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Crop bromide concentrations following methyl bromide fumigation for pale cyst nematode in southeastern Idaho

Christopher W. Rogers[1] | **Juliet M. Marshall**[2] | **Margaret Moll**[2] | **Cynthia Curl**[3]

[1]USDA-ARS, Northwest Irrigation and Soils Laboratory, Kimberly, Idaho, USA

[2]Plant Sciences Department, University of Idaho, Idaho Falls, Idaho, USA

[3]School of Public and Population Health, Boise State University, Boise, Idaho, USA

Correspondence
Christopher W. Rogers, USDA-ARS, Northwest Irrigation and Soils Laboratory, Kimberly, ID, USA.
Email: christopher.w.rogers@usda.gov

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Abstract

Methyl bromide (MeBr) is a sterilizing fumigant used to control quarantine pests that is restricted due to its detrimental atmospheric effects. The degradation of injected MeBr produces crop-available Br^-. Up to five applications of MeBr were used in southeastern Idaho fields to combat the pale cyst nematode (*Globodera pallida*). Data regarding the uptake and partitioning of Br^- in crops following MeBr application in the region were unavailable. Research determined background concentrations of Br^- in alfalfa (*Medicago sativa* L.), barley (*Hordeum vulgare* L.), corn (*Zea mays* L.), potato (*Solanum tuberosum* L.), and wheat (*Triticum aestivum* L.) compared to MeBr-treated fields. Background Br^- concentrations ranged from nondetectable (ND) to 33.0 mg Br^- kg^{-1}; vegetative tissue concentrations were greater than reproductive, except corn where there was no difference. Nearly all crops grown in MeBr-treated fields had greater Br^- concentrations than background. Background-baled-alfalfa tissue Br^- concentration was 33.0 mg kg^{-1} compared to 117.8 mg Br^- kg^{-1} from a MeBr-treated field. Br^- concentration in green alfalfa decreased from 79.8 to 36.5 mg Br^- kg^{-1} at the final cutting in a MeBr-treated field, where time after application decreased crop Br^- concentrations. Small grains had low Br^- concentrations in reproductive tissue (1.7 mg Br^- kg^{-1}) compared to vegetative tissue (106.5 mg Br^- kg^{-1}). Corn stover concentration (12.7 mg Br^- kg^{-1}) was low relative to small-grain straw, but corn ear (5.8 mg Br^- kg^{-1}) was greater than small-grain reproductive tissue in the MeBr-treated field. Crop selection following MeBr applications should consider the likelihood of elevated Br^- concentration for the plant fractions intended end use.

Abbreviations: Br, bromide; HSD, honest significant difference; MeBr, methyl bromide; ND, nondetectable; PCN, pale cyst nematode; TIF, totally impermeable film.

1 | INTRODUCTION

Methyl bromide (MeBr) is an effective pre-plant soil fumigant for the management of pests in agricultural crop production (Villalobos & Weber, 2005). Usage has become increasingly uncommon in the United States as MeBr is known to cause damage to the ozone layer (Birmpili, 2018) and is highly toxic if inhaled by farm workers and other off-target organisms (Thompson, 1966; USEPA, 2022b). Historically, MeBr has been used to control a range of agricultural pests, weeds, and insects but was largely phased out on January 1, 2005, in the United States with only a small number of specific exemptions (Mulder, 1979; USEPA, 2022b). Currently, the usage of MeBr is confined to critical use exemptions in the United States that include quarantine pests in a defined geographical area and preshipment for certain commodities (USEPA, 2022b).

The pale cyst nematode (PCN) (*Globodera pallida*) was discovered in specific potato (*Solanum tuberosum* L.) production fields in southeastern Idaho in 2006 (Hafez et al., 2007). The PCN is deemed a quarantine pest in many countries globally. For a period of time, Japan closed the importation of all potatoes produced in the United States, and many other countries closed potato imports from Idaho specifically (Dandurand et al., 2019; EPPO, 2017). Nearly 4000 ha of agricultural production land in or near Bingham County, ID, USA, has been managed in a PCN eradication program developed by the Idaho State Department of Agriculture (ISDA) and the United States Department of Agriculture's Animal and Plant Health Inspection Service (USDA-APHIS, 2012). This program was critical for ensuring the stability and future of the nearly $1 billion Idaho potato industry (USDA-APHIS, 2012). The PCN eradication program sought and received a United States Environmental Protection Agency (USEPA) exemption for the usage of MeBr as a fumigant to eradicate the damaging PCN in the region. The Idaho PCN program utilized multiple measures, but MeBr was the primary treatment intended to eradicate PCN with up to five applications occurring in a 5-year period in certain fields (USDA-APHIS, 2011). Subsoil injections were applied based on label guidelines at rates of 448 kg ha^{-1} (USEPA, 2023). In the PCN program, 98/2 MeBr and chloropicrin were applied, and polyethylene tarps were used prior to 2013 (USDA-APHIS, 2007, 2022). An 80/20 mixture of MeBr and chloropicrin was used subsequently, and tarping was changed to a vapor barrier (Raven "Vapor Safe" totally impermeable film [TIF], Raven Industries) due to changes in provisions (USEPA, 2022a, 2023).

