Spatial and Temporal Variation in Toxicity and Inorganic Composition of Hydraulic Fracturing Flowback and Produced Water

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Abstract

Hydraulic fracturing for oil and gas extraction produces large volumes of wastewater, termed flowback and produced water (FPW), that are highly saline and contain a variety of organic and inorganic contaminants. In the present study, FPW samples from ten hydraulically fractured wells, across two geologic formations were collected at various timepoints. Samples were analyzed to determine spatial and temporal variation in their inorganic composition. Results indicate that FPW composition varied both between formations and within a single formation, with large compositional changes occurring over short distances. Temporally, all wells showed a time-dependent increase in inorganic elements, with total dissolved solids increasing by up to 200,000 mg/L over time, primarily due to elements associated with salinity (Cl, Na, Ca, Mg, K). Toxicological analysis of a subset of the FPW samples showed median lethal concentrations (LC_{50}) of FPW to the aquatic invertebrate *Daphnia magna* were highly variable, with the LC_{50} values ranging from 1.16 to 13.7% FPW. Acute toxicity of FPW significantly correlated with salinity, indicating salinity is a primary driver of FPW toxicity, however organic components also contributed to toxicity. This study provides insight into spatiotemporal variability of FPW composition and illustrates the difficulty in predicting aquatic risk associated with FPW.

1. Introduction

Unconventional oil and natural gas (UOG) extraction has increased in prevalence over the past 50 years and there is a growing need to understand the environmental risk associated with such practices. Hydraulic fracturing (HF) is one such method of UOG extraction where water and a mixture of proprietary chemicals are pumped into a low-permeability geologic

formation under high pressure to fracture the substrate, releasing oil and gas [1–4]. This method allows for extraction of oil and natural gas reserves that would otherwise have been historically inaccessible [4,5]. Due to technological advancements and economic drivers, HF has increased substantially in the past decades [3,4,6–8].

Hydraulic fracturing is a water intensive process, using 2,000 to 100,000 m^3 of water per well ($2x10^6$ to $1x10^8$ L) for the injection fluid [5,9–11]. The fluid includes friction reducers, biocides, scale-inhibitors, gelling agents, and corrosion inhibitors (many of which are proprietary chemicals), as well as proppants, such as sand - which infiltrate fractures to prevent closure once pressure is released [4,8,12]. Post-fracturing, anywhere from 5% to 100% of the injected fluid will return to the surface combined with formation-derived waters [5,9,13,14]. The fluid that initially returns to the surface generally possesses the characteristics of the injection fluid and is termed flowback water, while fluids returning later which are characteristic of the formation waters and hold the targeted hydrocarbons are referred to as produced water [6,12,15,16]. The two waste products are not easily distinguishable and are collectively known as flowback and produced water (FPW), with the produced waters often representing a greater fraction of the volume [16].

Flowback and produced water is a complex mixture containing a range of organic and inorganic constituents derived from both the formation and injection fluid, with concentrations of components varying between wells, well pads, and geologic formations [15]. In general, FPW is highly saline, with sodium (Na) and chloride (Cl) concentrations frequently exceeding 50,000 mg/L and 100,000 mg/L, respectively [17–20]. Total dissolved solids (TDS) measurements can reach concentrations of upwards of 150,000 mg/L, due to high concentrations of Na, Cl, and other major ions (e.g., calcium (Ca), magnesium (Mg), potassium (K), strontium (Sr)) [21–23].

This salinization stems from the subsurface mixing of injection fluids and hyper-saline groundwaters - called formation brines, which differ based on the composition of surrounding rock and the source of the waters [16,24]. The organic fraction of FPW is primarily dictated by organics present in the injection fluid itself, and concentrations of these constituents peak early in the flowback period as these chemicals are depleted. However, it should be noted that formation-derived organics (e.g., polycyclic aromatic hydrocarbons (PAHs), phthalates) can be present throughout the well's production [15,17,25–28]. Other FPW constituents may include naturally occurring radioactive material (NORM) and transformation products resulting from chemical reactions within the well-bore environment [6,27,29–31].

