CHAPTER 2

Nutrient bioavailability of soils and sediments in an Australian estuary influenced by agriculture: linking land to sea

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Abstract

Nutrient bioavailability of runoff from agricultural soils was investigated in the Maroochy River watershed, Australia, a coastal watershed influenced by agriculture. Suspended sediments, river and estuarine sediments and deposited sediment in the near-shore coastal ocean were collected and analyzed for nutrient bioavailability using chemical analyses and phytoplankton (Skeletonema costatum) bioassays. Suspended sediments in the Maroochy River, which consisted of silt and clay-sized particles, had elevated Fe-oxide-extractable P and total P concentrations comparable to fertilized soil. Similarly, the deposited sediment sampled offshore of the river mouth had elevated total P, Fe-oxide-extractable P and total N concentrations that were much greater than the underlying marine sediment. The deposited offshore sediment contained mainly clay-size particles and appeared to be terrigenous in origin due to its similar composition (total P, Fe oxide P, total N, total carbon, total aluminum, and total silicon) to estuarine suspended sediments and terrestrial soils. This study demonstrated that nutrient-rich clay-sized particles, of terrigenous origin, are being transported and deposited offshore during erosion events. This highlights the need for multifaceted watershed management that encompasses a) erosion control measures that reduce suspended sediment loads of nutrient-rich clay- and silt-sized fractions to coastal waters, and b) nutrient-reduction strategies. Effective management must consider both agricultural productivity and potential environmental impacts, as what is economically viable may not be environmentally sustainable.
1 Introduction

The potential impact of increased nutrient and sediment loads to coral-reef ecosystems, especially inshore reefs of the Great Barrier Reef [1–3] and an increase in algal blooms (toxic and nontoxic) in several Australian estuaries, bays and coastal lakes [4, 5, 6, 7] has necessitated research on the downstream effects of land use on Australian waters. Globally, coral-reef ecosystems are declining due to the impacts of sediment, nutrients and other pollutants attributed to poor land-management practices [8]. Models estimate that 22% of coral reefs worldwide are threatened by soil erosion and land-based pollution [9]. Detrimental effects of phosphorus loss from agricultural land to freshwater rivers and lakes have become increasingly apparent, particularly in North America and Europe [10, 11]. In these regions much research has focused on increasing P retention on land and assessing P bioavailability in agricultural soils and runoff [11, 12].

Agricultural runoff is a major nonpoint source of phosphorus (P) and nitrogen (N) into rivers and estuaries [13]. During rainfall events excess nutrients can be transported from streams to rivers, estuaries and eventually to the coastal ocean. The majority of P (>90%) which is transported from rivers to the ocean is in particulate form [e.g. 14, 15], some fraction of which is desorbable and thus potentially bioavailable [14]. Conversely, most nitrate is lost via leaching from agricultural soils and is readily bioavailable, whilst ammonium is strongly sorbed to soil particles and transported in particulate form [16].

Although several studies have measured sediment nutrients, and/or water quality in estuaries impacted by agriculture [17–19], few have examined nutrients associated with suspended sediments [20], or examined these collectively [21, 22]. Most research has been confined to the watershed, receiving estuary, or near-shore coastal zone, with few studies examining their connectivity [18, 19, 21]. Thus comparisons between nutrient bioavailability of soil, suspended sediments, sediments in the receiving estuary as well as offshore sediments are rare.

Accurate and comparable assessments of sediment nutrient bioavailability have also been troubled by the lack of standard methodology for assessing bioavailable P. An accurate measure of algal available P was identified in Chaston [23], by correlating chemical measures of sediment P with maximum algal biomass of the euryhaline diatom Skeletonema costatum. Fe-oxide extractable P [24] and bicarbonate extractable inorganic P [25, 26] were highly correlated with bioavailable P in suspended sediments [23]. The Fe-oxide strip method was recommended for future analyses as it provides a stronger mechanistic basis than chemical extraction for estimating bioavailable P [27]. In addition, the technique has previously been used in both freshwater [27] and marine conditions [28] and is not influenced by sediment or soil type [28, 29], thus making it suitable for assessment of bioavailable P in coastal watersheds that have a broad range of sediment types distributed over a salinity gradient.

The main aim of this study was to assess nutrient bioavailability of runoff from agricultural soils in Australian estuarine and coastal marine ecosystems. Nutrient bioavailability from soil, suspended sediment, estuarine and deposited offshore sediment was determined in a subtropical Australian estuary impacted by agriculture,
using chemical analyses and algal bioassays. Results were used to formulate a conceptual model of sediment and nutrient transport in subtropical and tropical Australian estuaries and to demonstrate the link from land to sea.

2 Materials and methods

2.1 Study site

The study was conducted in the Maroochy River Watershed, Sunshine Coast, southeast Queensland, Australia (Fig. 1). The Maroochy River is 27 km long and drains a relatively small (~600 km²), predominantly rural watershed. Most of the upper watershed is forested (~10%), with the remainder cleared for rural (74%) and urban (~10%) uses, leaving only narrow riparian vegetation in most areas [30]. Major land uses in the watershed include sugar-cane, horticultural tree crop production, tropical fruit, vegetables and pastures for dairy and beef cattle [31]. Sugar-cane is the dominant crop covering 60 km², which is approximately 10% of the watershed [30]. Crops are supported on a variety of soils that vary in drainage, P-sorbing ability and bioavailable P content. The major soil types utilized for agriculture in the watershed include Red Kandosols, Yellow Kandosols, Chromosols, Redoxic Hydrosols, Podosols and Yellow Kurosols (classified according to [32]).

![Figure 1: Location of study sites in the Maroochy River and adjacent to the river mouth. Distance is given as kilometers from the river mouth. The shaded area represents cropped land. The patterned area represents the approximate bounds of river plume.](image-url)
According to the U.S. Taxonomy [33], these soils comprise 5 Alfisols, 1 Ultisol (Redoxic Hydrosol) and 1 Spodosol (Podosol). Fertilisers are applied to these soils in ammonium (N) and orthophosphate (P) forms. The Maroochy River receives nutrients from various diffuse and point sources within the watershed; with sewage outfalls and watershed runoff delivering the most significant loads of N and P at approximately equal loadings [34].

There are several near-shore reefs adjacent to the Maroochy river mouth (Fig. 1), with the reef around Mudjimba Island being a popular SCUBA diving site. The climate of the region is subtropical with typically wet summer and dry winter seasons.

