The Occurrence of Legacy P Soils and Potential Mitigation Practices Using Activated Biochar

Vasile Cerven1,*, Jeff M. Novak1, Ariel A. Szögi1, Kenneth Pantuck2, Don W. Watts1, Mark G. Johnson3

1Water and Plant Research Center, Coastal Plains Soil, Agricultural Research Service, United States Department of Agriculture, 2611 W. Lucas Street, Florence, SC 29501, USA
2State Assistance & Partnerships Branch Infrastructure and Assistance Section, Water Division, U.S. Environmental Protection Agency, Philadelphia, PA 19103, USA
3Center for Public Health and Environmental Assessment, Pacific Ecological Systems Division, U.S. Environmental Protection Agency, Corvallis, OR 97333, USA

Abstract

The long-term application of manures in watersheds with dense animal production has increased soil phosphorus (P) concentration, exceeding plant and soil assimilative capacities. The P accumulated in soils that are heavily manured and contain excess extractable soil P concentrations is known as legacy P. Runoff and leaching can transport legacy P to ground water and surface water bodies, contributing to water quality impairment and environmental pollution, such as eutrophication. This review article analyzes and discusses current and innovative management practices for soil legacy P. Specifically, we address the use of biochar as an emerging novel technology that reduces P movement and bioavailability in legacy P soils. We illustrate that properties of biochar can be affected by pyrolysis temperature and by various activating chemical compounds and by-products. Our approach consists of engineering biochars, using an activation process on poultry litter feedstock before pyrolysis to enhance the binding or precipitation of legacy P. Finally, this review article describes previous examples of biochar activation and offers new approaches to the production of biochars with enhanced P sorption capabilities.

Keywords

soils; legacy P soils; activated biochar

*Correspondence: vasile.cerven@usda.gov.

Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

Author Contributions: All authors contributed to this project. Individual contributions to the following categories are as follows: Conceptualization, J.M.N., M.G.J., and K.P.; methodology, J.M.N., M.G.J., K.P., and D.W.W.; funding, K.P. and M.G.J.; formal analysis, J.M.N., A.A.S., M.G.J., and V.C.; writing—original draft preparation, V.C., J.M.N., A.A.S., M.G.J., and D.W.W.; writing—review and editing, J.M.N., A.A.S., M.G.J., V.C., and D.W.W. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.
1. Introduction

The intensification of agricultural production through inorganic and organic fertilizers leads to crop yield increase and productivity in higher scale livestock operations. Although these agricultural intensifications are increasingly benefiting sustainable food production and security, they also increase concerns about the deterioration of environmental quality, soil nutrient balance, and crop productivity. This environmental concern is significant when agricultural waste products are used as a soil amendment, particularly in fields close to watersheds with intensive livestock production operations. For example, the intensive animal production system in the Chesapeake Bay Watershed area generates about 36 million metric tons of livestock manure per year [1].

Manure, (Figure 1) especially from poultry, is a leading source of P pollution in Chesapeake Bay [2], containing on average 32.6 kg ton⁻¹ of total N and 31.3–35.4 kg ton⁻¹ P₂O₅ of chicken litter [3,4]. A long-term trend for P accumulation was observed in topsoil (0–30 cm) over 12 years, as reported by [5]. In their study, P from poultry manure accumulated beyond plant nutritional requirements because the manure was applied at the agronomic N-recommended rates in a corn–soybean rotation system.

While livestock manure is a valuable resource for sustainable soil management and the supply of plant nutrients (e.g., N, nitrogen; P; and K, potassium), implementation of appropriate livestock manure management protocols is crucial for sustainable crop production and environmental quality. The need for manure guidelines becomes apparent when it is indiscreetly applied to soil as an organic fertilizer in small geographic areas with intensive animal production systems. It has been reported that manure application based on plant N nutrient requirements accumulates heavy metals [6,7] and excess soil P [8,9]. Current manure management practices based on crop N uptake requirements are unsustainable because of high risks of water quality impairment and soil nutrient and heavy metal concentration imbalances.

Although the agronomic soil P test is extensively used for making soil fertility recommendations, the soil P storage capacity (SPSC) concept has been proposed as a diagnostic tool for the assessment of the potential of P movement from the field environment to surface waters; SPSC can also be used to estimate legacy P loss at excessive concen [10] rations for soils in the eastern and central parts of the United States. The SPSC is based on a threshold molar ratio of extractable P/(Al + Fe) called the soil P saturation ratio (PSR), above which water soluble P abruptly increases. The research results revealed that [11] the degree of P saturation (DPS), which relates a measure of P already adsorbed by the soil to its adsorption capacity, could be an indicator of the soil’s P release capability. Particularly, the threshold DPS (Mehlich-1 extract) of 30% is recommended for Florida sands, while DPS values of 31–60% warrant caution with regard to the further addition of P to land, and DPS values of >60% indicate soils as contributors to water quality impairment [12]. As a result, P stability in soil with values below the threshold indicate that P release from the soil is minimal [13]. Kleinman and Sharpley’s [14] research results showed that Mehlich-3 extractable P can effectively be used to estimate P sorption saturation for over a wide range of acidic and alkaline soils as well.
Research results revealed that the long-term application of manure above plant nutritional requirements led to soil P accumulation, which is a potential source of environmental pollution [15]. For example, Sharpley et al. [16] reported higher water-extractable (11–85 mg kg\(^{-1}\)) and Mehlich-3 extractable P concentrations (82–2840 mg kg\(^{-1}\)) in 0–5 cm of soils following 10–25 years of manure (dairy, poultry, and swine) applications, as compared to water-extractable P (0.6–6 mg kg\(^{-1}\)) and Mehlich-3 extractable P (4.0–64 mg kg\(^{-1}\)) concentrations in untreated soils. The increase in both water- and Mehlich-3 extractable P in the heavily manured soil is 18–14 and 20–44-fold, respectively, higher than that for soil without manure application. Indeed, applied manure N and P are higher than the soil’s assimilative capacity and plant’s nutrient needs. This condition can result in promoting quality declines in water resources through soil leaching and runoff [17,18].

