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Characteristics of solids produced from coal mine drainage and their suitability for phosphorus control in dairy manure management

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Abstract

One strategy to limiting eutrophication in waterways is to reduce the concentration of water-extractable P (WEP) in land-applied manure. In this study, we investigated the feasibility of using mine drainage residuals (MDR), waste solids produced in large quantities from coal mine drainage treatment, to reduce WEP in dairy manure. Twenty MDRs from treatment systems in Pennsylvania were collected and analyzed to determine concentrations of pollutants that may limit land application. Laboratory dose-response tests were conducted using the selected MDRs to determine the effectiveness and kinetics of WEP reduction, and three field-scale MDR application tests were conducted to demonstrate the process of using MDR to decrease manure WEP. The MDR–manure mixtures investigated in this study do not exceed biosolid land application concentration limits set by the USEPA. Amendment rates of 5–10 g MDR L^{-1} of manure provided significant reductions in WEP. Iron-rich MDR, produced from passive and oxidant treatment of mine drainage, required 1–4 d to reduce WEP to an equilibrium concentration, while Ca-rich materials, produced from lime treatment, required 4–7 d. Three field studies at operating dairy farms confirmed the reduction in WEP when manure was amended with MDR. Unit costs calculated for a 1,900-m^3 manure tank treated with 4.4 g L^{-1} MDR were US\$2.16 per 1,000 L of manure and \$30 kg^{-1} WEP removed. These findings indicate that the WEP of dairy manure is not a fixed chemical parameter and can be modified with amendments such as MDR.

1 | INTRODUCTION

Land application of manure can be a significant source of environmentally mobile P and contribute to the eutrophication of receiving waters (Carpenter et al., 1998). The control of P losses from agricultural practices involves consideration of transport and source factors (Sharpley et al., 2003). Source controls include the rate, timing, and method of manure applications and the chemical characteristics of the manure. A commonly used measure of a manure's chemistry is the water-extractable P (WEP), which is a strong predictor of the environmental mobility of its P content immediately following land application (Kleinman et al., 2007; Kleinman, Sharpley, Wolf, Beegle, & Moore, 2002). In most manure management efforts, the WEP is a fixed parameter that is either measured on the raw manure or assumed from default published values (Weld et al., 2007).

Abbreviations: AASL, Agricultural Analytical Services Laboratory; MDR, mine drainage residual; WEP, water-extractable phosphorus.

One approach for controlling environmentally mobile P is the use of P sorbing materials that remove P from surface and subsurface waters draining from agricultural fields or operations. A variety of commercial and industrial byproducts have been evaluated for P control (Leader, Dunne, & Reddy, 2008; Stoner, Penn, McGrath, & Warren, 2012; references included in Penn & McGrath, 2014). In their review of the research, Penn and McGrath (2014) divided P-sorbing materials into two chemical groups with differing P-removal mechanisms. Iron- and aluminum-dominated solids remove P through rapid ligand exchange reactions. Calcium- and magnesium-dominated solids remove P through slower precipitation reactions.

Mining commonly results in metal-contaminated discharges whose treatment annually results in hundreds of thousands of tonnes of solids rich in Fe, Al, Ca, and Mg that must be managed at significant cost (Younger, Banwart, & Hedin, 2002). The solids, hereafter referred to as mine drainage residuals (MDRs), are typically treated as wastes and disposed of by landfilling, burial, or injection into abandoned mines. The identification of beneficial uses for MDRs has been a goal of private, public, and nonprofit groups for decades. Mine drainage residuals have potential value arising from their elemental composition (Stewart, Capo, Hedin, & Hedin, 2017) and pigmentary characteristics (Hedin, 2003), but markets for these uses are currently limited. The sorptive and reactive capacities of metal oxides (Cornell and Schwertmann, 2003; Dzombak & Morel, 1990) provide opportunities for the use of MDR in remediation efforts. Iron-rich MDRs have been shown to decrease Cd, Cu, and Zn concentrations in contaminated soils (Liu, Altschul, Hedin, Nakles, & Dzombak, 2014), decrease the release of Se from Se-rich coal refuse (Donavan & Ziemkiewicz, 2014), and decrease the release of H_2S from gypsum-amended dairy manure (Chen et al., 2018). The sorptive and chemical properties of MDR are the basis for its use for P management in water treatment and agronomic applications (Adler & Sibrell, 2003; Heal et al., 2005; Penn, Bryant, & Callahan, 2005; Penn, Bryant, Callahan, & McGrath, 2011). Columns of pelletized MDR have been used to treat wastewater (Littler, Geroni, Sapsford, Coulton, & Griffiths, 2013; Sibrell & Tucker, 2012; Sibrell, Montgomery, Ritenour, & Tucker, 2009) and fish hatchery effluent (Sibrell & Kehler, 2016). Troughs containing pelletized MDR have been used to treat wastewater (Dobbie et al., 2009) and runoff from dairy operations (Penn, Bryant, Kleinman, & Allen, 2007). The direct application of MDR to soils has been shown to increase P retention capacity (Evenson & Nairn, 2000) and decrease concentrations of P in field runoff (Fenton, Healy, & Rodgers, 2009; Penn & Bryant, 2006).

This study explored the use of MDR amendments to modify the WEP of dairy manure. Two benefits could result from this practice. First, a simple amendment-based method for managing the environmental risks of manure management could

Core Ideas

- Residuals produced from coal mine drainage (MDR) have P removal capabilities.
- Amending dairy manure with MDR at rates of 4–10 g/L decreases water-extractable P.
- The hazardous metal content of dairy manure amended with MDR is low.
- The cost to decrease water-extractable P of dairy manure with MDR was US$30/kg WEP.

be attractive to operators who cannot afford to upgrade to new technologies (Maguire, Kleinman, & Beegle, 2011). Second, the creation of a beneficial product from mine water systems could lessen the cost of mine water treatment. In an earlier phase of this work, the chemical characteristics of three MDRs and the ability of two of the MDRs to decrease P in monopotassium phosphate solutions and two dairy manures were presented (Sibrell, Penn, & Hedin, 2015). This phase of the study continued investigation of the ability of MDRs to lessen the WEP of dairy manure. The chemical characteristics of 20 MDRs collected from a variety of mine water and treatment environments are described along with an assessment of their hazardous metal content. The ability of multiple MDR amendments to decrease WEP in dairy manure was also assessed through laboratory dose and effect experiments. The results of three field trials where MDR was incorporated into manure management operations at dairy farms are presented and a cost developed for decreasing WEP in dairy manure using MDR amendments.