Historically, the use of MeBr was primarily for the production of fruit and vegetable crops harvested for direct consumption, predominately strawberry (*Fragaria x ananassa*), tomato (*Solanum lycopersicum* L.), peppers, and cucurbits (*Cucurbitaceae*) (Johnson et al., 2012). While potatoes are within the nightshade family (*Solanaceae*) and thus have some similarity with tomatoes and peppers, the other major crops grown in southeastern Idaho differ greatly from these vegetable crops and include alfalfa (*Medicago sativa* L.), wheat (*Triticum aestivum* L.), corn (*Zea mays* L.), and barley (*Hordeum vulgare* L.). Alfalfa is a leguminous perennial plant with a deep root system that is used for its biomass as animal feed, where the aboveground portion is harvested multiple times within a single growing season (Shewmaker, 2005). Barley and wheat are largely grown for their seed, while the straw is widely used in the cattle and dairy industries (Tarkalson et al., 2011). Barley produced in the region is primarily used for malting and brewing, while wheat is used for various end use products intended for human consumption. Potato is grown for the edible tuber; the potato leaves and aboveground plant tissues are poisonous to both humans and livestock due to the high concentration of the glycoalkaloid solanine. Potato aboveground dry matter (ADM) remains in the field after harvest and is recycled through the agroecosystem. This material is rapidly broken down due to its low C:N ratio. Corn can be harvested for its edible seeds, but due to the short growing season in southeastern Idaho, it is predominately produced for silage (68%) and harvested for animal feed (USDA-NASS, 2022).

Following MeBr application, degradation occurs in the soil, often rapidly, largely by chemical hydrolysis and methylation resulting in increased Br^- available to the crop (Dungan & Yates, 2003; Gan et al., 1994; Villalobos & Weber, 2005). While Br is not one of the 17 essential elements needed for crop growth, Br and a wide range of other elements are taken up in varying quantities by plants depending on both the element of interest and the soil environment (Yamada, 1968). In most scenarios, Br^- is of little interest biologically as it is not generally found in large quantities in the native environment and has a relatively low degree of toxicity (Flury & Papritz, 1993; WHO, 2009). However, concerns occur when excessive accumulation and elevated concentrations of Br^- are found in drinking water (WHO, 2009) and plants that are consumed (Knight & Costner, 1977). In sufficient quantities, Br^- can

Core Ideas

- Mean Br^- concentrations were less in nearly all crop materials from untreated compared to MeBr-treated fields.
- There were greater Br^- concentrations in vegetative compared to reproductive tissue in untreated and MeBr-treated fields.
- Br^- concentration in green alfalfa tissue decreased over the duration of the study.
- Third and fourth cutting green alfalfa tissue Br^- concentration was less than baled alfalfa.
- Whole-corn (vegetative + reproductive) Br^- concentration was less than other whole plants in a MeBr-treated field.

have negative health effects, particularly neurological, on both humans and animals (de Souza et al., 2013; Mulder, 1979; Van Leeuwen et al., 1987).

Similar to Flury and Papritz (1993) and due to the variation in methodologies used, we use the terms “bromine,” “Br,” and “mg kg^{-1}” to denote the bromine element regardless of chemical form and report concentrations of inorganic bromide as “bromide,” “Br^-,” and “mg Br^- kg^{-1}” based on the authors’ reporting in the article. We would note that research by Mino and Yukita (2005) determined that >95% of measured Br was in the Br^- form in select vegetable crops indicating the majority of crop Br is in the Br^- form, and thus, likely relatively comparable.

