Hydrological and Chemical Controls on Phosphorus Loss from Catchments

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INTRODUCTION

Phosphorus (P) contamination of surface water is of growing concern in many areas of the world. When in excess, the role of P in generating unwanted algal production in freshwater lakes and reservoirs is well documented. Most of the strategies designed to limit P entry to susceptible lakes and reservoirs are land or land-management based. Much of this P control strategy has focused on agricultural land uses and managements because agriculture is a dominant land use in many catchments.

A land-based control strategy presumes the linkage between P source (land) and impact areas (freshwater bodies) to be simple and direct. This typically is not true. First, not all P contributes to the problem; the bioavailability of the inflow P depends on its chemical form and the nature of the receiving water. Inflow P ranges from dissolved and desorbable sediment P (most bioavailable) to crystalline mineral and refractory organic P associated with sediment (least bioavailable). Most of the dissolved P (DP), especially orthophosphate, is readily available. The methods for estimating bioavailable P (BAP) of exported suspended sediment (subsequently referred to as sediment) range from algae to resin (chloride (Cl), iron (Fe))-, to chemical (sodium hydroxide (NaOH))based extractions and provide results that are useful as indices. However, these measures may overestimate the true algal-available P in a small, rapidly sedimenting reservoir and underestimate it in a large, partly or periodically anoxic reservoir. Second, a catchment or basin is a collection of P sources, storages and sinks tied together by a flow framework. The position of the P sources, storage and sinks relative to the primary flow

pathways and each other defines the key linkages from source to impact area. Clearly, flow and proximity to flow are critical. All else being equal, the sources, storages and sinks closest to the primary flow pathways will have the largest and quickest impact. The nature of the sources, storages or sinks is also important. Flow considerations being equal, their intensity, capacity and efficiency will affect the extent of their impact. Practically, P sinks are not important unless water or sediment containing P is transferred out of the catchment. Third, the importance of intensity, capacity and efficiency of sources and storages applies to flow and erosion (sediment) as well as P. Sources with low P contents and high runoff and/or erosion potentials can be major P sources, whereas those with high P concentrations but low runoff and erosion potentials may be minor P sources. For a hill-land catchment in the northeastern USA, Gburek and Pionke (1995) and Zollweg et al. (1995) provide good examples of this situation.

The focus of this chapter will be on the small catchment, a step above the farm and field scale. It will establish the critical P source areas in the context of the catchment flow system. This critical source area is a special condition of the critical zone, defined earlier by Pionke and Lowrance (1991) as 'a bounded area or volume within which one or a set of related processes dominate to provide excessive production (source), permanent removal (sink), detention (storage) or dilution of NO₃-N'. When applied to P, the focus is more on an area than a volume and less on sinks and dilution, due to the differences between nitrate (NO₃) and P. Our goals are: (i) to describe some basic controls on P losses from critical source areas; (ii) to describe and evaluate a simulation-based approach to delineate critical P source areas in the context of a small catchment; and (iii) to examine these ideas in terms of remediation and controlling P export from catchments. We shall focus on a small agricultural hill-land catchment located in east-central Pennsylvania, USA.

METHODS

The following describes the simulation methodology and basis of application. The simulation results were compared with measured runoff and DP response to storms on the experimental catchment. Earlier results show this simulation methodology to be useful and applicable to this catchment (Zollweg et al., 1995).

Runoff Generation Using the Soil-Moisture-Based Runoff Model

The soil-moisture-based runoff model (SMoRMod) developed by Zollweg (1994) has been shown to successfully simulate both the long-term daily hydrograph and individual storm hydrographs for small to medium non-

winter storms on small (< 200 ha) New York and Pennsylvania catchments (Zollweg et al., 1995, 1996). It is a physically based, spatially distributed model of catchment processes, using climatic variables as input and requiring topography, land use and soil distribution as data layers. It includes the hydrological processes of infiltration, soil-moisture redistribution, groundwater flow and surface-runoff generation. It divides the catchment into homogeneous small rectangular cells, for which calculations are performed.

