegetation and measured Hg net-ecosystem exchange, whereas, Pulganbar measurements were conducted over bare soil and dominated by Hg emissions. Bare soils have been shown to exhibit greater rates of surface emissions due to increased exposure to incoming solar radiation increasing photo-reduction occurring within the substrate and enhanced volatilisation from the substrate (Gustin et al., 2002). Vegetated ecosystems often experience lower rates of emissions primarily due to surface shading and vegetation uptake (Graydon et al., 2006).

Annual cumulative Hg flux based on April 2017 to April 2018 was 1.8 µg m$^{-2}$ yr$^{-1}$, suggesting there was a small net source of Hg. Cumulative Hg flux shown in Figure 1 indicates that the site was dominated by net deposition until early spring. The site then switched to net emission which continued through summer to mid-autumn 2018, when cumulative fluxes began to decline again. The net Hg cumulative emission stage was greater than the net cumulative deposition stage at Oakdale, with cumulative Hg flux maximum reaching 2.7 µg m$^{-2}$ (on 30 April 2018) while cumulative flux minimum was −1.0 µg m$^{-2}$ (13 September 2017) (Figure 1), further suggesting the site was a small net source of Hg to the atmosphere. These values aligned with other annual Hg$^{0}$ measurements made at background sites. Castro and Moore (2016) estimated an annual contribution of −3.3 µg m$^{-2}$ yr$^{-1}$ for a combination grassland and deciduous forest ecosystem, while Osterwalder et al. (2017) and Stamenkovic et al. (2008) estimated 9.4 (boreal peatland) and 2.5 µg m$^{-2}$ yr$^{-1}$ (grassland), respectively.

Average ambient Hg values at Oakdale (0.68 ng m$^{-3}$ (SD± 0.22 ng m$^{-3}$) over the study duration) are well below the global background concentration of 1.2 ng m$^{-3}$ (Sprovieri et al., 2016) and below values reported for the Southern Hemisphere or Australia (<1 ng m$^{-3}$) (Howard et al., 2017; Slemr et al., 2015). Atmospheric Hg concentrations echoed observed flux trends with highest concentrations occurring during summer (0.88 ng m$^{-3}$) and lowest in winter (0.43 ng m$^{-3}$). Howard and Edwards (2018) did observe similar concentrations at an alpine site in south-eastern Australia.
Table 1: Seasonal means and standard deviations (SD) for Hg flux measurements and measured environmental variables across the study duration (3 April 2017 to 21 June 2018) at Oakdale, NSW. Averages were separated into day and night to show diel variability for those variables known to exhibit diel variability. Net all-wave radiation (Net Rad) provides day maxima and nighttime minima. Total solar is the net short-wave radiation (incoming – outgoing). DOI: https://doi.org/10.1525/elementa.423.t1

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<th>Soil Temperature (5 cm)</th>
<th>Net Rad (W m(^{-2}))</th>
<th>Total Solar (W m(^{-2}))</th>
<th>VWC (5 cm)</th>
<th>Sensible Heat Flux</th>
<th>CO(_2) Flux ((\mu)mol m(^{-2}) s(^{-1}))</th>
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Australia, with an atmospheric Hg concentration of 0.6 ng m$^{-3}$. Low atmospheric concentrations at Oakdale were attributed to lack of any significant anthropogenic sources in the region. The majority of atmospheric Hg$^0$ in the Southern Hemisphere is from long-range transport from the Northern Hemisphere and ocean evasion (Slemr et al., 2015). The combination of high oxidative conditions over the ocean and transport likely means that Hg$^0$ is deposited to the ocean surfaces before reaching the Oakdale field site and leading to overall lower atmospheric concentrations.