Phosphorus movement and accumulation in soils have been under investigation for several decades [19]. Novak et al. [17] reported P accumulation in soil and movement to a greater soil depth (60–152 cm) beneath a spray field that applied swine manure to a grass crop. These researchers speculated that severe P leaching was due to an exceedance of the soil’s profile P sorption capacity. Other researchers reported similar findings where the intensive over-application of swine manure to the same field might have overwhelmed the P sorptive capacity of Coastal Plain soils, which subsequently affected shallow groundwater quality [11,20]. Additionally, storm events will exacerbate water quality impairment linked to soil P buildup by increasing P runoff into waterways, leading to eutrophication and negatively impacting water quality [21,22]. Therefore, the development of a new management strategy to eliminate legacy P losses from P-overloaded soils is vital for environmental sustainability. Moreover, P as a resource is needed since global P supplies are not infinite [23].

### 2. Management Practices That Reduce Agricultural Losses of Legacy P

It is important to develop the best agronomic management practices capable of controlling legacy P losses in agricultural soils, especially its dissolved forms. The overall goal is to minimize P movement and not to create water quality impairment that exacerbates environmental pollution. These practices intend to reduce legacy P leaching as one of the main pathways of its loss, largely in sandy soils in the Southeastern USA, which have limited soil phosphorus storage capacity and high infiltration rates [11,24]. As the research results have revealed [17,25], the long-term application of animal manure caused strong accumulation and the downward movement of dissolved P through the soil profile. Phosphorus movement through the soil profile also presents threats to water quality. For example [26], reported that during storms, the rain infiltrating high P topsoil mobilized the dissolved P into groundwater, causing considerable P movement as deep as 1.5 m. Similarly, Kleinman et al. [27] also observed that overland flow from fields to ditches accounted for about 8% of annual ditch P export, and that more than 90% of P transport from fine-textured Delmarva soils to field ditches occurred in subsurface flow. Therefore, controlling dissolved P losses from agricultural soils to surface waters is challenging because conservation practices mostly prevent (particulate) soil P losses.
2.1. Agronomic Practices

Here we describe management practices that reduce legacy soil P, which is vital to the minimization of P losses from agricultural soils, and those that mitigate the risk of eutrophication. A variety of agronomic practices exist to reduce legacy P concentrations and movement from agricultural soils. These agronomic practices target the P transport pathway and involve the implementation of soil and nutrient management practices [28]. Several agronomic practices addressing legacy P losses include conservation tillage [29,30] and cover crops [31,32]. These practices create vegetative buffer strips along water bodies [33,34]. The implementation of these buffer strips also includes grass–legume forage systems [35] combined with the best nutrient management efforts such as the land application of P-sorbing materials; treating manure with aluminum sulfate; increasing plant P use efficiencies; and increasing the N:P ratio of manure [36,37]. However, these best management practices can be more effective on sediment-bound P in the runoff, but less effective in reducing dissolved P loss from sandy soils on the Delmarva Peninsula [38,39].

2.2. P-Hyperaccumulator Plants

An emerging technology that ameliorates the legacy P issue is phytoremediation. This technology involves the use of plants for the uptake of pollutants from the environment. Several plant species such as Indian mustard (Brassica juncea L.), corn (Zea mays L.), and annual ryegrass (Lolium multiflorum) grown on a highly phosphorus-enriched soil exhibited higher P uptake and can thus be employed for P phytoremediation [40,41]. White lupin (Lupinus albus L.) responded to the level of soil residual P in the Coastal Plain of South Alabama and can hyperaccumulate P [42]. Indeed, Novak and Chan [43] proposed to reduce higher concentrations of soil P in the fields with excess P levels by using P-hyperaccumulator plants or by growing plants that are genetically modified through traditional breeding and transgenic technique strategies in order to increase their P-uptake characteristics. A recent study revealed that P adsorption in transgenic plants increased 3-fold as compared to that in host plants (Torenia hybrid cv. Summer wave blue; Petunia hybrid cv. Surfinia purple mini; and Verbena hybrid cv. Temari scarlet), according to [44]. The transgenic plants showed hyperaccumulation of inorganic P in their leaves and accelerated their absorption rates in hydroponic solutions.

2.3. P-Binding Technologies

2.3.1. P-Sorbing Materials—P-sorbing materials offer a new approach to the reduction of dissolved P concentration and its movement. Natural and industrial by-products commonly contain chemical compounds such as iron (Fe), aluminum (Al), calcium (Ca), and magnesium (Mg) oxides or oxyhydroxides. P-sorbing materials have been applied as a soil amendment at rates of 2.5%, 5.0%, 7.5%, and 10% (w/w) [45]. These compounds can potentially chemically bind P through various sorption mechanisms or through the formation of insoluble precipitation phases [46,47]. For example, the removal efficiencies for cumulative P from swine wastewater using the marl gravel media filter system ranged from 37% to 52% [48]. Another industrial by-product—the acid mine drainage (AMD) treatment residuals—was found to decrease plant available P in poultry litter [49], in soil [50,51], as well as when used in a drainage ditch [52]. Water treatment residuals (WTR),
a by-product of municipal drinking water treatments plants, have a strong affinity to sorb P as well [53], and its adsorption capacity can vary depending on WTR application rates [54]. Research results obtained using P-enriched Coastal Plain sandy soils revealed [45] that applying alum-based WTR into an Autryville and Norfolk soil series significantly increased their Pmax values relative to soils with no WTR addition. Furthermore, the results showed that WTR incorporation into soils with high P concentrations caused larger relative reductions in extractable water soluble P than Mehlich-3 P concentrations [55]. Moreover, coarse-sized WTR aggregates (between 1.0 and >4.0 mm) showed less adsorption capacity than fine-sized (<1.0 mm) aggregates [56]. The addition of Fe/Mn- and P-modified Al-WTR to the soil significantly reduced the concentrations of Pb (up to 60% by Fe/Mn-Al-WTR and 32% by P-Al-WTR) and Cu (up to 45% by Fe/Mn-Al-WTR and 18% by P-Al-WTR) in the shoots and roots of ryegrass as compared to raw Al-WTRs and untreated soil, according to [57].