The soil-moisture submodel simulates daily variations in soil-moisture status and groundwater conditions for each cell over the catchment and estimates a daily stream flow at the catchment outlet. For each daily time step, water can be added to or removed from the soil, split into the rootzone layer, the subroot-zone layer and the subsoil plus bedrock layer by the processes of evapotranspiration, precipitation, interflow, percolation and surface runoff.

The runoff-generation submodel computes the storm hydrograph from the rainfall amount, rainfall intensity and initial soil-moisture conditions. This submodel provides a variable source area (VSA) response (Ward, 1984), where storm runoff is produced from expanding and contracting zones of filled storage, due to high water-tables or soil moisture. Surface runoff due to rainfall in excess of soil infiltration capacity is also computed.

The outflow hydrograph for the storm event combines the runoff amounts generated with the times for these to reach the catchment outlet. From overland flow velocities and travel times calculated for each cell, based upon the slope and land use (SCS, 1975), the travel times along the optimal flow paths are summed to generate total travel times to the catchment outlet. Organized by equal travel times, the total runoff delivered to the outlet over time becomes the storm hydrograph.

Dissolved Phosphorus Generation Using the Soil-Moisture-Based Runoff Model

The SMoRMod was modified to combine P input from the land surface with the generated surface runoff and route this mix to the catchment outlet, using the time–area approach previously described. The DP in surface runoff was computed from Bray P for both cropland and forest–grassland soils, using the linear relationships presented in Daniel *et al.* (1994). The Bray P values for each field within the Brown catchment were obtained by analysing multiple soil samples collected from the top 15 cm during May 1985. The storm runoff is diluted in the stream by subsurface flow, which is assigned a DP concentration of 0.007 mg l⁻¹ (Pionke *et al.*, 1988). Baseflow rate is simulated by the long-term hydrological submodel of SMoR-Mod.

Erosion and Sediment Bioavailable Phosphorus Generation

Erosion was computed for each model cell using the soil loss equation (soil loss = RKSLCP) developed by Wischmeier and Smith (1965). Cells with no surface runoff were designated as non-contributing. The soil loss terms were determined directly from maps and available data. The sediment BAP was computed directly as enrichment ratio (ER) \times Bray P \times soil loss, where ER is computed as: $\ln(ER) = 1.21 - 0.16 \ln(\text{soil loss})$ (Sharpley, 1985). Bioavailable P was computed as the sum of sediment BAP and DP.

STUDY CATCHMENT

The 25.7 ha Brown catchment is typical of small, first-order, upland agricultural catchments in the north-eastern USA. It is located approximately 40 km north of Harrisburg, Pennsylvania, within the Susquehanna River Basin (Fig. 10.1). The climate is temperate and humid. Precipitation is approximately 1100 mm year⁻¹ and stream flow about 450 mm year⁻¹. Land use is almost entirely agricultural. Figure 10.2 shows land-use distribution and elevation with respect to mean sea level. The universal transverse Mercator (UTM) geographical coordinate system (zone 18) is used as a reference. A small amount of forest and a non-harvested grass strip borders the lower portion of the stream channel. The typical crop rotation is maize, small grain and hay, with about 35% of the catchment being in maize in any year. The soils are all shaly or channery silt loams that range in depth from 25 to 120 cm but are otherwise hydrologically similar. The Bray P concentration, expressed in terms of 1 cm depth, ranged from 6 kg ha⁻¹ cm⁻¹ in permanent grass and woods to 36 kg ha⁻¹ cm⁻¹ in the intensively cropped areas.

The topographic data were derived from a US Geological Survey topographical map augmented by a local survey. Soil properties and related hydrological characteristics were taken from the Soil Conservation Service (SCS, 1969). Agricultural field distribution and associated land use were determined from our own survey.

RESULTS AND DISCUSSION

Basic Controls on Phosphorus Losses from Critical Source Areas

The critical source area, as defined earlier, can be critical in hydrological, erosional, chemical and P-use terms. The source areas of surface runoff and erosion within the catchment provide the underlying control on P export. Clearly, without surface runoff, neither eroded soil, DP nor sediment BAP will be exported and thus that area cannot be a P critical source area.