Five study sites that are influenced by various watershed activities were selected in the Maroochy River and offshore of the river mouth (Fig. 1). The five river sites covered the transition from freshwater to marine waters and were located within a forested area (23 km upstream from the river mouth), a cane drain (19 km upstream), a sugar-cane area (15 km upstream), at a sewage-treatment outfall (STP) (3 km upstream) and a well-flushed site close to the river mouth (0.5 km upstream). The freshwater stream located in the forested area flows into Yandina Creek during high flow events only and does not flow in dry conditions.

The sites adjacent to the river mouth were located within the flood plume of the Maroochy River (Fig. 1). The extent of the river plume was assessed by aerial observation during a large flood event in May 1999. The first site was located close to the river mouth (1 km downstream from the mouth), two sites were located at Surprise Reef (2 and 2.5 km downstream) with the remaining two sites at Mudjimba Island (3.5 km and 4 km from the mouth).

The seven major agricultural soil types in the watershed (mentioned above) were also sampled. The surface layer (top 10 cm) of soil was collected from various locations within the watershed (Fig. 2).

![Figure 2: Location of bulk soil samples in the Maroochy River Catchment, Queensland, Australia.](image-url)
2.2 Sampling strategy

Water and sediment samples were collected during 4 separate trips to the Maroochy River between May 1999 and November 2000 during wet and dry conditions (Fig. 3). The river flooded in May 1999 and a plume stretching past Mudjimba Island was visible from the air (Fig. 1). Due to difficulties in obtaining sufficient suspended sediments for analysis, a transect extending from the Maroochy River mouth to Mudjimba Island was planned to locate and sample sediments that had settled from the plume, or previous run-off events. The trip was delayed for several months to October 1999, due to unsuitable sampling conditions (big seas and strong wind) after the flood. Despite the delay, deposited sediments were located and sampled. Sediment samples from the Maroochy River were taken 1 month later in November 1999 for comparison. Following more than a year of above average rainfall, a drought occurred from August to October 2000. The river was sampled during September 2000 to capture the dry conditions. The final sampling was conducted after the first big rainfall following the drought in November 2000. Bulk soil samples were collected in January 1999.

2.3 Water quality

Physical aspects of water quality measured in this study included total suspended solids (TSS), secchi depth, salinity, chlorophyll a (Chl a), pH and temperature. Salinity, pH and temperature were measured in the field using a Horiba Water Quality Checker Model U-10. The Horiba was calibrated, as per manufacturers instructions, prior to every sampling. On return from the field, salinity and pH were checked against standard solutions to monitor for instrument drift (which was negligible).

![Figure 3: Daily rainfall data (mm) recorded at Maroochydore during the study. Arrows denote time of sampling.](image)
Water was sampled at approximately 0.1 m depth using a bucket on the top of the flooding tide (river sites) and opportunistically at sites that were not tidally influenced. Triplicate water samples for Chl a analysis were collected and filtered (Whatman GF/F filters), then stored on dry ice. In the lab, the filter was ground in 90% acetone to extract Chl a, spectral extinction coefficients were determined on a spectrophotometer and chlorophyll a concentrations calculated according to Parsons et al. [35]. Triplicate 2 L samples of water from each site were stored in rinsed plastic containers until return to the laboratory where samples were filtered through a preweighed Whatman GF/F filters for determination of TSS using method SM 2540D [36]. A known volume of water was filtered onto a preweighed and predried (110 °C; 24 h) Whatman GF/C glass-fiber filter. The filter was then oven dried at 60 °C for 24 h and total suspended solids calculated by comparing the initial and final weights [36].

To assess dissolved nutrients (ammonium, nitrate/nitrite, phosphorus) samples were filtered in the field to remove particulate matter using a 60-mL syringe and Sartorius Minisart 0.45 µm disposable membrane filters. Total nutrients (total Kjeldahl nitrogen and total phosphorus) were collected using a 60-mL syringe without a filter in order to obtain a whole water sample. Collected samples were stored in plastic 100-mL bottles. Filtered and unfiltered water samples were frozen immediately using dry ice and transported to the laboratory where they were analyzed using the standard auto-analyzer chemical techniques of Clesceri et al. [36].

2.4 Suspended sediments

Bulk water samples (~100-L) were collected at the water surface in 25-L acid-washed opaque plastic drums. Samples were kept out of direct sunlight to minimize heating in the field and stored at 4 °C in the laboratory prior to analysis. Water samples were then centrifuged (in 600-mL aliquots) at 2000 rpm for 15 min. The overlying water was then decanted and the suspended sediment slurry collected and oven-dried. Collected sediments were analyzed for total P (TP) [37], Fe-oxide extractable P (FeO-P) [24], total N (TN) and total organic C (TC) by combustion analyzer and total aluminum (Al) by XRF. Analyses were conducted in triplicate or duplicate (depending on sample availability). Particle size was determined using the laser optical particle-sizing method [38], Calgon dispersant and ultrasound were used to fully disperse the dry sediment samples prior to analysis with a Malvern laser-diffraction instrument.

2.5 River and oceanic sediment

Sediments were sampled from the Maroochy River and adjacent to the river mouth by divers using SCUBA or snorkeling gear. River samples were taken from subtidal areas of the riverbank, not the scoured floor of the river channel. Near-shore samples were collected from various depths shallower than 15 m. The upper layer (~top 2 cm) of sediment was scraped using a stainless steel scraper and placed directly into a zip-lock plastic bag. The sediment slurry was then transported to the surface and snap frozen using dry ice. Syringes (60 mL) were used to collect the
fine clay layer of deposited sediments found at several locations outside the river mouth. This fine clay layer was dark colored and resembled deposited sediment, and was easily distinguished from the underlying marine sediment. Samples were frozen immediately and stored at −20 °C prior to analysis. In the laboratory, the deposited sediment samples were thawed and then shaken to resuspend the sediments. Sand particles were then separated from the finer clay- and silt-sized particles and the remaining mixture centrifuged to collect the deposited sediment.

Sediments were analyzed for total P, Fe-oxide extractable P, total N, total C, total Al and Si as described above. Analyses were conducted in duplicate, where possible (depending on sample volume). Particle size was also determined using the laser optical particle-sizing method described above.

