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Passive Biological Treatment of Mine Water to Reduce Conductivity: Potential Designs, Challenges, and Research Needs

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Abstract

The remediation of mine water to preserve receiving water quality has advanced substantially over the past half century, but prospective regulations to limit the conductivity of mining-impacted waters pose a significant new challenge. Conventional approaches to reduce high levels of conductivity in these mine waters are often costly, requiring high levels of maintenance and significant inputs of energy and refined chemicals. In contrast, passive biological treatment (PBT) systems are a relatively low-cost, low-maintenance treatment technology for mine waters that have been used for over three decades. However, their practical ability to reduce conductivity is unclear, given previous research reports focused on the removal of metals, acidity, and solids. A systematic literature review to identify previous reports of PBT systems at the laboratory or field scale that include evaluations of changes in conductivity suggests that decreases in conductivity of 30 to 40% are achievable. Substantial variability in performance is common, however, and conductivity increased markedly in some systems. This variation may be associated with the dissolution of limestone, which is a key treatment material in some systems. Although the development of PBT to serve as pre-, post-, or stand-alone treatment systems targeting conductivity may reduce overall treatment cost in some settings, optimization of these designs requires an increase in the number of published conductivity datasets from similar systems, detailed reports on the key ions contributing to elevated conductivity region to region, and further investigation of the underlying biochemical processes responsible for conductivity reductions.

Core Ideas

- Passive treatment of mine waters is a low-maintenance option for conductivity reduction.
- Passive treatment systems can reduce conductivity by 30–40%, but efficacy is variable.
- The use of limestone in passive treatment systems may prevent conductivity reduction.
- More datasets on conductivity reduction by passive treatment systems are needed.
- Regional ionic profiles of conductivity will improve passive treatment system design.

COAL MINING remains a major industry in the United States, with nearly 1 Pg (~1 billion short tons) of coal produced annually to supply both domestic and international demands (US EIA, 2016). Although coal mining provides a significant source of domestic energy, concerns regarding the environmental and community health impacts associated with the mining process have been raised by both scientists and community action groups for many years (e.g., Palmer et al., 2010; Holzman, 2011; Hendryx, 2015). Despite both societal and regulatory pressures on the coal mining industry, as well as the rise of natural gas extraction via hydraulic fracturing, recent projections indicate that at least 1000 km² of new surface mining to extract coal reserves is expected in the next 20 yr in the Central Appalachian region alone (Strager et al., 2015).

Both active and shuttered (“closed” or “abandoned”) mine sites are associated with a large number of environmental concerns and general aquatic habitat degradation, including burial of aquatic habitat by valley fills, sedimentation of receiving waters, and the discharge of either alkaline (neutral pH) or acidic (low pH) mine drainage, depending on the underlying geology and type of mining (Holzman, 2011). However, over the past few years, regulation of mine waters, particularly in the Appalachian region of the United States, is increasingly focused on receiving water measures of specific conductance (temperature-corrected conductivity, henceforth “conductivity”) as a proxy for the potential degradation of downstream aquatic ecology (Sarver and Cox, 2013). Elevated measures of conductivity downstream from mining sites are common, as previously unexposed rock weathers and releases various ions into groundwater and stormwater runoff.

Multiple field surveys of streams in the Appalachian region have observed reductions in the abundance and diversity of benthic macroinvertebrates when aquatic conductivity is elevated, and debate as to a level of conductivity that is inherently harmful to aquatic ecology persists (Hartman et al., 2005; Merricks et al., 2007; Pond et al., 2008; Pond, 2010; Cook et al., 2015). Although a recent USEPA report suggests an ambient criteria level of <300 $\mu\text{S cm}^{-1}$ (USEPA, 2011), laboratory studies have observed no change in the survival and reproduction of a wide

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Abbreviations: CWA, Clean Water Act; PBT, passive biological treatment; RAPS, reducing and alkalinity producing systems; SMCRA, Surface Mining Control and Reclamation Act; TMDL, total maximum daily load; VFB, vertical flow bioreactor.

variety of species at levels $>1000 \mu\text{S cm}^{-1}$ (Yeager-Armstead et al., 2013). It is quite likely that the degree of stress placed on a benthic community depends on the specific mix of constituent ions contributing to conductivity, the particular aquatic species present, and habitat quality (Cook et al., 2015; Smith et al., 2015; Timpano et al., 2015; Cañedo-Argüelles et al., 2016; Clements and Kotalik, 2016).

Despite the uncertainties surrounding specific acceptable standard levels, the mining industry in the United States is under increasing pressure to reduce conductivity levels in waters receiving mine discharges to maintain compliance with Clean Water Act (CWA) regulations (Sarver and Cox, 2013). At present, acceptable water treatments designed to reduce conductivity are quite expensive and energy intensive (e.g., reverse-osmosis technology) and require considerable capital investments, in addition to ongoing maintenance and monitoring. Passive biological treatment (PBT) systems (e.g., wetlands, vertical flow bioreactors, etc.), which are generally less expensive and rely on low-maintenance technologies without ongoing energy or material inputs, have been used in previous efforts to remove or transform a variety of contaminants from mine waters (Younger et al., 2002; Watzlaf et al., 2004). The potential of both passive and more intensive (active) treatment technologies in reducing conductivity, in keeping with proposed surface water quality goals, was recently reviewed by Pinto et al. (2016); while this work provides significant information regarding the removal of various mine water contaminants that may contribute to conductivity, it does not explicitly report actual experimental or field-monitoring observations of conductivity reduction.

