Addressing Variable Phosphorus Solubility of Organic Amendments Inthe Chesapeake Bay Program's Phase 6 Watershed Model

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June 2017

Executive Summary

Because land-applied organic amendments (manures and biosolids) have widely differing susceptibilities to phosphorus (P) solubilization by water, total P (TP) content is an unreliable indicator of their potential to impact water quality. While P can be transported by erosion of P-enriched soil particles, much research has addressed P loss to surface runoff and subsurface drainage in the form of dissolved reaction P (DRP) because it is this dissolved P that is algae available and which stimulates eutrophication in aquatic systems.Numerous research studies have shown that P loss as DRP is directly correlated with the water extractable P (WEP) content of surface-spreadsoil amendments. To account for this variable P release to runoff and drainage, states (DE, MD, PA, VA) within the Chesapeake Bay Program (CBP) watershed have P indices which allow for differential weighting of applied P sources based on their WEP. Additionally, the APLE (Annual Phosphorus Loss Estimator) model used in the Phase 6 CBP watershed model (CBP WSM) to simulate P losses allows the percent water extractable P (%WEP = WEP/TP × 100) to be supplied as an input variable for conventional manures.

While the water solubility of P in organic amendments depends on a number of parameters (animal species, diet, storage, treatment, etc.), the chemical composition (aluminum (Al) and iron (Fe) content) is of overriding importance. These elements tend to form insoluble P-containing compounds and thus reduce WEP and environmental P loss. Because Al and Fe are intentionally added in wastewater treatment and chemical modification of manures, biosolids and alum-treated manures are characterized by low dissolved P loss following land application. Additionally, when incorporated into the soil, high Al/Fe containing amendments have lower P phytoavailability, meaning that the soil P pool is less bioavailable and, in turn, less environmentally relevant. The current APLE model does not account for the impact of Fe and Al content on P loss potential, thus overestimating their load response following land application. It is important that the CBP watershed model accurately addresses the P loss potential for land-based recycling of such amendments.

In the Phase 6 model, the starting point for the land-to-water delivered nutrient (e.g., P) load for any land use in a given land segment is calculated based on the watershed-wide spatially averaged nutrient loading rate (Average P Load) as follows:

Delivered P Load = Average P Load +Σ[Δ input × sensitivity]

The delivered load is subsequently modified by various BMP efficiencies and delivery ratios. The sensitivity represents the change in delivered (export) load for a unit change from the overall

Bay-wide average in any input. The original Phase 6 APLE sensitivity analysis concluded that delivered P loads were relatively insensitive to changes in the amount of P supplied by sources such as manures, fertilizer, and biosolids.Thus, the summation term in the above equation included sensitivities only for soil P, stormwater runoff, and sediment washoff. However, the APLE model limitations in terms of not addressing organic amendments high in Al and Fe meant that the environmental benefit they confer in reduced loss of dissolved Pwas not originally reflected in the CBP WSM. This resulted in over-prediction of export loads for such amendments. Through interaction with the Modeling Workgroup, a WEP sensitivity parameter has been added which will bring the simulated export loads from these amendments more in line with the actual loads documented in numerous research studies.

Fully addressing this issue could involve two additional approaches. First, a post-process best management practice (BMP) could be formulated which addresses P sources with high Al/Fe that reduce P availability. In the CBP WSM model, BMPs reduce loads by a given percentage as a pollutant moves from the field scale to the watershed scale. Such a BMP could be applied to the acres within a land segment that have received biosolids or chemically treated manures. This approach would require engagement in the expert panel process for adding new BMPs—and could be done without the need to calibrate a new version of the model, although any changes in model output would not be recognized before a two-year no-change lock-down period for the model. A second approach would involve revision of the APLE model algorithm to allow for some added P from such sources to be immediately placed into the soil stable P pool that is unavailable to P loss. This longer-term approach would require: (1) collaboration between the APLE model developers and scientists knowledgeable of P fate and transformations in residual-amended soils, and (2) recalibration of the CBP WSM.

Without these further modifications, the watershed model will likely continue to overestimate loads for P soil amendments with high Fe/Al content, although the lumping of parameters at the county scale makes it difficult to quantify the resulting inaccuracy and limits precise allocation of delivered P loads among the various P-source inputs in a given land segment. Continued stakeholder engagement in the CBP model development is needed to accurately address biosolids and chemically treated manures characterized by low water extractable P (WEP) arising from compositionally elevated Al and Fe.