### 2.6 Soil samples

Bulk soil samples (0–10 cm depth) were collected at each site. Half of each bulk sample was enriched with P (as solution K$_2$HPO$_4$) at concentrations comparative to sugar-cane fertilizer applications (solution P concentration of 0.2 mg P L$^{-1}$). Phosphorus is usually applied as either mono- or di-ammonium phosphate fertilizer. Simulated aquatic sediments (comprising clay- + silt-sized particles <20 µm diameter) were prepared, as follows, from collected soils. Air-dried (<2 mm) soil samples (300 g) and deionized water were added to perspex cylinders (30 cm long × 7 cm internal diameter) to give a final soil and water volume of 1.2 L. Cylinders were then inverted several times over 30 s and allowed to stand without agitation for 4.5 min at 22 °C, after which the top 10 cm of the suspension was removed by suction. Based on Stokes’ Law, at 22 °C all particles with diameters >20 µm (i.e. fine and coarse sands) should have vacated the top 10 cm in this time, leaving the suspended clay- + silt-sized (<20 µm diameter) fraction [39]. The suspension was then left for a further 4.5 min without agitation, to enable particles >20 µm to settle out of the next 10 cm, thus enabling further collection of clay + silt-sized particles. Deionized water was then added to the cylinder to bring the volume back to 1.2 L, and the shaking and settling process was repeated four times to collect the remaining particles <20 µm diameter. The collected suspensions were centrifuged (20 min, 4000 g), the supernatant discarded, and the sediment plugs were oven dried at 40 °C for 2 days. Particle size was also determined using the laser optical particle-sizing method of [38].

### 2.7 Sediment bioassays

Sediment bioavailable P was determined using the sediment bioassay technique developed in Chaston [23]. Nonaxenic unialgal cultures of *Skeletonema costatum* were obtained from the culture collection of CSIRO Marine Research, Tasmania, Australia. Bioassays were conducted in triplicate using 250 mL Erlenmeyer flasks with 100 mL of modified f/2 media (without P) inoculated with approximately 200 000 cells L$^{-1}$ of *Skeletonema costatum*. One hundred mg L$^{-1}$ of air-dry sediments (clay and clay + silt, with and without P enrichment) were used as the sole source of P in the sediment bioassays. Control bioassays that had no sediment additions,
only modified f/2 media (f/2–P), were conducted to assess any growth associated with carry over P in the internal nutrient pools of the algal cells or seawater used in the media. Growth under optimum nutrient conditions (complete f/2 media) was also measured as a control response that could be compared between experiments to monitor natural growth fluctuations. Flasks were continually shaken to prevent CO₂ limitation and pH was assumed constant [23].

In-vivo Chl a fluorescence was used as a proxy of algal biomass to monitor the bioassay response. Fluorescence was measured at identical circadian times daily with a Turner TD 700 fluorometer fitted with a 13-mm test tube adapter to hold small test tubes, a red photomultiplier, daylight white lamp and broad-band Chlorophyll filter kit (340–500 nm excitation, >665 nm emission). Five-milliliter sub-samples were taken aseptically, dark adapted for 30 min prior to fluorescence measurements then discarded. Algal growth was measured daily until a decline in biomass was observed, which usually occurred within 7 days. Maximum growth was defined as the maximum fluorescence standard units (fsu) attained prior to cells reaching stationary growth [(when daily growth was not significantly higher (p < 0.05)]. Maximum fsu was not used due to the error associated with fsu/cell variability when cells are nutrient limited. The maximum growth (fsu) was then converted into Chl a (µg L⁻¹) using the correlation between extracted and in-vivo data from different stages of the S. costatum growth cycle (Chl a = 2.5115 × fsu). Chaston [23] determined that direct conversion was possible as long as bioassays were in exponential growth and not nutrient limited. Algal biomass related to internal nutrient pools or seawater used in the media was corrected for by subtracting the maximum control biomass (no added P) from the maximum sediment biomass. This was termed the ‘maximum algal biomass’. The maximum algal biomass of each sediment type was then correlated against the measured chemical fractions of P to determine which fractions best reflected algal bioavailable P.

3 Results

3.1 Water column and sediment nutrients

Total water column nutrients (N and P) were higher than dissolved nutrients at all sampling locations along the river and adjacent to the river mouth during low-flow conditions (Fig. 4). Total P was approximately 10 times greater than dissolved reactive P (DRP) in the upstream cane area (~15 km), which was most likely attributable to high suspended sediment (Fig. 4a). Total P and DRP were most elevated at the sewage outfall (~3 km). Phosphorus concentrations dropped in the middle reaches of the river (~15 km) and close to and adjacent to the river mouth. Total P was only 2 times greater than DRP at the oceanic sites.

Sediment Fe-oxide-extractable P followed a similar trend to water column P within the river and was lowest at the upstream cane area (4.2 mg kg⁻¹) and highest at the sewage outfall (7.3 mg kg⁻¹) (Fig. 4c). However, sediment P remained elevated at the river mouth and at several oceanic sites, which varied from 1.5 mg kg⁻¹ just outside the river mouth to 7.6 mg kg⁻¹ at Surprise Reef.
Nutrient Bioavailability of Soils and Sediments

Water column total N decreased from 70 µM upstream (cane area) to 16 µM at the river mouth, averaging 7 µM outside the river (Fig. 4b). In comparison, there was little difference in DIN between the upstream cane area (10 µM) and sewage outfall (8 µM), indicating that elevated TN upstream was most likely attributable to suspended sediments or dissolved organic N, although there was a large drop in DIN from the sewage outfall (8 µM) to the mouth (0.6 µM). Conversely, sediment total N content in the Maroochy River was lowest upstream (500 mg kg\(^{-1}\)) and highest at the sewage outfall (1160 mg kg\(^{-1}\)) (Fig. 4d), similar to sediment P content. Sediment N content decreased close to the river mouth (50 mg kg\(^{-1}\)) and increased with distance outside the mouth to 180 mg kg\(^{-1}\) at Mudjimba Island.