The goals of this manuscript are therefore (i) to discuss the evolution of strategies and goals used to regulate mine waters, (ii) to briefly review available PBT systems for the treatment of mine water and discuss mechanisms relating to conductivity reduction, (iii) to present and evaluate available publications that explicitly report conductivity changes observed in PBT systems, and (iv) given datasets available from the literature directly observing conductivity reduction, to identify primary challenges to implementation of these systems, as well as immediate and long-term research needs for optimization of mine water treatment. It is worth noting that while this review and discussion is largely anchored by the current water quality issues and associated regulatory disputes in the Appalachian Coalfields region of the United States, these issues are global. Recognition of the negative ecological impacts of elevated conductivity on freshwaters and an accompanying desire for regulatory limits to restore aquatic integrity are also increasing in Europe, Australia, and New Zealand (Cañedo-Argüelles et al., 2016). Despite this broad interest, no focused synthesis of available information regarding the potential for passive biological treatment to reduce conductivity is currently available.

Common Biological Strategies to Mitigate Mining Impacts on Receiving Waters

Review of Applicable Regulations and Existing Debates

Given the substantial geologic disturbance wrought by subsurface and surface mining, effects on regional hydrology and water quality are inevitable. To minimize negative impacts and preserve aquatic integrity, mining operations are subject

to multiple regulatory requirements, including the Surface Mining Control and Reclamation Act (SMCRA) and multiple specific sections of the CWA.

Under SMCRA, new mining operations are required to file for a permit and submit a mitigation plan to counter any negative environmental consequences; recent proposed revisions under the new Stream Protection Rule aim to require monitoring and remediation to more specifically target the protection of native species and hydrologic integrity (OSMRE, 2015). Sections 402 and 404 of the CWA are administered by the United States Army Corps of Engineers and require plans for compensatory mitigation of valley fills and stream burials, e.g., stream restoration (USEPA, 2016b). A recent review of over 400 restoration projects in Central Appalachia subject to Section 404 questions the administration of this effort, as it appears that the majority of projects target perennial streams, even though intermittent and ephemeral streams are more commonly impacted by surface mining and valley fills (Palmer and Hondula, 2014). More broadly, there is concern that the original pledged mitigation funds may no longer be available for restoration due to recent bankruptcies and restructuring in the coal industry (Storrow, 2016).

While SMCRA and Sections 402 and 404 of the CWA are specific to land-moving activities with the potential for future environmental impacts, Section 303(d) of the CWA, commonly referred to as the Total Maximum Daily Load (TMDL) program, aims to identify currently impaired waterbodies and then link the potential for remediation to reductions in multiple associated watershed pollutant sources (USEPA, 2016a). Following identification of a water body that fails to meet its designated use (e.g., fishing, swimming, preservation of aquatic life), TMDL assessments are conducted to identify and quantify pollutant sources and to determine the necessary pollutant load reductions from each source to bring the water back into compliance with applicable standards. Conductivity is frequently identified as the primary stressor for degraded aquatic integrity, which is often measured in terms of benthic macroinvertebrate abundance and diversity (Palmer et al., 2010; Cañedo-Argüelles et al., 2016). Reductions in loads of chemicals contributing to conductivity from upland sites, including mines, are considered necessary to restore macroinvertebrate communities. At present, the ability to practically apply the TMDL watershed remediation strategy to conductivity impairments remains in question. Uncertainties surrounding the lack of a specific macroinvertebrate “stressor” in cases of conductivity impairments waylaid efforts to address these impairments via TMDL load reductions in West Virginia. In the 2015 case “Ohio Valley Environmental Coalition (OVEC) et al. v. Gina McCarthy et al.,” the West Virginia federal district judge ruled that, because conductivity was a proxy for the actual ionic stressors (e.g., SO_4^{2-}) and not the stressor itself, the development of TMDL plans targeting reductions in conductivity loadings could not be required (DiCosmo, 2015).

Effective remediation of streams to restore aquatic integrity in watersheds impacted by mine waters has proven difficult due to issues of jurisdiction, economics, and scientific uncertainty. However, given the repeated identification of conductivity as a primary stressor of concern, it is likely that future regulatory requirements will increasingly focus on either this broad surrogate for water quality or a collection of specific primary ions responsible for ecological stress (Sarver and Cox, 2013; Cañedo-Argüelles et al., 2016).

Common Design Strategies and Water Quality Targets

Biological strategies to reduce contamination in mine waters discharged to the environment have existed for decades and have primarily been directed at pH increase and the removal of various metals. Conductivity reduction has not traditionally served as a water quality mitigation target. Iron, Al, and Mn are the most commonly targeted metals in coal-mining regions, but other metals and metalloids such as As, Cd, Co, Cu, Ni, Se, Sn, Sb, Pb, and Zn may be targeted in hard-rock mining operations (Younger et al., 2002; Peer et al., 2015).