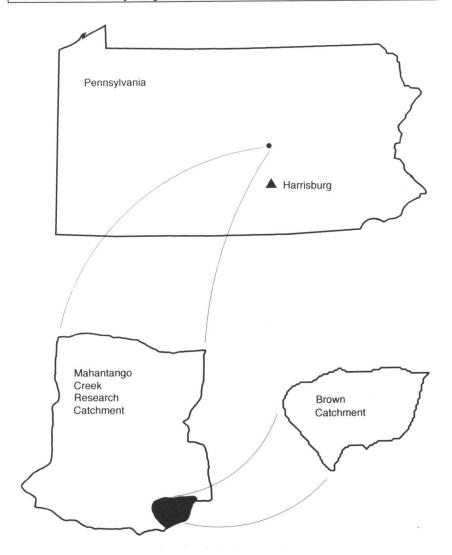


Fig. 10.1. Brown catchment – location.

$Surface ext{-runoff controls}$

Surface runoff in our study catchment can be generated by two processes. One is by generation of precipitation excess, which occurs when the rainfall rate exceeds the soil infiltration capacity (Smith and Williams, 1980). Accumulated over the storm, this excess becomes surface runoff. This process is typically controlled at the soil scale, and the infiltration curve very much depends on the properties of the surface and shallow soil. The other is the conversion of precipitation to surface runoff where potential soil-

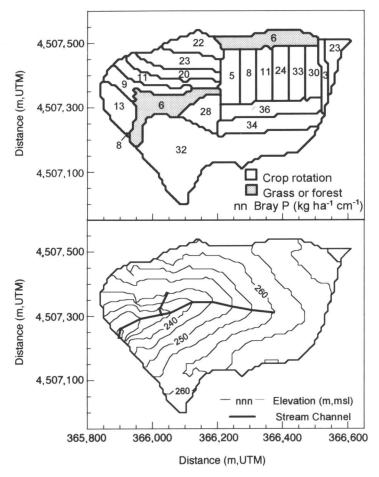


Fig. 10.2. Brown catchment - topography, land use and soil-P fertility levels.

water storage is filled. This control is at the catchment scale and results from the close proximity of the water-table to the land surface, primarily in near-stream zones (Ward, 1984). Here, soil properties are much less important, because the control is lack of water storage, not infiltration capacity. In fact, many of these soils exhibit high infiltration rates when not saturated. In our study catchment, the VSA system is the dominant control on where and how much surface runoff is generated. The VSA control is common to humid, temperate, hill-land regions (Dunne and Black, 1970) and is well known, with work having been done in Canada, the UK, New Zealand, the USA and Scandinavian countries.

Erosion controls

Erosion in the Brown catchment is typically very low, but has been severe when a certain combination of conditions is met, such as very intense storms on already wetted bare soils. Also, much of the gully erosion occurs in concentrated flow zones within the VSA rather than up on the steeper slopes. In terms of the soil loss equation parameters, the cover (C) factor appears critical, particularly in the VSA. The C factor ranges over two orders of magnitude from permanent grass to row crops (Musgrave, 1947). The soil loss equation, although instructive, estimates total erosion at the soil scale over the long term (Wischmeier and Smith, 1965). In a critical-area context, we are more interested in those erosion source areas that deliver most of the sediment BAP to the catchment scale. For 56 sediment-bearing storms in the Brown and encompassing 7.4 km² Mahantango Creek research catchment (Pionke and Kunishi, 1992), nearly all the sediment exported was clay and fine silt (< 5 µm diameter). However, the source soils ranged from 29 to 53% sand. Thus, the conversion of soil to exported sediment is mostly due to the much reduced export of sand. This sand fraction consists of primary particles, not sand-sized aggregates. The aggregates found in these soils are observed to be unstable and break down to primary particles when wetted. We concluded that most sand is left behind where erosion occurs, with the rest being deposited during transport to the catchment scale.

To relate eroded P to its soil-source P contents, Menzel (1980) proposed expressing this as an ER. Summarizing his own and Menzel's work, Sharpley (1992) showed: (i) the eroded materials to be enriched in both BAP and clay relative to its soil source; and (ii) the BAP and clay contents in the eroded materials to be highly related. This implies that the critical source area for sediment may need to be redefined in terms of supplying the fine sediments being exported from the catchment. In the Brown catchment, which is small, well drained and without apparent storages for fine sediments *en route*, we hypothesize a direct and quick connection between critical sediment source areas and the catchment scale. Here, the much used sediment delivery ratio (SDR), showing sediment loss per unit land area to decrease with increasing catchment size (Walling, 1977), reflects sand deposition *en route* from source to catchment. Thus, the SDR is not an issue and does not alter sediment BAP export from the Brown catchment.