Environmental P Losses from Land-Applied Manures and Biosolids

Biosolids and livestock manures both contain P, but the forms in which this P exists is quite different. Whereas the P in manures tends to be bound with calcium (Ca) and magnesium (Mg), biosolids P is predominantly associated with iron (Fe) and aluminum (Al) (O'Connor et al., 2002). These differences result in widely differing susceptibility to P solubilization by water (Brandt et al., 2004). To quantify this variability, a methodology has been developed for measuring the water extractable P (WEP) of organic amendments (Kleinman et al., 2007). Based on WEP, P solubility follows the order: inorganic P fertilizer (triple superphosphate - TSP) > manures (dairy, poultry) >> biosolids (see Figure 1). The

APLE User's Manual (APLE, 2013) provides default values for the %WEP (percent of total P extractable by water): 50% dairy/beef manure, 20% for poultry manure, 35% for swine manure, and 10% for manures amended to reduce soluble P (i.e., poultry litter amended with alum). The APLE model provides no %WEP for biosolids; however, Brandt et al. (2004)reported the mean %WEP values of <3% for 19 biosolids (Figure 1). The low %WEP of biosolids has been confirmed by the recent work of Jameson et al. (2016) who reported the average %WEP of 81 biosolids samples from 26 POTWs in North Carolina to be 5%.

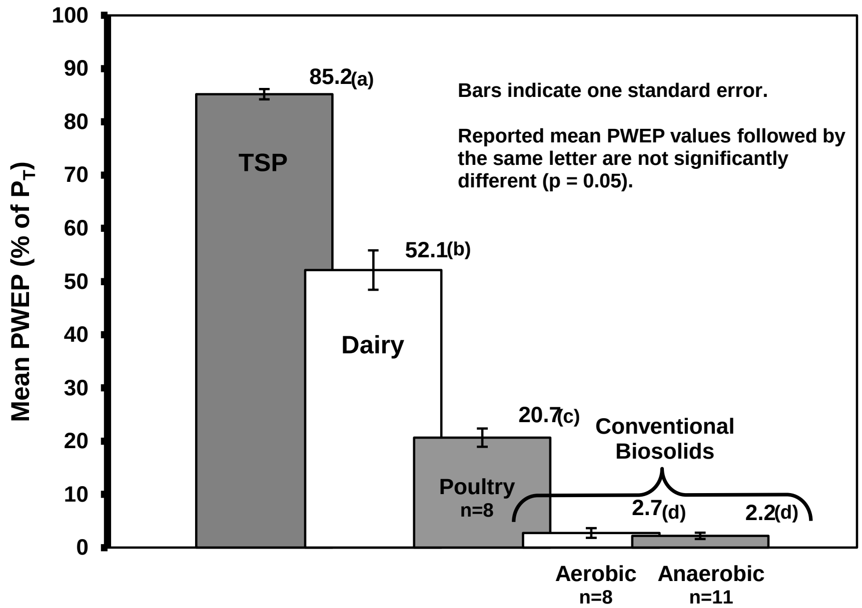

Figure 1.Comparison of PWEP for TSP, manures and biosolids (Brandt et al., 2004).

While the water solubility of P in organic amendments depends on a number of parameters (animal species, diet, storage, treatment, etc.), the chemical composition (aluminum (Al) and iron (Fe) content) is of overriding importance. These elements tend to form insoluble P-containing compounds and thus reduce WEP and environmental P loss. Figure 2 shows the %WEP as a function of the total molar Al plus Fe content for manures and biosolids. The manures have low Al + Fe (< 0.1 mol kg^{-1}) and are characterized by relatively high %WEP. Biosolids tend to have higher Al + Fe, reflecting intentional addition of these elements for P removal, clarification, dewatering, and odor control.