3.2 Sediment and soil nutrients

Total P content of the deposited sediment at Surprise Reef and Mudjimba Island (1290 mg kg\(^{-1}\)) was much higher than the P content of river (420 mg kg\(^{-1}\)) and marine (103 mg kg\(^{-1}\)) sediment as well as bulk soil (410 mg kg\(^{-1}\)) (Table 1). The total P content was comparable to fertilised soil (888 mg kg\(^{-1}\)) and suspended sediment (990 mg kg\(^{-1}\)) in the Maroochy River. The Fe-oxide-extractable P content of the deposited sediment (49.7 mg kg\(^{-1}\)) was also more elevated than the river (4.2 mg kg\(^{-1}\)) and marine sediment (5.3 mg kg\(^{-1}\)) as well as soil (7.4 mg kg\(^{-1}\)), although less than fertilised soil (68.5 mg kg\(^{-1}\)) and suspended sediment (90.2 mg kg\(^{-1}\)). It is interesting to note that although the total P content of the river sediment...
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was approximately 4 times higher than the marine sediment, Fe-oxide-extractable P content was similar. This indicates that most bioavailable P in the river sediments is either desorbed/fluxed from the sediment, or associated with organic matter (organic P) that is not measured as Fe-oxide P (as total C is 2–3 times higher in the river than the marine sediments).

Total N content of the deposited sediment (3630 mg kg\(^{-1}\)) was approximately two times greater than the soil (1980 mg kg\(^{-1}\)), three times higher than the river sediment (1363 mg kg\(^{-1}\)), and 30 times higher than the marine sediment (110 mg kg\(^{-1}\)). The total carbon content of the deposited sediment (4.4%) was comparable to bulk soil (3.5%) and was greater than the river sediment (1.9%) and marine sediment (0.8%). Total silicon content varied from 26.8% (suspended sediment) to 42.6% (marine sediment). Soil (35.1%) and river sediment (33.7%) had similar silicon contents, as did the suspended sediment (26.8%) and deposited sediment (28.3%).

The total aluminum content of the soil (4.56%), deposited sediment (5.76%) and river sediment (6.46%) were comparable. Suspended sediment had the highest Al content (10.25%) and the marine sediment contained the lowest (0.52%). Similarly, the total iron content of deposited sediment (3.3%) was comparable to the suspended sediment (4.8%) and river sediment (3.3%), and approximately two times greater than the bulk soil (1.7%). The marine sediment was markedly different; with the total Fe content being an order of magnitude lower (0.2%) than the other sediment samples and the bulk soil. Al and Fe are terrestrial elements found commonly in soil [40], and thus are not naturally abundant in marine sediments [41]. The similarities in the composition of deposited sediment with estuarine suspended sediments and bulk soils, particularly Al and Fe, indicates that the deposited sediments are more likely terrigenous in origin than marine.

Table 1: Mean nutrient content of different sediment types in the Maroochy River Catchment.

<table>
<thead>
<tr>
<th>Sediment type</th>
<th>Total P (mg kg(^{-1}))</th>
<th>FeO-P (mg kg(^{-1}))</th>
<th>Total N (mg kg(^{-1}))</th>
<th>Total C (%)</th>
<th>Total Si (%)</th>
<th>Total Al (%)</th>
<th>Total Fe (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>410 (140)</td>
<td>7.4 (2.4)</td>
<td>1980 (881)</td>
<td>3.5 (1.3)</td>
<td>35.1 (2.9)</td>
<td>4.6 (1.5)</td>
<td>1.7 (0.4)</td>
</tr>
<tr>
<td>Fertilized soil</td>
<td>888 (346)</td>
<td>68.5 (21.7)</td>
<td>NA (NA)</td>
<td>NA (NA)</td>
<td>NA (NA)</td>
<td>NA (NA)</td>
<td>NA (NA)</td>
</tr>
<tr>
<td>Suspended sediment</td>
<td>990 (637)</td>
<td>90.2 (46.0)</td>
<td>NA (376)</td>
<td>(1.6) (0.5)</td>
<td>(2.3) (1.41)</td>
<td>(4.8) (0.5)</td>
<td></td>
</tr>
<tr>
<td>River sediment</td>
<td>420 (119)</td>
<td>4.2 (1.2)</td>
<td>1363 (376)</td>
<td>1.9 (0.5)</td>
<td>33.7 (2.8)</td>
<td>6.5 (0.2)</td>
<td>3.3 (0.1)</td>
</tr>
<tr>
<td>Marine sediment</td>
<td>103 (37)</td>
<td>5.3 (1.05)</td>
<td>110 (18)</td>
<td>0.8 (0.4)</td>
<td>42.6 (2.8)</td>
<td>0.5 (0.2)</td>
<td>0.2 (0.1)</td>
</tr>
<tr>
<td>Deposited sediment</td>
<td>1290 (159)</td>
<td>49.7 (8.8)</td>
<td>3630 (479)</td>
<td>4.4 (0.6)</td>
<td>28.3 (3.9)</td>
<td>5.8 (1.1)</td>
<td>3.3 (0.8)</td>
</tr>
</tbody>
</table>

Value in brackets denotes standard error of mean. N = 3. NA = not available.
3.3 Suspended sediment

During wet conditions suspended sediments from the cane area (16 km upstream) had the highest total P content (2260 mg kg\(^{-1}\)), which was approximately double the total P in the deposited sediment samples (1290 mg kg\(^{-1}\)) and 1.5 times greater than sediments simulated from fertilized soils (silt-sized 1417 mg kg\(^{-1}\), clay 1602 mg kg\(^{-1}\)) (Table 2). Total P of the deposited sediment was comparable to the fertilized simulated sediments and greater than the nonfertilized simulated sediments. The forested stream and cane drain had the lowest total P concentrations.

The bioavailable P content of the suspended sediments in the Maroochy River (measured as Fe-oxide-extractable P) was lowest at the forested stream site (3.3 mg kg\(^{-1}\)) and cane drain (13.4 mg kg\(^{-1}\)), then decreased with proximity to

### Table 2: Comparison of suspended sediment nutrient content and grain size between field and simulated suspended sediments and deposited sediment.