Phosphorus use and chemical controls

The P use and chemical controls can vary, depending on the chemical and mineralogical nature of the soil and sediment system under study.

The soil-P content or fertility level is typically the dominating control in determining P critical source areas from P use and chemical perspectives. For our catchments, we have examined and considered P exposure, soil properties and vegetation as controls on BAP export. We

have concluded these to be important, but their effects were largely overshadowed by P fertility level over the longer term and at larger scales.

Increased P fertility level of a soil translates into increased DP in runoff and BAP in sediment (Romkens and Nelson, 1974; McCallister and Logan, 1978; Sharpley, 1992; Daniel et al., 1994; Pote et al., 1996). The relationship between DP and sediment or soil BAP is curvilinear (McCallister and Logan, 1978; Wolf et al., 1985; Sharpley, 1992), with DP increasing much more rapidly than sediment or soil BAP as P fertility increases to some limit established by the solubility of Fe, aluminium (Al) or calcium (Ca) phosphorus compounds, depending on the mineralogy. The relationship can be linearly approximated (Pote et al., 1996), especially at the lower P fertility levels (McCallister and Logan, 1978; Wolf et al., 1985; Daniel et al., 1994).

Surface placement or exposure of manure or P fertilizer to surface runoff can greatly increase DP concentrations in surface runoff (Timmons et al., 1973; Sharpley et al., 1994, 1996). The question relative to selecting P critical source areas is: will exposure be sufficiently long-term and spatially extensive to control BAP export at the catchment scale? We concluded no, because here surficial P applications tend to be incidental and local and the effects transitory. However, the timing of the runoffgenerating storm following application is critical. Sharpley (1980) and Westerman and Overcash (1980), respectively, have shown the DP and total P concentration in runoff to decrease greatly within a relatively few days following surface application. Apparently, diffusion and infiltration redistribute surface-applied P into the soil profile. In most field situations, dew and small rainfall events occur much more often than major runoff events soon after application. Where P is surface-applied concurrently over most of the critical surface-runoff areas and quickly followed by a major runoff event, P exposure may well control P export from the catchment for that storm event. However, the contribution from this single event needs to be assessed in terms of the long-term P losses and impact downstream.

Soil properties are clearly important in defining P critical source areas. These properties can greatly affect runoff (where precipitation excess is the cause), erosion, P bioavailability and the P distribution between sediment and surface runoff. In terms of P chemistry, the primary control in our catchments is on the relationship between solution, sorbed and the remaining sediment BAP. Based on our own unpublished work and that of Sharpley (1983), the changes in isotherm shape and buffering capacity seem mostly to depend on the clay content, although we expect some lesser effects due to Fe content (Wolf *et al.*, 1985). However, where all soils are developed from the same parent material and subject to similar P fertilizer-management strategies as in this catchment, the soil-P chemistry and mineralogy are not expected to be differentiating criteria for defining critical source areas.

In our catchments, the surface-runoff critical areas (VSA) are generally

grassed. This results from a strong conservation ethic among local farmers and because these areas are often too wet to plant in spring. These grassed riparian zones have two other effects. One, they act as buffer strips and are effective in removing the sand fraction from erosion-containing through flows. Two, vegetation can be a source of DP and may set the lower limit on P export from the catchment. Schreiber (1990), Sharpley (1981), Sharpley and Smith (1991), and Gburek and Broyan (1974) examined the DP concentration in leachate from simulated rainfall on soybeans, cotton, sorghum and orchardgrass. The overriding effect appeared to be the extent of vegetative leaching, with an initially high DP concentration in leachate $(0.06-0.27 \text{ mg l}^{-1})$ rapidly declining to a much lower $(0.015-0.1 \text{ mg l}^{-1})$ and stable concentration at storm's end. For orchardgrass (Gburek and Broyan, 1974), the ending values for a 12 and 150 mm rainfall were 0.05 and 0.035 mg l⁻¹ DP, respectively. Because the channel in the Brown catchment is neither a sediment source nor storage, these extended leaching values may represent the lower DP concentration limit achievable in surface runoff by improved P management or remediation.