Research on Br accumulation in plants was largely conducted prior to the removal of MeBr as a common soil fumigant in the 1970s and 1980s prior to the development of TIF tarps. That older work typically showed elevated Br concentrations in fumigated crops compared to check plots (Beckman et al., 1967; G. Brown & Jenkinson, 1971; A. Brown et al., 1979; G. Brown et al., 1974; Kempton & Maw, 1972, 1973, 1974; Masui et al., 1978, 1979; Nazer et al., 1982; Yuita, 1994). The magnitude of the differences in the crop tissue Br concentrations in these studies between untreated checks and fumigated soils was crop dependent. For example, barley whole plants harvested near the boot stage prior to seed development averaged tissue concentrations of 106 mg Br^- kg^{-1} in checks but up to 1788 mg Br^- kg^{-1} in fumigated plots (A. Brown et al., 1979). This was a much greater Br^- concentration than in a crop such as strawberry, where leaf concentrations only ranged from an average of 63 mg Br^- kg^{-1} in untreated checks to 88 mg Br^- kg^{-1} in fumigated plots (A. Brown et al., 1979). In contrast to the high concentrations seen in whole plants, previous work showed much less variation in wheat seed Br concentrations that only ranged from 4.5 to 44 mg kg^{-1} when grown and sampled from 1.5 to 3.5 years after MeBr applications of 975 kg ha^{-1} (G. Brown et al., 1974).

Br^- concentrations up to 10,000 mg Br^- kg^{-1} were reported in Idaho from alfalfa bales produced in MeBr-fumigated fields in the PCN effected area (Hu et al., 2017). Hu et al. (2017) also reported mean Br measured in baled alfalfa from nonfumigated fields at 4.6 mg kg^{-1}, while in fumigated fields, Br in tissue samples averaged 3300 mg kg^{-1}. These reported tissue concentrations from fumigated samples were greater than the normal range of Br concentrations summarized by Shtangeeva (2017) of <1–285 mg kg^{-1} in dry tissue of terrestrial plants. Reported fumigated concentrations from baled alfalfa samples collected in the PCN affected area were also greater than the previous USEPA tolerance level for alfalfa hay of 50 mg Br^- kg^{-1} (Inorganic Bromide Residues, 2022) that was phased out in 2011.

Studies on plant uptake following MeBr application were largely conducted prior to the widespread implementation of TIF tarps and conducted on crops and in regions that are markedly different from the high-input, irrigated production system common to southeastern Idaho. Additionally, studies measuring Br^- concentrations in alfalfa tissue following MeBr applications have not been conducted to our knowledge. Thus, the objectives of this research were to (a) measure background concentrations (uptake and partitioning) of Br^- in alfalfa, barley, corn, potato, and wheat in non-fumigated fields; (b) determine the uptake and partitioning of Br^- between both vegetative plant tissue and the reproductive tissue (seed, ear, or stem tuber) as applicable in crops grown on previously fumigated plots in affected fields; (c) determine Br^- concentrations in green and baled alfalfa tissue over the typical within-season harvest time frame; and (d) compare the background Br^- concentrations in the plant parts of crops in the region to those grown on previously fumigated soils.

2 | MATERIALS AND METHODS

2.1 | Research area

The research was conducted in Bingham County, ID, USA, south of Idaho Falls, ID, USA, where nearly 4000 ha of land has been regulated for PCN since its discovery in 2006 (USDA-APHIS, 2022). The area is classified as a warm summer humid continental climate (Dfb) in the Köppen–Geiger climate classification system with low rainfall (Kottek et al., 2006). The region is dependent on irrigation to supply annual crop needs as it receives only around 330 mm of precipitation annually with the lowest amounts in the summer months (NOAA, 2021).

2.2 | Background alfalfa, barley, corn, and potato Br concentrations

Background Br^- concentrations can no longer be assessed in fields where MeBr was applied and therefore, we collected background samples from non-fumigated fields with no previously documented PCN and no known MeBr application history to determine background Br^- concentrations for the area. Four non-fumigated fields for each of the five study crops were selected within 40 km of the MeBr-treated area in the fall near the end of the growing season in 2016. Four subsamples were collected using a 1-m^2 quadrat from each field. “Green” alfalfa was harvested (Table 1) for hay under normal production protocols near the bud stage during active plant growth (Shewmaker, 2005). Whole aboveground plant samples were collected and homogenized, and an approximate 25 g subsample was collected for analysis. Baled alfalfa samples were collected using standard collection procedures with a forage probe (Putnam, 2003). Approximately 10 subsamples

TABLE 1 Crop production and sampling timeline for research conducted to measure crop Br⁻ concentrations following MeBr applications in Bingham County, ID, USA.