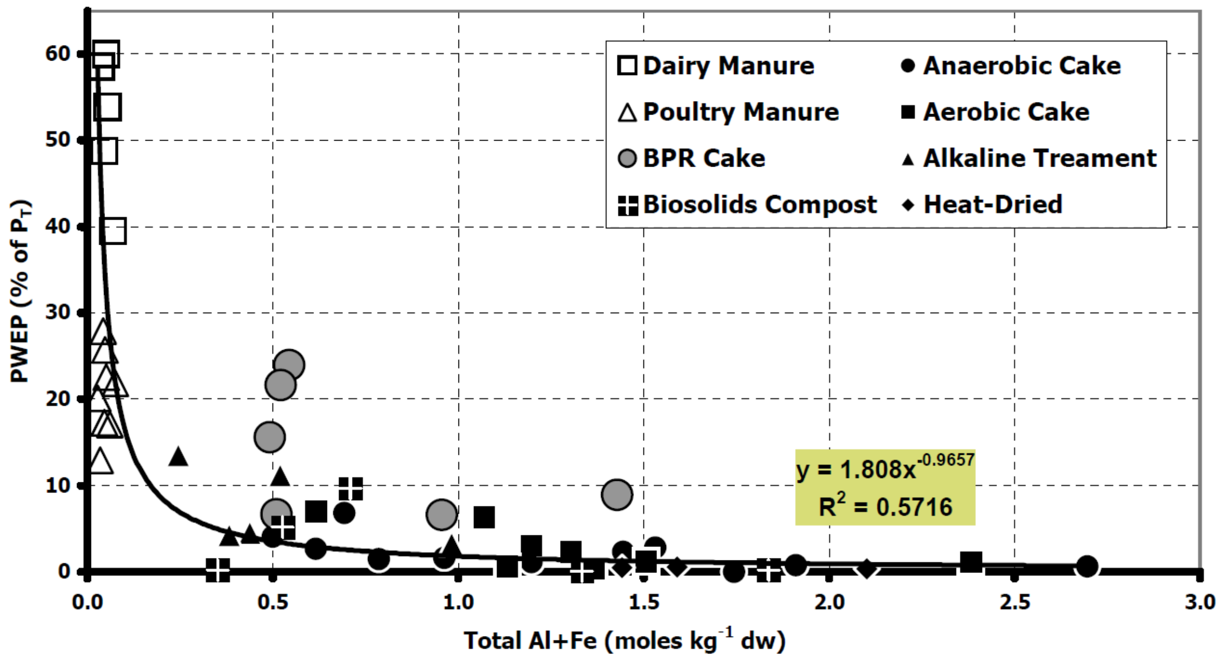

Figure 2. Percent water extractable P as a function of total molar Al plus Fe content of biosolids and manures (Brandt et al., 2004).

This means that P applied to soils in biosolids is dramatically less prone to runoff and subsurface drainage than the same amount of P applied in livestock manures and chemical fertilizers. For example, leaching of P from six biosolids applied to sandy, low-P sorbing soils was statistically lower than from chicken manure or triple superphosphate (TSP) fertilizer (applied at the same total P rate) and not statistically different from the unfertilized controls (Elliott et al., 2002).

Runoff studies also demonstrate that biosolids are typically prone to less P loss than other nutrient sources. Figure 3 shows the runoff dissolved P (RDP) of dairy manure compared to four bisolids surface applied to both high- and low-P soils. All materials were applied at the same total P rate (100 lbs. P ac^{-1}). The dairy manure exhibited significantly higher P loss that all the biosolids. It is noteworthy that the RDP for two of the biosolids was not different from the control (unamended) soil. These two biosolids contain elevated Fe from discharge of Fe-based water treatment residuals into the sewer system. A related study was conducted in which 8 biosolids and 3 dairy manure samples were applied at the same total N loading rate and subjected to rainfall (Elliott et al., 2005). Dairy manure has statistically higher total dissolved P (TDP) and total P (TP) in runoff than seven of the biosolids. The TDP and TP in runoff from 6 of the biosolids did not differ statistically from the untreated soil control.