Designs for PBT of mine waters stem from observations of the positive effects (increasing pH and lowering metal concentrations) that *Sphagnum* bogs had on the water quality of coalmine waters in the late 1970s (Huntsman et al., 1978; Weider and Lang, 1982). Engineered *Sphagnum* bogs for mine water treatment were attempted in the early 1980s but did not elevate pH or remove metals adequately because they are low-productivity systems with low tolerance to high Fe concentrations (Weider et al., 1985; Spratt and Weider, 1988). To counter these issues, subsequent efforts focused on the design of more traditional types of treatment wetlands with emergent macrophytes, similar to systems used for municipal wastewater treatment many decades prior (Kadlec and Wallace, 2009). Treatment wetlands vegetated with *Typha* spp. proved effective at Fe and Mn removal and were commonly employed in the late 1980s after being developed in West Virginia and Pennsylvania (Younger et al., 2002). Eventually, the aerobic treatment wetland system approach was extended to include simple open-water ponds as well. These ponds, typically dubbed “oxidation ponds,” were often, and still are, interchanged or used in concert with treatment wetlands.

In the 1990s, the menu of PBT options for mine waters was extended with the development of successive alkalinity-producing systems (SAPS; Kepler and McCleary, 1994) and other types of vertical flow bioreactors (VFBs). Successive alkalinity-producing systems, reducing and alkalinity-producing systems (RAPS), vertical flow ponds, vertical flow wetlands, vertical flow systems, and VFBs are all names for the suite of systems that consist of a pond filled with influent mine water overlying organic substrates that are underlain by stone (most often limestone of relatively high purity) with a networked drainage system of perforated piping. For ease of discussion, these are subsequently referred to as VFBs. These systems vary greatly in the depth of ponded water, with a few shallow enough that emergent wetland vegetation grows. Vertical flow bioreactors also vary greatly in the thickness and mixture of organic substrate; thickness can vary from a few centimeters for traditional RAPS treating coalmine drainage to over a meter for VFBs treating hard-rock mine drainage. The substrate is generally composed of various organic wastes, usually compost (e.g., spent mushroom compost), and with amendments of limestone and/or recalcitrant organic materials (e.g., wood chips).

Vertical flow bioreactors for mine water treatment have typically been applied to remove metals from solution and/or to generate alkalinity to raise and buffer pH. In an oxygenated system, Fe will passivate or “armor” the surface of limestone, severely decreasing dissolution efficiency. In most VFBs, the primary purpose of the organic substrate is to strip oxygen and reduce any Fe(III) to Fe(II), preventing it from precipitating within the limestone bed. However, over the last decade and a

half, more systems have been installed that rely primarily on the organic substrate for alkalinity generation via SO_4^{2-} reduction and metal and metalloid removal via metal sulfide formation, sorption, or other redox reactions (e.g., conversion of selenite or selenate to the insoluble elemental Se; Liang, 2014); often, this is for removal of the more trace elements (e.g., Cd, Ni, Se, Sn, Zn). Vertical flow bioreactor design has only recently been optimized for SO_4^{2-} reduction, not specifically to meet conductivity recommendations, but to meet SO_4^{2-} discharge limits or maximize metal removal via metal sulfide formation.

Processes in Passive Biological Treatment Systems That Reduce Conductivity

Since conductivity measures the collective effect of ions in solution (McCleskey et al., 2012), its reduction requires the removal of ions from solution or their replacement with ions of lower characteristic conductivity (referred to as molal or equivalent conductivity, see Table 1 in McCleskey et al. [2012] for details). Although not previously a formal design objective, PBT systems can theoretically reduce the conductivity of mine waters by removing or exchanging ions via various physical, chemical, and microbiologically-mediated processes, as summarized in Fig. 1. Dilution of settling ponds by rain, runoff, or groundwater influx can lead to conductivity reductions, particularly in regions that receive high levels of seasonal precipitation. Adsorption of ions onto charged surfaces or particles can also reduce conductivity, although most of the major ions contributing to conductivity in these discharges (SO_4^{2-} , Ca^{2+} , and Mg^{2+}) do not adsorb strongly onto the typical types of materials found in PBT systems (Pokrovsky and Schott, 2002). In addition, it is critical to note that substantial conductivity reduction via adsorption likely requires both anions and cations to be adsorbed to maintain charge balance. Nevertheless, a number of modified materials such as clay minerals, fly ash, zeolites, and biochars have shown promise for removing these major ions as well, with removal efficiencies of ~50 and 75% observed for SO_4^{2-} and Mg^{2+} , respectively (Gitari et al., 2006; Phillips et al., 2016; Pinto et al., 2016). In addition, the oxic hydrolysis and precipitation of metal ions such as Fe^{3+} and Al^{3+} can also cause a reduction in conductivity, particularly if other ions become associated with these coagulant-like precipitates. The formation of mineral precipitates such as jarosite [$\text{KFe}(\text{OH})_6(\text{SO}_4)_2$] or schwertmannite [$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$], which is dependent on pH, could also reduce conductivity by removing both Fe and SO_4^{2-} from solution (Biggam et al., 1996).