**Mercury flux variation across seasons**

Meteorological variables measured throughout the study peaked during summer with a mean air temperature, soil temperature and maximum daytime net radiation, 19.0°C, 24.8°C and 818.1 W m$^{-2}$ respectively (Table 1). Austral winter presented with the lowest mean air temperature (12.4°C), soil temperature (11.6°C) and maximum daytime net all-wave radiation (547.4 W m$^{-2}$). Total cumulative rainfall over the 445 day study period was 972.4 mm. Volumetric soil water content (VWC) peaked in winter and was always highest at 30 cm (maximum of 30.1% in June) (Figure 2). Little difference was seen between VWC at 5 cm and 15 cm, except in July and August when 5 cm VWC was higher.

Observed relationships between environmental variables and net Hg$^0$ fluxes were generally too low to be deemed significant (Table 2). Emission and dry deposition (positive and negative fluxes) Hg$^0$ fluxes when separated presented with a much larger proportion of significant

![Figure 2: Monthly mean Hg flux and associated environmental variables at Oakdale, New South Wales, 3 April 2017 to 21 June 2018. Means for April, May, and June are based on all available data from these months in both 2017 and 2018. For Hg flux (a) columns are the monthly mean and bars represent standard deviation. For the environmental variables (b–e), solid line is mean value and shading is the standard deviation. VWC is the volumetric water content. DOI: https://doi.org/10.1525/elementa.423.f2](https://doi.org/10.1525/elementa.423.f2)
Table 2: Spearman correlations with all Hg fluxes and emission and deposition (Dep.) Hg fluxes for each season and across the entire study duration at Oakdale, NSW. T is the soil temperature at each measured depth, VWC is the volumetric water content at each measured depth, RH is the relative humidity and Q* is the net all-wave radiation. Bold values indicate significant correlations (p-value < 0.01). DOI: https://doi.org/10.1525/elementa.423.t2

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correlations. The strongest correlation with net Hg fluxes was found to be sensible heat during summer (r = 0.13). However, as sensible heat is used as the momentum scalar when calculating Hg fluxes using the aerodynamic gradient method, sensible heat cannot be assumed to be a completely independent variable, therefore the correlations are most likely a reflection of this. Across the entire study period, net Hg\textsubscript{0} fluxes were found to have a significant relationship (p-value < 0.01) with net radiation, air temperature, relative humidity, and soil temperature at all depths, however correlations were low. When Hg fluxes across the entire study period were isolated to just emission fluxes the only variable not to have a significant correlation was air temperature and correlations remain low. Soil temperatures at all depths presented with a negative correlation with emission Hg fluxes across the entire study period, contrary to what has been observed in the literature. These relationships do however vary between seasons.

The winter Hg flux minima closely aligns with the minima observed for net all-wave radiation, air temperature and soil temperature, all of which occur around July (Figure 2). The maximum Hg flux in February is slightly offset from the peaks in temperature and net all-wave radiation that were observed in November–January. Australia’s winters are commonly warmer than those reported throughout the literature. Oakdale experienced a mean winter temperature of about 12°C, compared to both North America’s and Asia’s mean winter temperatures of 3°C, where 56.6% and 25.1% of Hg flux studies have taken place, respectively (Agnan et al., 2016). Most of south-eastern Australia does not experience freeze-thaw cycles or snowfall, and rarely sees temperatures below 0°C. Additionally, winter experienced less rainfall than other parts of the year, with a mean of 1.5 mm d\textsuperscript{–1} compared to the yearly average of 2.2 mm d\textsuperscript{–1}.

Winter was the only season to have a statistically significant two-way t-test (p-value < 0.05, t-score = –2.41) for diel composite day and nighttime measurements (Supplementary Table S1). Winter diel trends saw near zero emissions overnight (Figure 3), which follows the trends commonly observed in the literature (Baya and Van Heyst, 2010; Converse et al., 2010; Osterwalder et al., 2017). Low Hg\textsubscript{0} surface emissions was caused by the cooler soil temperatures which limit the substrate’s ability to uptake and release Hg\textsubscript{0} back to the atmosphere (Bahmann et al., 2006; Baya and Van Heyst, 2010).