FPW has been shown to be potentially hazardous to aquatic organisms, with salinity associated ions (Cl^-, Na^+, Ca^{2+}, Mg^{2+}, K^+), organic constituents, or a combination of the two being primarily responsible for the toxic effects observed [17,27,32–35]. The driver of toxic effects varies between FPW sample, model organism, and biological endpoint assayed. In addition to lethal effects, low concentration FPW exposure may induce sublethal effects, including alterations to metabolism, fecundity, development, behaviour, and/or cell functioning in both aquatic invertebrates [34,36–38] and vertebrates [39–43]. Risk assessment is complicated by the highly variable composition of these wastes. FPW toxicity has been shown to change within a single well over production time, as well as between different wells within a geologic formation, making assessing and tracking toxicity outcomes difficult [17,36].

While FPW composition is variable, some degree of toxicity prediction may be possible due to commonalities between FPWs, namely high salinity. While the salinity varies between samples, increased ion content is universal in FPW and is known to elicit toxic effects [17,34]. Unlike salinity, other toxic constituents of FPW (e.g., organics, metals, radionuclides) do not

exhibit this relative similarity, varying in both species and presence depending on geologic formation and composition of the injection fluid [15]. Furthermore, inorganic constituents represent an easily measured component of these wastes, unlike other constituents which pose much greater quantification difficulties, namely the numerous organic compounds present.

Due to this commonality, the degree of salinization is an easily measured parameter that could potentially be used to gauge FPW toxicity and estimate the risk associated with accidental release and spills of FPW. The current study investigates the variability of FPW inorganic composition sampled across wells/locations within the Montney and Duvernay Formations of Alberta and British Columbia, Canada, and relates this to acute lethal toxicity. Overall, the goal was to determine if the inorganic composition of FPW could be used to assess the potential toxicity associated with the sample. Inorganic compositional data was compiled from 140 FPW samples taken from 10 wells across the two geologic formations, at various flowback times. This allowed for comparison of FPW composition between wells on the same well pad, different well pads within the same formation, and between different formations using multivariate analysis. A subset of FPW samples were used for acute toxicity testing on the model freshwater invertebrate, *Daphnia magna,* to evaluate the relationship between inorganic composition and toxicity, allowing for determination of how aquatic risk of FPW releases may vary spatially and temporally. To our knowledge this is the first study to analyze a collection of FPW samples of this magnitude, thus providing a novel opportunity to thoroughly compare the spatial and temporal heterogeneity of these wastes, evaluate the toxic risk they pose, and evaluate the correlation between inorganic composition and overall toxicity to allow for better estimation of aquatic risk.

2. Methods

2.1 FPW sampling

FPW samples were collected between 2016 and 2019 from 10 HF wells across six well pads (surface locations). FPW was collected from each well at multiple timepoints during the flowback period, for a total of 140 FPW samples from the 10 wells. Wells from both the Montney (northern Alberta and British Columbia, Canada) and Duvernay (central and northern Alberta) Formations were sampled. Sampling methods for these wells have been previously published [43–46]; briefly, at each sampling time, samples were collected in 20L polyethylene buckets, sealed with minimal headspace and transported to the University of Alberta and stored at 4°C in the dark until use. In the current text well naming nomenclature indicates the location of the geologic formation of the well (M = Montney, D = Duvernay), a numerical indicator to designate the well pad (1-3), and, when required, a letter to designate the well on a well pad with multiple wells sampled (M1a-d & D3a-b). The names, sample number, formation, sampling times, and complete inorganic composition for each timepoint for each well are given in Table S1.

2.2 Inorganic analysis

Methodologies for inorganic characterization as well as the inorganic composition of a subset of the FPW samples have been published previously for both 2016 (see [43,44,47]) and 2019 samples (see [36,45]). Briefly, FPW samples were filtered through 0.2 μm nylon membranes, diluted with 18.2 MΩ·cm ultrapure water, and acidified with 12 μL 70% HNO_3 per 10 mL sample. Dilution factor was determined by sample specific TDS, as determined via evaporation of FPW and subsequent weighing of resultant solids. Inorganic quantification was performed using an Agilent 8800 Triple Quadrupole inductively coupled plasma mass spectrometer (ICP-MS/MS). A gas collision cell utilizing either He, O_2, or H_2 was used for most

elements, except heavy metals and low mass elements which were quantified in no-gas mode. Chloride of the 2016 FPW samples was quantified via ion chromatography using a Dionex DX, and via ICP-MS/MS in H_2 mode for the 2019 samples. Instrumentation drift was accounted for via an inline internal standard addition of Sc, Ge, In, Lu, and Bi. TDS was measured via evaporation of FPW and subsequent weighing of resultant solids.