Field operation	Study timeline
MeBr fumigations of crop test field (tested potato field only fumigated in 2014)	2013 and 2014
Commercial alfalfa production	2015
Crop test initiation	2016
Barley, wheat, and potato planting	April
Corn planting	May
Alfalfa cutting 1	June 2[a]
Alfalfa cutting 2	July 11 and 12
Barley and wheat sampling	August 15 and 16
Alfalfa cutting 3	August 23
Corn sampling	September 1
Potato sampling	September 22
Alfalfa cutting 4	October 10
Baled alfalfa cutting 2 sampling	December 21
Baled alfalfa cutting 3 sampling	January 26, 2017

[a] Samples from alfalfa cutting 1 were not analyzed due to logistical issues.

were collected from each bale for a total of 100 g or greater, which was homogenized, and a 25 g subsample was collected for Br⁻ analysis. Barley and wheat whole aboveground plant tissue was collected and subsequently threshed to separate the seed and vegetative tissue, and a 25 g subsample was collected of each for analysis. Corn was collected using a 1-m^2 quadrat as above, and ears and vegetative tissue (stover) were separated. After each part was homogenized, a 25 g subsample was collected separately for Br⁻ analysis. For the corn ear, the entire ear (seed plus cob) was homogenized together. Barley and wheat are at low moisture content at the time of harvest, whereas alfalfa and corn, particularly for silage, are still at high moisture contents. Potato Br⁻ concentrations were measured in production fields where vine (ADM) kill had already occurred prior to harvest. Therefore, only the tuber was collected. In the field, samples of alfalfa, corn, and potato were immediately placed into sealable plastic bags (opaque bags for potato to exclude light) in a cooler with dry ice and refrigerated until the time of analysis. Samples for barley and wheat were transported back to the laboratory as complete bundles to allow threshing, cleaning, and subsequent separation for tissue analysis.

2.3 | Crop Br⁻ uptake and partitioning following MeBR application

Study design concessions were necessary due to the PCN quarantine status of the area where research was being conducted. The crop test trial was conducted in 2016 and arranged in an RCB design for alfalfa, barley, corn, and wheat in a field (Field A) that had previously received MeBr applications in 2013 and 2014. Field A had previously tested positive for PCN and was still under regulations where potato was not permitted to be grown. Therefore, it was necessary to plant potatoes in a nearby smaller field (Field B) on the same farm that was only fumigated a single time in 2014, had never tested positive for PCN, and where potato production was not restricted. Plant samples were processed as in the background test samples described in detail above. Samples were collected for green alfalfa from four cuttings per year. Logistical issues resulted in the loss of data from cutting 1. Individual plots were baled, and samples were collected from the second and third baled cuttings in late December and January, respectively. The fourth cutting did not produce sufficient biomass for bailing. Barley and wheat were sampled at crop maturity in mid-August, corn at the first of September, and potato in mid-September (Table 1).

2.4 | Analysis of Br⁻ concentration in plant materials

Samples were labeled, bagged, and shipped overnight on dry ice to GEL Laboratories (Charleston) where they were analyzed for Br⁻ via ion chromatography using EPA method SW-846 9056A (USEPA, 2000). Plant material was extracted with deionized water at a 1–10 (w/v) ratio, stirred, and then filtered through a 0.45-μm membrane filter. Filtrate was measured using a Dionex Ion Chromatography System 3000 (Thermo Fisher Scientific) equipped with a 50-μL sample loop, an AS23 separation column, an AG23 guard column, a DRS 600 dynamically regenerated suppressor, and a Dionex conductivity detector. Moisture content was determined by drying to constant mass at a temperature of 110°C based on ASTM method D 2216 (ASTM, 2019). All results were moisture corrected based on measured values and are reported on a dry-weight-equivalent concentration. The laboratory reported that all samples were delivered with proper chain of custody and no signs of tampering or breakage. All data met the laboratory acceptance criteria for initial calibration, continuing calibration, instrument, and process controls as submitted or were diluted until concentrations were within the calibration range.