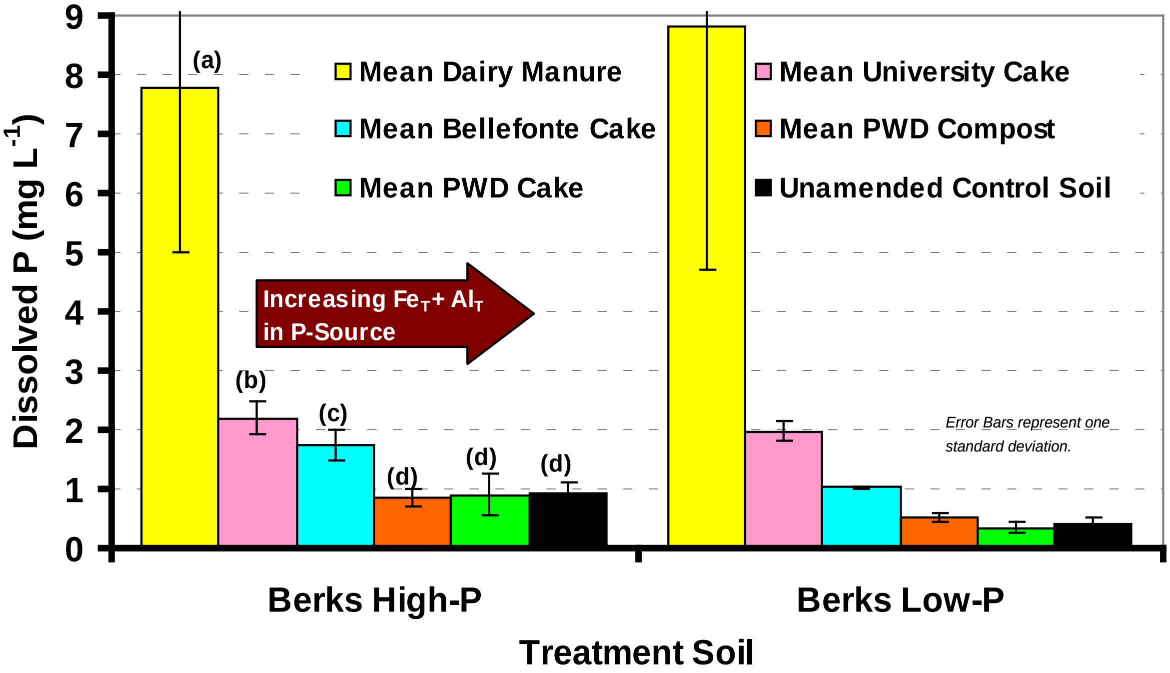

Figure 3. Runoff dissolved P for dairy manure and four biosolids (Brandt, 2003).

Sims et al. (2003) conducted runoff studies in Howard County, Maryland and reported that the bioavailable P in runoff from high-Fe biosolids-amended soil was not significantly different from un-amended soil despite very high total biosolids-P loading rates (292 pounds P per acre).

Fertilizer Replacement Value of Biosolids Relative to Chemical Fertilizers

Another reflection of the differences between biosolids and other land applied P sources is the manner in which crops respond to the added P; that is, the phytoavailability of P. Conventional thinking is that the total P content of land-applied materials is a measure of phytoavailability. Hence, in using soil test P levels to gauge the need to add additional P, it is typical to assume all added P can be used to satisfy crop requirements. Such rationale does not distinguish P phytoavailability differences among various P sources. This is particularly critical for biosolids because of the wide variation in relative P phytoavailability (RPP) among biosolids products.

Perhaps the most comprehensive study of the RPP of biosolids is that conducted by O'Connor et al (2004) who compared the phytoavailability of 12 biosolids (representative of residuals produced nationally) to a commercial inorganic fertilizer (TSP) on P-deficient soils. Figure 4 summarizes the results of this research. They found the phytoavailability of 12 biosolids could be grouped into three categories relative to inorganic P fertilizer (TSP): high (>75% of TSP), moderate (25-75% of TSP), and low (<25% of TSP). Where a biosolids fits into this categorization is largely determined by the manner in which it is generated (the nature of the wastewater treatment process) and how it is handled post-generation. In the highest category were biosolids produced by biological P removal (BPR) processes which largely mimic fertilizer P with regard to phytoavailability. This was confirmed recently by Kahiluoto et al. (2015) who found that biosolids P captured biologically was more plant available than the P in inorganic fertilizer.

The low category included materials treated by advanced alkaline stabilization, and heat-dried or composted biosolids with high Fe or Al content. Huang et al.(2012) also found that the P-phytoavailability of iron-treated and composted biosolids was much lower than chemical fertilizer (KH_2PO_4). Penn and Sims (2001) reported that a high-Fe biosolids applied to a P-saturated soil actually decreased the P that could be extracted from the soil. This suggests that some Fe-rich biosolids actually *decrease* the plant available P in soils.

Most of the biosolids in the study (O'Connor et al., 2004) were produced by conventional wastewater and solids processing and fell in the moderate category. The mean RPP of the biosolids in the intermediate category was 49%, meaning than the total P application rate for such materials should be twice the P crop requirement to satisfy the agronomic need of the crop.