2.3 Daphnia colony maintenance

Daphnia magna were sourced from Aquatic Research Organisms (ARO, USA, September 2019) and cultured in the Department of Biological Sciences Aquatics facility at the University of Alberta following Organization for Economic Cooperation and Development (OECD) guidelines [48,49]. *Daphnia* colonies were held in 1 L of water at 20 ± 1°C in 2 L glass beakers, with a 14:10 light:dark photoperiod. Complete water changes occurred thrice weekly using culture water consisting of moderately hard dechlorinated City of Edmonton water (pH ≈ 7.6, hardness ≈ 180 mg/L as $CaCO_3$, conductivity ≈ 385 µS/cm [39]) supplemented with 2 mM $CaCl_2 \cdot 2H_2O$, 0.5 mM $MgSO_4 \cdot 7H_2O$, 0.77 mM $NaHCO_3$, and 0.08 mM KCl. Each *Daphnia* colony was fed 3 mL of green algae (*Raphidocelis subcapitata*) (ARO, USA) and 3 mL of yeast, cereal leaf, and trout chow mixture (ARO, USA) daily, and 100 µL Roti-Rich invertebrate food (VWR, USA) once weekly. Colony health was monitored throughout this work, with monthly toxicity assays performed using a reference toxicant (copper) to ensure the *D. magna* responded to toxicant exposure as expected.

2.4 Toxicity testing

48-hour acute toxicity tests were carried out according to OECD guidelines [48], with slight modifications to determine the concentration of FPW causing 50% lethality (LC_{50}) in *D.*

magna. Exposure solutions were prepared by diluting raw FPW samples (100% FPW) in culture water to achieve the desired FPW concentrations (reported as a dilution percent). *Daphnia* neonates (< 24 h old) were group exposed in 20 mL glass scintillation vials (5 neonates per vial) containing 20 mL of the appropriate exposure solution for 48h without renewal or feeding and repeated 6 times (n = 6 replicates per concentration per test). Exposure concentrations were 0 (control), 1, 5, 7.5, 10, 12.5, 15, and 20% FPW or 0, 0.01, 0.1, 0.5, 1, 5, 10, and 15% FPW, depending on preliminary range finding tests. Toxicity testing was carried out on a subset of the 140 FPW samples collected, specifically 13 samples were evaluated for toxicity from 8 wells: well D3a (0, 8, 120h), well D3b (0, 8, 408h), well M1a (48h), well M2 (0, 48, 168), and well M3 (1, 24, 48h). Acute toxicity tests were performed according to the same methodology used by Boyd et al., in a previous study analyzing 3h samples from wells M1a-d [36], these results are included in this study as well (Table 1). Samples assayed were stored at 4°C in the dark from time of collection in 2016 or 2019 until use in toxicity assays in 2020.

2.5 Data analysis

All statistical analysis was carried out using RStudio version 1.3.1093 [50]. LC_{50} analyses were performed with the "ecotox" package. LC_{50} values are considered significantly different when the 95% confidence intervals (CIs) do not overlap. Spearman correlation coefficients were calculated with the "Hmisc" package. Principal component analyses (PCA) were used to evaluate correlations in inorganic composition of FPW between wells at different flowback times and locations. Prior to PCA, inorganic chemistry results that were below detection limit (BDL) or not tested (NA) were imputed via log-ratio expectation-maximization algorithms using the "zCompositions" R package using the lrEMplus function. Elements with BDLs or missing values exceeding 30% prevalence were eliminated from principal component

analyses. Samples taken at time 0 were eliminated from analysis as these samples are characteristic of solely the injection fluid, not FPW. Principal component analyses and visualization were performed via the "FactoMineR" and "factoextra" R packages, with all values standardized by scaling to unit-variance. FPW inorganic composition data from ICP-MS/MS and ion chromatography analyses were used as the input variables for PCA analyses. For analysis of spatial trends in FPW compositional variability, 95% CI ellipses were calculated based on unifying geographic groupings of the FPW samples (geologic formation, well pads, or individual wells).