Critical Source Delineation in the Context of a Small Catchment

The surface runoff, erosion, DP and sediment BAP critical areas were delineated for the Brown catchment when subject to a 21 mm rainfall. These delineations were based on simulations applied to this 25 April 1992 storm for the particular set of initial conditions existing then. For a different-size storm under different initial conditions, the storm yields could change greatly and the areal extent of the response might expand (larger storm) or contract (smaller storm). However, the landscape pattern of surface runoff should change little. The erosion and P loss patterns may change more, but only in response to major changes in key parameters, such as C factor or P fertility levels.

The simulations of surface runoff and DP in storm flows from the Brown catchment were found to reasonably approximate storm data collected from this catchment during 1983–1985 and in 1992 (Zollweg et al., 1995). The erosion and sediment BAP simulations were not tested or compared against collected data and are used for demonstration only.

The results show surface runoff and erosion to be generated from very limited areas within the Brown catchment (Fig. 10.3). Most surface runoff originates near the stream channel, with 98% being produced from about 14% of the catchment area. There is some surface runoff generated along slope breaks that parallel the channel. Basically, this is a VSA hydrological system, where the location of surface runoff is controlled by catchment (water-table position)- rather than soil (infiltration)-scale processes. The erosion critical source areas are even more limited, located primarily in the lower catchment, where a sloped maize field intersects the hydrologically

active area. Very little erosion occurs elsewhere in the surface-runoff critical area because of the excellent vegetative cover.

The critical source areas of surface runoff and erosion establish the outer boundaries for DP and sediment BAP loss (Fig. 10.4). Within these boundaries, most of the DP is lost from cropland, where the Bray P concentrations in soil are highest, within and about the ephemeral upper stream channel. In contrast, the much lower Bray P values associated with the permanently grassed area around the lower channel negate the effect of the high surface runoff on DP export. The sediment BAP is more localized, primarily in cropland near the lower channel, because of the high erosion rate. Combined as BAP loss (Fig. 10.4), there are two very small areas that contribute most of the BAP total. Based on the simulation, DP

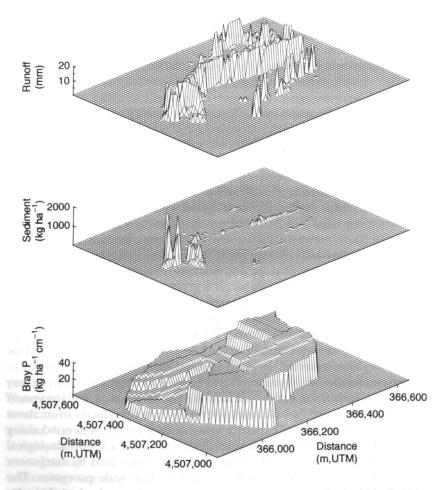


Fig. 10.3. Brown catchment – simulated surface runoff and erosion for the 25 April 1992 storm.

 $(68~\rm g)$ and sediment BAP $(77~\rm g)$ losses from the catchment are about equal. In terms of area, 98% of the sediment BAP loss is from 6% of the catchment and most of the DP loss is from 11% of the catchment. About 20–30% of the BAP originates from 1% of the catchment area.

This analysis shows that a very small portion of the catchment is the source of most of the exported BAP. It also shows where these BAP losses are concentrated within the catchment. With this simulation approach, it is possible to better target monitoring, research and remediation programmes and more realistically explore the impact of alternative land use and P-management options.

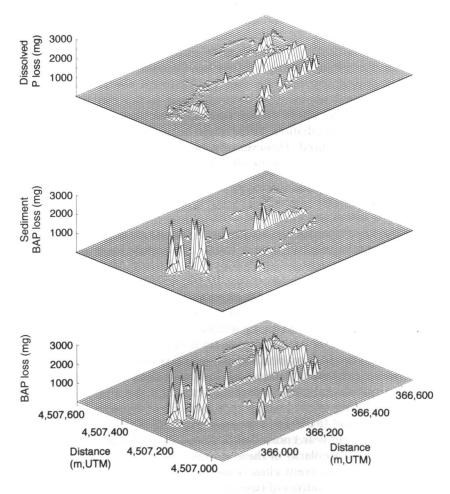


Fig. 10.4. Brown catchment – simulated dissolved P, sediment bioavailable P and bioavailable P losses for the 25 April 1992 storm.