Sulfate reduction, which occurs in the anoxic sediments of PBT systems, represents a major route for decreasing conductivity, since SO_4^{2-} is often a primary contributor to conductivity in many mine waters due to its high concentration and characteristic conductivity (Watzlaf et al., 2004; McCleskey et al., 2012; Cook et al., 2015; Cravotta and Brady, 2015). Reducing SO_4^{2-} concentrations may also be critical to preserving sensitive species (Clements and Kotalik, 2016). However, the rate and efficiency of SO_4^{2-} reduction can be limited by the quantity and quality of organic matter available as primary substrate for SO_4^{2-} -reducing microorganisms (Harris et al., 2006; Neculita et al., 2011; Sánchez-Andrea et al., 2014). Finally, the sulfide and bicarbonate that are formed during SO_4^{2-} reduction can also bring about further conductivity reductions. Sulfide reacts with metal ions to form metal sulfides that rapidly precipitate from solution or with

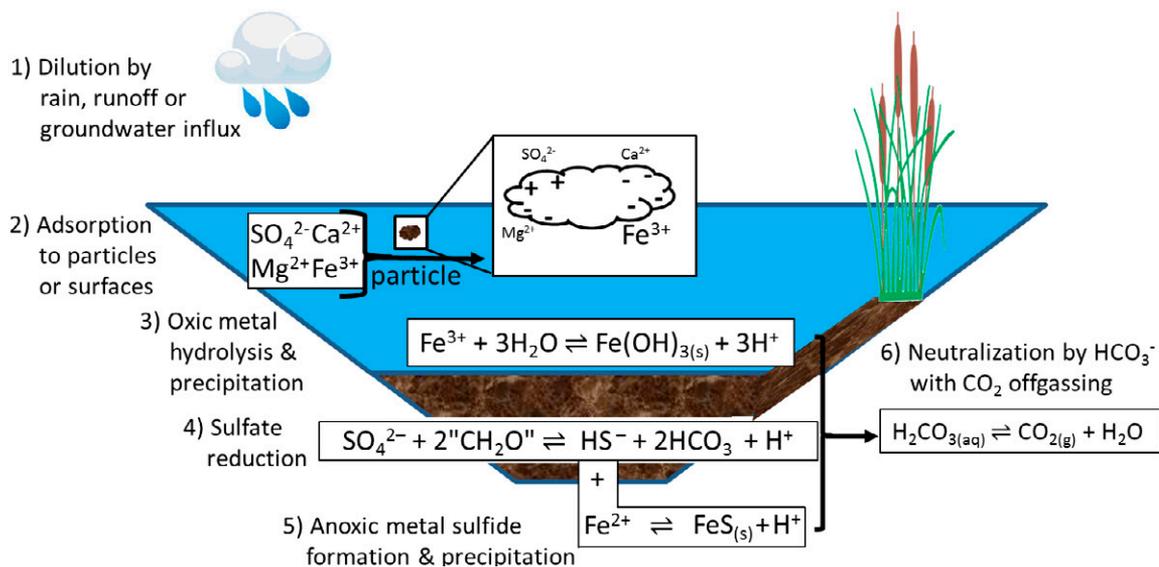


Fig. 1. Principal processes within passive biological treatment systems that reduce conductivity. The upper layer represents an oxic water layer, while the lower, dark-colored layer represents anoxic sediment. The smaller size of the sulfate, calcium, and magnesium ions adsorbed onto the particle represent the fact that these ions often adsorb only weakly to most surfaces and particles. Organic matter consumed during sulfate reduction is represented by "CH₂O"

protons in acidic conditions to form hydrogen sulfide gas, which has very low solubility. Bicarbonate can react to neutralize acidity and form carbonic acid, which in turn can be degassed from solution as carbon dioxide. Further details on the mechanisms associated with these processes that reduce conductivity can be found in Kadlec and Wallace (2009) and Pinto et al. (2016).

Published Research with Conductivity Data from Passive Biological Treatment Systems

Conductivity is often measured in system influent and effluent as a general water quality parameter; however, as the reduction of conductivity has not been a primary design objective until recently, actual published reports on PBT performance that include conductivity measures are somewhat uncommon. To determine whether past research existed that reported conductivity reductions by these systems, an initial literature review effort used searches with Google Scholar and WorldCat for the following terms in various combinations: "mine water," "passive treatment," "acid mine drainage," "biological treatment," "conductance," and "conductivity." In keeping with expectations and previous experience, a number of articles noted that conductivity data were collected alongside pH and temperature measurements, but these data were rarely then reported in the publication. Only 10 publications in peer-reviewed journals on treatment of mine waters were identified that included conductivity performance data. To supplement this handful of peer-reviewed articles, proceedings from the International Mine Water Association (1980–2014), the American Society for Mining and Reclamation (1980–2015), and the West Virginia Mine Drainage Task Force (1980–2016) conferences were searched for additional relevant studies. Review of these articles yielded an additional 18 studies, a number of which included data on multiple treatment systems that varied in their primary media materials. A summary of the 28 studies identified and the associated conductivity changes reported is provided in Table 1. It is worth noting that some studies did not specify whether they reported specific conductance, which is corrected for variation in temperature, or conductivity, which is not. However,

since specific conductance is directly proportional to conductivity, their relative changes are directly comparable.