<table>
<thead>
<tr>
<th>Sample location</th>
<th>Total P (mg/kg)</th>
<th>FeO-P (mg/kg)</th>
<th>Total N (mg/kg)</th>
<th>Mean particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forested stream (−23 km)</td>
<td>260 (0.1)</td>
<td>3.3 (0.1)</td>
<td>NA</td>
<td>29.9</td>
</tr>
<tr>
<td>Cane drain (−19 km)</td>
<td>450 (0.3)</td>
<td>13.4 (0.3)</td>
<td>NA</td>
<td>15.7 (5.8)</td>
</tr>
<tr>
<td>Cane area (−16 km)</td>
<td>2260 (3.7)</td>
<td>258 (3.7)</td>
<td>NA</td>
<td>28.3</td>
</tr>
<tr>
<td>Sewage outfall (−3 km)</td>
<td>NA</td>
<td>106 (1.5)</td>
<td>NA</td>
<td>27.2</td>
</tr>
<tr>
<td>River mouth (−0.5 km)</td>
<td>NA</td>
<td>69.8</td>
<td>NA</td>
<td>32.7</td>
</tr>
<tr>
<td>Deposited sediment (+1.5–3 km)</td>
<td>1290 (159)</td>
<td>49.7 (8.8)</td>
<td>3630 (480)</td>
<td>7.3 (0.0)</td>
</tr>
</tbody>
</table>

**Suspension sediment source**

<table>
<thead>
<tr>
<th></th>
<th>Total P (mg/kg)</th>
<th>FeO-P (mg/kg)</th>
<th>Total N (mg/kg)</th>
<th>Mean particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulated silt + clay (silt-sized particles)</td>
<td>677 (142)</td>
<td>13.4 (4.0)</td>
<td>3861 (540)</td>
<td>10.1 (0.9)</td>
</tr>
<tr>
<td>Simulated silt + clay (+P) (silt-sized)</td>
<td>1417 (266)</td>
<td>95.5 (25.1)</td>
<td>5413 (805)</td>
<td>4.7 (0.7)</td>
</tr>
<tr>
<td>Simulated clay (clay-sized particles)</td>
<td>851 (139)</td>
<td>15.1 (4.2)</td>
<td>5413 (805)</td>
<td>4.7 (0.7)</td>
</tr>
<tr>
<td>Simulated clay (+P) (clay-sized particles)</td>
<td>1602 (245)</td>
<td>95.6 (22.0)</td>
<td>5413 (805)</td>
<td>4.7 (0.7)</td>
</tr>
</tbody>
</table>

Values in brackets indicate standard error of mean when enough sample was available. Some analyses were not replicated or conducted (NA) due to limited sediment quantities.
the river mouth. Suspended sediments collected from the cane area (16 km upstream) had the highest Fe-oxide-extractable P (258.4 mg kg\(^{-1}\)) in the Maroochy River (Table 2). Fe-oxide-extractable P was approximately 2.5 times greater than suspended sediments simulated from fertilized soil (silt-sized = 95.5 mg kg\(^{-1}\), clay = 95.6 mg kg\(^{-1}\)) and 5 times higher than deposited sediment (49.7 mg kg\(^{-1}\)). Suspended sediments collected at the sewage outfall (105.82 mg kg\(^{-1}\)) and river mouth (69.8 mg kg\(^{-1}\)) had comparable Fe-oxide-extractable P to simulated fertilized sediments. Suspended sediments in the cane drain had comparable Fe-oxide-extractable P to sediments simulated from nonfertilized soils (silt-sized 13.42 mg kg\(^{-1}\); clay 15.1 mg kg\(^{-1}\)). The forested stream site had the lowest Fe-oxide-extractable P (3.3 mg kg\(^{-1}\)). The deposited sediment samples contained approximately half of the Fe-oxide-extractable P bound to the simulated fertilized sediments and had more than double the P bound to simulated sediments derived from nonfertilized soils.

The deposited sediment and simulated silt-sized sediments had comparable total N contents (3630 and 3861 mg kg\(^{-1}\), respectively). The simulated clay sediments (5412 mg kg\(^{-1}\)) had approximately 1.5 times more total N than the deposited sediment and silt-sized sediments, and were approximately 2.5 times more enriched than the soil they were simulated from.

Mean particle size was very fine within the Maroochy River and varied between 16 µm (cane drain) and 33 µm (river mouth). The deposited sediment samples (7.3 µm) were at least half the size of the river samples and were intermediate between the simulated silt-sized (10.1 µm) and clay (4.7 µm) suspended sediments.

Due to the amount of water required to sample suspended sediments during low-flow conditions, insufficient quantities were obtained for sediment analysis except at the sewage outfall during the September 2000 drought. Mean sediment size (9.6 µm) was approximately one third the size of sediments sampled during wet conditions (27.3 µm). There was also variation in particle size between wet sampling [Feb. 1999 (data not presented) and November 2000] at the upstream cane site (28.31 µm Nov. 00, 17.7 µm Feb. 99) and pristine site (29.9 µm Nov. 00, 6.3 µm Feb. 99). The sediment that was sampled was much finer than the sediment captured during the initial ‘flush’ of sediments in November 2000. This highlights the pulsed nature of sediment transport and the difficulty in accurately capturing the pulse of suspended sediments.

### 3.4 Deposited sediment bioassays

Sediment deposited at Mudjimba Island and Surprise Reef contained a high content of measured bioavailable P (Fe-oxide-extractable P) (Table 2). When deposited sediment was used as the sole source of P in sediment bioassays, maximum *Skeletonema costatum* biomass reached 450–500 µg Chl a L\(^{-1}\) (Fig. 5). In comparison the underlying sand at each site only produced a maximum biomass of 150 µg Chl a L\(^{-1}\). There was little variation between the sand collected from Surprise Reef (sand 1,2) and Mudjimba Island (sand 3).
Conversely, the maximum biomass differed with deposited sediment type, although there was little variation within replicates. This was attributable to the varying Fe-oxide-extractable P content of the deposited sediment sampled from different sites (Fig. 6). The maximum algal biomass correlated well with Fe-oxide-extractable P content of simulated sediment, sand and deposited sediment.
(r = 0.944 p < 0.001) (Fig. 6). This demonstrates the suitability of Fe-oxide P as a measure of bioavailable P in both marine and terrigenous sediments.

3.5 Transport of suspended sediments and deposited sediment

It was apparent from visual observation in the field that suspended sediment load in the Maroochy River was heaviest during heavy rainfall conditions. This was particularly apparent at the well-flushed river mouth, which normally had clear, blue water in dry conditions. The transport of large amounts of suspended sediments outside the river mouth was easily visible.