2.3.2. Naturally Occurring and Waste Materials—It appears that the use of gypsum is a valuable strategy for controlling P movement [58,59]; likewise, there is a large potential in the use of waste materials such as bauxite residuals, fly-ash, wood ash, and slag [52]. Pen et al. [60] observed that using steel slag as the P sorption material in the P removal structure resulted in the removal of 25% of all dissolved P from rainfall and irrigation events during the first five months of structure operation. The other study demonstrated that the maximum adsorption capacity of the fly-ash and bauxite residuals were 29 and 25 g kg\(^{-1}\), respectively [61], and P removal varied based on the chemical properties of the by-products [62,63]. Therefore, P mobility can be controlled by Al, Fe, or Ca depending on their pH. As an example, the P removal by AMD residuals and WTRs was a result of the adsorption to Al- or Fe-oxides/hydroxides or the precipitation of Al- or Fe-phosphates. In contrast, P removal from stormwater by slag materials used in field scale filtration structures occurred through both Ca and Al/Fe mechanisms [64]. The mobility of P is also highly pH dependent. Lee et al. [65] observed that a higher P adsorption rate onto WTR was obtained at low reaction media (pH 4) as compared to neutral media, with the lowest P adsorption rate at pH 9. As Silva [66] reported, the two highest peaks occur in the soil pH acid range of pH 4–5.5, where P precipitates with Fe and Al, while the third peak occurs in alkaline soils at around pH 8.0, when P is precipitated primarily by Ca.

2.4. Biochar

Among the several chemical/physical methods developed to reduce legacy soil P [55,56], biochar emerges as a novel technology for the binding of P-forms [67,68]. Biochar is the carbonaceous by-product from the thermochemical conversion of organic materials that commonly contain high amounts of cellulose, hemicellulose, or lignin [69]. Kang et al. [70] observed that biochar application improved the soil bulk density, soil organic carbon, pH, and cation exchange capacity in field soil, which positively affected corn and Chinese cabbage growth. Biochar can be produced from a wide range of biomass feedstocks including woodchips from cedar, cypress, bamboo, pine sources [71,72], agricultural by-products, or residues of agricultural wastes including pecan shells, peanut shells, cotton gin trash, wheat straw, corn straw, corn cobs, rice husk [73,74], and livestock manure [75,76].
The pyrolysis temperature for biochar derived from poultry litter, cattle manure, rice straw, soybean straw, and corn was 450 °C [76]; the temperatures from peanut hull were 400, 500 °C; those from pecan shell were 350, 700 °C; those from switchgrass were 250, 500 °C [73]; that from pine chips, poultry litter was 500 °C [75]; and those from wood chips: Japanese cedar, Japanese cypress, bamboo chips, rice husks, sugarcane bagasse, and poultry manure were 400, 600, and 800 °C [71]. The choice of feedstock for the production of biochar is often decided by local availability of waste produce and transport distance to the pyrolyzer plant [77,78]. After pyrolysis, biochar properties are often modified physically [79,80] or chemically [81,82] to increase its surface area, pore size distribution, and form surface functional groups to increase the biochar’s adsorption capacity [83,84]. Physical biochar engineering techniques include ball milling modification, gas/steam activation, magnetization, and microwave irradiation [85]. Recent research results showed the potential for improving biochar P adsorption capacities by chemical modification [86,87], which includes its activation by different acids (HCl, HNO₃, H₂SO₄, H₃PO₄ and H₂O₂), with different alkali (NaOH, KOH), with other oxidizing agents (KMnO₄, Fe(III)) [85] and salts (MgCl₂, CaCl₂) [82,87,88]. Although recent studies and review papers [75,89] describe biochar’s properties and its role in soil remediation, the efficacy of activated biochar on soil legacy P remediation requires further investigation due to diverse feedstock chemistry [69], activation technologies [90,91], and the complexity of biochar structural properties as well as soil properties [92,93].

We compiled a list of published works that used various chemical/physical activation processes on biochar produced from various feedstocks and how they responded in P sorption experiments. Results in Table 1 reveal that the P adsorption capacity among the biochars varied considerably. We report that from these studies, the Pmax values ranged from 13.6 to 153.4 mg⁻¹.

The studies cited in Table 1 used a number of chemical and physical activation processes on the biochars to improve their physicochemical properties and enhance their adsorption performance. Generally, chemically activating these biochars with these salts resulted in the biochar’s higher P adsorption capacity. MgO-biochar showed better phosphate adsorption in saline soils and the maximum phosphate adsorption capacity was 1.46 times higher than biochar [94]. Phosphates were bound to the Mg-biochar not only by electrostatic adsorption but also by covalent bonds to form magnesium phosphate crystals [88,94]. Moreover, as observed by [83], the P removal efficiency increased with the increasing adsorption dosage. Zheng et al. [96] reported that P was adsorbed by the Mg-Al modified biochar through co-precipitation reaction and an Al-designed biochar showed the highest aqueous stability with little metal dissolution. This designed biochar showed an increase in P adsorption with an increase in metal loading. Additionally, physical activation by modifying feedstock pyrolysis conditions (e.g., temperature, residence time, etc.) resulted in an increasing biochar adsorption capacity with higher pyrolysis temperatures [87,99], which varied across different feedstocks [95].