The literature review identified VFBS and wetlands as the two main categories of PBT systems with reported changes in conductivity. In some cases, the systems consisted of a combination of multiple components such as oxidation ponds or anoxic limestone drains, in addition to a wetland or VFB. The scale of the systems varied from small, laboratory benchtop investigations to large, field-scale projects, and they spanned many geographic regions in the United States and internationally (South Korea, Australia, India, and England; Table 1). The chemical composition of the mine water, the hydraulic retention time, and the materials used in the treatment system construction also varied substantially between studies. Both VFBS and wetlands typically contained a mixture of complex organic materials such as compost, sawdust, manure, hay, foodstuffs, sediment, wood chips, and wastewater sludge, but simple carbon sources including sucrose, ethanol, and acetic acid were also used in some studies. In addition, the results from most systems varied temporally and often reflected a period of time beginning shortly after the system startup and lasting for <1 yr. Where possible, the mean conductivity values or the reported range of values were listed in Table 1.

Despite these design variations, the inclusion of limestone appeared to be a key factor that affected system ability to reduce mine water conductivity. Limestone-free systems reduced conductivity of mine water influents to a significantly greater extent than systems with limestone (two-sample *t* test, *p* = 0.003; Fig. 2); this was observed for both the VFB and wetland systems. Only 3 out of 25 of the systems that did not contain limestone exhibited an increase in conductivity following passive treatment, while most of the limestone-containing systems showed increases in conductivity. This suggests that limestone dissolution in these PBT systems may override their potential conductivity reduction mechanisms. Limestone-free systems exhibited four of the five largest decreases in conductivity (>30% reduction), which indicates that these systems may offer the best potential for optimizing conductivity reduction via PBT.

Table 1. Literature records of changes in conductivity following passive biological treatment of waters affected by mine drainage.

Reference	No.	Region	Treatment type	Influent		Effluent		Change
				$\mu\text{S cm}^{-1}$		$\mu\text{S cm}^{-1}$		
Fyson et al., 1998	1	Germany	Laboratory-scale VFB†	1600	1200	1200	1200	-25‡
Kepler et al., 1999	2	West Virginia & Pennsylvania	Field-scale VFB	1000–3400	930–2560	930–2560	930–2560	-30 to +30
Fyson et al., 2006	3	Germany	Laboratory-scale VFB	1033	576	576	576	-44‡
Pahler et al., 2007	4	Colorado	Field-scale VFB	3430–5760	3360–5560	3360–5560	3360–5560	-18 to +10
Blumenstein et al., 2008	5	California	Laboratory-scale VFB	2900	3700–4700	3700–4700	3700–4700	28 to 62
Gusek et al., 2008	6	California	Field-scale VFB	1453	1027	1027	1027	-29
Blumenstein and Gusek, 2009	7	California	Field-scale VFB	3000	3000	3000	3000	0
Kumar et al., 2011	8	Australia	Laboratory-scale VFB	11000	10700	10700	10700	-3‡
Kumar et al., 2011	8	Australia	Laboratory-scale VFB	10300	7100	7100	7100	-31‡
Gandy and Jarvis, 2012	9	England	Laboratory-scale VFB	580	615	615	615	6
Gandy and Jarvis, 2012	9	England	Field-scale VFB	580	604	604	604	4
Song et al., 2012	10	South Korea	Field-scale VFB	2400	2500	2500	2500	4
Santamaria, 2014	11	Oklahoma	Laboratory-scale VFB	1200–1320	1150–1550	1150–1550	1150–1550	-10 to +29
Yim et al., 2015	12	South Korea	Field-scale VFB	2000	2000	2000	2000	0‡
Marcillo et al., unpublished data, 2015	13	Pennsylvania	Laboratory-scale VFB	863	635	635	635	-26‡
Tarutis and Unz, 1990	14	Pennsylvania	Constructed wetlands	711	592	592	592	-17
Wildeman et al., 1993	15	Colorado	Constructed wetlands	8000–10830	9240–12200	9240–12200	9240–12200	-6 to 44
Stark et al., 1994	16	Ohio	Constructed wetlands	1790	1702	1702	1702	-5
Sikora et al., 1996	17	Alabama	Constructed wetlands	1120	1230–1270	1230–1270	1230–1270	9.8 to 13
Heil and Kerins, 1988	18	Montana	Constructed wetlands	3349	3440	3440	3440	3
Heil and Kerins, 1988	18	Montana	Constructed wetlands	2414	2559	2559	2559	6
Skousen et al., 1999	19	West Virginia	Constructed wetland & anoxic limestone drain	900	880–1400	880–1400	880–1400	-2 to +56
Skousen et al., 1999	19	West Virginia	Constructed wetland & anoxic limestone drain	4700	1200–4500	1200–4500	1200–4500	-47 to -4
Hilton et al., 2003	20	Pennsylvania	VFB & constructed wetland	1880	1760	1760	1760	-6‡
Hilton et al., 2003	20	Pennsylvania	VFB & constructed wetland	1432	1335	1335	1335	-7‡
Hilton et al., 2003	20	Pennsylvania	VFB & constructed wetland	1140	939	939	939	-18‡
Rose et al., 2004	21	Pennsylvania	VFB & constructed wetland	1100–3210	900–3210	900–3210	900–3210	-18 to +23
Sheoran, 2005	22	India	Natural wetland	7240–8153	7082–5474	7082–5474	7082–5474	-15 to -30‡
Behum et al., 2006	23	Oklahoma	Constructed wetland	480	500	500	500	4
Sheoran, 2006	24	India	Laboratory-scale constructed wetland system	1520–1590	737–1810	737–1810	737–1810	-52 to +14‡
Cravotta, 2007	25	Pennsylvania	Oxidation pond & constructed wetlands	517	513	513	513	-1‡
Eger, 2007	26	Minnesota	Natural wetland	1100	600	600	600	-45‡
Hedin, 2013	27	Pennsylvania	Oxidation pond & constructed wetlands	2688	2434	2434	2434	-9‡
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	504	477	477	477	-5‡
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	2040	2030	2030	2030	0‡
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	1510	1390	1390	1390	-8‡
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	866	590	590	590	-32‡
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	2600	2570	2570	2570	-1‡
Cravotta and Brady, 2015	28	Pennsylvania	Oxidation pond & constructed wetlands	650	696	696	696	7‡
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	1980	1930	1930	1930	-3‡
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	2100	1920	1920	1920	-9‡
Cravotta and Brady, 2015	28	Pennsylvania	Constructed wetland	992	1080	1080	1080	9‡