Implications for Remediation and Control of Phosphorus Export from the Catchment

This section provides additional observations and interprets key catchment processes and responses in terms of remediation. These interpretations also serve to summarize key points developed in the chapter. Remediation is defined broadly to include assessment and prevention, not just the application of remedial practices to critical source areas.

Delineation and evaluation of critical source areas

Typically, small areas within the total catchment are the source of most BAP export. The base control for these BAP critical source areas is where surface-runoff occurs. In VSA-controlled catchments, the location of surface-runoff critical areas is predictable and follows a pattern, even when hydrological conditions change. If BAP loss from the catchment is a major issue, the critical source areas can be identified for remediation. In addition, optional remediation strategies and tactics can be tested via simulation. Knowing where surface runoff is least likely to occur can also be important for remediation. These might be the best areas for land-based disposal of P if required. However, this becomes more complicated with manurial P sources because of the nitrogen (N) component, a situation that will be addressed last.

Delineation of critical source times and events

Analogous to critical source areas, there can be critical time or storm periods when relatively little time or few storms account for most of the BAP lost from the catchment. Using data from the 7.4 km² Mahantango Creek research catchment (Pionke et al., 1996), which contains the Brown catchment, nearly 70% of the DP exported occurred during the 10% of time dominated by the larger runoff events (Fig. 10.5). This increased to about 90% BAP exported when the sediment BAP was included. These data represent the mean DP by flow interval for over 1000 observations (samples collected from two to three times weekly over 9 years) and are used instead of the Brown catchment data, which indicated similar patterns but with fewer observations (about 240 over 31/2 years). Of the 1000 samples, 109 were taken during storm hydrographs, with 62 of these included in the highest flow period (> 3001 s⁻¹) shown in Fig. 10.5. These 62 storm events, averaging seven per year, controlled BAP loss. We have not yet determined the seasonality or similarity of these storms. The remedial implications of a time period or an event class being critical are several. First, we can probably ignore the sources of base flow and the small storm events, which together export most water but very little of the BAP. Secondly, we can develop design or index storms to represent the range in size, intensity and initial conditions for the 62 controlling events. These can be used to do

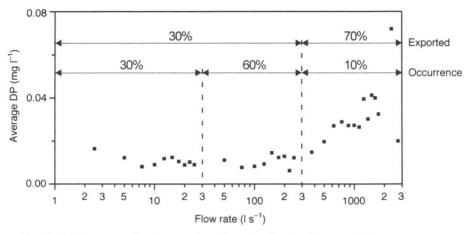


Fig. 10.5. Mahantango Creek research catchment – dissolved P concentration, occurrence and export summarized for 1984 to 1993.

simulations, as well as to establish the location and dimensions of critical source areas for these critical storms.

Critical process or characteristics at source areas that can be managed

At the catchment scale, relatively few processes and parameters in source areas control BAP export and even fewer are efficiently or readily manageable. The amount and location of surface runoff are not typically or readily managed on site. Erosion is more manageable, particularly by manipulating the C factor directly or indirectly through a conservation practice, such as modified tillage. Dissolved P is managed by controlling the P fertility level in surface-runoff zones, and sediment BAP is managed by controlling erosion and/or P fertility level in the primary erosion zones. In terms of remediation, how might we simply examine, contrast and identify potential control strategies? In Fig. 10.6, sediment, runoff, sediment BAP and DP in catchment outflow are compared for this purpose. These curves represent conceptual, not data-derived, equations. The parameters used are the sediment-to-solution ratio, expressed as sediment concentration, and the concentration ratio of sediment BAP to DP, which is defined as r. For high sediment concentrations, i.e. above 10,000 mg l⁻¹, erosion controls BAP export, and clearly erosion control is the primary remedial candidate. For low sediment concentrations, i.e. below 100 mg l⁻¹, most of the BAP is dissolved and the main control will be to reduce the P fertility level in the surface-runoff critical zones, unless the surface runoff volume can be greatly reduced, a much less likely option. Between 100 and 10,000 mg l⁻¹ sediment, curve selection, representing the different sediment BAP-to-DP ratios, exerts control on whether water- or sediment-phase P dominates.