On a wider scale of use, our proposed concept of “designer” or engineered biochar may provide the means of making biochar to specifically address a targeted contaminant or ameliorate soil deficiency. It was suggested that biochar properties can also be modified...
to remediate problem soils [73]. For example, water holding capacity limitations of sandy soils can be improved with biochar made from pine chips, switchgrass made at 350 °C or miscanthus at 459 °C [100,101]. Similarly, [102] reported that date palm-derived biochar produced at low pyrolysis temperatures (300 °C and 400 °C) improved water retention in sandy soil by 46%. Moreover, biochar with particle sizes <1 mm can increase water conservation in sandy soil more than larger (1–2 mm) particle sizes [103]. As a result, designer biochar applied to nutrient-poor soils have been reported to increase soil fertility properties [104–106] and improve crop growth [107–109].

3. Conclusions and Prospects

Our review article summarizes recent research results using agronomic, physical, and chemical methods as best management practices in soil legacy P reduction. The review highlights the significant inter-relations between biochar properties vs. feedstock source, role of pyrolysis temperature, choice of activation chemical materials, and examples of using designer biochar to decrease soil legacy P concentrations. Additionally, we showed that designer biochar can be produced by chemically activating its parent feedstock with metal salts or other amendments, or through physical processes such as pyrolysis temperature modifications. These last two physico-chemical approaches produce biochar with enhanced P sorption capabilities and serve as alternative management practices in the reduction of legacy P soils. The overall benefit is the reduction of both extractable P concentrations and dissolved P concentrations in legacy P soils with the subsequent benefit of rebalancing soil P levels and reducing non-point source P pollution. Furthermore, biochar can be used as a soil amendment to improve soil quality by reducing the presence of heavy metals in contaminated soils, and as a slow-release fertilizer for improving the fertility of the agricultural soils. However, we suggest that further biochar research needs to adjust biochar application rates under field environment conditions. In this way, high-risk pollution from heavy metals contained in those by-products will be reduced.

Acknowledgments:

This work was made possible through an Interagency Agreement between the U.S. Department of Agriculture-Agricultural Research Service and the U.S. Environmental Protection Agency (EPA Agreement Number 60-6082-8-002). The mention of tradenames or commercial products in this article was solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. The U.S. Department of Agriculture is an equal opportunity employer.

Funding:

This research was funded by the U.S. Department of Agriculture, Agricultural Research Service, Project Number 6082-12630-001-15I, Accession No. 435628.

Data Availability Statement:

Not Applicable.
References

1. Kleinman P; Blunk KS; Bryant R; Saporito L; Beegle D; Czymmek K; Ketterings Q; Sims T; Shortle J; McGrath J. Managing manure for sustainable livestock production in the Chesapeake Bay Watershed. J. Soil Water Conserv 2012, 67, 54A–61A.

2. Sutton R; Cox C. Bay out of Balance: Broken System Allows Phosphorus Pollution to Worsen. Environmental Working. 2010, pp. 1–33. Available online: https://www.ewg.org/bay_out_of_balance_full_report (accessed on 4 May 2021).

3. Chastain JP; Camberato J; Skewes P. Poultry Manure Production and Nutrient Content 2001, 3b-1–17. Available online: https://www.clemson.edu/extension/camm/manual/poultry/pch3b_00.pdf (accessed on 4 May 2021).

4. Davis MA; Sloan DR; Kidder G; Jacobs RD. Poultry Manure as a Fertilizer. UF IFAS Extension Publication PS1/AA205. 2017. Available online: https://edis.ifas.ufl/publication/AA205 (accessed on 4 May 2021).

5. Hoover NL; Kanwar R; Soupir ML; Pederson C. Effects of Poultry Manure Application on Phosphorus in Soil and Tile Drain Water Under a Corn-Soybean Rotation. Water Air Soil Pollut. 2015, 226, 1–12.

6. Provolo G; Manuli G; Finzi A; Lucchini G; Riva E; Sacchi GA. Effect of Pig and Cattle Slurry Application on Heavy Metal Composition of Maize Grown on Different Soils. Sustainability 2018, 10, 2684.

7. Haroon B; Hassan A; Abbasi AM; Ping A; Yang S; Irshad M. Effects of co-composted cow manure and poultry litter on the extractability and bioavailability of trace metals from the contaminated soil irrigated with wastewater. J. Water Reuse Desalination 2019, 10, 17–29.

8. Toth JD; Dou Z; Ferguson JD; Galligan DT; Ramberg CF Jr. Nitrogen-vs. phosphorus -based dairy manure application to field crops. J. Environ. Qual 2006, 35, 2302–2312. [PubMed: 17071901]

9. Sadeghpour A; Ketterings QM; Vermeulen F; Godwin GS; Czymmek KJ. Soil Properties under Nitrogen- vs. Phosphorus-Based Manure and Compost Management of Corn. Soil Sci. Soc. Am. J 2016, 80, 1272–1282.

10. Dari B; Nair VD; Sharpley AN; Kleinman P; Franklin D; Harris WG. Consistency of the threshold phosphorus saturation ratio across a wide geographic range of acid soils. Agrosyst. Geosci. Environ 2018, 1, 1–8.

11. Nair VD; Harris WG. Soil phosphorus storage capacity for environmental risk assessment. Adv. Agric 2014, 2014, 723064.

12. Nair VD; Portier KK; Graetz DA; Walker ML. An environmental threshold for degree of phosphorus saturation in sandy soils. J. Environ. Qual 2004, 33, 107–113. [PubMed: 14964364]

13. Nair VD. Soil phosphorus saturation ratio for risk assessment in land use systems. Front. Environ. Sci 2014, 2.

14. Kleinman PJA; Sharpley AN. Estimating soil phosphorus sorption saturation from Melich-3 data. Commun. Soil Sci. Plant Anal 2002, 33, 1825–1839.