† VFB, vertical flow bioreactor.

‡ The treatment did not include limestone

Potential Design Challenges

The high variability of PBT systems in reducing conductivity (Fig. 2) highlights a number of design challenges. From a theoretical standpoint, it is important to recognize that a 30 to 40% decrease in conductivity in a SO_4^{2-} -dominated system is approximately the maximum predicted by stoichiometry when considering SO_4^{2-} reduction alone. Sulfate reduction, which represents the major pathway for conductivity reduction in these systems, results in the production of two moles of bicarbonate for every one mole of SO_4^{2-} reduced:



Since bicarbonate also contributes to conductivity, there is a limit to the reduction in conductivity that can be achieved via SO_4^{2-} reduction alone. This limitation relates to the ionic molal conductivities at infinite dilution for the SO_4^{2-} and bicarbonate ions (159.8 and 44.1 $\text{mS kg cm}^{-1} \text{ mol}^{-1}$, respectively) and the pH of the water (McCleskey et al., 2012). The theoretical decrease in conductivity due to SO_4^{2-} reduction can be calculated for the range of SO_4^{2-} concentrations typically found in mine water (0.001–0.025 mol L^{-1} of SO_4^{2-}) using the recently validated approach by McCleskey et al. (2012). This approach predicts that replacing all SO_4^{2-} ions with bicarbonate ions in a 1:2 molar ratio results in a reduction in conductivity of 27 to 37% over this concentration range, assuming the sulfide produced either degasses (since typical systems have $\text{pH} < 7$ and the $\text{pK}_a = 7$ for