3. Results & Discussion

3.1 FPW toxicity

Acute toxicity of FPW to *D. magna* neonates varied substantially, with LC_{50} values ranging over an order of magnitude (ranging from 1.16 – 13.7%) (Table 1), with a significant inverse correlation ($p < 0.05$) between LC_{50} and several elements primarily associated with salinity: e.g. (Na, Mg, Sulfur (S), Cl, K, Ca, Bromine (Br), as well as, Sr, Molybdenum (Mo), and Barium (Ba)). This suggests salinity was one of the major drivers of acute FPW toxicity, as toxicity generally increased (i.e., LC_{50} decreases) as salinity increased, which is in agreement with previous work evaluating FPW toxicity to *D. magna* [33,34] and other aquatic organisms [17,27,32,37]. Salinity is also believed to be the primary driver of sublethal effects of FPW exposure observed in *D. magna*, including reduced brood size, lowered metabolic rate, and altered behaviour [33,34,51]. Increased salinity has been shown to induce both hyperosmotic stress, impacting the organisms ability to osmoregulate, and oxidative stress, with reactive oxygen species inducing cellular damage [15] which are predicted to be the modes of action in the current study as well. The inverse correlation between LC_{50} and salinity suggests the acute

toxicity of FPW can be estimated by the salinity of the sample, simplifying estimation of potential risk in the assessment of other FPW samples.

Surprisingly, no trend between geologic formation and toxicity was observed, with the most and least toxic FPW being from Montney wells, and the intermediate LC_{50} values displaying no formation influence (Table 1). This result was somewhat surprising as it was predicted that Montney FPW samples would, on average, be less toxic than Duvernay FPWs due to their lower average salinity (Table 2). The difference between predicted and observed results is likely due to the relatively small subsample of FPWs used in toxicity testing (n=17), of which only six Duvernay samples were tested from two wells on a single well pad. Additionally, increased salinization of FPW occurs with increasing flowback time as a larger proportion of the returning FPW is composed of hypersaline formation brines rather than injection fluids [52]. Most of the samples tested in the current study were from early in the flowback period (0-8h), rather than time-periods that would be likely to have significant salinization by formation brines (Fig. 1), thus potentially masking the salinity differences between the two formations. Previous work has found several Duvernay FPW samples taken later in the flowback period ($\geq$ 72h) are highly toxic, with *D. magna* acute LC_{50} values of less than 1% reported [17,34], supporting the hypothesis that Duvernay FPW would be more toxic than Montney FPW as the formation brine begins to dominate the FPW composition.

While salinity was a primary cause of acute toxicity, the organic chemicals in FPWs, including both anthropogenic and formation derived organics, are known contributors to toxicity. Several studies have found raw FPW (i.e., with organics present) to be significantly more toxic than those lacking organics [17,27,32,34,53]. Organic constituents primarily contribute to sublethal toxic effects, with reduced aerobic scope and increased developmental deformities in

zebrafish (*Danio rerio*), and increased immobilization in *D. magna* only observed when organic constituents of FPW were present [41,42,51]. Accurate prediction of FPW toxicity is further complicated by spatial and temporal variation in organics, as FPW composition varies with injection fluid composition, well location, and flowback time [25–28,54]. Therefore, while acute toxicity of FPWs can be estimated from salinity, differences of organic compounds present could contribute to the observed variation. The contribution of non-saline FPW components to toxicity may increase with exposure time, making organic composition of increased concern under chronic exposure scenarios, where salinity may be insufficient to elicit acute toxic effects due to more dilute FPW exposures. Furthermore, organic complexation with other FPW constituent, such as saline ions and metals, may alter exposure of the complexed ions to biota, impacting toxicity as organic species and concentration changes throughout the flowback period. Consequently, such salinity-based estimations are better suited to acute, spill-type exposure scenarios and less relevant in low-dose, chronic exposure scenarios such as leaching from containment infrastructure. Chronic raw-FPW exposure has an increased impact on survival, growth, and reproduction-based endpoints in several species compared to the saline component of the wastes alone [21,34], suggesting organics may be important drivers of toxicity in these exposures in addition to salinity. In addition to the toxic contributions of salinity and organics, other toxic substances, such as NORM and metals, also vary between wells and injection fluid composition [6,29,47], and could further affect toxicity. Several metals quantified in the current study were at concentrations sufficient to induce toxicity, including Sr and Cd which reach levels up to 1307 mg/L (D1 18d) and 1.49 mg/L (M1d 1h), 10x and 400x their respective EC_{50}s for *D. magna* immobilization [55].