Results that fell below the analytical detection limit were reported by GEL Laboratories as “ND” or nondetectable. To account for the lognormal nature of the data, and for any sample where Br⁻ concentrations were not detectable, a substitute value was used in the analysis defined as the value of the detection limit divided by the square root of 2. Table S2 provides detection limits, which varied by media and analysis batch (Hornung & Reed, 1990).

2.5 | Statistical analysis

All raw data were log transformed due to skewness and to conform to assumptions of normality and homogeneity of variance. Reported values were back-transformed to original concentration units (mg Br$^-$ kg^{-1}). Summary statistics for the raw data are available in Table S1 and represent the measured concentrations in the study. Background Br$^-$ concentrations were analyzed based on a completely randomized design with subsampling where crop material was the fixed factor and subsamples within fields were the random factor. This allowed the evaluation of whether Br$^-$ differed based on crop material (baled vs. green alfalfa or reproductive and vegetative portions for other crops). The MeBr-fumigated field crop comparison test was analyzed based on an RCBD with subsampling with crop material as a fixed factor and subsample within blocks as a random factor. Potatoes were analyzed separately but using the same methods as Field A. This was for consistency as we were unable to include potatoes in Field A due to quarantine restrictions along with the fact that Field B had a different cropping history with only a single MeBr application in 2014. All analyses were conducted in SAS using the GLIMMIX procedure. Mean comparisons were conducted using Tukey's honest significant difference (HSD) and deemed significant if $p < 0.05$.

3 | RESULTS

3.1 | Background alfalfa, barley, corn, and potato Br concentrations

Bromide is naturally occurring, and most crops will contain some amount of Br$^-$ even when grown in fields never treated with MeBr. Raw summary data for the current study are available in Table S1. Here, we report average background back transformed concentrations of Br$^-$ measured in alfalfa, wheat, barley, potato, and corn samples collected in 2016 from southeastern Idaho fields (Figure 1).

Comparison of all crop material was conducted using Tukey's HSD ($p < 0.05$) and resulted in the greatest measured concentrations in baled alfalfa tissue at 33.0 mg Br$^-$ kg^{-1} compared to green alfalfa tissue at 5.0 mg Br$^-$ kg^{-1}. The lowest concentrations were measured in the barley and wheat seed that were both 0.6 mg Br$^-$ kg^{-1}. Differences within a crop occurred between vegetative tissue and reproductive tissue (seed) for all crops excluding corn where no difference in the corn stover (1.6 mg Br$^-$ kg^{-1}) and corn ear (1.9 mg Br$^-$ kg^{-1}) Br$^-$ concentration was measured. Wheat straw concentrations of 11.3 mg Br$^-$ kg^{-1} were greater than seed at 0.6 mg Br$^-$ kg^{-1}. Barley straw concentrations of 8.3 mg Br$^-$ kg^{-1} were greater than seed at 0.6 mg Br$^-$ kg^{-1}. Potato samples collected from non-fumigated fields indicated that background Br$^-$ concentrations in potato tubers were all ND (Table S1).

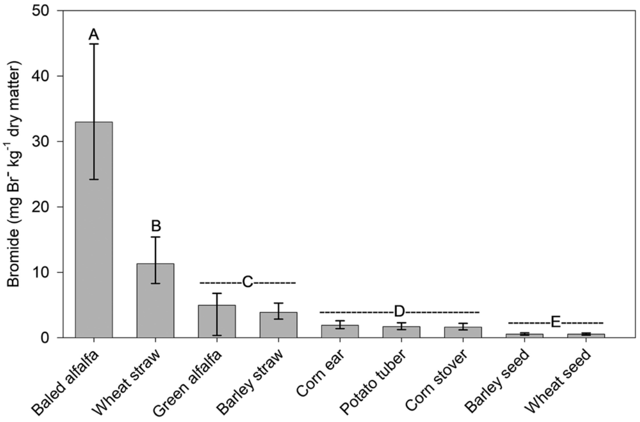

FIGURE 1 Back-transformed background Br$^-$ crop sample mean concentrations and 95% confidence intervals for baled alfalfa, green alfalfa, crop vegetative tissues, and reproductive tissues (seed/ear/tuber) collected near harvest during the 2016 growing season from untreated fields in Bingham Country, ID, USA ($n = 16$). Different letters indicate significant differences when Tukey's HSD was significant ($p < 0.05$).