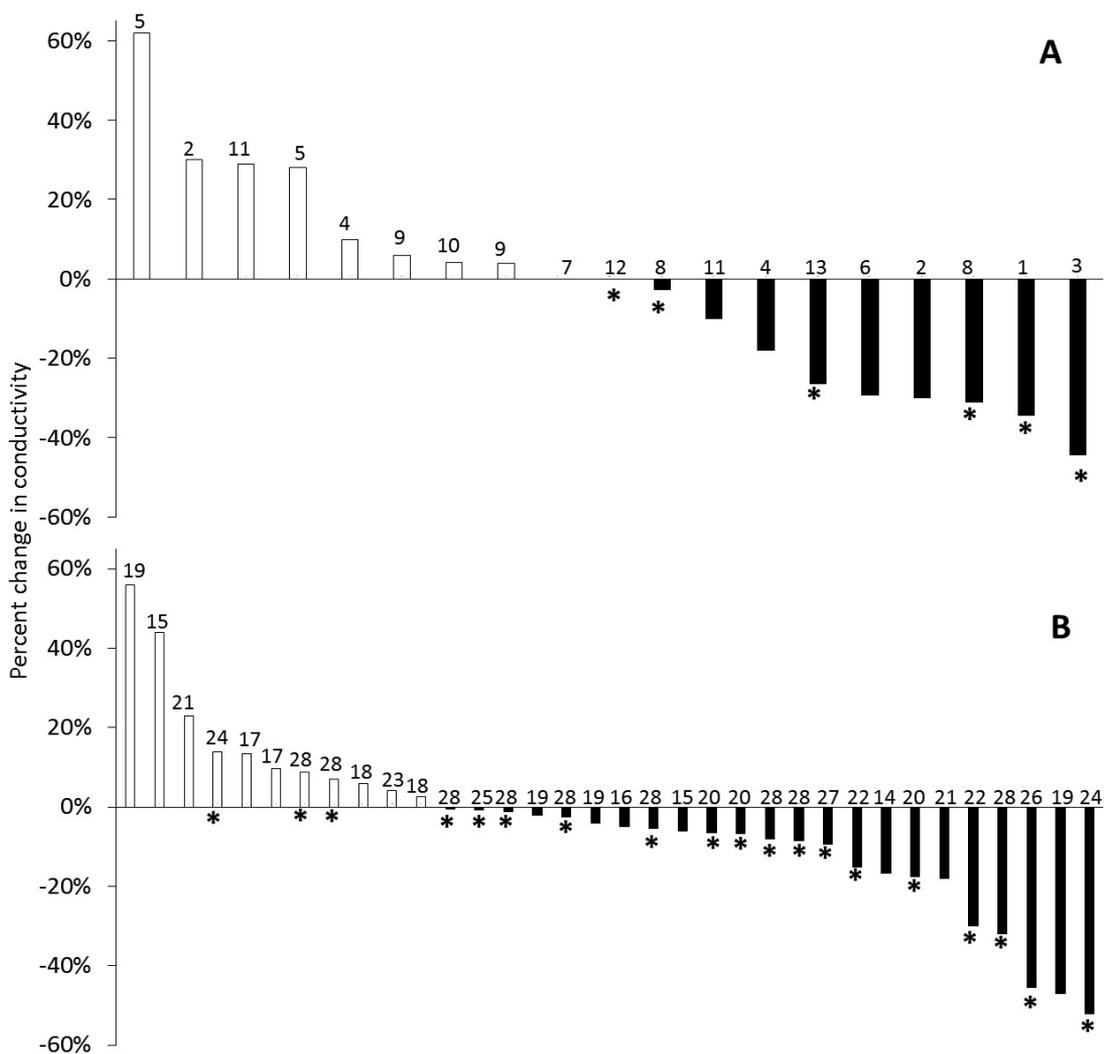


Fig. 2. Percent change in conductivity of mine water after passive biological treatment with (A) vertical flow bioreactors or (B) wetlands systems. White bars indicate increases and black bars indicate decreases in conductivity. The numbers above the bar refer to the study referenced in Table 1, and * below the bar indicates that the treatment did not include limestone.

H₂S) or reacts rapidly to form metal-sulfide precipitates. However, at pH <6.3, the bicarbonate produced via SO₄²⁻ reduction could rapidly react with hydronium ions to form dissolved carbon dioxide, thereby potentially reducing the conductivity further. The reaction of Fe and other hydrolyzable metals with sulfide to form metal-sulfide precipitates may also reduce conductivity. As a general theoretical estimate, conductivity reductions of approximately 33% are possible for these systems, which agrees well with the upper range of observed conductivity reductions reported in the available literature, particularly for the limestone-free systems (Fig. 2).

Another challenge in the design of PBT systems to meet effluent conductivity goals relates to the particular characteristics of the mine water requiring treatment. Since SO₄²⁻ reduction is a key process involved in these types of treatment approaches, mine waters that are dominated by high SO₄²⁻ concentrations may be the best candidates for effective reductions in conductivity by PBT systems. In addition, acidic mine waters may be treated more effectively than alkaline mine waters, since the removal of acidity by the bicarbonate produced during SO₄²⁻ reduction offers an additional pathway to reduce conductivity. Also, the higher bicarbonate concentrations that tend to be associated with net alkaline mine waters may not be removed easily during PBT. Finally, better

conductivity reductions may be achieved in softer waters, since PBT systems generally do not remove Ca and Mg efficiently (Pinto et al., 2016). The geology of the region and type of discharge source (e.g., flooded subsurface mine, partially flooded subsurface mine, surface mine, mine spoil) determines mine water chemistry (e.g., Cravotta et al., 1999; Strosnider et al., 2014) and therefore which PBT systems for conductivity reduction may be applicable.

A final constraint on the design of PBT systems to reduce conductivity relates to seasonal variations in precipitation, which can affect the flow rate of the mine water through the treatment system. High flow rates during rainy periods can decrease the retention time of a treatment system, potentially lowering the degree of conductivity reduction that can be achieved. However, the dilution of the mine water by rainfall and runoff during a large precipitation event may counteract this lower reduction efficiency to a certain extent. In addition, lower temperatures during the winter months could also substantially lower the reductions in conductivity that could be achieved, since the activity of the SO₄²⁻-reducing bacteria driving this key process is limited by temperature (Sawicka et al., 2012). Some of the variability for conductivity reduction by PBT systems from the literature (Fig. 2) may be due to these types of seasonal, climate-related factors.