15. Sharpley A; Jarvie HP; Buda A; May L; Spears B; Kleinman P. Phosphorus legacy: Overcoming the effects of past management practices to mitigate future water quality impairment. J. Environ. Qual 2013, 42, 1308–1326. [PubMed: 24216410]

16. Sharpley AN; McDowell RW; Kleinman PJA. Amounts, forms, and solubility of phosphorus in soils receiving manure. Soil Sci. Soc. Am. J 2004, 68, 2048–2057.

17. Novak JM; Watts DW; Hunt PG; Stone KC. Phosphorus movement through a Coastal Plain soil after a decade of intensive swine manure application. J. Environ. Qual 2000, 29, 1310–1315.

18. Szogi AA; Vanotti M; Ro K. Methods for treatment of Animal manures to reduce nutrient pollution prior to soil application. Curr. Pollut. Rep 2015, 1, 47–56.

19. Sims JT; Simard RR; Joern BC. Phosphorus loss in agricultural drainage: Historical perspective and current research. J Environ. Qual 1998, 27, 277–293.

20. Azevedo RP; Salcedo IH; Lima PA; Fraga VDS; Lana RMQ. Mobility of phosphorus from organic and inorganic source materials in a sandy soil. Int. J. Recycl. Org. Waste Agric 2018, 7, 153–163.
21. Sharpley AN; Chapra SC; Wedepohl R; Sims JT; Daniel TC; Reddy KR Managing agricultural phosphorus for protection of surface waters: Issues and options. J. Environ. Qual 1994, 23, 437–451.

22. Novak JM; Stone KC; Watts DW; Johnson MH Dissolved phosphorus transport during storm and base flow conditions from an agriculturally intensive southeastern coastal plain watershed. Trans. ASAE 2003, 46, 1355–1363.

23. Cordell D; White S. Life’s bottleneck: Sustaining the world’s phosphorus for a food secure future. Annu. Rev. Environ. Resour 2014, 39, 161–188.

24. Kleinman PJA The persistent environmental relevance of soil phosphorus sorption saturation. Curr. Pollut. Rep 2017, 3, 141–150.

25. Koopmans GF; Chardon WJ; McDowell RW Phosphorus movement and speciation in a sandy soil profile after long-term animal manure applications. J. Environ. Qual 2007, 36, 305–315. [PubMed: 17215240]

26. Vadas PA; Srinivasan MS; Kleinman PJA; Schmidt JP; Allen AL Hydrology and groundwater nutrient concentrations in a ditch-drained agroecosystem. J. Soil Water Conserv 2007, 62, 178–187.

27. Kleinman PJA; Allen AL; Needelman BA; Sharpley AN; Vadas PA; Saporito LS; Folmar GJ; Bryant RB Dynamics of phosphorus transfers from heavily manured coastal plains soils to drainage ditches. J. Soil Water Conserv 2007, 62, 225–235.

28. Dodd RJ; Sharpley AN Conservation practice effectiveness and adoption: Unintended consequences and implications for sustainable phosphorus management. Nutr. Cycl. Agroecosyst 2015, 104, 373–392.

29. Uribe N; Corzo G; Quintero M; Van Griensen A; Solomatine D. Impact of conservation tillage on nitrogen and phosphorus runoff losses in a potato crop system in Fuquene watershed, Columbia. Agric. Water Manag 2018, 209, 62–72.

30. Osmond D; Shober A; Sharpley AN; Duncan EW; Hoag DLK Increasing the effectiveness and adoption of agricultural phosphorus management strategies to minimize water quality impairment. J. Environ. Qual 2019, 48, 1204–1217. [PubMed: 31589706]

31. López-Vicente M; Calvo-Seas E; Álvarez S; Cerdà A. Effectiveness of cover crops to reduce loss of soil organic matter in a rainfed vineyard. Land 2020, 9, 230.

32. Aronsson H; Hansen EM; Thomsen IK; Liu J; Ogaard AF; Kankanen H; Ulen B. The ability of cover crops to reduce nitrogen and phosphorus losses from arable land in southern Scandinavia and Finland. J. Soil Water Conserv 2016, 71, 41–55.

33. Roberts WM; Stutter MI; Haygarth PM Phosphorus retention and remobilization in vegetated buffer strips: A review. J Environ. Qual 2012, 41, 389–399. [PubMed: 22370401]

34. Singh G; Kaur G; Williard K; Schoonover J; Nelson KA Managing phosphorus loss from agroecosystems of the Midwestern United States: A review. Agronomy 2020, 10, 561.

35. Mclennon E; Solomon JKQ; Davison J. Grass-legume forage systems effect on phosphorus removal from a grassland historically irrigated with reclaimed wastewater. Sustainability 2020, 12, 2256.

36. Sharpkey AN; Daniel T; Sims T; Lemunyon J; Stevens R; Parry R. Agricultural Phosphorus and Eutrophication, 2nd ed.; ARS-149; USDA: Springfield, VA, USA, 2003; 38p. Available online: https://naldc.nal.usda.gov/download/26693/pdf (accessed on 20 May 2021).

37. Qin Z; Shober A. The challenges of managing legacy phosphorus losses from manure-impacted agricultural soils. Curr. Pollut. Rep 2018, 4, 265–276.

38. Kleinman P; Sharpley A; Buda A; McDowell R; Allen A. Soil controls of phosphorus in runoff: Management barriers and opportunities. Can. J. Soil Sci 2011, 91, 329–338.

39. Kleinman PJA; Fanelli RM; Hirsch RM; Buda AR; Easton ZM; Wainger LA; Brosch C; Lowenfish M; Collick AS; Shirimorehammad M; et al. Phosphorus and the Chesapeake Bay: Lingering issues and emerging concerns for agriculture. J Environ. Qual 2019, 48, 1191–1203. [PubMed: 31589735]

40. Delorme TA; Angle JS; Coale FJ; Chaney RL Phytoremediation of phosphorus-enriched soils. Int. J. Phytoremediation 2000, 2, 173–181.