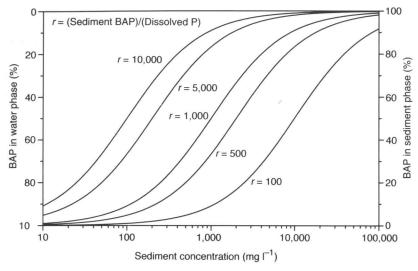


Fig. 10.6. Implications for controlling BAP export based on sediment and BAP concentrations in catchment outflow.

The change in sediment BAP/DP lumps the effects of soil properties and P fertility levels together. Assuming P equilibrium, this ratio (r) will decrease as the P fertility level is increased, simply due to the curvilinearity of the isotherm. Consequently, the DP concentration will increase more rapidly than sediment BAP as more P is added to the soil or sediment. Thus, as the P fertility level is raised (e.g. decrease r from 5000 to 500 at 1000 mg l⁻¹ sediment), the BAP export will be dominated by water and not sediment, which implies a very different remediation strategy. Conversely, a remediation strategy implemented to greatly reduce P fertility level in soil may eventually elevate erosion control to a realistic remedial approach if further BAP-loss control is needed. The Brown catchment averages about 200 mg l^{-1} sediment in storm runoff and an rvalue of about 5000 (298 mg kg^{-1} of 0.1 N NaOH-extractable P in sediment \div 0.053 mg l^{-1} DP), which puts 50% of BAP in the water phase. Thus, if a remedial control strategy is needed for the Brown catchment, it should include the reduction of P soilfertility levels in the critical surface-runoff areas in order to be effective.

Unified remedial strategies where nitrate losses must also be controlled

The selection of remediations for controlling BAP export from catchments should not cause or aggravate other water-quality problems. Bioavailable-P control strategies based on reducing surface-runoff losses either by increasing the infiltration rate or by placing most P in non-runoff zones may well increase NO₃ recharge to groundwater. This is an issue where the application of manure or organic materials is the primary source of BAP

excess. Thus, remedial approaches in these circumstances must be developed and selected to optimize BAP control relative to achieving these other nutrient-control objectives.

CONCLUSION

Control of BAP export from a catchment must be examined at the catchment, as well as farm and field, scale. There are two reasons. First, hydrologically related processes that dominate at the catchment scale can control which farms or fields contribute most of the exported BAP. Second, catchment elements that exist between field and catchment outlets may alter the timing, amount and concentration of BAP exported. These elements can include wetlands, channels, reservoirs and flow confluences. Although the impact of these elements is important, it is catchment-specific and beyond the scope of this chapter. Instead, we delineated major BAP source areas from a catchment-scale hydrological perspective, which are not predictable using a field- or farm-scale approach. Only after hydrological and erosion source areas were established was it appropriate to bring in soil, chemistry and P-use information. After doing this, we found that nearly all of the BAP exported from this catchment originated from less than 10% of the land area. To tie off-site impacts of BAP export to field use and management, it will be necessary to integrate field use and management with the dominant catchment-scale processes, as was done here.

ABSTRACT

This chapter explores the controls on loss of bioavailable phosphorus (BAP) from catchments. It establishes the concept of critical BAP source areas in the context of a flow framework. The hydrological, erosion, chemical and phosphorus (P)-use controls on BAP loss from critical source areas are identified and discussed in terms of BAP export from hill-land agricultural catchments located in the humid north-eastern USA. The application of the concept and its importance are demonstrated for an experimental Pennsylvania catchment, using a simulation method based on data collected from this catchment. The results show most exported BAP to originate from small and predictable hydrological source areas within the catchment. These ideas, simulations and additional data are summarized and used to show that most of the BAP loss is concentrated in space and time and by process, so that relatively small areas, few storm events and few processes control BAP export from catchments. These implications are discussed in terms of remediation strategies and options likely to be most effective.

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