2 | MATERIALS AND METHODS

Mine drainage residual samples were collected from 20 sites selected to represent the range in mine drainage chemistry and treatment technologies currently existing in the eastern U.S. coal fields. Samples of the untreated mine drainage water at each site were collected and analyzed for inorganic parameters. Alkalinity (Standard Method [SM] 2320B) and pH were measured in the field. Raw and acid-preserved samples were delivered to a Pennsylvania Department of Environmental Protection accredited laboratory (G&C Coal Analysis Laboratory) for analysis of acidity (SM 2310B) and total concentrations of Fe, Al, Mn (SM 3120B), and sulfate (SM 4500 SO_4^{2-} E) (American Public Health Association, 2017).

Solid samples were collected from settling basins associated with the treatment systems or from natural deposits of solids downstream of mine water discharges. Two- to four-liter samples were collected wet and later dewatered by

decanting free water and straining the solids through 100-μm filter bags. The dewatered solids were dried at 100–110 ˚C to a constant weight and stored in sealed plastic bags. Dried solids were used in chemical testing, particle size measurements, and dose-effect experiments.

The sample pH was measured on a prepared slurry (1:2 solid/deionized water). Neutralization potential was measured by acid titration (Sobek, Schuller, Freeman, & Smith, 1978). Solid samples were submitted to Activation Laboratories for analysis of 55 elements and parameters by lithium metaborate/tetraborate fusion followed by inductively couple plasma–mass spectroscopy (Actlabs, 2020). Major cations were reported as oxide compounds and were converted to elemental concentrations. All MDR analytical results are expressed on a solid (dry weight) basis. Detailed chemical composition of the MDR samples was presented by Stewart et al. (2017) in an analysis focused on the rare earth elements. This study focused on the bulk elemental and hazardous metal content of the MDR solids. Concentrations of hazardous metals were evaluated with respect to limits established by Standards for Use and Disposal of Sewage Sludge (1994), the USEPA standards for land application of biosolids).

Particle size distributions for the dried MDR samples were determined by hand shaking dried MDR solids on stacked 10-, 4-, 1-, 0.6-, and 0.18-mm sieve screens. The weight of MDR collected on each screen was measured and used to develop a particle size distribution.

Manure used in the laboratory experiments was obtained from storage tanks, sumps, or tanker trucks at dairy farms in central Pennsylvania. All manure analyses were conducted by the Agricultural Analytical Services Laboratory (AASL) at Pennsylvania State University. Raw manure samples were analyzed for total solids (SM 2540G), total N (dry combustion analysis; Watson, Wolf, & Wolf, 2003), P, K, and Fe (HNO_3 and H_2O_2 digestion followed by analysis using inductively coupled plasma–optical emission spectrometry; USEPA, 1996a, 1996b), and water-extractable P (WEP) (Kleinman et al., 2007).

A temporal study was conducted to investigate the kinetics of the MDR–WEP reaction. The study measured the effect on WEP of two MDRs at two dosing rates during a 14-d period. A single stock dairy manure with 5.8% solids was used for all tests. Prior to initialization of the experiment, stock manure was stored at 4 ˚C. Two-liter high-density polyethylene containers with 1 kg of manure were prepared, allowed to come to temperature and pre-incubated for 4 d, and amended with no MDR (control), Brandy Camp MDR at 6 or 12 g kg^{-1}, and Blue Valley MDR at 6 or 12 g kg^{-1}. Each treatment was duplicated for a total of 10 experimental units. Both MDRs were screened to <0.18-mm particle size before dosing. Containers were maintained at 22 ± 2 ˚C throughout the experiment. At predetermined sampling times, containers were vigorously shaken by hand for 30 s and 34-g subsamples (2 g dry

weight equivalent assuming the original 5.8% solids content) removed and measured for WEP. Time periods tested were: 4, 8, 16, 36, 48, 96, 168, 240, and 336 h after MDR addition. The change in WEP with time was fit to a three-parameter exponential decay model:

$$y = a \times \exp(-bx) + y_0$$

where y is WEP (mg kg^{-1}), x is time (h), a is the difference between the initial and final WEP at the asymptote, y_0 (mg kg^{-1}), and b is a rate constant (h^{-1}). Model coefficients were estimated for each rate of both MDRs by the PROC NLIN procedure of SAS using the Marquardt option (SAS Institute, 2019). Comparisons were made between model coefficients for each MDR at both rates using the Contrast statement of the PROC NLMIXED procedure of SAS.

The effects of various amendments and doses on manure chemistry were evaluated by amending dairy manure with MDR and measuring WEP after an incubation period of approximately 5 d. The experiment included sand, gypsum, and nine MDRs selected to represent the range in compositional chemistry. Sand was included as an inert solid control. Gypsum was included because of its use for P control in other manure management applications (Moore & Miller, 1994). All amendments were screened to <1-cm particle size prior to addition. A common dairy manure sample, previously characterized for solids and chemical composition, was used for all dose–effect tests. The density of the manure was determined, and weighed samples of manure were amended with sand and gypsum at rates of 2, 4, 8, and 16 g kg^{-1} and with MDR at rates of 1, 2, 4, 6, 8, 12, and 24 g kg^{-1}. Solid–manure mixtures were shaken vigorously by hand for 30 s, agitated on a laboratory shaker at 180 excursion per minute for 1.5–2.5 h, and then delivered to AASL for analyses of WEP. Water-extractable P as a function of amendment rate was fitted to the same three-parameter exponential decay model used for the temporal study using the PROC NLIN procedure of SAS. In addition to evaluating each amendment individually, data from Fe-rich and Ca-rich MDRs were pooled, fit to the model, and coefficients compared using the Contrast statement of the PROC NLMIXED procedure of SAS.