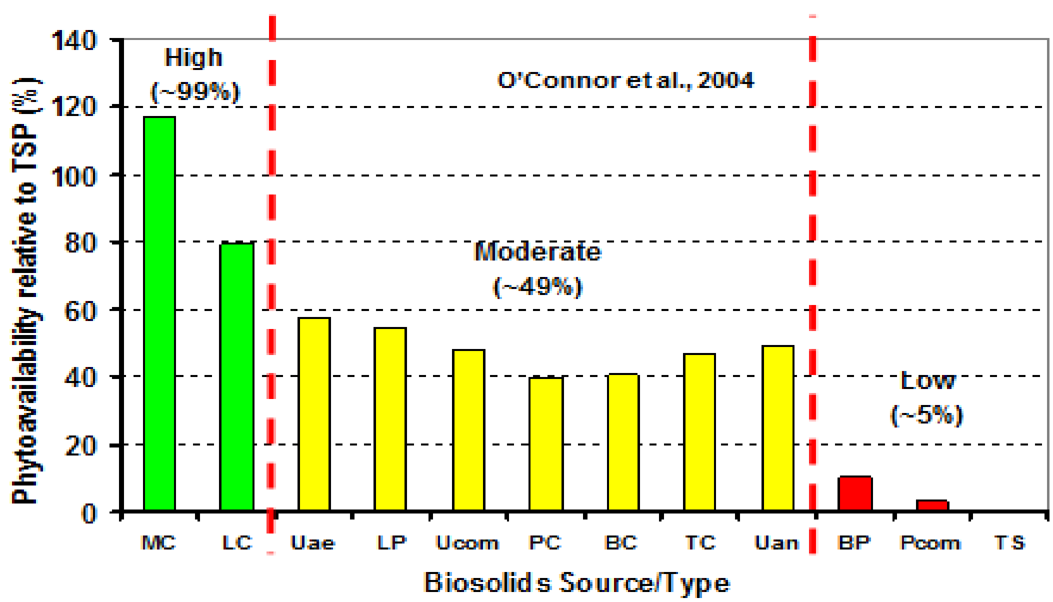

Figure 4. Phytoavailability values of biosolids-P relative to TSP fertilizer.

Miller and O'Connor (2009) investigated long-term (16-month) phytoavailability of biosolids-P by harvesting growing vegetation every 4-8 weeks. Even with multiple plant tissue removal events, they concluded that the P phytoavailability of less-soluble P biosolids was ~50-80% that of TSP. They suggest a biosolids P saturation index (PSI) is directly related to the usefulness of the biosolids in supplying crop P. The PSI is the molar ratio of oxalate-extractable P to the oxalate-extractable Fe + Al. Other researchers have recognized that total P content is an unreliable measure of plant-available P in biosolids, just as the total P content of soils is not well correlated with crop response. Maguire et al. (2001) investigated the P availability of two Maryland soils (Elkton silt loam and Suffolk sandy loam) where biosolids were applied for crop production. They conclude "the testing of biosolids for P availability, rather than total P, is more appropriate tool for predicting extractable P from the biosolids-amended soils".

Accurate determination of the relative biosolids P phytoavailability (biosolids-P compared to fertilizer P) is essential to applying biosolids at rates agronomically equivalent to fertilizer P (O'Connor et al., 2004; Miller and O'Connor, 2009). The EPA Process Design Manual (USEPA, 1995) on land application of sewage sludge (biosolids) assigns a 50% relative effectiveness factor for biosolids, meaning that the phytoavailability of biosolids is typically half that of commercial P fertilizer.

Long-term Effects of High Al/Fe P Sources

Analogous to the inherently high Al/Fe of biosolids is the practice of adding alum to poultry litter to reduce P loss following land application (Huang et al., 2016). This practice has received extensive investigative research over the past 2-3 decades, allowing its long-term sustainability to be studied. For 20 years (1995-2015) poultry litter was applied with and without alum addition annually in paired watersheds. The conclusions of this work (Huang et al., 2016) are noteworthy:

"In this study, additions of alum-treated litter resulted in higher M3-P contents in surface soils and less WEP in comparison with soil fertilized with untreated litter. Because P runoff from pastures is predominantly soluble P rather than particulate P, <u>higher M3-P at the surface does not result in higher P runoff</u>. In addition, deep profile sampling revealed that M3-P contents in the 10- to 50-cm profile of soils fertilized with high rates of untreated litter were 266% higher with untreated litter than with alum-treated litter. <u>The average annual P load from the watershed fertilized with untreated litter (1.96 kg P ha^{-1}) was 231% higher than with alum-treated litter (0.85 kg P ha^{-1}). This study provided evidence that poultry litter treated with alum can greatly reduce P losses from both surface runoff and vertical downward movement for long time periods, which may improve the sustainability of fertilizing with poultry litter.</u>" (emphasis added)

Thus, land application of materials high in Al (or Fe) relative to P have lower environmental P loss over long time periods, despite the fact that soil test P levels (e.g., Mehlich 3-P) is higher. This has resulted in the development of adding Al to poultry litter as a best management practice (BMP) for mitigating P loss from fields (discussed below).

The Phase 6 Watershed Model Approach

The Phase 6 CBP WSM, first released in 2016, is slated for final release in 2017. It represents the latest efforts to enhance the ability of the WSM to serve as the framework for designing implementation plans and tracking BMP implementation progress. Figure 5 shows the Phase 6 overall schemefor calculating delivered pollutant loads from any land segment (primarily counties) in the watershed. The following narrative will address the Phase 6 model in the context of P, the focus of this paper.