241 The LC_{50} values for Duvernay well pad D3 varied by approximately two-fold and had an
242 inconsistent temporal variation (Table 1). Well D3a samples at 8 and 120 h showed similar
243 toxicity (LC_{50} 6.03% and 5.46%, respectively), while the 0-hour sample showed much lower
244 toxicity, suggesting the injection fluid (0 h) was less toxic than the later FPWs that had been
245 salinized by formation brines (LC_{50} 11.4%). Conversely, well D3b showed similar toxicity at 0
246 and 408 h (LC_{50} 5.39% and 5.02%, respectively), while the 8 h sample was significantly less
247 toxic with an LC_{50} of 8.14%. This may be due to the injection fluid and later produced waters
248 having similar toxicity, while at 8 h the mixing of remaining injection fluids and the formation
249 brines diluted the toxic constituents of both, thus increasing the LC_{50}. The inconsistent toxicity of
250 D3a and D3b, both in terms of LC_{50} values and temporal trends, is interesting as both wells
251 utilized the same hydraulic fracturing methods, began production on the same day, and produced
252 FPW with similar inorganic compositions (Fig. S1b). This variability illustrates the contribution
253 of non-saline constituents in dictating toxicity, including the organic fraction. The increased
254 toxicity of well D3b samples compared to D3a at initiation of flowback (0 h) is likely due to
255 differing injection fluid composition between the two wells, with differences between the two
256 wells subsiding later in the flowback period (>120 h) and LC_{50} values become similar as the
257 injection fluid is cleared and the formation derived organics and inorganics dominate both the
258 composition and toxicity of the FPW.

259 Montney FPW also showed inconsistent temporal changes in toxicity. Well M2 FPW
260 increased in toxicity later in the flowback period as formation derived constituents increased
261 with LC_{50} values of 1.16% and 3.47% after 48 and 168 h of flowback, respectively, compared to
262 the significantly less toxic FPW/injection fluid at the start of flowback (0 h LC_{50} 9.48%) (Table
263 1). Conversely, M3 FPWs decreased in toxicity as the toxic injection fluid-derived constituents

were cleared from the well (1 h LC_{50} 1.85%), and later samplings showed consistent toxicity, with 24 and 48 h LC_{50} values of 6.76 and 6.47%, respectively (Table 1). Sampling time did not correlate with toxicity ($p = 0.11$), supporting this inconsistent variability in temporal trends. Similar to D3a and D3b, studies with Montney wells on the same well pad (M1a-d FPW) exhibit variable toxicity despite substantial similarities in their fracturing approach and inorganic composition of FPWs (Table S1 & [36]). Comparison of the 3-hour samples from the four wells on well pad M1 showed a nearly two-fold difference in LC_{50} values between the least toxic (M1b 13.7%) and most toxic (M1c 7.2%) samples, with M1d also being significantly more toxic than M1b (LC_{50} 9.89%) (Table 1). Previous chronic (21 day) low-concentration exposures using these 3 h FPW samples corroborate these differences in toxicity, as exposure to M1c FPW caused substantial mortality and a significant delay in reproduction in *D. magna* at a concentration of only 0.75%, while exposures to 2% FPW from M1a, b, and d, failed to yield similar results [36]. Collectively these results indicate that FPW toxicity is highly variable, and that although salinity is a primary driver of acute lethality to *D. magna*, other components, such as organic compounds, may elicit a high degree of toxicity regardless of salinity.

Overall, these results suggest that while prediction of FPW toxicity based on salinity measurements alone may underestimate overall toxicity to a degree, this approach provides a reasonable prediction of risk for acute exposures without requiring complex organic compositional characterization. This approach could help simplify preliminary risk assessment after application of a correction factor to overcome the underestimation of risk, prior to site-specific determination of risk. Additionally, characterization of many organics in FPW is further complicated by the proprietary nature of many constituents of the injection fluid, thus further supporting salinity-based estimates for preliminary risk assessment. Such salinity-based

287 predication may also be applicable in assessment of conventional oil and gas wastewater toxicity,
288 where salinity also acts as a primary driver [56].