Field trials were conducted at three operating dairy farms. All trials utilized Brandy Camp MDR that had been milled to <0.18-mm particle size with a Pulva Model A Pulverizer. Field Trial 1 was conducted at a 3,000-cow dairy operation where barn floors were flushed several times a day with liquid manure. The wash water was collected in a 380-m^3 concrete tank from which the manure was pumped through a solids separator. The solids produced were used for bedding while the liquids were recycled as wash water. The system accumulated excess liquid that was stored in several concrete tanks and eventually land applied. Brandy Camp MDR was added directly to the 380-m^3 tank during a wash cycle. The amended

manure was mixed in the tank for 15 min with in-place equipment and discharged to the solids separator. Manure samples were collected from the tank before addition of the MDR, after addition of the MDR and mixing, and from both discharges of the solids separator.

Field Trial 2 was conducted at a 170-cow dairy farm. The milking cows were penned in a free-stall barn that received sawdust bedding that was periodically washed into a sump and pumped to an earthen storage lagoon. Mine drainage residual was added by the operator directly to the animal bedding in bulk quantities. The dose of MDR in the manure samples was dependent on the mixture of MDR and sawdust that the operator prepared, the amount applied to the barn, and the amount of manure produced by the cows. The MDR dose (g L^{-1}) was estimated from the increase in Fe concentration in the manure–bedding mixture as

$$MDRdose = \frac{ManureFe - 0.62}{(11\%Fe \times 85\%solids)/(2.2/3.75)}$$

where the manure Fe content is expressed in pounds per 1,000 gallons; 0.62 lb per 1,000 gallons is the measured Fe content of untreated manure at the farm, the MDR contained 11% Fe and 85% solids, and 2.2 and 3.785 convert from English to metric units.

Field Trial 3 was conducted at a 100-cow dairy farm where manure was stored in a 1,900-m^3 open concrete tank and periodically spread on local fields. The trial involved treatment of the full manure storage tank several days before manure removal and land application. Brandy Camp MDR (8.2 t) was added directly to the manure storage tank while it was stirred with a manure pump. Three days later the manure was removed and spread on local fields by a contract manure hauler. Samples of manure were collected from the tank before MDR addition and from the manure tanker as it was being spread.

Manure samples for all three field trials were collected before and after the addition of MDR and analyzed by AASL for total solids, P, K, Fe, and WEP. The hold time between sample collection and fixation of P by the laboratory was at least 7 d.

3 | RESULTS

3.1 | Sampling sites: Mine water characteristics and treatment technologies

The MDR sampling sites were selected to represent a range of mine drainage chemistry and treatment technologies. Sites that already produced solids in large quantities or had the potential in the future to produce large quantities were prioritized. Table 1 shows the general mine drainage water chemistry and the treatment technology used at each site. Additional mine drainage water chemistry is shown in Supplemental Table S1. Mine water chemistry varied from circumneutral pH alkaline flows contaminated with Fe to low pH acidic flows contaminated with Fe, Al, and Mn. Treatment technologies included natural, passive, and active processes. Three of the sites did not contain treatment systems, and solids were collected from areas of natural precipitation. Three of the passive systems were aerobic ponds and wetlands that treated naturally alkaline Fe-contaminated water. Two of the passive systems received alkaline water that had been pretreated with a buried bed of limestone. One passive system (Mitchell) was an open bed of limestone that treats water by precipitating metals within the aggregate. The MDR sample was collected from the solids produced when the bed was mechanically cleaned. Two of the chemical treatment systems used oxidants (H_2O_2 or $KMnO_4$) to treat alkaline Fe-contaminated water. Nine of the chemical systems used various forms of lime (lime slurry, CaO, Ca(OH)$_2$, or waste lime).

3.2 | MDR Composition

The major element compositions of MDR samples are shown in Table 1. The slurry pH of the MDRs ranged from 2.7 to 11.2. Two samples with pH <3 were collected from sites where Fe had precipitated naturally from acidic Fe-contaminated water. The pH of the MDRs collected from passive treatment systems were generally circumneutral. The pH of MDRs from lime treatment systems ranged between 8 and 11. Five of the MDRs had pH values >10, which is indicative of unreacted Ca(OH)$_2$.

The chemistry of the MDRs was dominated by either mine drainage metals (Fe, Al, and Mn) or byproducts of lime treatment (Ca and Mg) (Figure 1). Eleven of the MDRs were Fe rich, containing 40–54% Fe. For reference, pure ferrihydrite, Fe(OH)$_3$, contains 52% Fe and pure goethite, FeOOH, contains 63% Fe. The Fe-rich MDRs were all collected from sites with high concentrations of Fe, and treatment was natural, passive, or with oxidants. The chemical composition of MDR collected from lime treatment systems reflected a mixture of byproducts of lime addition and the metals contained in the mine drainage water. The dominant elements in seven of the lime-treatment MDRs were Ca and Mg (Ca + Mg). These elements are present due to incomplete reactivity of the lime reagent or the formation of calcite and dolomite during treatment. Mine drainage residuals with high Ca + Mg also had high neutralization potential, which arises from lime and calcite. The most inefficient lime treatment was the Antrim plant, where the MDR was 34% Ca + Mg and the neutralization potential was 92% CaCO$_3$ equivalent. The most efficient lime treatment was the Hollywood plant, where the MDR contained only 4% Ca +

TABLE 1 Chemical composition of mine drainage water at sample collection sites and solids collected. Solids pH was measured on a prepared slurry of 1:2 solids/deionized water