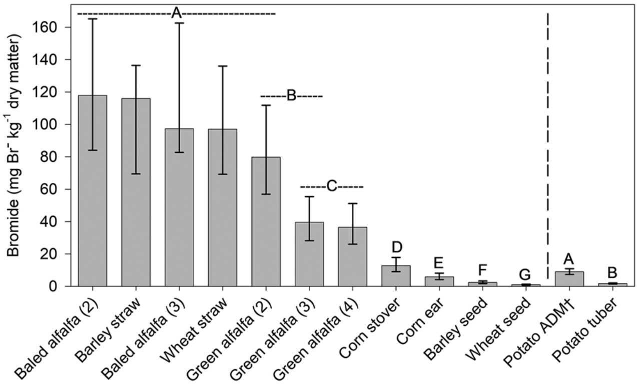

FIGURE 2 Back-transformed Br$^-$ crop sample mean concentrations and 95% confidence intervals from a MeBr-treated field (2013 and 2014) for baled alfalfa, green alfalfa, crop vegetative tissues, and reproductive tissues (seed/ear/tuber) collected near harvest during the 2016 growing season. Fields were in Bingham Country, ID, USA ($n = 16$). †Potato was grown in a separate field treated once in 2014 and analyzed separately. Different letters indicate significant differences when Tukey's HSD was significant ($p < 0.05$). ADM, aboveground dry matter.

3.2 | Crop test in previously MeBR-fumigated soils

Differences based on Tukey's HSD ($p < 0.05$) in Br$^-$ concentrations were measured based on crop material (Figure 2). Baled alfalfa cuttings 2 and 3, barley straw, wheat straw, and green alfalfa cutting 2 samples were not significantly different from each other and averaged >100 mg kg^{-1} Br^-. Baled alfalfa tissue concentrations from cutting 2 (117.8 mg Br^- kg^{-1}) and cutting 3 (97.3 mg Br^- kg^{-1}) did not differ but were both greater than tissue concentrations from green alfalfa cuttings 3 and 4. Green alfalfa cutting 2 sample concentrations of 79.8 mg Br^- kg^{-1} were similar to baled alfalfa and green alfalfa cutting 3 of 39.5 mg Br^- kg^{-1}. However, by green alfalfa cutting 4, Br^-concentrations decreased to 36.5 mg Br^- kg^{-1}, which were less than cutting 2 but similar to cutting 3. Barley and wheat straw tissue concentrations of 116.0 and 97.0 mg Br^- kg^{-1} were greater than their seed concentrations of 2.4 and 1.0 mg Br^- kg^{-1}, respectively. Small-grain seed concentrations were less than all other measured crop materials. Corn stover concentrations of 12.7 mg Br^- kg^{-1} were less than either barley straw (116.0 mg Br^- kg^{-1}) or wheat straw (97.0 mg Br^- kg^{-1}) and were greater than corn ear concentrations of 5.8 mg Br^- kg^{-1}.