289 *3.2 FPW compositional variation between geologic formations*

290 Comparison of all FPW samples showed the inorganic composition was primarily influenced by
291 the geologic formation of the well. Montney and Duvernay FPW samples clustered separately
292 from each other, separating along both PC1 and PC2, representing 70.6% and 9.2% of the
293 variance respectively (Fig. 2a). Increasing PC1 score correlates with most elements measured,
294 with the main contributors to PC1 being increases in Li, Na, Cl, K, Ca, Br, and Sr. The clustering
295 of Duvernay samples at higher PC1 scores is due to the increased concentration of these
296 elements over Montney samples. The distinct inorganic composition of Montney and Duvernay
297 samples is also evident at the well pad level, with Duvernay FPWs (locations D1-3) and
298 Montney (M1-3) samples separating along PC2 (Fig. 2b), due primarily to Mg, S, Manganese,
299 and Iron. While separation based on geologic formation is observed along PC2, substantial
300 overlap does occur along PC1 (Fig. 2), indicating that while Duvernay samples generally have
301 higher Li, Na, Cl, K, Ca, Br, and Sr concentrations, there is appreciable overlap in the
302 concentration ranges observed for these elements. This is evident with Montney wells on well
303 pad M2 having similar PC1 scores to the Duvernay samples from wells D1 and D2, due to
304 similar concentrations of Li, Na, Cl, K, Ca, Br, and Sr (Fig. 2b).

305 Most of the elements contributing to Montney and Duvernay separation along PC1 are
306 salinity associated, suggesting much of the difference in the FPW produced from these
307 formations is due to the higher average salinity of Duvernay FPWs (Table 2). The salinity of
308 FPW is primarily dictated by the formation brines that leach into the well bore, mixing with the
309 injection fluid to formulate the FPW [52]. These brines differ between locations, but normally

range from 100-300 ppt in the Western Canadian Sedimentary Basin, in which the Montney and Duvernay formations reside [57]. These differences in inorganic FPW composition between Montney and Duvernay samples are consistent with other formations, where concentrations of salinity associated elements (Na, Cl, K, Ca) are similar within a formation, suggesting FPW from other formations may exhibit similar intra-formation grouping and inter-formation separation as Montney and Duvernay. While there is substantial variation in FPW composition within a single formation, relative similarity in range of variance within a formation is observed in formations outside Montney and Duvernay. Montney and Duvernay FPWs have higher concentrations of saline elements than FPWs from the Denver-Julesburg (DJ) basin of Colorado, USA [6,11,58–60], suggesting formation brines of the DJ basin are less concentrated than Montney or Duvernay brines. Duvernay derived FPWs are similar in composition to the those from the Marcellus shale of the northeastern United States and the Permian basin of Texas and New Mexico [13,18–20,61–64]. The Montney derived FPWs quantified here are most similar to Marcellus FPWs, but generally with lower enrichment of Cl [13,18,20,61–63]. Montney FPWs have lower enrichment of all major elements than Permian basin FPWs [19,20,64], consistent with less concentrated formation brines in the Montney formation.

3.3 FPW compositional variation within a geologic formation

3.3.1 Montney formation FPW variation

Inorganic analysis of Montney FPW shows there is substantial variability in FPW composition between well locations targeting the same geologic formation. FPW samples from wells at three well pads in the Montney formation were compositionally distinct, with M2 FPW having the most unique composition, separating substantially from M1 and M3 samples along PC1, representing 70.2% of the variation (Fig. 3a). Separation along PC1 is dictated primarily by

Na, Mg, Cl, K, Ca, Br, and Sr. M1 and M3 derived FPWs are relatively similar in composition, with slight separation along both PC1 and PC2, the latter representing 19.6% of the variance with primary contributors being Fe, Mo, and Mn. The higher salinity of M2 samples is a major driver of its dissimilarity from other Montney samples. Concentrations of salinity-associated elements are on average 2.3 - 3.3x higher in M2 FPW than M3 (Table 2). M1 and M2 exhibit a 2.9x difference in average TDS, with differences in average content of major contributing elements varying from 2.4 – 5.5x higher in M2 than M1.

The differences in inorganic composition of FPW between M2 and M3 samples (Fig. 3a) could be due to spatial variation in formation brines as the two well locations are 120 km apart, so spatial variation in formation brine chemistry was expected to alter the inorganic makeup of the FPW. The substantial compositional dissimilarity between M1 and M2 FPW (Fig. 3a) is noteworthy as these two wells are less than 12 km apart and terminate at a similar depth in the formation. This difference suggests large variations in formation brine composition can occur over small distances. Complicating the interpretation of spatial variability is the relative compositional similarity between M1 and M3 FPW (Fig. 3a) despite the sites being nearly 130km apart, thus were expected to be more compositionally distinct, however little variation is seen in the major contributing elements. However, some elements do exhibit variation, for example M3 FPW having 2.3x higher boron and 44x higher S than M1 FPW (Table S1). These results suggest a heterogenous spatial distribution of solute content within formations, thus impacting FPW composition. This heterogeneity in FPW composition is not observed over smaller distances, with the four wells located at well pad M1 (wells M1a-d) showing little variability in FPW composition (Fig. 3b).