The deposition trend seen in winter may be due to the influence of vegetation on the uptake of Hg compared to other variables during winter. Diel CO\textsubscript{2} fluxes during winter had a mean value of −0.80 μmol m\textsuperscript{–2} s\textsuperscript{–1} (SD ± 2.00 μmol m\textsuperscript{–2} s\textsuperscript{–1}) during the day and 1.27 μmol m\textsuperscript{–2} s\textsuperscript{–1} (SD ± 1.79 μmol m\textsuperscript{–2} s\textsuperscript{–1}) overnight, suggesting that plant uptake is still occurring during this time, unlike in other regions of the world where winter conditions mean plant growth is dormant (Sommar et al., 2016). However, despite daytime Hg\textsubscript{0} deposition (−0.99 ng m\textsuperscript{–2} h\textsuperscript{–1}) corresponding to CO\textsubscript{2} uptake, correlations between CO\textsubscript{2} fluxes and Hg fluxes in winter were weak (deposition Hg\textsubscript{0} fluxes with CO\textsubscript{2} flux, r = 0.12). Soil emissions were also reduced during this time as lower net all-wave radiation and temperatures observed during winter reduce the ability for volatilisation and reduction reactions to occur in the substrate which may be allowing vegetation uptake to drive Hg flux trends. Spring deposition Hg fluxes had the strongest correlation with CO\textsubscript{2} fluxes (r = 0.22) of all seasons (Table 2). Stronger springtime correlations are also seen between

![Figure 3: Diel mean composite trends for Hg\textsubscript{0} flux (navy blue line), soil temperature at 5 cm (orange line), air temperature (green line), net all-wave radiation (red solid line), total solar radiation (red dashed line) and CO\textsubscript{2} flux median diel composite (purple line) across each season at Oakdale, NSW, 3 April 2017 to 21 June 2018. Navy blue shaded area is Hg\textsubscript{0} flux standard deviation and purple shaded area is CO\textsubscript{2} flux inter-quartile range. Dotted vertical lines indicate median sunrise and sunset times for each season. Axis label colour corresponds to line colour on graph, except for temperature (shown in legend). DOI: https://doi.org/10.1525/elementa.423.f3](https://doi.org/10.1525/elementa.423.f3)
net radiation, both soil and air temperature and Hg emission flux, suggesting that the influence of these parameters on the evasion of Hg from the substrate is greater than the rate of uptake by vegetation at this site. Correlations between Hg\(^8\) deposition fluxes and CO\(_2\) fluxes suggest that Hg deposition is greater during times of high CO\(_2\) uptake. Lack of diel trends during spring could be caused by a combination of increased deposition, due to plant uptake, combined with higher soil emissions, due to increased solar radiation and temperatures, resulting in minimal net Hg\(^8\) exchange. Hg\(^8\) dry deposition is often found to increase during spring in response to rapidly growing vegetation (Fritsche et al., 2008). However, mean Hg fluxes during spring suggest net Hg emission was occurring, despite a daytime CO\(_2\) uptake of \(-1.54\) µmol m\(^{-2}\) s\(^{-1}\), the second highest uptake after autumn 2017.

Summer predominantly showed emission during the day and deposition overnight (Figure 3). However, two-way \(t\) tests between daytime and nighttime mean Hg\(^8\) fluxes had a \(p\)-value of 0.67, indicating diel trend was not statistically significant. Baya and Van Heyst (2010) saw similar diel trends during both summer and spring where Hg fluxes experienced net emissions during high net all-wave radiation and increased surface temperatures. Further, diel CO\(_2\) fluxes during summer showed the least variability, with median diel values ranging between \(-1.25\) and 3.35 µmol m\(^{-2}\) s\(^{-1}\) (Figure 3), indicating little influence from vegetation during this time, allowing soil emissions to be the key sources of Hg to the atmosphere. Reduced CO\(_2\) uptake during summer is likely caused by the hot dry conditions as indicated by the higher temperature and lower soil volumetric water content (VWC) (Figure 2). During periods of low water availability stomatal resistance increases, thereby reducing the amount of stomatal uptake occurring and simultaneously reducing Hg uptake (Emmerich and Verdugo, 2008). Reduced CO\(_2\) uptake is evident by the slight dip in CO\(_2\) diel flux compared to the stronger diel trends observed in other seasons. Osterwalder et al. (2020), observed a similar phenomenon where drought conditions at a grassland site in Switzerland resulted in reduced CO\(_2\) and Hg stomatal uptake. As intense drought conditions are a defining feature of Australia’s environment it is plausible that during drought Australia’s grasslands could become a greater source of atmospheric Hg.