4 | DISCUSSION

4.1 | Background alfalfa, barley, corn, and potato Br^- concentrations

Bromine concentrations in terrestrial plant tissue vary due to species differences and natural availability in soil where coastal areas and volcanic ash-derived soils are the most likely to have elevated soil concentrations (Flury & Papritz, 1993; Martin, 1966; Shtangeeva, 2017; Yuita, 1994) and subsequently plant tissue concentrations. The Br content of terrestrial plant ranges from <1 to 285 mg kg^{-1} with most samples being on the lower end as summarized by Shtangeeva (2017). In the current study, measured Br^- concentration maxima in background samples were the greatest from vegetative tissue with a nearly sixfold difference between the vegetative and reproductive maxima for wheat (Table S1). Alfalfa is a deep-rooted perennial forage crop primarily grown for the aboveground vegetative tissue that is used for animal feed. Research on Br^- uptake following MeBr applications in green alfalfa is highly limited with Magarian et al. (1998) reporting little uptake in a study using Br^- as an environmental tracer. Hu et al. (2017) measured concentrations of 4.2 mg Br^- kg^{-1} in baled alfalfa tissue from untreated fields, similar to our background green alfalfa samples (6.8 mg Br^- kg^{-1}) but much lower than our background baled alfalfa (33.0 mg Br^- kg^{-1}); however, we have no indication from which cutting the sample was derived or the length of time from bailing. In the current study, background baled alfalfa Br^- concentrations were greater than those of all other crop materials including green alfalfa. Elevated Br^- concentrations in baled alfalfa may be due to degradation and loss of more easily decomposed vegetative material during harvest and storage that resulted in a concentration effect of Br^- in plant tissue. The pattern of greater Br concentration in the vegetative tissue compared to the seed for small-grain cereal crops, primarily wheat, has been previously reported. Our results are similar to previous research on barley in Turkey where Br concentrations in the seed portion (spike) at harvest were <10 mg kg^{-1}, while vegetative tissue (leaf) concentrations exceeded 25 mg kg^{-1} (Birsin et al., 2010). Similarly, concentrations of Br in the wheat seed of ∼10 mg kg^{-1} were measured compared to concentrations of nearly 50 mg kg^{-1} from stem and leaf samples in Spain (Fransi et al., 1987). Bromine seed concentrations of around 1 mg kg^{-1} for wheat were also reported from trials in England (G. Brown et al., 1974). In our study, the concentration of Br^- in corn stover of 1.6 mg Br^- kg^{-1} did not differ from corn ears concentrations of 1.9 mg Br^- kg^{-1}. This is comparable to the concentrations reported in corn samples by Jemison and Fox (1991) of <10 mg Br^- kg^{-1} where no additional Br^- was applied. Bromine concentrations in potato were low in the tubers sampled in the study by G. Brown et al. (1974) where potato vegetative tissue (potato ADM) had greater concentrations of up to 48 mg kg^{-1} compared to potato tubers where concentrations were only 3 mg kg^{-1}. Our data were similar to previous reports and clearly indicated the likelihood of elevated Br^- concentrations in baled compared to green alfalfa, greater Br^- concentrations in aboveground vegetative tissue than small-grain seeds, as well as the relatively low concentrations in the corn plant (both ears and stover), indicating the importance of considering both the crop and the plant part of interest when crops are produced following MeBr applications.

4.2 | On-farm crop test

The magnitude of Br concentrations found in crops following MeBr applications is dependent on the initial rate of application, the crop produced, the crop part harvested, cultural management practices, and the environmental movement of Br within the agroecosystem in the time period from application to production (G. Brown et al., 1974; Chao, 1966; Iragavarapu et al., 1998). Consistent with previous research, elevated Br^- concentrations were measured in crops grown on soils previously treated with MeBr in our study (Figure 2). Measured Br^- concentration maxima from the crop test were upward of three times greater than the mean within a crop material with particularly high values for specific vegetative crop material (Table S2). As historical use of MeBr was largely focused on high-value vegetable crops, most of the available research reported in the literature excluded traditional agronomic field crops (Beckman et al., 1967). Data on alfalfa are quite limited, but in our study, Br^- concentrations in baled alfalfa were greater than concentrations measured in many crop materials including green alfalfa. This increased concentration in baled alfalfa compared to green alfalfa is likely related to plant tissue degradation during storage.

