Processes of P mobility from Fitzgerald river catchment following application of different p rates

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Abstract
Phosphorus (P) export by erosion, surface runoff, throughflow and leaching are considered the main sources of P loss from agricultural land. The present study was conducted on the upper Fitzgerald River Catchment in the South coast region of Western Australia (WA) to examine the process of P mobilization at different P rates (0, 20 and 40 kg P/ha). Intact column leaching, packed box and field runoff plot studies were conducted on contrasting soils from the catchment. Soil solution was collected at 5, 10 and 15 cm by installing Rhizon soil solution samplers, and leachate collected at 30 cm. Runoff and soil solutions were analysed for particulate P (PP), dissolved reactive P (DRP), and total dissolved P (TDP) and dissolved organic P (DOP) was calculated by difference (TDP-DRP). Overall, DRP comprised <35 % of TP in runoff while about 90% or more of relative P losses via runoff, throughflow and leachate were in DOP and PP forms. The DOP and soluble organic carbon (SOC) in soil solution were well correlated in sand (R^2 = 0.78, P <0.05) and clay soils (R^2 = 0.56, P <0.05) at 0-5 cm suggesting that amounts of organic matter dissolved in soil solution influences P sorption and mobility. The higher PP concentration for the clay soil at the interface of clay and sandy layers indicates subsurface lateral flow is exacerbated by dispersive clay which might be an additional concern regarding P mobility in clay and duplex soils of the catchment. Ponding of water at the surface or lateral movement of water at the interface of sand and clay layers in the profile would increase the risk of P losses in the form of DP or PP in dispersion-prone sodic soils.

Key Words
Subsurface flow, hydrological risk, eutrophication, colloidal P, colloidal organic compounds.

Introduction
Phosphate fertilizers played an important role in the agricultural development of the south west of WA but continuous use of P fertilizers for several decades led to a gradual build up in soil P (Samadi and Gilkes 1998). These accumulated P inputs coupled with recent adoption of minimum tillage for crop establishment and a strong affinity of soils for P, results in the accumulation of P near the soil surface, where it has the greatest potential for P loss though overland flow (Sharpley 1995). Most of the research on understanding this process of P loss from agricultural land in WA has concentrated on identifying the sources and processes of nutrient export from pasture land in the coastal zone to wetlands, estuaries and streams (McKergow *et al.* 2002). In contrast, very little research has been carried out on the nutrient export from cropping land in medium to low rainfall zones (Weaver *et al.* 2003) where fertilizers account for much of the agricultural nutrient inputs. Until recently, study of the impact of management programs on nutrient delivery at the catchment scale was very limited. However, modeling by Weaver *et al.* (2003) and Wong *et al.* (2006) for catchments on the south and west coast of Western Australia has begun to address these issues. Phosphorus is transported from soil to surface water in two major forms, DRP and PP, from agricultural land by runoff, erosion and leaching (Sharpley 1985a). Studies have reported that runoff generation in the south west of WA is dominated by throughflow and George and Conacher (1993) found that runoff mechanisms on a small hill slope near Narrogin were dependent on the extent and development of variable source areas of the catchment. Phosphorus export to surface waters via leaching (as opposed to erosion and surface runoff) is also an important source of P loss from soil to water (Hesketh and Brookes 2000). To quantitatively study the effects of soil type on P transport from cropping landscapes in the South coast region of WA, this study was carried out on intact columns, field runoff plots and packed boxes. The present research was thus designed to understand: (1) the mechanisms of P transfer to surface waters (either by runoff, throughflow or leaching) either in solution or attached to suspended sediments and (2) effects of rates of P application on P loss.