Site	Treatment	Mine drainage water				Solids													
		pH	Fe	Al	Mn	pH	Al	C	Ca	Fe	K	Mg	Mn	Na	P	Si	S	LOI	NP
			—mg L^{-1}—											—%—						
Hall	natural	5.1	186	<1	24	2.7	0.1	0.5	<0.1	54.3	0.02	0.0	0.01	0.02	0.12	0.2	1.6	20.2	−1
Hughes	natural	4.1	140	11	3	2.9	0.4	0.9	0.1	47.5	0.10	0.0	0.01	0.03	0.02	1.4	3.4	27.1	−6
Honeypot	natural	6.2	53	<1	3	6.3	0.1	0.5	0.4	54.3	0.02	0.0	0.10	0.05	0.03	2.1	0.4	14.5	1
Marchand	PA	6.3	73	<1	1	6.9	0.2	0.7	0.6	52.6	0.03	0.1	0.04	0.12	0.04	2.0	0.2	17.1	1
Latrobe	PA	6.3	42	<1	3	6.2	0.2	0.5	0.7	53.7	0.03	0.1	0.05	0.06	0.21	2.3	0.3	13.8	1
Hoyman	PA	6.3	34	<1	8	7.6	2.4	1.6	2.3	40.7	0.50	0.2	0.93	0.09	0.02	6.2	0.1	15.4	7
SR114D	PLA	6.4	40	<1	<1	6.4	0.4	1.4	0.3	49.5	0.10	0.1	0.05	0.07	0.20	4.0	0.2	14.4	<1
Wolford	PLA	5.8	93	2	2	4.4	2.2	1.2	0.8	44.4	0.20	0.1	0.02	0.13	0.02	3.5	1.6	20.3	−2
Mitchell	PLA	3.0	7	22	12	6.5	15.0	8.3	3.9	3.9	0.80	0.3	1.92	0.07	0.01	10.8	1.5	31.2	6
Mathies	oxidant	6.7	90	4	2	7.6	2.8	1.0	2.1	47.0	0.10	0.1	0.06	0.33	0.03	1.2	0.5	19.1	6
Blue Valley	oxidant	6.8	16	<1	3	6.6	0.5	2.4	2.2	52.1	0.05	0.1	0.29	0.06	0.02	1.7	0.3	16.2	7
Toby	LimeSl	3.7	23	10	13	10.0	4.4	3.2	18.7	11.2	0.10	3.5	1.24	0.07	0.01	3.0	3.7	25.6	42
Greene	CaO	3.2	8	3	45	9.7	1.3	3.9	9.5	4.8	0.10	12.5	7.40	0.07	0.01	3.8	1.3	30.3	74
Manor	CaO	3.3	247	14	4	11.2	2.5	2.9	13.4	27.8	0.02	1.6	0.28	0.04	0.02	2.1	1.5	21.6	40
Colver	CaO	6.1	67	<1	1	9.2	0.6	8.2	27.4	10.5	0.10	0.8	0.15	0.16	0.02	2.4	0.5	34.0	69
Clyde	Ca(OH)$_2$	6.1	175	<1	4	10.9	0.9	7.6	30.0	5.3	0.10	1.6	0.19	0.19	0.02	2.8	1.8	33.2	76
Hollywood	Ca(OH)$_2$	3.2	75	25	2	8.2	9.2	0.4	2.7	25.6	0.02	1.1	0.34	0.02	0.01	7.8	0.5	21.0	10
Delmont	Ca(OH)$_2$	2.5	101	105	8	11.1	1.7	2.9	20.1	17.7	0.02	1.3	0.26	0.04	0.04	1.1	6.3	20.1	36
Brandy Camp	Ca(OH)$_2$	5.1	68	8	9	8.4	1.3	6.9	25.5	10.6	0.10	1.2	1.24	0.00	0.00	1.9	1.1	35.3	67
Antrim	waste lime	3.2	25	22	22	11.2	1.5	9.4	32.6	1.2	0.10	1.6	1.22	0.08	0.01	1.7	0.6	38.4	92

Note. LOI, loss on ignition; NP, neutralization potential as CaCO$_3$ equivalence; PA, passive aerobic treatment; PLA, passive aerobic treatment with limestone; LimeSl, lime slurry treatment.
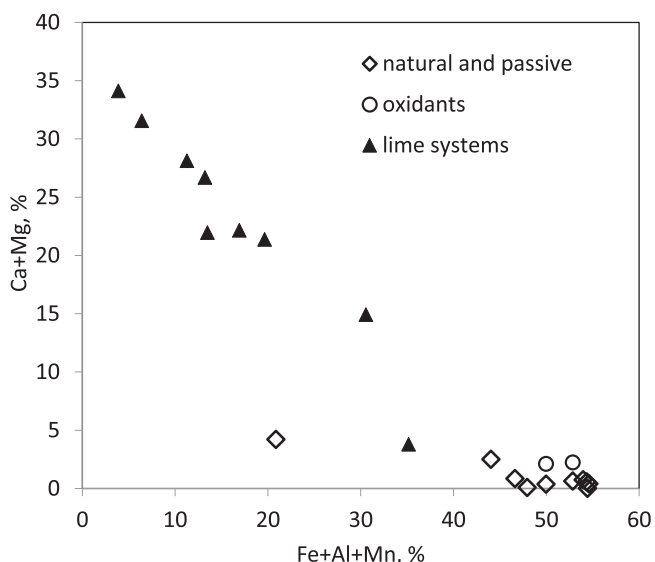
FIGURE 1 Solid concentrations of (Ca + Mg) plotted against (Fe + Al + Mn) for mine drainage residual samples

Mg and had a neutralization potential of only 10% $CaCO_3$ equivalent.

Concentrations of selected trace elements of concern in the MDR solids are shown in Table 2. Mercury, Mo, and Se were near or below the detection limit (1–3 mg kg^{-1}) and Cd was <4 mg kg^{-1} for all MDRs. Lead was below detection (5 mg kg^{-1}) for 11 samples and ranged up to 36 mg kg^{-1} for nine samples. Chromium ranged up to 61 mg kg^{-1} and Cu ranged up to 53 mg kg^{-1} for 19 samples. A measurement of 251 mg kg^{-1} Cu at the Mitchell passive limestone treatment system was confirmed through additional sampling of solids. Arsenic, Ni, and Zn varied widely among MDRs, with low values 5–10 mg kg^{-1} and high values >200 mg kg^{-1} As, >600 mg kg^{-1} Ni, and >1,000 mg kg^{-1} Zn.

Table 2 includes ceiling (maximum) metal concentration values contained in Standards for Use and Disposal of Sewage Sludge (1994). Manure is not considered a biosolid, and its land application is not subject to the limits. However, the limits provide a useful point for evaluation of the environmental significance of the metals in manure amended with MDR. None of the raw MDR samples exceeded the limits for Cd, Cu, Hg, Mo, Pb, Se, or Zn. Three MDRs exceeded the Ni limit. All three were collected from systems that received low pH mine water. Two MDRs exceeded the As limit. Both samples were from systems that receive alkaline Fe-contaminated mine water in an industrial–urban setting. When added to manure (before land application), the metals contained by the MDR solids are diluted and the metal concentrations are below the ceilings.