We are unaware of specific research comparing Br$^-$ uptake in alfalfa to other crops following MeBr applications. Br$^-$ concentrations in alfalfa from non-fumigated feedstuff samples for animal consumption were reported to range from 4 to 12 mg Br$^-$ kg^{-1} from samples in California (Lynn et al., 1963). Research on background concentrations and crop Br$^-$ concentrations following MeBr applications for small grains is limited, but in the present study, background Br$^-$ concentrations were generally similar to or less than those previously reported (Birsin et al., 2010; A. Brown et al., 1979). In barley grown in previously MeBr-treated fields from the current study in Idaho, Br$^-$ concentrations were generally less than those reported by A. Brown et al. (1979) in California where maximum tissue concentrations from MeBr-treated plots exceeded 5000 mg Br$^-$ kg^{-1}. Despite this difference, the results are consistent with the previous research determining maximum Br$^-$ concentrations in plant materials in the season immediately following applications. The samples in the current study were collected in the second season after the final MeBr application. Based on the results of the current study, and a reported concentration of 10,000 mg Br^{-1} kg^{-1} from Hu et al. (2017), it is highly likely that all plant samples would have had greater Br$^-$ concentrations if planted and sampled closer to the time of MeBr treatments. Furthermore, G. Brown et al. (1974) grew wheat that was harvested 1.5, 2.5, and 3.5 years after MeBr application and measured decreasing Br concentrations over time of 44.0, 15.0, and 4.5 mg kg^{-1} for these timeframes, respectively. This is also supported by the reduced concentration in alfalfa throughout the growing season measured in the current study. Increased Br$^-$ concentrations were previously measured in corn stover samples following MeBr application with corn sample concentration of 13.5 Br$^-$ kg^{-1} in treated samples compared to 6.9 mg kg^{-1} in nontreated corn; Br$^-$ corn seed concentrations were not reported (Ellis et al., 1995). Similar to Jemison and Fox (1991) who used KBr as an environmental tracer in their studies, we measured lower concentrations of Br$^-$ in both corn ear and stover in background samples than from crops grown in treated areas. In their research, KBr-treated plots exceeded 5880 mg Br$^-$ kg^{-1} in the stover with corn seed having 300 mg Br$^-$ kg^{-1}. Corn yields in the irrigated production region of southeast Idaho where this study was located are large, approaching 30 Mg ha^{-1}. Corn is also one of the latest planted crops in southeastern Idaho, which may have led to lower Br$^-$ concentrations in the corn crop following irrigation of the other crops prior to planting corn. Silage corn is commonly grown in the region for total biomass (ear and stover), but the Br$^-$ concentrations reported here from ears and stover indicate that corn is likely to have lower Br$^-$ concentrations than other vegetative material such as alfalfa or small-grain straw that is used for animal feed rations and bedding. However, specific measured concentrations were still quite elevated from corn stover indicating the potential for increased uptake (Table S2), especially if testing had occurred in the crop season following MeBr application. Potato tubers had lower Br$^-$ concentrations than potato ADM in the current study similar to the results from G. Brown et al. (1974) where plant tissue concentrations from the highest MeBr application rate were 280 mg kg^{-1} in tubers compared to 6675 mg kg^{-1} for potato ADM (Figure 2).

Comparisons of Br$^-$ concentrations in a crop should be considered in relation to desired end use of the crop in the specific growing environment to ensure accurate understanding of the expected response to MeBr fumigation. Little work has compared large scale commercially important agronomic crops directly to one another while also differentiating vegetative and reproductive tissues in fields previously treated with MeBr. This research provides clear evidence of Br$^-$ accumulation in crops following MeBr applications up to 2 years post application as evidenced by the values in our crop tests compared to background concentrations. Vegetative tissue had a greater concentration of Br$^-$ compared to reproductive parts. Thus, the end use of the crop must be considered when determining how to sample to evaluate crop Br$^-$ concentrations. Corn stover had a reduced Br$^-$ accumulation compared to small-grain straw in the region. Potatoes had relatively low uptake, particularly in tubers, compared to the other crops; however, the fact that it was necessary to grow potatoes in a location with a different MeBr application history and the lack of background potato ADM data limits this conclusion.

5 | CONCLUSIONS

MeBr field applications have been utilized to reduce or eliminate specific quarantine pests. Following MeBr application, crops are expected to have increased Br$^-$ concentrations compared to background concentrations for crop materials produced on untreated fields. Vegetative tissue concentrations of Br$^-$ were greater when compared to reproductive tissue. In a MeBr-treated field, alfalfa (green and baled) and small-grain straw had the greatest concentration of Br$^-$. While elevated crop Br$^-$ uptake may occur, corn silage appears to be a better option if decreased Br$^-$ concentrations are needed based on a whole-plant end use (e.g., animal forage) compared to alfalfa or small-grain straw. Time after MeBr application and irrigation/precipitation events are expected to reduce Br$^-$ concentrations over time; however, the rate of this is unpredictable due to the multitude of environmental factors affecting Br$^-$ reduction. When evaluating crop tissue Br$^-$ concentrations, sampling based on the end use of the crop is critical to ensure that the concentrations accurately measure the portion to be used. Thus, consideration of the crop of interest, the part of the crop, and the timing of sampling after application must be considered when determining the potential for crop Br^- uptake and removal following MeBr application.

AUTHOR CONTRIBUTIONS

Christopher W. Rogers: Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; visualization; writing—original draft; Writing—review and editing. **Juliet M. Marshall**: Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; visualization; writing—review and editing. **Margaret Moll**: Data curation; formal analysis; investigation; methodology. **Cynthia Curl**: Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; project administration; resources; software; supervision; validation; visualization; writing—review and editing

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

ORCID

Christopher W. Rogers https://orcid.org/0000-0002-1989-1582

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