The influence of freshwater was apparent with a large drop in salinity during the wet season (Fig. 7a). Salinity decreased ~30‰ at the sewage outfall (3 km from the river mouth) to only 5‰. The suspended sediment load varied within the river as well as with sampling time (wet vs. dry) (Fig. 7b). During the wet sampling turbidity was highest in the cane drain (70 mg L\(^{-1}\)) and dropped significantly to

![Graphs showing salinity, total suspended sediments, dissolved inorganic nitrogen, dissolved reactive phosphorus, and Secchi depth during wet and dry conditions.](image-url)
15 mg L\(^{-1}\) in the upstream cane area. Turbidity increased to 20 mg L\(^{-1}\) at the sewage outfall and decreased to 10 mg L\(^{-1}\) at the mouth. The opposite occurred during the dry sampling, with maximum turbidity at the sewage outfall (~45 mg kg\(^{-1}\)) and lowest upstream (10 mg L\(^{-1}\)) at the cane drain. The forested stream located 23 km upstream did not flow during dry conditions. The secchi depth was inversely related to water-column turbidity, with the secchi depth increasing in proximity to the river mouth during both dry and wet seasons (Fig. 7f).

The Chl \(a\) concentration also varied within the river and between sampling times (Fig. 7c). In the wet sampling, the Chl \(a\) maximum occurred upstream in the cane area (~20 µg Chl \(a\) L\(^{-1}\)). Chl \(a\) concentration was similar in the cane drain and downstream at the sewage outfall (~5 µg Chl \(a\) L\(^{-1}\)). Chl \(a\) was not detected at the forested site (~23 km) and was also low at the river mouth (2.5 µg Chl \(a\) L\(^{-1}\)). In the dry sampling the maximum occurred in the cane drain and was only 5 µg Chl \(a\) L\(^{-1}\) (4 times lower than the wet maximum).

Concentration of Chl \(a\) was inversely related to the suspended sediment load in the water with maximum Chl \(a\) corresponding to low water-column turbidity. In dry conditions, phytoplankton biomass was highest in the cane drain, which had lower turbidity than sites downstream (except for the mouth). In wet conditions turbidity was highest in the cane drain thus phytoplankton biomass was low as light probably limited growth. During wet conditions the Chl \(a\) maximum occurred at the upstream cane site, which had lower turbidity than the cane drain and sewage outfall. The chlorophyll maxima also corresponded to DIN, which was greatest in the cane area in the wet season and cane drain in the dry (Fig. 7d). Chl \(a\) was continually low at the well-flushed river mouth during wet and dry conditions. Although nutrients are flushed through the river mouth, phytoplankton is unlikely to assimilate nutrients within such short water residence times. The forested stream (23 km upstream) also had low Chl \(a\) biomass. This may be attributable to low dissolved nutrient concentrations and its ephemeral nature as the stream flowed for only short periods. Algal biomass appeared to be influenced by DIN rather than DRP as Chl \(a\) maximum corresponded to elevated DIN not DRP. However, it should be noted that additional nutrients, particularly P, would be associated with the suspended sediments, which were not quantified. Elevated DIN in the cane area may be caused by fertiliser run-off and leaching of NO\(_3^-\) from the land to the water. Elevated P levels are most likely caused by desorption of P from sediment particles eroded from nearby agricultural soil.

4 Discussion

4.1 Delivery of nutrients to the coastal ocean

4.1.1 Phosphorus and nitrogen pathways

Phosphorus (as orthophosphate) and nitrogen (as ammonium) are applied as fertilizers to the seven major agricultural soils in the Maroochy Watershed. It is well known that crops do not assimilate all of the P and N added as fertilizer [42], thus a significant fraction is dissolved in the soil porewater or bound to soil particles.
The major pathways of P and N movement from land to water vary due to different cycling processes in the soil (Fig. 8). Most P will be transported to waterways in particulate form via sorption to soil particles [14, 17, 21, 43], as P sorption readily occurs by covalent bonding of phosphate ions to hydrous oxides of iron (Fe) and aluminum (Al) on particle surfaces [44]. A fraction of the particulate P is desorbable and thus potentially bioavailable (Froelich, [14]). Turnover times for inorganic phosphorus in the water column of the GBR range from hours to weeks [45]. Conversely, the majority of bioavailable N enters the marine environment in dissolved form, either as nitrate or ammonium or adsorbed to particles (ammonium) [13]. Nitrate is the dominant form, transported via surface run-off and through leaching processes into the ground water [13] (Fig. 8). In addition, there is increasing evidence that transport of N by the intertidal and subtidal flux of ground water is significant for coastal ecosystems [46]. As ammonium is not readily leached, it is either a) dissolved in the soil pore water or b) adsorbed to the surface of clay and organic matter by ion exchange or c) fixed within layers of the clay structure and is not available for biological uptake [16]. However N can be released once sediments are deposited through biological regeneration, remobilization and sediment resuspension [47]. Once transported into marine waters, dissolved ammonium and nitrate are readily assimilated by phytoplankton or other marine plants as N often limits productivity in marine environments [42, 48, 49]. Estimates of N demand by phytoplankton on the GBR indicate dissolved inorganic N pools have turnover times of the order of hours to days [45].

4.1.2 Sediment and nutrient transport

During high-intensity rainfall events P-rich agricultural soils (sand, silt and clay-sized particles) are eroded into nearby streams and rivers (Fig. 8). Coarser soil particles (sand) settle out first and are deposited as river sediments; the finer fractions (silt and clay) eventually deposit close to the coast [50, 51] (Fig. 8). The large difference in particle size between suspended sediments at the Maroochy River mouth (>20 μm) and sediment deposited outside the river mouth (silt-sized <20 μm) (Table 2), indicates that this settling process occurred in the Maroochy River. The suspended sediment and deposited silt-sized particles were enriched with total P comparable to fertilized soil from the watershed. Finer-sized particles have an increased adsorption capacity due to their large surface area [52], thus contain the highest concentration of bioavailable P per unit weight [53]. In addition, the deposited sediment also had elevated TN concentration (3630 mg kg⁻¹) which was almost double the TN measured in the watershed soils. This indicates that nutrient-rich sediments are being eroded from the Maroochy Watershed, flushed into the Maroochy River during heavy rainfall events and deposited offshore. The chemical composition of the deposited offshore sediment was more comparable to the bulk soil, suspended sediment and river sediment than the underlying marine sand (Table 1). The dissimilarities between the deposited sediment and the underlying marine sand, suggest that the deposited sediment was not marine in origin and more likely terrigenous. The large difference in total Al and Total Fe content of the deposited sediment and marine sediment further validates this, as Al and Fe
Figure 8: Conceptual model of the movement and processing of sediment and nutrients in the Maroochy River and offshore (see text for explanation).
are terrestrial elements [40], which do not naturally occur in high concentrations in marine sediments [41].