Standards for Use and Disposal of Sewage Sludge (1994) contains limits on the cumulative amount of hazardous metal that can be land applied (Table 2). A calculation was made of

the MDR dosing rate necessary to exceed the cumulative limits assuming 100,000 L yr^{-1} of manure applied for 20 yr. All calculated doses were >1,000 g L^{-1} for Cd, Cr, Cu, Hg, Pb, Se, and Zn. The most limiting MDR was the Latrobe MDR, which would meet the As limit if applied at a rate of 82 g L^{-1}. This dose is an order of magnitude larger than the recommended dosing rates developed in this study.

3.3 | Temporal MDR–WEP Experiment

Results of the temporal MDR dosing experiment are shown in Figure 2 and Table 3. The experiment utilized a single stock manure dosed with 6 or 12 g L^{-1} of either Brandy Camp (BC), a Ca-rich MDR, or Blue Valley (BV), an Fe-rich MDR. The concentration of WEP in the control dairy manure used in the experiment increased during the course of the experiment, from an initial concentration of 3,031 ± 172 mg kg^{-1} (mean ± 95% confidence interval) to a final concentration of 3,964 ± 137 mg kg^{-1} (Supplemental Figure S1). The observed increase in WEP is of unknown origin but is suspected to be probably related to a temperature-induced increase in biological activity in the manure after it was moved from the storage cooler for the laboratory bench study.

All four MDR treatments decreased WEP during the 14-d period (Figure 2), but the rate of WEP removal (b) of treatments varied (Table 3). The Fe-rich BV MDR removed WEP faster than Ca-rich BC MDR at both the 12 g kg^{-1} rate ($b = 0.0503$ h^{-1} vs. 0.0113 h^{-1}, respectively; $p < .0001$) and the 6 g kg^{-1} rate ($b = 0.0116$ h^{-1} vs. 0.00547 h^{-1}, respectively; $p < .0001$). The rate of WEP reduction for both the BV and BC MDR was higher with the 12 g kg^{-1} addition than the 6 g kg^{-1} addition ($p < .0001$ and $p = .0033$, respectively). The 6 g kg^{-1} addition of BV reduced WEP at a similar rate as the 12 g kg^{-1} addition dose of BC ($p = .87$).

While there were significant differences between the rates of WEP removal, all of the treatments eventually decreased WEP to <1,000 mg kg^{-1}solid (Figure 2). The modeled asymptotes (y_0) for the four treatments ranged between 343 and 524 mg kg^{-1}solid, and contrast comparisons found no difference in the values ($p \geq .4$).

3.4 | MDR Dosing Experiments

The effect of MDR, sand, and gypsum amendments on WEP was assessed through a dose–effect experiment (Figure 3). Sand was included as a nonreactive solid control. The raw manure contained 4,546 mg kg^{-1} WEP. Sand and gypsum had negligible effects on WEP. All MDR treatments decreased concentrations of WEP, with greater WEP reductions at higher MDR dosing. Eight MDRs decreased the WEP by at least 50%. The MDRs were grouped by their chemical

TABLE 2 Concentrations of selected trace elements of concern in mine drainage residual (MDR) samples, ceiling limit and cumulative loading limits from Standards for the Use or Disposal of Sewage Sludge (1994), and MDR dose to manure to exceed the cumulative limit over 20 yr at a manure application of 100,000 L ha^{-1} yr^{-1}

MDR	As	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn
					—mg kg^{-1}—					
Hall	9	2.4	6	9	<1	<2	8	11	<3	32
Hughes	57	1.7	20	17	<1	<2	7	11	<3	34
Honeypot	229	2.4	10	10	<1	3	29	<5	<3	34
Marchand	23	2.0	14	10	<1	<2	9	11	<3	23
Latrobe	251	1.5	14	10	<1	<2	13	10	<3	31
Hoyman	42	1.8	26	9	<1	<2	300	<5	<3	1,370
SR114D	56	1.7	17	10	<1	<2	21	<5	<3	52
Mitchell	6	2.7	61	251	<1	<2	606	18	<3	1,180
Wolford	49	1.6	20	9	<1	<2	17	8	<3	69
Mathies	5	3.8	<1	20	<1	<2	80	36	<3	317
Blue valley	64	2.2	10	9	<1	3	38	<5	<3	232
Toby	3	0.9	15	31	<1	<2	216	<5	<3	462
Greene	3	0.5	<1	10	<1	<2	857	12	<3	774
Manor	5	1.6	16	24	<1	<2	158	<5	<3	358
Colver	27	<0.5	9	8	<1	<2	25	<5	<3	16
Clyde	10	<0.5	12	6	<1	<2	31	<5	<3	17
Hollywood	8	2.2	31	53	<1	<2	840	<5	<3	1,330
Delmont	73	0.8	7	6	<1	<2	63	<5	<3	175
Brandy Camp	6	<0.5	9	11	<1	<2	254	8	<3	278
Antrim	2	0.5	11	17	<1	<2	184	<5	<3	345
USEPA limits										
ceiling limit, mg kg^{-1}	75	85	na	4,300	57	75	420	840	100	7,500
cumulative loading limit, kg ha^{-1}	41	39	3,000	1,500	17	na	420	300	100	2,800
MDR dose to meet USEPA cumulative limit										
Minimum, g L^{-1}	82	>1,000	>1,000	>1,000	>1,000	>1,000	245	>1,000	>1,000	>1,000
Median, g L^{-1}	891	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000	>1,000

composition into Fe rich (Hughes, Lowber, Mathies, and Blue Valley) and Ca rich (Colver, Delmont, Brandy Camp, Antrim, and Toby). Figure 4 shows the aggregated data fitted with three-parameter exponential decay models. Model coefficients, fit statistics, and contrasts are summarized in Table 4. For both MDR types, increased dosing lowered WEP ($p < .001$). At low doses, the two types of MDR behaved similarly, but as dosing increased, the Ca-rich MDRs became less effective relative to the Fe-rich MDRs. This trend resulted in a divergence of the asymptotes ($p < .0196$).