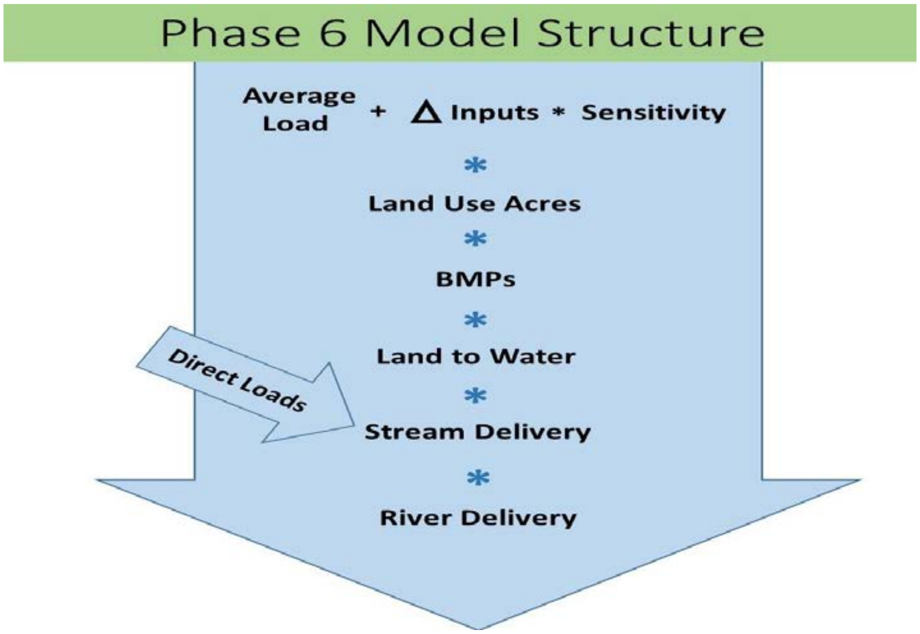

Figure 5. The Phase 6 Watershed Model Structure

In the Phase 6 model, the starting point for the land-to-water Delivered P Load for any land use in a given land segment is calculated based on the watershed-wide spatially averaged P loading rate (Average P Load) as follows:

$$\text{Delivered P Load} = \text{Average P Load} + \Sigma[\Delta \text{ input} \times \text{sensitivity}] \qquad \text{Equ. 1}$$

The Average P Load is subsequently modified by various BMP efficiencies and delivery ratios. The sensitivity represents the change in delivered (export) P load for a unit change in any P input. The units for the terms in this equation are pounds P per acre per year.

The Modeling Workgroup found that the APLE (Annual Phosphorus Loss Estimator) model was most appropriate for simulating P in Phase 6 and calculating P sensitivities in agricultural soils. The original Phase 6 APLE sensitivity analysis concluded that delivered loads were only slightly sensitive to changes in the amount of P supplied by sources such as manures, fertilizer, and biosolids. Thus, the summation term in the above equation included sensitivities only for soil P, stormwater runoff, and sediment washoff (Phase6 WM4, 2016). And the environmental benefit of reduced dissolved P loss from organic amendments high in Al and Fe was not reflected originally in the CBP WSM.

The omission of the importance of P source characteristics in the first sensitivity analysis was likely due to the fact that the APLE model simulations were confined to manure-conventional tillage systems where the %WEP of the P source is not considered. However, in Pennsylvania, for example, 81.7% of the acres planted in corn and 92.8% of the acres planted in soybeans in 2013 involved no-till or other conservation tillage practices (Penn State Agronomy Guide, 2015-16). Table 1 shows the results of a 10-year APLE model run for spring application of dairy manure via incorporation to provide 150 pounds of plant-available N. Note that the Manure Dissolved P loss in Table 1 is zero even when the manure loading rate is doubled.

P loss (lbs/ac)	**Loading Rate 31.4 wet tons/ac**	**Loading Rate 62.8 wet tons/ac**
Sediment P	2.92	4.60
Soil Dissolved P	0.18	0.58
Manure Dissolved P	0.00	0.00
Total P Loss	3.11	5.19
Mehlich-3 P	67	227

Table 1. APLE output for dairy manure incorporated in spring

However, when a surface-spreading dairy manure scenario is considered for manures having very different P solubility (%WEP of 50% verses 5%), the Manure Dissolved P is a substantial contribution to the Total P Loss (Table 2). This table also shows the significant influence of %WEP on the total P loss over a 10-year period.

P loss (lbs/ac)	**%WEP = 50**	**%WEP = 5**
Sediment P	3.93	4.02
Soil Dissolved P	0.42	0.44
Manure Dissolved P	4.21	1.69
Total P Loss	8.56	6.15
Mehlich-3 P	152	162

Table 2. APLE output for dairy manure surface spread in spring

Given this significant influence of the water solubility of the P source as reflected in the %WEP, the Modeling Workgroup added a WEP sensitivity term in Equation 1.