In subtropical and tropical systems, such as the Maroochy Watershed, the transport and deposition of silt and clay and associated nutrients offshore are most often associated with pulsed storm events [20, 22]. During flood conditions, estuarine processes may be bypassed and freshwater, sediments and nutrients discharge directly onto the continental shelf [54, 55]. Additional sediment and nutrients may also be supplied by erosion and scouring of the estuary floor during these conditions [54, 55]. As storm events occur over short time frames, Australian rivers and estuaries only contribute a significant amount of material to the continental shelf for short periods [56]. Although plumes spread in a band up to 50 km from the coast, particulate material is trapped within 10 km of the coast [57]. Fine-sized particles have been shown to deposit and accumulate close to the shore, with silt and clay being found 5–20 km offshore in the Johnstone River watershed (North Queensland, Australia) [19]. In the Maroochy watershed a thin film of clay and silt deposited in grooves and sheltered areas on a rocky near-shore reef located 2.5–4 km from the Maroochy River mouth. Sediment movement may also occur with the continual resuspension and redistribution of sediment at the river mouth due to tidal flushing and wind resuspension [47]. Flushing and exchange of clean oceanic water with estuarine water at the river mouth, improves water clarity (measured by secchi depth) with distance downstream (Fig. 7).

4.1.3 Cycling of nitrogen and phosphorus

Once soils are eroded into waterways, some P may be desorbed from particle surfaces into the water column and be assimilated by marine plants such as phytoplankton [14]. The remaining P may either be deposited with silt and clay particles in the river or transported offshore with suspended clay particles as previously mentioned. Ammonium will also be deposited in the river and transported offshore, due to strong sorption to particle surfaces. This is reflected in the high total N concentration of the deposited sediments outside the Maroochy River (Table 1).

Once sediments (mostly silt and some clay) deposit in the river, microbial mineralization may generate additional release of ammonium and P out of the sediments into the water column. Additional desorption or sorption of P to particles may also occur when sediments are resuspended by wind, waves or tides [14].

The deposition of clay and silt particles offshore provides a source of bioavailable P, total P, total N (Table 1), and ammonium. Although the ammonium content of the sediments was not measured in this study, previous research (Chaston, [23]) found the ammonium concentrations in silt and clay particles collected from the Maroochy watershed were elevated. Although ammonium does not appear to be immediately bioavailable when sediments are in suspension (Chaston, [23]), biological processing in the sediments may facilitate further N release once sediments are deposited [13]. The deposited sediment was a significant source of bioavailable P (Fig. 4), in contrast to the underlying marine sand (Fig. 5). Additional release of sediment bound P and N may occur during sediment resuspension events [58–60].
In the Great Barrier Reef lagoon, algal blooms have been linked to wind resuspension of sedimentary nutrients [61, 62]. The regeneration of P is so efficient in coastal systems that only a small proportion is lost permanently to the sediments by burial [13]. Microbial mineralization of organic N released from resuspended shelf sediments in the GBR has been associated with elevated water-column dissolved inorganic concentrations after a cyclonic disturbance [61]. In the Moresby River estuary (North Queensland), estuarine sediments appeared to be a source of nitrate during the dry season [21].

4.2 Environmental implications

4.2.1 Impact on river and estuary ecosystem health

Although elevated nutrient concentrations may not cause excessive algal growth in turbid waterways where light limits algal growth [63], the movement and deposition of suspended sediments to estuaries and the coastal ocean where light is not limiting, may enhance growth. This is particularly significant in areas where algal productivity is limited by nutrients. Although N usually limits productivity in estuarine and coastal waters [42, 49, 64], increased bioavailable P could further strengthen N limitation, favoring N-fixing cyanobacteria [65]. Nutrient enrichment can also alter the phytoplankton community composition [66], which can have significant impacts on grazers and predators, although this is not well studied [42].

4.2.2 Impact of offshore sediment and nutrient deposition

The impact of sediment and nutrient movement offshore of the Maroochy River is likely to have a localized, small impact due to the dilution of nutrients and dissipation of sediments by the ocean. The Maroochy River drains directly onto the continental shelf of the Pacific Ocean, thus nutrient-rich plume waters are quickly diluted. However, flood plumes extending to Mudjimba Island did persist for several days during the study, and deposited clay and silt was found 5 months after the flood event. Nutrient enrichment is likely to be restricted to localized areas where nutrient-rich clay and silt particles are deposited. Benthic microalgae and macroalgae growing in these areas can potentially take up nutrients from these enriched sediments [67–69]. In addition, marine phytoplankton will quickly assimilate any nutrients that are released into the water column [46]. Although these impacts are localized, they may have a detrimental effect on the recreational value of the near-shore reefs in the area, due to increased turbidity. Continual nutrient enrichment can also lead to the detrimental impacts mentioned above.

In comparison, the movement and deposition of sediments and nutrients offshore to areas with restricted tidal exchange and long residence times, such as enclosed bays and lagoons, may have more significant and detrimental impacts. In other areas of southern Queensland, there have been several reports of very significant impacts of sediment loads on downstream coastal seagrass areas, including extensive loss of seagrass areas in Hervey Bay, following flood events [70], and the loss of seagrass in southern Moreton Bay associated with general increases
in turbidity [71]. Nutrient- and sediment-rich river flow, often associated with increased agriculture, has also had significant impacts worldwide. Increased nutrient load in river flow, has seen an increase in hypoxia in the Gulf of Mexico, causing the formation of a huge ‘dead zone’ [72]. Increased hypoxia has also been reported in the Adriatic Sea due to nutrient-rich water from the Po River [73]. Deterioration of water quality from nutrient enrichment and sediment inputs has also caused hypoxic or anoxic conditions in Chesapeake Bay (USA), causing declines in living resources [74].

Locally, movement and deposition of suspended sediments offshore may also have significant ramifications in the Great Barrier Reef Lagoon, Australia. Terrestrial runoff of sediment and nutrients (mostly N and P) to the GBR has increased 2- to 4-fold over the last century [75, 76]. Many tropical rivers and estuaries discharge into the lagoon, which has been described as a semi-enclosed sea that annually receives an increasing load of nutrients [2]. Gradients in reef and community structure, biodiversity and ecological function in near-shore coral reef systems have been associated with environmental gradients influenced by terrestrial runoff [77].