The importance of MDR particle size on WEP removal was evaluated through a dose–effect experiment on four MDRs selected based on the established effectiveness and availability for field trials. The experiment demonstrated increased WEP removal with decreasing particle size (Supplemental Figure S2). All four <0.18-mm particle size preparations affected WEP similarly. As a result of this finding, the Brandy

Camp MDR used in subsequent dose–effect testing and for field trials was milled with a Pulva Corporation Model A pulverizer to a powder with <0.18-mm particle size. This material will be referred to as Pulva Brandy Camp MDR.

Dose–effect tests were conducted with the Pulva Brandy Camp MDR on four dairy manures (Figure 5) with WEP ranging from 2,228 to 4,795 mg kg^{-1}. The MDR effectively decreased WEP for the high-WEP manure but had less effectiveness on the WEP of the low-WEP manures.

3.5 | Field Trials

Results from the field trials are shown in Table 5. Field Trial 1 occurred at a large dairy operation where the barns are washed with liquid manure twice a day and the wash water is treated with a mechanical solids separator. Pulva Brandy Camp MDR
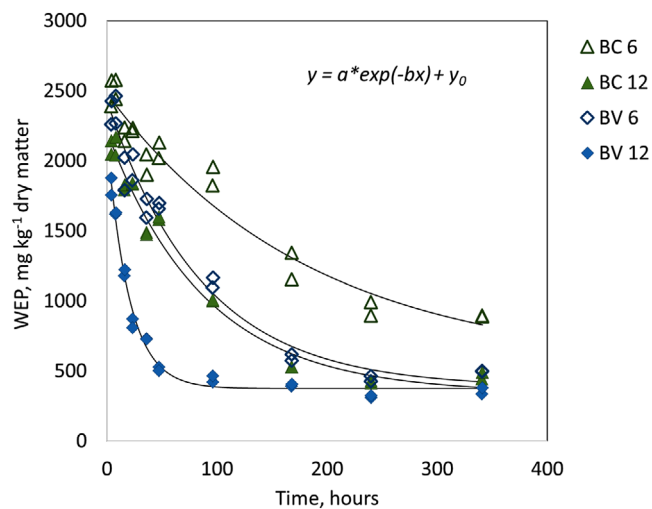
FIGURE 2 Change in water-extractable P (WEP) from manure treated with Blue Valley (BV) or Brandy Camp (BC) mine drainage residuals at a rate of 6 and 12 g kg^{-1} for 340 h (14 d). Data were fit to the function $y = a \times \exp(-bx) + y_0$. Model coefficients and fit statistics are presented in Table 3

was added to the sump that receives wash water (Supplemental Figure S3). The liquid manure had low WEP. Nonetheless, MDR addition decreased the WEP from 2,200 to <1,000 mg kg^{-1}. The only problem noted by the operator was dust.

Field Trial 2 occurred at a free-stall dairy operation where Pulva Brandy Camp MDR was added to bedding before use (Supplemental Figure S4). The WEP in the raw manure–bedding mixture, 3,300–4,700 mg kg^{-1}, was decreased to <1,000 mg kg^{-1} in samples receiving MDR. While the calculated dosing, 24–41 g L^{-1}, was very high, no negative impacts on milk yield or cow hygiene were reported while the animals were bedding in sawdust amended with MDR.

Field Trial 3 occurred at a small dairy operation where manure is stored in a 1,900-m^3 open-top concrete tank that is emptied twice a year. The entire tank was dosed with Pulva Brady Camp MDR prior to the manure's removal (Supplemental Figure S5). The 4.4 g L^{-1} MDR dose decreased WEP from 4,100 to 3,200 mg kg^{-1}. No negative impacts on subsequent crop yield were reported by the operator.

4 | DISCUSSION

The elemental compositions of 20 MDR samples produced from coal mine drainage were analyzed in detail. In addition to the major composition of Ca, Mg, Fe, Al, and Mn, the MDRs contain trace elements whose presence and release is a concern in the use of these materials in agronomic applications. For example, Fenton, Healy, and Rodgers (2009) reported that solids collected from a copper–sulfur mine released hazardous metals when used to treat waste waters at a dairy operation. Appalachian coal mine drainage typically contains low concentrations of hazardous metals (Cravotta, 2007), and MDR is not considered hazardous by U.S. regulators. Sibrell et al. (2015) conducted water extractions on three Appalachian MDRs and concluded that the release of hazardous metals was minimal, especially under circumneutral pH conditions as exist in manure systems.