Path Forward: Future Research Needs

Although regulatory strategies, economic pressures, and geological limitations differ widely by country, the treatment of mine waters is an international problem. There is a need to develop and share strategies to ameliorate the various impacts of mine waters across the broad geographic regions that it affects. Many researchers emphasize that the specific mine water characteristics and the geographic setting often require a uniquely tailored remediation approach (Pinto et al., 2016). However, the collective experience of researchers and restoration practitioners can facilitate the selection of effective solutions and help to avoid costly mistakes. Given the current review of past studies of PBT of mine waters, as well as a review of the underlying chemistry, it seems unlikely the biological treatment of high-conductivity (e.g., $>1000 \mu\text{S cm}^{-1}$) mine water alone would be sufficient to meet new federal recommendations for surface waters ($300\text{--}500 \mu\text{S cm}^{-1}$). However, the substantial cost savings of these designs, especially in terms of maintenance, in comparison to traditional wastewater treatment plants, may make them suitable for lower-strength mine water as pretreatment prior to active treatment, as a finishing step prior to discharge to surface waters, or in the management of legacy sites. In addition, there may be opportunities to combine a PBT system with adsorbent-based technologies to harness the benefits of SO_4^{2-} reduction and sorption within a multistage passive system. However, this approach remains untested at present and would be an avenue for future research.

A number of other key areas for immediate, mid-term, and long-term research on the use of PBT systems for conductivity reduction are listed in Fig. 3. These research areas focus on publishing more conductivity data for the influents and effluents from these systems and also characterizing the main ionic constituents that contribute to conductivity across regions of varying geology. In particular, the recent work by Cravotta and Brady (2015) reporting on conductivity reduction by passive systems in Pennsylvania provides a model

example of a monitoring and analytical strategy that provides these data. Similar treatment monitoring approaches used to identify changes in key contributors to conductivity prior to discharge could be paired with downstream ecological studies to determine the importance of individual or combined ionic effects on sensitive species. The effects of combinations of ions on ecosystems and species is especially encouraged because of the competitive inhibition of relatively toxic ions (e.g., Al^{3+} , Zn^{2+}) by relatively benign ions (e.g., Ca^{2+} , Mg^{2+} ; Smith et al., 2015). Information from such investigations would facilitate designs of PBT systems that are focused on removing the relevant ions for conductivity reduction. Finally, longer-term research could involve the design and testing of systems that include PBT as one component of a larger system. The combination of these research efforts will enable PBT systems to become a more effective remediation solution for mine water.

Conclusion

Passive biological treatment systems can be quite effective in the removal of acidity and metals from mine water, but their ability to reduce conductivity appears somewhat limited based on an assessment of the current literature data. Nevertheless, some systems, particularly those that do not incorporate limestone into their construction materials, have been observed to reduce conductivity by 30 to 40%, which may prove useful as a pretreatment or finishing component of a larger treatment system, or in the treatment of legacy discharges. Design optimization will require identification of the ionic constituents responsible for primary conductivity constituents in various regions, long-term monitoring data of current systems that may not have been designed primarily to treat conductivity, and evaluation of the environmental factors governing underlying biogeochemical processes responsible for specific ion removals. Ideally, field-scale monitoring efforts will concurrently evaluate downstream impacts on aquatic ecology to better inform continually adapting regulatory strategies to prevent species extirpation.

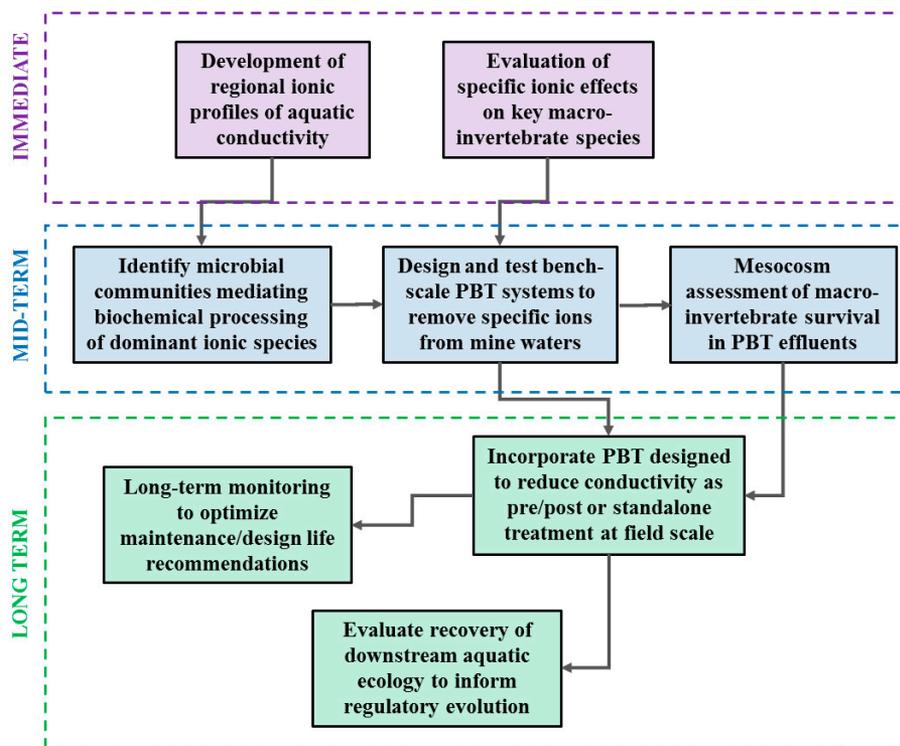


Fig. 3. Summary of immediate, mid-term, and long-term research needs for the use of passive biological treatment systems to decrease conductivity in mine waters.

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