The higher rate of Hg surface emissions during summer is largely attributed to the higher net all-wave radiation and soil and air temperatures, which were also highest at this time. High net all-wave radiation and soil temperatures enhance photoreduction and volatilisation occurring in the substrate allowing emissions to dominate (Carpi and Lindberg, 1997; Choi and Holsen, 2009). This is further confirmed by the Spearman correlations, which showed these parameters had the strongest correlations with positive Hg fluxes. Converse et al. (2010) observed that despite summer being the dominant growing period, solar radiation and temperature relationships allowed more Hg to be released from the substrate than was being taken up by the surrounding vegetation. The low CO\(_2\) uptake observed at Oakdale suggests similar is happening here.

Diel trends for both spring and autumn were not significant, with both seasons shifting continually between emission and deposition over the 24 hour period. Spring exhibited diel bidirectional exchange with a daytime average of 0.81 ng m\(^{-2}\) h\(^{-1}\) and nighttime average of –0.19 ng m\(^{-2}\) h\(^{-1}\) (Table 1). Autumn 2017 observed the opposite trend with deposition occurring during the day (–0.65 ng m\(^{-2}\) h\(^{-1}\)) and emission occurring at night (0.79 ng m\(^{-2}\) h\(^{-1}\)). Spring’s diel trends indicated higher variability during the day than overnight, as indicated by the SD (±10.51 ng m\(^{-2}\) h\(^{-1}\), day and ±7.73 ng m\(^{-2}\) h\(^{-1}\), night). However, the mean 24 hour values did not reflect this to the same extent.

Autumn Hg fluxes indicated little influence from environmental variables, with diel composite trends showing little diel variation (Figure 3). This is largely attributed to a reduction in solar radiation (mean total solar = 117.96 W m\(^{-2}\), 2017 and 138.11 W m\(^{-2}\), 2018) and temperature (mean air temperature = 14.40°C, 2017 and 16.43°C, 2018). Of all seasons autumn correlations between net Hg flux and measured environmental variables were the lowest and had the least number of significant correlations, 3 out of 15 variables were significant, and all remained low. Like the other seasons, autumn emission and deposition fluxes presented with stronger and more statistically significant correlations (13 out of 15), however, correlations remained low. Autumn was also the only season to not have a statistically significant correlation with air temperature and had the second lowest correlation between Hg emission and total solar radiation (\(r = 0.14\)). These trends were similar to those observed at a high alpine grassland site by Converse et al. (2010), who noted weak correlations with the majority of environmental variables. The lack of relationship was likely caused by decreases in photoreduction occurring in the substrate, reducing evasion, and senescence causing a reduction in deposition.

Autumn 2018 experienced significantly lower CO\(_2\) fluxes than 2017, mean daytime fluxes –0.66 µmol m\(^{-2}\) s\(^{-1}\) compared to –6.41 µmol m\(^{-2}\) s\(^{-1}\), with warmer temperatures and drier conditions (Table 1) likely as a result of increasing drought conditions. As a result, autumn 2018 diel Hg\(^8\) flux trends were different to 2017, with reduced daytime deposition and continued deposition overnight. This further indicates that drought conditions could significantly influence the rate of surface emissions occurring within Australian grasslands.