This study provides additional information regarding the hazardous metal content of the MDRs recovered from coal mine drainage (Table 2). At the dosing rates considered in this study, the hazardous contaminants arising from MDR in land-applied manure do not exceed the USEPA ceiling concentrations and would not exceed the cumulative loading limits for decades.
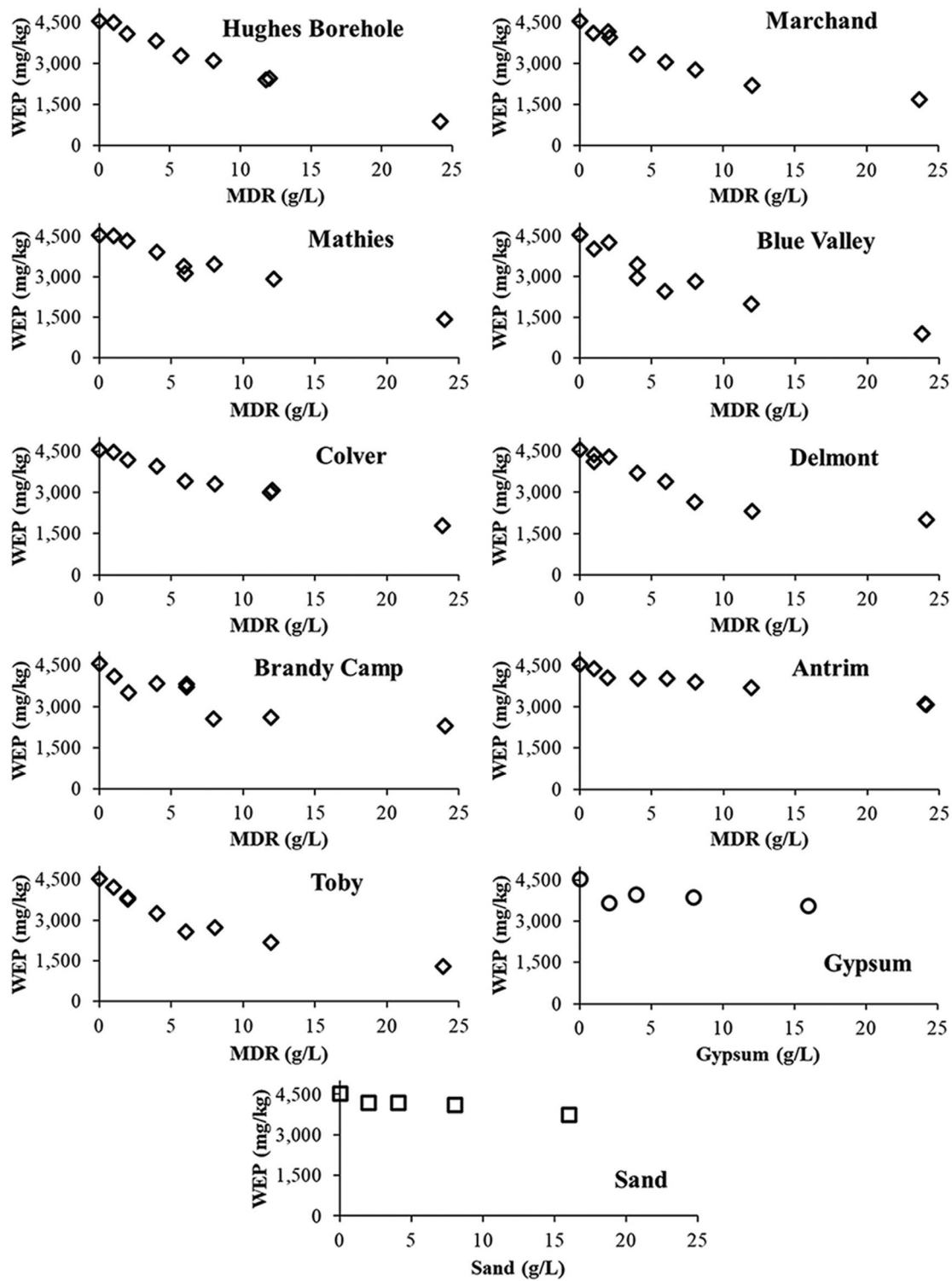
TABLE 3 Estimated model coefficients and fit statistics for the function $y = a \times \exp(-bx) + y_0$ describing the relationship between water-extractable P (WEP) from manure treated with Blue Valley (BV) or Brandy Camp (BC) mine drainage residuals at a rate of 6 or 12 g kg^{-1} for 340 h (14 d). Contrast statements are for the hypothesis that model coefficients are different within mine drainage residuals applied at different rates, between mine drainage residuals applied at the same rate, and between mine drainage residuals applied at different rates

Source	Rate	a	b	y_0	R^2	Pr < F
	g kg^{-1}	mg kg^{-1}	h^{-1}	mg kg^{-1}		
Brandy Camp	6	1,955	0.00547	523.8	0.95	<.0001
	12	1,866	0.0113	343.3	0.98	<.0001
Blue Valley	6	2,046	0.0116	381.7	0.97	<.0001
	12	1,796	0.0503	372.8	0.99	<.0001
Contrasts			Pr > F			
BC6 vs. BC12		.66	.0033	.41		
BC6 vs. BV6		.69	.0040	.56		
BC12 vs. BV12		.42	<.0001	.60		
BV6 vs. BV12		.022	<.0001	.90		
BC6 vs. BV12		.41	<.0001	.4265		
BC12 vs. BV6		.076	.87	.69		

FIGURE 3 Changes in water-extractable P (WEP) measured for different doses of mine drainage residual (MDR). The experiment used a common manure. The MDRs were sieved to a particle size of <1 cm for all trials. The raw unamended manure contained 4,546 mg kg^{-1} solid WEP

The addition of MDR to dairy manure was found to be an effective method for decreasing WEP. Both laboratory and field experiments indicated that for high-WEP manure, a dose of about 8 g L^{-1} can decrease WEP to values considered to be environmentally benign. However, the effectiveness of MDR amendments for WEP management was influenced by the chemical compositions of the MDR and manure. The chemical composition of the MDR solids sorted into two groups: Fe-rich solids produced from the treatment of Fe-contaminated water by natural or passive processes or through the addition
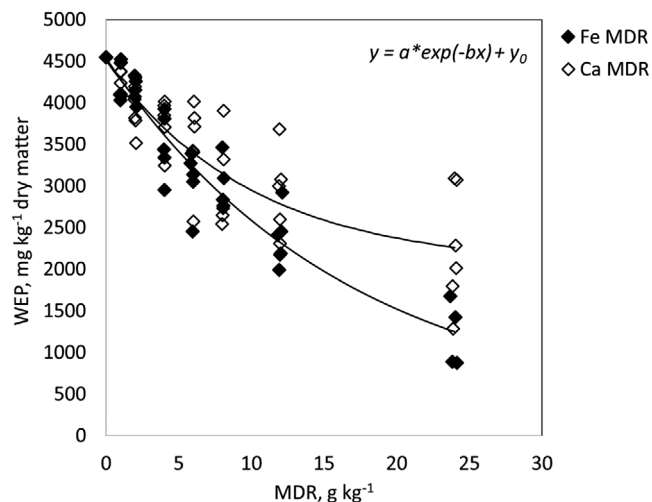
FIGURE 4 Change in water-extractable P (WEP) from manure treated with Fe-rich and Ca-rich mine drainage residuals (MDRs) at varying application rates. Data were fit to the function $y = a \times \exp(-bx) + y_0$. Model coefficients, fit statistics, and contrasts are presented in Table 4

of oxidants; and Ca-rich solids produced from lime treatment. The temporal study established that while Fe-rich and Ca-rich materials were both capable of decreasing WEP to low concentrations, the rate of WEP removal by Fe-rich MDR was faster than that of Ca-rich MDR. The high-dose Fe-rich BV MDR lowered WEP in a dairy manure by 2,279 mg kg^{-1} (73%) after 1 d of contact, while the high-dose Ca-rich BC MDR required 4 d to achieve a similar result. This is consistent with the findings of Penn and McGrath (2014) that P removal by Fe-rich solids is faster than that of Ca-rich solids because of different chemical mechanisms.