So, for example, the delivered P load from cropland is calculated as:

$$
\begin{aligned}
\text{Delivered P Load} &= \text{Average P Load} + \Sigma[\Delta \text{ input} \times \text{sensitivity}] \\
&= 1.39 \text{ lbs. P/ac} + [\Delta \text{ inches of stormwater runoff} \times 0.057] \\
&\quad + [\Delta \text{tons/ac of sediment washoff} \times 0.168] \\
&\quad + [\Delta \text{ M3-P} \times 0.015] \\
&\quad + [\Delta \text{ WEP} \times 0.018]
\end{aligned}
$$

Inclusion of this final term will account for the differential solubility of manures, biosolids, and other land applied P sources for which the APLE model permits selection of %WEP. Currently APLE only has %WEP values for dairy, poultry, and swine manures and manures amended to reduce soluble P. Mean %WEP values for biosolids will be proposed.

Fully addressing this issue could involve two additional approaches. First, a post-process best management practice (BMP) could be formulated which addresses P sources with high Al/Fe that reduce P availability. A second approach would involve revision of the APLE model algorithm to allow for some added P from such sources to be immediately placed into the soil stable P pool that is unavailable to P loss. These approaches are addressed below.

Best Management Practices (BMPs) for Reducing Dissolved P

The CBP Watershed Model BMP adoption document (Simpson and Weammert, 2009) includes the practice of adding alum to poultry litter to reduce ammonia emissions (p. 30, Simpson and Weammert, 2009). The documentation states that "alum will also reduce phosphorus runoff", and "reduced leaching and runoff of soluble phosphorus" is cited as a co-benefit of this practice. Yet the effectiveness estimates table at the beginning of the document indicates a 50% reduction in TN but states "N/A" (not applicable) for TP.

The BMP adoption manual contains the following statement: "If these practices become widely implemented research should be designed to quantify its ability to remove phosphorus. Self-Davis and Moore (1998) found with land application of alum treated litter to pasture, soluble reactive P concentrations in runoff were 87% lower compared to the control (untreated litter) for the first runoff event and 63% less for the second event."

A BMP for chemical treatment of manures has been published by SERA-17 (Moore, nd). The Southern Extension and Research Activity (SERA)-17 is a group of university and USDA research scientists, policy makers, and extension personal formed "to develop and promote innovative solutions to minimize phosphorus loss from agriculture". This document states: "Treating poultry litter with alum is one of the most effective methods of reducing phosphorus runoff from fields fertilized with litter. Alum applications to poultry litter have been shown to reduce phosphorus runoff by 87 percent from small plots and by 75 percent from small watersheds."

This BMP states that "alum should be applied to poultry litter at a rate equivalent to 5-10 percent by weight (alum/manure)." In one of the original studies, the alum-treated manure had an Al/P molar ratio of about 1(Moore et al., 2000). The concept is to have enough Al (and/or Fe) to bind the all the P in the land-applied material. Table 3 shows the constituent concentrations and the molar ratio of [Al+Fe] to [P] for some manures and biosolids.

Material	Al (g/kg)	Fe (g/kg)	P (g/kg)	Molar (Al+Fe)/P
Dairy manure (PA)	0.45	0.74	7.06	0.141
Poultry litter (DE)	1.5	3.4	18.9	0.178
Alum-treated poultry litter (AR)	18.7	1.72	18.9	1.19
DC Water biosolids	4.0	88.0	30.4	1.75
Hampton Roads (VA) biosolids	13.7	56.0	30.1	1.56

Table 3. Molar ratio of [Al+Fe] to [P] in manures and biosolids

The important feature of the data in Table 3 is that biosolids can have more Al +Fe than P, similar to the alum-treated poultry litter. A large body of research has shown that such materials have lower environmental P loss when spread on soils. Thus, the inclusion of a BMP to account for this behavior is scientifically justified and sufficient data exist on the benefits of this practice to enable the Bay Program to convene an expert panel to define such a BMP.

Modification of APLE Model

A second possible approach for modifying the CPB WSM to more accurately address materials with high [Al+Fe]/[P] ratio is to alter the APLE model algorithm code. Based on analysis of the original research papers which form the basis of the APLE model, Figure 6 was developed which shows the way in which P added to the soil is distributed between three soil pools. In APLE, all added P initially is place in the labile P pool, which, as the name implies, is readily available for crop uptake or environmental loss. This is in rapid equilibrium with the active P pool. The active P pool represents P loosely bound to the soil that replenishes the labile P as it is lost via crop removal or runoff/leaching. Extraction of P in soil testing (e.g., Mehlich3-P) is generally considered to be a measure of the combined labile and active P pools. Transfer of P from the active to the stable pool is based on slow adsorption kinetics of P in soils.