3.3.2 Duvernay formation FPW variation

Similarly, Duvernay FPW demonstrated compositional variability within a formation. Wells on well pad D3 produced FPWs that were compositionally distinct from the other two locations (D1 & D2) with lower Li, Na, Cl, K, Ca, Br, and Sr in D3 samples compared to D1 or D2 (Fig. S1a). Little variation was observed between FPW sampled from the two wells on the well pad D3 suggesting compositional similarity (Fig. S1b). This variation between well pads is also likely due to differences in formation brine composition, with the average TDS of D1 and D2 FPWs being more than twice that of D3. The difference being primarily due to 2-3x higher average Na, Ca, and Cl (Table 2). This variation in composition is noteworthy as all three of these well locations are within 20 km of each other, further showing substantial compositional variability over short geographical distances. The comparatively dilute FPW of D3 was likely influenced by only using freshwater for injection fluid formulation and the relatively short shut-in time [44] limiting interaction with formation brines. The lower salinity of D3 compared to D1 and D2 beyond the initial stages of flowback (Fig. 1) similarly indicates geographic heterogeneity in the formation brine composition, suggesting formation brines in this location are less concentrated than those found in the other two Duvernay wells.

The composition of D1 & D2 FPW suggests that FPW rapidly takes on the inorganic characteristics of the underlying formation brines, regardless of the composition of the injection fluid. The injection fluid used in well D1 was made solely using freshwater, while D2 utilized a combination of freshwater and reused FPW [44]. Reuse of FPW increases the solute content of the injection fluid, with D2 having 18x higher TDS at initiation of flowback (characteristic of the injection fluid), compared to D1 (5,310 mg/L vs 288 mg/L, respectively) (Table S1). Despite the difference in injection fluid composition, both wells took on similar hypersaline compositions within hours of flowback initiation (TDS at 8h sampling: 153,000 mg/L for D1 and 168,000

mg/L for D2), characteristic of the formation brines. This indicates the inorganic composition of FPW is likely dictated by the underlying hydrogeochemistry for much of the flowback period, with injection fluid only substantially influencing composition during the earliest phases of the flowback period.

3.4 Temporal variation in FPW composition

FPW composition was also changes over time, with initial samples having a lower salinity, and the concentration of many elements increasing with sampling time as formation brines contribute more to the composition of the FPW [52]. The FPW returning during the initial stages of flowback are compositionally similar to the injection fluid, which are normally of lower salinity and increased organic content. The lower salinity injection fluids are gradually removed from the well and/or mix with the formation brines resulting in higher salinity wastes with time.

In the FPWs characterized here, concentration of most inorganics increased over time, with Cl and Na increasing the most with flowback time (Table S1). Chloride concentration in Duvernay wells increased by an average of 78,500 mg/L per well over the sampling timeframes (range 46,000 to 136,000 mg/L increase per well), yielding maximal Cl concentrations of 140,000 mg/L (Table 2). Montney FPW Cl concentration increased by an average of 28,000 mg/L over time (range 6,000 to 57,000 mg/L increase per well), with maximal concentrations of 68,000 mg/L. Sodium concentration also increased temporally, with an average increase in Duvernay FPW of 37,000 mg/L and in Montney FPW of 22,000 mg/L (range 24,000 to 58,000 mg/L increase per Duvernay well; 4,500 to 44,000 mg/L increase per Montney well), yielding maximal concentrations of 67,000 mg/L and 56,000 mg/L respectively. Inclusion of M3 FPWs skews these relationships somewhat due to the short sampling period (48 h), which was likely insufficient to completely clear the injection fluids. Averages increase in Cl and Na for Montney

wells when excluding M3 increased to 34,000 and 27,000 mg/L, respectively. The large increases in inorganic ions such as Na, Cl, and Ca drive the temporal increase in TDS observed (Fig. 1). This increase in TDS has been shown in previous work investigating both Montney and Duvernay FPW [17,23] as well as FPW from other formations [11,13,18,58,62,63,65].