The slow kinetics of WEP removal by Ca-rich materials is an important consideration in the evaluation and use of these materials for WEP management. Most studies that screen materials for their ability to remove soluble P from wastewaters utilize sorption tests where capacity is evaluated after a 24-h incubation (Cucarella & Renman, 2009). While this approach may be appropriate for evaluating the ability of Fe-rich solids to decrease dissolved P in artificial solutions, it is not appropriate for testing on complex solutions like manure

or for Ca-rich materials. The complete reaction of Ca-rich solids with WEP in dairy manure can require 7–10 d of incubation. Tests done at shorter incubation periods are probably underestimating the solid's capacity for WEP removal. When evaluating a solid for its capacity to decrease P in animal manures, testing should include a range of incubation periods that extend to 14 d. Additionally, in field applications, the length of time between dosing manure with MDR and spreading the manure on fields will influence the impact on WEP. In applications that involve <1 wk of contact time between the MDR addition and field application, Fe-rich MDR will be more effective for WEP reduction than Ca-rich MDR. In applications where the contact time is >1 wk, Ca-rich MDR will be equally effective as Fe-rich MDR.

The effectiveness of an MDR for WEP removal is dependent not only on the MDR but also the concentration of WEP in the manure. Mine drainage residual was most effective on manures with high WEP but had little effect on manures with low WEP (Figure 5). When conducting experiments that utilize P-removing solids such as MDR, the presence of excessive WEP in the raw manure should be confirmed.

These results indicate that the WEP of dairy manure is not a fixed chemical characteristic. The ability to modify WEP can be a valuable tool in manure management application where the WEP is an important component of the manure management plan. When these plans suggest a high risk of P release, the use of amendments to decrease WEP may be a viable management option. This study demonstrated the utility of using MDRs produced from coal mine drainage for WEP reduction.

4.1 | MDR Treatment Cost

A unit cost for P management using MDR to decrease WEP was developed from Field Trial 3. The addition of 8.2 t of Pulva Brandy Camp MDR to 1,900 m^3 of dairy manure with 8.1% solids decreased the WEP by 894 mg kg^{-1} and removed 138 kg of WEP. The cost to treat the manure included the material and its addition and mixing. Dried powder MDR is estimated to cost US$450 t^{-1} (delivered to the site) and $50 t^{-1} to apply and mix with manure. The total cost of the

TABLE 4 Estimated model coefficients and fit statistics for the function $y = a \times \exp(-bx) + y_0$ describing the relationship between water-extractable P (WEP) from manure treated with Fe-rich or Ca-rich mine drainage residuals (MDRs) at various doses. Contrast statements are for the hypothesis that model coefficients are different between the two types of mine drainage residuals

Source	a	b	y_0	R^2	Pr < F
	mg kg^{-1}	kg g^{-1}	mg kg^{-1}		
Fe MDR	4289.1	0.0606	244.5	0.92	<.0001
Ca MDR	2470.1	0.0994	2034.4	0.75	<.0001
Contrast	Pr > F				
Fe vs. Ca MDR	.0116	.1779	.0196		

TABLE 5 Results of the three field trials where dairy manure was amended with Pulva Brandy Camp mine drainage residual (MDR). Manure samples were collected before and after MDR addition

Treatment	MDR dose	WEP	Solids	N	K$_2$O	P$_2$O$_5$	Fe
	g L^{-1}	mg kg^{-1} solid	%			—kg m^{-3}—	
Field trial 1							
Wash	0	2,220	5.6	3.2	1.8	0.8	0.2
Sump	6.1	794	6.2	3.3	1.8	0.7	0.6
Sump	6.1	751	6.3	3.9	1.8	0.8	0.7
Solids separation		479	8.9	4.0	1.8	0.8	0.8
Liquid separation		914	5.1	3.0	1.8	0.7	0.6
Field trial 2							
Raw	0	4,697	6.8	2.9	1.9	0.8	0.1
Raw	0	3,251	6.9	2.9	2.4	0.8	0.4
Barn sump	23.7[a]	360	7.8	7.7	1.9	0.7	2.4
Barn sump	40.7[a]	662	14.1	4.7	3.4	1.3	3.9
Field trial 3							
Raw manure	0	4,116	8.1	3.5	3.4	1.3	0.1
Field applied	4.4	3,222	8.0	3.6	3.4	1.3	0.5

[a]MDR dose calculated from increase in Fe concentrations.
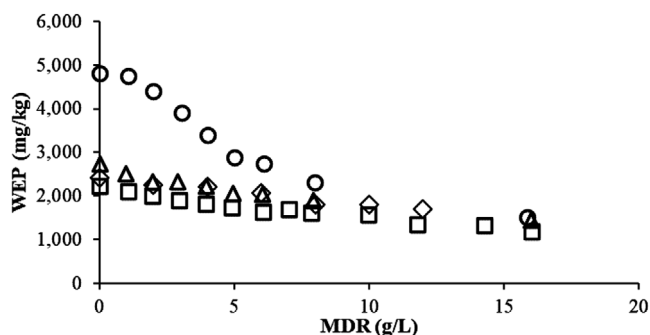
FIGURE 5 Dose-response curves generated for four dairy manures that varied in water-extractable P (WEP). The same Pulva Brandy Camp mine drainage residual (MDR) was used in each experiment

treatment was $4,100. The calculated unit costs were $30 kg^{-1} WEP removed and $2.16 per 1000 L of manure treated.

5 | CONCLUSIONS

The results of this study support the use of MDR to decrease the WEP of dairy manure. The MDR–manure mixtures investigated did not exceed concentration and loading limits established for land-applied biosolids by the USEPA. The MDRs sorted into Fe-rich and Ca-rich types based on the types of mine water treatment utilized. Dose–effect testing determined that while both types of MDR eventually decrease WEP to low concentrations, the Fe-rich solids remove WEP faster. The findings demonstrate that the WEP of dairy manure is not a fixed parameter and can be modified with amendments such as MDR. A field trial with 1,900 m^3 of dairy manure demonstrated reductions of WEP using MDR at a unit of cost of $30 kg^{-1} WEP.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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