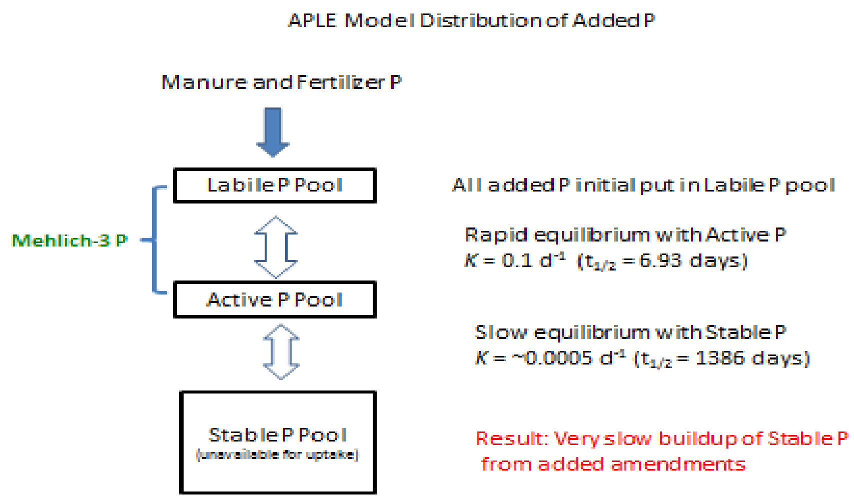

Figure 6. Existing APLE distribution of P added to the soil.

One possible means of modifying the APLE model to address P sources with inherently high Al + Fe content is to initially allocate some of the added P into the stable P pool (Figure 7). This would be logical since the stable P pool is regarded as P that is fixed by precipitation or adsorption to oxides of Al and Fe in the soil. The effect of this allocation would be a reduction of P susceptible to environmental loss, which would be consistent with the large body of supporting research.

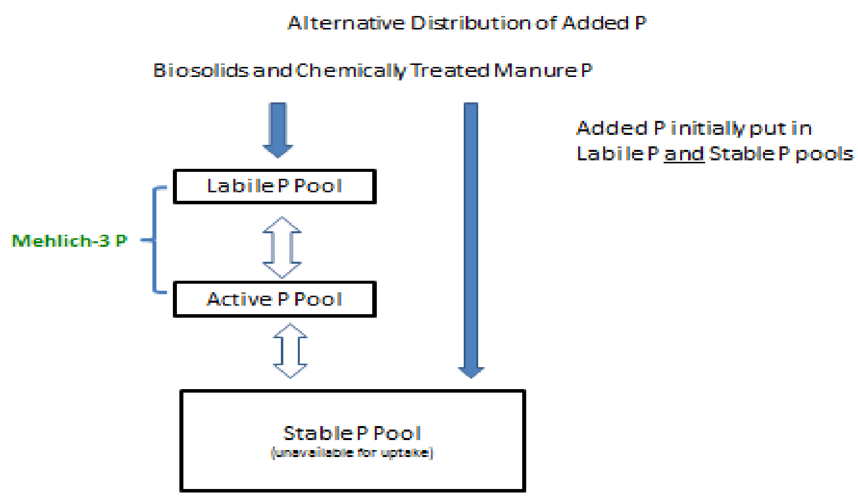

Figure 7. Proposed APLE distribution of P added to the soil.

Conclusions

The 2010 Chesapeake Bay Total Maximum Daily Loads (TMDL) establishes limits on the amounts of N, P, and sediment pollution necessary to meet water quality goals in the Bay. The Phase 6 Watershed Model will be used to predict loads from various land segments that comprise the watershed and "as the primary accounting tool for designing implementation plans and tracking progress in BMP implementation" (Phase 6 WM1, 2016). Many changes have been made to improve the ability of the model to accurately quantify these delivered loads from the land segments. One enhancement needed was the ability of the model to account for the fact that manures and biosolids have widely differing susceptibility to phosphorus (P) solubilization by water and, in turn, dissimilar potential to impact water quality when land applied within the Bay watershed. Through participation with the Modeling Workgroup, a WEP sensitivity parameter has been added which will result in bringing the simulated export loads more in line with the actual loads documented in numerous research studies.

Fully addressing this issue could involve: (1) developing a post-process BMP which addresses P sources with high Al/Fe that reduce P availability, and (2) revising the APLE model algorithm to allow for some added P from such sources to be immediately placed into the soil stable P pool that is unavailable to P loss. Without further modification, the Watershed Model will likely overstate the load implications for such soil amendments, although the lumping of parameters at a county-scale level makes it difficult to quantify the resulting inaccuracy and limits precise allocation of delivered P loads among the various P-source inputs in a given land segment. An iterative validation process accompanying modifications can evaluate if model output accurately captures the documented lower P loss potential of biosolids and chemically treated manures characterized by low water extractable P. The Bay Program should pursue continued stakeholder engagement to implement changes and enhance the accuracy of the CBP Watershed Model.

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