Distinct phases of flowback are observed because of this changing composition, where samples cluster together based on relatively similar composition when analyzed by PCA. For all wells the PC1 scores increased with time as formation brines increased the TDS (Fig. S2), consistent with previous work which found FPW samples from a single well in the DJ basin grouped into three distinct phases over time [11]. These DJ basin samples were found to be significantly different during the first two days of flowback compared to later samplings, with a further shift in composition after 21 days of flowback. These results echo the changes observed in this study, with greater compositional change occurring in the earliest samples as the injection fluid is cleared from the well, and less variation being observed at later samplings (Fig. S2). Analysis of more than one well obscures these groupings, with no discernible clustering observed between all Duvernay (Fig. 4a) or Montney (Fig. 4b) FPWs. A general trend of increasing PC1 score over time is observed as formation brines salinize the returning waters, but no substantial clustering of sampling times is observed due to substantial variation in FPW composition between wells.

4. Conclusions

Determination of the ecotoxicological risks posed by FPW is needed to determine the best approaches to treatment and disposal that will ensure adverse effects are avoided. This aim is complicated by the complex composition of FPWs as differences prevent extrapolation of risk assessment, treatment, and disposal methods between different FPWs. To better understand these

risks and complications, comparison of a variety of FPWs is needed to determine the degree to which they vary.

The present study provides a spatial and temporal analysis of inorganic variation in FPWs, providing insight into the degree of heterogeneity of these wastes. FPW is a highly heterogenous mixture enriched in various, mainly saline, elements with levels of salinization varying significantly both between and within geologic formations. This heterogeneity prevents generalizations of FPW composition across sites as short physical separation in drilling location can lead to large differences in FPW inorganic makeup. FPW also varies temporally, with most inorganic solutes increasing with flowback time as the wastes are salinized by formation brines, however the extent of this salinization is variable between wells.

This study also provides insight into the acute toxicity of a variety of FPW samples. The use of *D. magna* in these investigations is pertinent due to their wide-ranging distribution and known sensitivity to FPW. Extirpation of these primary consumers from FPW release would be detrimental not only to *D. magna*, but also to higher trophic levels that rely upon these basal members of the aquatic food chain. The hypersaline composition of FPWs is a major driver of toxicity in *D. magna*, with toxicity increasing in concert with salinity. These results allow for an evidence-based approach to FPW toxicity estimation using salinity measurements alone, but the contributions of organic components to toxicity cannot be overlooked. Substantial variation in the toxicity of FPWs that are inorganically indistinguishable and sourced from the same well pad further demonstrates the importance of FPW constituents other than salinity. Further work is needed to evaluate the extent to which this salinity-based risk estimation can be extrapolated to longer term exposures, where low abundance constituents may contribute more to toxicity than in shorter term acute exposures. Temporal analysis of FPW toxicity reveals large variations in

toxicity of a single well over time. This variation is inconsistent between wells, with some wells increasing in toxicity over the time periods analysed, while others decrease or even display biphasic relationships, with higher or lower toxicity observed at intermediate timepoints. Despite this, increasing salinity with sampling time is predicted to drive an overall trend of increasing toxicity with flowback time, however toxic constituents of some injection fluids may also induce toxicity early in flowback.

Overall, the results presented here demonstrate the substantial compositional and toxicological variability of FPW, with large differences observed over short distances and times. These results reiterate the need for case-specific approaches to risk assessment and disposal methods of FPWs, as application of a 'one-size-fits-all' approach will prove insufficient in light of this variability.

CRediT authorship contribution statement

Connor B. Stewart: Formal analysis, Data Curation, Visualization, Writing - Original Draft. **Hannah M. Lowes:** Investigation, Writing - review & editing. **W. Tyler Mehler:** Conceptualization, Writing – review & editing. **Katherine N Snihur:** Investigation, Writing - review & editing. **Shannon L. Flynn:** Investigation, Writing - review & editing. **Daniel S. Alessi:** Resources, Writing - review & editing. **Tamzin A. Blewett:** Supervision, Conceptualization, Resources, Writing - review & editing.

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Data availability

Compositional data is available in Table S1. All other data will be made available on a public repository upon acceptance of the manuscript for publication.

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