41. Sistani KR; Pederson GA; Brink GE; Rowe DE Nutrient uptake by ryegrass cultivars and crabgrass from a highly phosphorus-enriched soil. J. Plant Nutr 2003, 26, 2521–2535.
42. Mullins GL; Reeves DW Response of lupin to soil pH and residual phosphorus. In Proceedings of the Eighth International Lupin Conference, Asilomar, CA, USA, 11–16 May 1996; p. 4. Available online: https://cdn.sare.org/wp-content/uploads/20171204123943/904LS93-053.020.pdf (accessed on 6 May 2021).

43. Novak JM; Chan ASK Development of P-hyperaccumulator plant strategies to remediate soils with excess P concentrations. Crit. Rev. Plant Sci 2002, 21, 493–509.

44. Matsui K; Togami J; Mason JG; Chandler SF; Tanaka Y. Enhancement of phosphate absorption by garden plants by genetic engineering: A new tool for phytoremediation. BioMed Res. Int 2013, 2013, 182032.

45. Novak JM; Watts DW Increasing the phosphorus sorption capacity of southeastern coastal plain soils using water treatment residuals. Soil Sci. 2004, 169, 206–214.

46. Buda AR; Koopmans GF; Bryant RB; Chardon WJ Emerging technologies for removing nonpoint phosphorus from surface water and groundwater: Introducction. J. Environ. Qual 2012, 41, 621–627. [PubMed: 22565243]

47. Leader JW; Dunne EJ; Reddy KR Phosphorus sorbing materials: Sorption dynamics and physicochemical characteristics. J. Environ. Qual 2008, 37, 174–181. [PubMed: 18178890]

48. Szögi AA; Humenik FJ; Rice JM; Hunt PG Swine wastewater treatment by media filtration. J. Environ. Sci. Health Part B 1997, 32, 831–843.

49. McDonald LM Acid mine drainage treatment residuals to reduce phosphorus in poultry litter. J. Am. Soc. Min. Reclam 2011, 2011, 409–418.

50. Adler PR; Sibrell P. Sequestration of phosphorus by acid mine drainage floc. J. Environ. Qual 2003, 32, 1122–1129. [PubMed: 12809314]

51. Church CD; Hedin RS; Bryant RB; Wolfe AG; Spargo JT; Elkin KR; Saporito L; Kleinman PJA Phosphorus runoff from soils receiving liquid dairy and swine manures amended with mine drainage residuals. Appl. Eng. Agric 2021, 37, 351–352.

52. Penn CJ; Bryant RB; Kleinman PJA; Allen AL Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials. J. Soil Water Conserv 2007, 62, 269–276.

53. Ippolito JA; Barbaric KA; Heil DM; Chandler JP; Redente EF Phosphorus retention mechanisms of a water treatment residuals. J. Environ. Qual 2003, 32, 1857–1864. [PubMed: 14535330]

54. Ippolito JA Aluminum-based water treatment residuals use in a constructed wetland for capturing urban runoff phosphorus: Column study. Water Air Soil Pollut. 2015, 226, 1–8.

55. Novak JM; Watts DW An alum-based water treatment residuals can reduce extractable phosphorus concentrations in three phosphorus-enriched coastal plain soils. J. Environ. Qual 2005, 34, 1820–1827. [PubMed: 16151234]

56. Novak JM; Watts DW Water reatment residuals aggregate size influences phosphorus sorption kinetics and pmax values. Soil Sci. 2005, 170, 425–432.

57. Wang Q; Shaheen SM; Jiang Y; Li R; Slaňy M; Abdelrahman H; Kwon E; Bolan N; Rinklebe J; Zhang Z. Fe/Mn- and P-modified drinking water treatment residuals reduced Cu and Pb phytoavailability and uptake in a mining soil. J. Hazard. Mater 2021, 403, 123628.

58. Favaretto N; Norton LD; Johnston CT; Bigham J; Sperrin M. Nitrogen and phosphorus leaching as affected by gypsum amendment and exchangeable calcium and magnesium. Soil Sci. Soc. Am. J 2012, 76, 575–585.

59. Grubb KL; McGrath JM; Penn CJ; Bryant RB Effect of land application of phosphorus-saturated gypsum on soil phosphorus in a laboratory incubation. Appl. Environ. Soil Sci 2012, 2012, 506951.

60. Penn CJ; McGrath JM; Rounds E; Fox G; Heeren D. Trapping phosphorus in runoff with a phosphorus removal structure. J Environ. Qual 2012, 41, 672–679. [PubMed: 22565249]

61. Penn CJ; Bryant RB; Callahan MP; McGrath JM Use of industrial by-products to sorb and retain phosphorus. Commun. Soil Sci. Plant Anal 2011, 42, 633–644.

62. Stoner D; Penn C; McGrath J; Warren J. Phosphorus removal with by-products in a flow-through settings. J. Environ. Qual 2012, 41, 654–663. [PubMed: 22565247]