4.2.3 Nutrient limitation
It is generally accepted that N limits productivity in most coastal marine ecosystems and P limits freshwater productivity [42]. Although N limitation has been shown to occur in southern Queensland estuaries and coastal waters [28, 78, 79], there is increasing evidence that N also limits freshwater productivity in southern Queensland streams [80]. In addition, Australian freshwater systems with long residence times show stoichiometric evidence of N limitation [81].

Low N:P ratios in rivers, estuaries and coastal waters may be reinforced by the episodic transport and deposition of P-rich sediment to Australian coastal ecosystems. The release of bioavailable P from sediments and the release of additional micronutrients such as Fe, may account for the prevalence of N-fixing cyanobacteria such as *Trichodesmium* in coastal seas [2]. Biological cycling of N in the sediment may also result in loss of N via denitrification to N₂ gas, as well as N release through nitrification [13]. Thus, N limitation may be exacerbated if denitrification rates are high.

4.2.4 Watershed management
This study highlights the importance of effective land management and erosion control measures that reduce the suspended sediment load. Although agricultural practices are continually improving to reduce soil erosion and minimize nutrient loss both locally [82] and overseas [83, 84], practices need to encompass a broader approach that emphasizes the hydrological and nutrient link between land and sea. Effective management must consider both agricultural productivity as well as potential environmental impact as practices that are economically viable may not be environmentally sustainable [11]. Mitigation measures should encompass both sediment- and nutrient-reduction strategies in order to reduce particulate and dissolved nutrient transport. Nutrient management should focus on both N and P.
as measures that control only one nutrient may enhance loss of the other [85], or cause nutrient limitation to switch between N and P [42].

Soils with high Fe-oxide-extractable P or Colwell P, which correlates with bioavailable P (Chaston, [23]) must be targeted and managed effectively, particularly in areas prone to erosion. This will be specific for each watershed, depending on the dominant erosion processes occurring and watershed hydrology (e.g. stream gradient, watershed size, topography). Hill-slope erosion (sheet and rill erosion) is the dominant erosion process in most of northern Australia, including the Maroochy River watershed [86]. Cultivated land, which covers a large area of the watershed, is an important potential source of hillslope sediments. The majority of P export may be derived from only a small portion of the watershed over a short time period [11, 17]. Thus risk assessments within the watershed should be based on soil type, land use and position in the watershed.

The 7 major agricultural soil types in the Maroochy Watershed varied in chemical composition with the total P content of unfertilized soils ranging from 20-1120 mg P kg\(^{-1}\). Only two of the soils, the Chromosol and Redoxic Hydrosol, had TP concentrations greater than 400 mg kg\(^{-1}\). The average total P content of most Australian surface soils except those derived from basalt is less than 400 mg P kg\(^{-1}\) soil [87]. However, the silt- and clay-sized fractions of the soil were more elevated (220–1390 TP mg kg\(^{-1}\)), although this was not proportional to TP of the bulk soil. Although total P is commonly used to assess the sediment nutrient status, it does not accurately reflect bioavailable P at low total P concentration and should only be used to identify soils with potentially high bioavailable P, as high total P is often well correlated with high bioavailable P [23]. Identification of soils with high bioavailable P (e.g. Red Kandosol), and thus potential to cause algal blooms when eroded, could be used to set priorities for managing watershed areas and identifying potential problem areas in terms of offsite nutrient transport.

Colwell-extractable P is widely used in Australian soils to assess the availability of P to crops [44]. Colwell P values of less than 10 mg P kg\(^{-1}\) are considered very low, while values >100 mg P kg\(^{-1}\) are considered very high. Within the intensive land use zone of Australia, 1.6% of surface soils have Colwell P < 10 mg P kg\(^{-1}\), 3.6% have Colwell P > 80 mg P kg\(^{-1}\), and the majority (60.9%) have Colwell P ranging between 10 and 30 mg P kg\(^{-1}\) [88]. The 7 major agricultural soils in the Maroochy Watershed all fall below 100 mg P kg\(^{-1}\) prior to fertilizer application, and three have very low P values (<10 mg P kg\(^{-1}\)). However, after application of P fertilizers, most values would be considered very high (up to 430 mg P kg\(^{-1}\)). The silt-sized fraction had more elevated Colwell P values, with all values (except 3 nonfertilized soils) considered very high with up to 760 mg P kg\(^{-1}\). This indicates that the fertilized soils in the Maroochy Watershed are all sources of potentially high bioavailable P and need to be carefully managed.

Although suitable chemical analyses of bioavailable P in sediments and silt and clay-sized fractions of the soil have been identified [23] the next step is to relate this to bulk surface soil. Knowledge of the enrichment ratio of P between the bulk soil and resultant sediment will allow an assessment of the risk of sediment being a P source to algae, using analyses of the bulk surface soil, rather than the silt- and
clay-sized fraction. Thus, the challenge facing soil scientists will be to develop a realistic nutrient-enrichment ratio that represents sediment moving offsite. Currently, bioavailable P is usually predicted from bulk soils assuming a nutrient-enrichment ratio based on clays only, which is estimated at 10%.

The prioritization of watershed areas could extend to classification of rivers and estuaries, based on the potential for soil erosion, general ecosystem health (background nutrient levels, primary productivity) and residence time of water. Increased residence time caused by low river flow has stimulated algal blooms in Australian rivers and estuaries [4, 89]. Flushing times were also shown to be a dominant factor in controlling the degree of internal processing of nutrients in the Richmond River Estuary, Australia [54]. The amount and duration of rainfall will also influence the amount of nutrients and sediment transported [17].

5 Conclusions

This study indicates that fine, clay-sized particles, rich in total P, total N and bioavailable P, are being transported and deposited offshore during erosion events. These nutrient-rich particles are likely to be terrigenous in origin as their chemical composition is more comparable to the estuarine suspended sediments and surface soils than the underlying marine sand. This demonstrates the connectivity between the watershed, land and sea and highlights the need for multifaceted watershed management that encompasses; a) erosion control measures that reduce the suspended sediment load of nutrient-rich clay- and silt-sized fractions, and b) nutrient-reduction strategies. Effective management must consider agricultural productivity as well as the potential environmental impact, as what is economically viable may not be environmentally sustainable.

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