Hg deposition fluxes in autumn had the strongest relationship with relative humidity (\(r = 0.30\)). This relationship may explain why mean Hg\(^8\) fluxes indicated more deposition. Relative humidity has been suggested as an indicator of Hg deposition occurring via condensation of water onto the surface vegetation, whereby higher humidity indicates more potential for condensation to occur (Fritsche et al., 2008). Howard and Edwards (2018) suggested that nocturnal Hg depletion events were caused by dew formation and fog creating potential sinks of Hg. Spring diel trends exhibit deposition leading up to sunrise which then shift to emission shortly after sunrise (Figure 3). This could be an indication that Hg deposition with dew formation is
occuring which is then volatilising back into the atmosphere as the dew is evaporated at Oakdale (Converse et al., 2010). Reduced air temperatures and overnight temperature conditions and atmospheric stability during autumn is favourable for frequent fog and dew formation, allowing for greater Hg deposition to occur.

Conclusions
Mercury fluxes observed at Oakdale where highly variable and low throughout the study duration making it difficult to definitely determine the strength of relationships with environmental parameters. Mean Hg\(^2\) fluxes were close to zero, however cumulative fluxes over a 12 month period suggest that the dry grassland was a small net source of atmospheric Hg\(^2\). Variability in Hg\(^2\) trends was seen on seasonal scales, with the warmer months exhibiting net surface emissions and the cooler months exhibiting net deposition. This variation is primarily driven by changes in vegetation uptake, and photoreduction and volatilisation occurring at the surface. CO\(_2\) and Hg\(^2\) flux trends indicated that under hot dry conditions dry grassland stomatal uptake is reduced, leading to reduced Hg\(^2\) dry deposition and allowing increased surface emissions to occur.

Warmer air and soil temperatures and higher solar radiation, coupled with year-round plant productivity at Oakdale create a balance between Hg\(^2\) emission and deposition, leading to overall low fluxes. Hot dry conditions observed during austral summer reduced stomatal uptake of both CO\(_2\) and Hg\(^2\), causing a reduction in the rate of Hg\(^2\) dry deposition occurring. Substantially higher total solar radiation increased photoreduction occurring at the surface allowing for greater Hg\(^2\) emission to occur. Winter conditions show the opposite to occur. Low temperatures and solar radiation decreased the rate of surface evasion, while stomatal uptake was still efficient enough to increase Hg\(^2\) dry deposition, leading to net deposition during winter. Spring and autumn Hg\(^2\) fluxes both had low net exchanges. Springs low net exchange was attributed to increased vegetation (higher Hg\(^2\) deposition) coupled with increased surface emissions due to higher temperatures and incoming solar radiation, while autumns trends were found to have little influence from environmental variables. Increasing drought conditions in 2018 reduced vegetation productivity allowing net Hg\(^2\) emission to continue into autumn 2018.

This study clearly demonstrates that Australian dry grasslands are neither a source or sink of Hg\(^2\) and therefore contribute very little to the global Hg budget. However, more research is still needed to better understand how different vegetation types influence Australia’s Hg budget and to further understand how prolonged drought condition may influence Hg\(^2\) emission and deposition trends on inter-annual scales. Vegetation plays a key role in determining Hg deposition and storage. However, little is still known about how long-term changes in vegetation uptake from different vegetation types can influence Hg air-surface exchange at the ecosystem level. Under hot dry conditions, when vegetation uptake is reduced, Hg surface emissions dominate. Therefore, a better understanding of the drivers that influence Hg vegetation uptake will provide better parameterisation of Hg\(^2\) dry deposition.

Data accessibility statement

Supplemental files
The supplemental files for this article can be found as follows:

- **Figure S1.** Photos demonstrating change in vegetation coverage within the main measurement footprint at at Oakdale, New South Wales, from 3 April 2017 to 21 June 2018. DOI: https://doi.org/10.1525/elementa.423.s1
- **Table S1.** Student two-way t-tests for seasonal diel Hg flux composite day/night values at Oakdale, New South Wales, from 3 April 2017 to 21 June 2018. DOI: https://doi.org/10.1525/elementa.423.s2

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Competing interests
The authors have no competing interests to declare.

Author contributions
- Contributed to conception and design: KM, GCE
- Contributed to acquisition of data: KM, GCE
- Contributed to analysis and interpretation of data: KM
- Drafted and/or revised the article: KM, PJB
- Approved the submitted version for publication: KM, PJB

References


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