63. Agyin-Birikorang S; O’Connor GA; Jacobs LW; Makris KC; Brinton SR Long-term phosphorus immobilization by a drinking water treatment residual. J. Environ. Qual 2007, 36, 316–323. [PubMed: 17215241]
64. Qin Z; Shober A; Scheckel K; Penn CJ; Turner KC. Mechanisms of phosphorus removal by phosphorus sorbing materials. J. Environ. Qual 2018, 47, 1232–1241. [PubMed: 30272772]
65. Lee LY; Wang B; Guo H; Hu JY; Ong SL. Aluminum-based water treatment residue reuse for phosphorus removal. Water 2015, 7, 1480–1496.
66. Silva G. The Peaks and Valleys of Phosphorus Fixation. MSU Extension. Available online: https://extension.msu.edu (accessed on 12 June 2021).
67. Novak JM; Ro K; Ok YS; Sigua G; Spokas K; Uchimiya S; Bolan N. Biochars multifunctional role as a novel technology in the agricultural, environmental, and industrial sectors. Chemosphere 2016, 142, 1–3. [PubMed: 26166785]
68. Yang X; Zhang S; Lu M; Liu L. Preparation and modification of biochar materials and their application in soil remediation. Appl. Sci 2019, 9, 1365.
69. Spokas KA; Cantrell KB; Novak J; Archer DW; Ippolito JA; Collins HP; Boateng AA; Lima IM; Lamb MC; McAlloon AJ. Biochar: A synthesis of its agronomic impact beyond carbon sequestration. J. Environ. Qual 2012, 41, 973–989. [PubMed: 22751040]
70. Kang S-W; Yun J-J; Park J-H; Cho J-S. Exploring suitable biochar application rates with compost to improve upland field environment. Agronomy 2021, 11, 1136.
71. Kameyama K; Miyamoto T; Iwata Y; Shiono T. Influence of feedstock and pyrolysis temperature on the nitrate adsorption of biochar. Soil Sci. Plant Nutr 2016, 62, 180–184.
72. Novak JM; Sigua GC; Ducey TF; Watts DW; Stone KC. Designer biochars impact on corn grain yields, biomass production, and fertility properties of a highly-weathered ultisol. Environments 2019, 6, 64.
73. Novak JM; Lima I; Xing B; Gaskin JW; Steiner C; Das KC; Ahmeda M; Rehrah D; Watts DW; Busscher WJ. Characterization of designer biochar produced at different temperature and their effects on a loamy sand. Ann. Environ. Sci 2009, 3, 195–206.
74. Shen Y. Rice husk-derived activated carbons for adsorption of phenolic compounds in water. Glob. Chall 2018, 2, 1800043.
75. Novak JM; Johnson MG; Spokas KA. Concentration and release of phosphorus and potassium from lignocellulosic- and manure-based biochar for fertilizer reuse. Front. Sustain. Food Syst 2018, 2, 54.
76. Sarfaraz Q; da Silva LS; Drescher GL; Zafar M; Severo FF; Kokkonen A; Molin GD; Shafi MI; Solaiman ZM. Characterization and carbon mineralization of biochar produced from different animal manures and plant residues. Sci. Rep 2020, 10, 955. [PubMed: 31969672]
77. Ippolito JA; Cui L; Kammann C; Wrage-Mönning N; Estavillo JM; Fuertes-Mendizabal T; Cayuela ML; Sigua G; Novak J; Spokas K. Feedstock choice, pyrolysis temperature and type influence biochar characteristics: A comprehensive meta-data analysis review. Biochar 2020, 2, 421–438.
78. Keske C; Godfrey T; Hoag DL; Abedin J. Economic feasibility of biochar and agriculture coproduction from Canadian black spruce forest. Food Energy Secur. 2020, 9, 188.
79. Ro K; Lima IM; Reddy GB; Jackson MA; Gao B. Removing gaseous NH3 using biochar as an adsorbent. Agriculture 2015, 5, 991–1002.
80. Bergna D; Varila T; Romar H; Lassi U. Comparison of the properties of activated carbons produced in one-stage and two-stage process. J. Carbon Res 2018, 4, 41.
81. Shamsuddin M; Yusoff N; Sulaiman M. Synthesis and characterisation of activated carbon produced from kenaf core fiber using H3PO4 activation. Procedia Chem. 2016, 19, 558–565.
82. Yin Q; Wang R; Zhao Z. Application of Mg-Al-modified biochar for simultaneous removal of ammonium, nitrate, and phosphate from eutrophic water. J. Clean. Prod 2018, 176, 230–240.
83. Li J; Li B; Huang H; Lv X; Zhao N; Guo G; Zhang D. Removal of phosphate from aqueous solution by dolomite-modified biochar derived from urban dewatered sewage sludge. Sci. Total Environ 2019, 687, 460–469. [PubMed: 31212154]
84. Zheng Y; Zimmerman AR; Gao B. Comparative investigation of characteristics and phosphate removal by engineered biochars with different loadings of magnesium, aluminum, or iron. Sci. Total Environ 2020, 747, 141277.
85. Li S; Chan CY; Sharbatmaleki M; Trejo H; Delagah S. Engineered biochar production and its potential benefits in a closed-loop water-reuse agriculture system. Water 2020, 12, 2847.
86. Takaya C; Fletcher L; Singh S; Okwuosa U; Ross A. Recovery of phosphate with chemically modified biochars. J. Environ. Chem. Eng 2016, 4, 1156–1165.
87. Yin Q; Liu M; Ren H. Removal of ammonium and phosphate from water by Mg-modified biochar: Influence of Mg pretreatment and pyrolysis temperature. BioResources 2019, 14, 6203–6218.
88. Shin H; Tiwari D; Kim D-J Phosphate adsorption/desorption kinetics and P bioavailability of Mg-biochar from ground coffee waste. J. Water Process. Eng 2020, 37, 101484.
89. Sajjadi B; Chen W-Y; Egiebor NO A comprehensive review on physical activation of biochar for energy and environmental applications. Rev. Chem. Eng 2019, 35, 735–776.
90. Hagemann N; Spokas K; Schmidt H-P; Kägi R; Böhlma RA; Bucheli TD Activated carbon, biochar and charcoal: Linkages and synergies across pyrogenic carbon’s ABCs. Water 2018, 10, 182.
91. Ukanwa K; Patchigolla K; Sakrabani R; Anthony E; Mandavagane S. A review of chemicals to produce activated carbon from agricultural waste biomass. Sustainability 2019, 11, 6204.
92. Novak J; Busscher WJ; Watts DW; Armonette JA; Ippolito JA; Lima IM; Gaskin J; Das KC; Steiner C; Ahmedna M. Biochar impact on soil-moisture storage in an ultisol and two aridisols. Soil Sci. 2012, 177, 310–320.
93. Zheng X; Wu J; Yan X; Qin G; Zhou R; Wei Z. Biochar-induced soil phosphate sorption and availability depend on soil properties: A microcosm study. J. Soils Sediments 2020, 20, 3846–3856.
94. Wu L; Wei C; Zhang S; Wang Y; Kuzyakov Y; Ding X. MgO-modified biochar increases phosphate retention and rice yields in saline-alkaline soil. J. Clean. Prod 2019, 235, 901–909.
95. Jiang Y-H; Li A-Y; Deng H; Ye C-H; Wu Y-Q; Linnu Y-D; Hang H-L. Characteristics of nitrogen and phosphorus adsorption by Mg-loaded biochar from different feedstocks. Bioresour. Technol 2019, 276, 183–189. [PubMed: 30623874]
96. Zheng Q; Yang L; Song D; Zhang S; Wu H; Li S; Wang X. High adsorption capacity of Mg-Al-modified biochar for phosphate and its potential for phosphate interception in soil. Chemosphere 2020, 259, 127469.
97. Choi Y-K; Jang HM; Kan E; Wallace AR; Sun W. Adsorption of phosphate in water on a novel calcium hydroxide-coated dairy manure-derived biochar. Environ. Eng. Res 2018, 24, 434–442.
98. Riddle M; Bergström L; Schmieder F; Lundberg D; Condron L; Cederlund H. Impact of biochar coated with magnesium (hydro)oxide on phosphorus leaching from organic and mineral soils. J. Soils Sediments 2018, 19, 1875–1889.
99. Trinh VT; Nguyen TMP; Van HT; Hoang LP; Nguyen TV; Ha LT; Vu XH; Pham TT; Quang NV; Nguyen XC Phosphate adsorption by silver nanoparticles-loaded activated carbon derived from tea residue. Sci. Rep 2020, 10, 3634. [PubMed: 32107469]
100. Novak JM; Busscher WJ Selection and use of designer biochar to improve characteristics of southeastern USA coastal plain degraded soils. In Advanced Biofuels and Bioproducts; Lee J, Ed.; Springer: New York, NY, USA, 2012.
101. Carvalho ML; De Moraes MT; Cerri CEP; Cherubin MR Biochar amendment enhances water retention in a tropical sandy soil. Agriculture 2020, 10, 62.
102. Alotaibi KD; Schoenau JJ Addition of biochar to a sandy desert soil: Effect on crop growth, water retention and selected properties. Agronomy 2019, 9, 327.
103. Alghamdi AG; Alkhasha A; Ibrahim HM Effect of biochar particle size on water retention and availability in a sandy loam soil. J. Saudi Chem. Soc 2020, 24, 1042–1050.
104. Jien S-H; Wang C-S Effects of biochar on soil properties and erosion potential in a highly weathered soil. Catena 2013, 110, 225–233.
105. Karim MR; Halim MA; Gale NV; Thomas SC Biochar effects on soil physicochemical properties in degraded managed ecosystem in northeastern Bangladesh. Soil Syst. 2020, 4, 69.
106. Shetty R; Prakash NB Effect of different biochars on acid soil and growth parameters of rice plants under aluminium toxicity. Sci. Rep 2020, 10, 12249. [PubMed: 32704053]
107. Baronti S; Alberti G; Vedove GD; Di Gennaro F; Fellet G; Genesio L; Miglietta F; Peressotti A; Vaccari FP The biochar option to improve plant yields: First results from some field and pot experiments in Italy. Ital. J. Agron 2010, 5, 3–12.
108. Trupiano D; Cocozza C; Baronti S; Amendola C; Vaccari FP; Lustrato G; Di Lonardo S; Fantasma F; Tognetti R; Scippa GS The effects of biochar and its combination with compost on lettuce (Lactuca sativa L.) growth, soil properties, and soil microbial activity and abundance. Int. J. Agron 2017, 2017, 1–12.

109. Olszyk D; Shiroyama T; Novak J; Cantrell K; Sigua G; Watts D; Johnson MG Biochar affects growth and shoot nitrogen in four crops for two soils. Agrosyst. Geosci. Environ 2020, 3, 22.
**Figure 1.**
Chesapeake Bay region (A) containing high poultry populations (B), producing mounds of poultry litter manure (C), and a eutrophic wetland (D) from elevated stream water phosphorus concentrations (photos courtesy of Ariel Szögi and Jeff Novak, USDA-ARS).
Table 1.

Phosphorus (P) adsorption capacity of activated biochars derived from various feedstocks.

| Feedstock       | P Form | Activation | Carbonization | Adsorption | References |
|-----------------|--------|------------|---------------|------------|------------|
|     | Agents | Activation | Capacity     |            |            |
|     | (°C)   |            | qmax          |            |            |
| Peanut shells   | P      | 1 M MgCl₂  | 600           | 18.9       |            |
| Poplar chips    | PO₄⁻³  | 4% MgCl₂   | 600           | 89.9       |            |
| Soybean straw   | PO₄⁻³  | 2 M MgCl₂  | 500           | 74.5       |            |
| Ground coffee   | P      | 3 M MgCl₂  | 500           | 56         |            |
| Sewage sludge+  | PO₄⁻³  | Dolomite   | 800           | 29.2       |            |
| Banana straw    | P      | 1 M MgCl₂  | 430           | 31.2       |            |
| Wheat straw     | PO₄⁻³  | 0.5 M MgCl₂⁺|             |            |            |
|                 |        |            | 0.5 M AlCl₃  | 600        | 153.4      |
| Dairy manure    | PO₄⁻³  | 2 M CaCl₂  | 500           | 13.6       |            |
| Crop residuals  | P      | 3.1 M MgCl₂| 600           | 65.4       |            |
| Tea residuals   | PO₄⁻³  | 0.001 M AgNO₃|             | 13.6       |            |