Methods
Study site characteristics
This investigation was conducted on the upper Fitzgerald River catchment, 400 km south east of Perth. The

catchment covered an area of about 104,000 ha and has a Mediterranean-type climate with annual rainfall 400 to 450 mm (Hill and Schiller 2003). The soils in the catchment are classified as: Hypocalcic Mottled-Hypernatric Brown Sodosol; Acidic-Sodic Magnesic Brown Dermosol; Hypocalcic Petrocalcic Black Sodosol; Mottled-Sodic Eutrophic Brown Kandosol; Eutrophic Mottled-Mesonatric Brown Sodosol; Eutrophic Mesonatric Brown Sodosols (McArthur 2004).

Sampling
Intact soil cores (10 cm diameter × 20 cm length) were collected from moderate P-loss risk areas of the catchment from sand, clay and loam soils. The cores were irrigated with 25 mm of water (196 ml of deionised water per column) at 4-day intervals and a total of 20 irrigations were applied to each core. The packed box study was conducted on galvanized steel boxes constructed from sheet metal with dimensions of 100 cm (length) x 40 cm (width) x 30 cm (height) to collect runoff and throughflow at 10 and 30 cm depth. Simulated rainfall was applied at 100 mm/hr, which represents the intensity of storm events similar to those which occur in the rainy season at the catchment. Simulated rainfall was applied to the boxes at 1, 15 and 30 days. Rhizon soil solution (< 0.1 µm pore size) samplers were installed horizontally in the columns and runoff boxes at 5, 10 and 15 cm depth. The soil solution was removed periodically under vacuum and transferred immediately to a freezer at -20ºC. Twelve field runoff plots each measuring 2.0 x 1.5 m were installed in the upper Fitzgerald River catchment in February 2007. Runoff from all plots was collected in 2007 after two rainfall events through collection devices consisting of 70 L containers capable of containing 20% of runoff from rainfall events up to 50 mm rainfall. A trench was dug perpendicular to the slope direction and equipped with collectors to collect separately overland (surface runoff) and throughflow (lateral through the soil profile). Barley seed was drilled in the plot in May, 2007 with three rates of phosphate fertilizer (0, 20 and 40 kg P/ha as DAP), giving four replicates of each P treatment.

Laboratory methods
The pH and EC were measured for all samples and solutions were then filtered through a 0.45 µm membrane filter for DRP, TDP and SOC. Dissolved OP was calculated from the difference between TDP and DRP. Total solids (TSS) were determined by oven drying 20 ml of runoff and through flow samples at 105ºC for 24 hrs. Particulate P was determined by the difference between TP (unfiltered) and TDP concentration. The statistical analysis was carried out using Statistic 8 software.

Results
Runoff
The DRP load for sand and clay soil was <0.26 mg (4-25% of TP) and 0.04-1.10 mg (2-67% of TP) irrespective of events and increased with P rates ($P < 0.05$). The amount of DOP for sand and clay varied from 0.14-0.71 mg (2-80% of TP) and 0.06-1.19 mg (16-72 % of TP), and significantly increased with P rates ($P < 0.05$). Higher relative P loss in PP (> 68 %) forms was observed for runoff losses whereas DRP (< 49%) and DOP (< 35%) were lesser contributors to P transport in runoff (data not shown). In the field simulation study, DOP load was a major proportion (51-87%, data not shown) of TDP in runoff. Significantly higher P load occurred for broadcast P fertilizer application relative to drilled fertilizer ($P < 0.05$).

Throughflow
The amounts of DRP in sand and clay soil ranged from 0.01-0.47 mg and 0.04-3.24 mg (1-63% of TP) whereas DOP varied from 0.02-0.38 mg and 0.48- 17.7 mg (30-90% of TP). The PP ranged from 0.01-0.15 mg and 0.05-2.01 mg (2-58% of TP) for sand and clay. In sand soil, the amounts of DRP and DOP transported in throughflow at 30 cm varied from 0.01-0.81 mg (4-11% of TP) and 0.21-7.61 mg (68-90% of TP) and an increase in DOP as a percent of TP occurred with subsequent runoff events. Significant increase in DRP and DOP concentrations occurred with P rates of application but no effect of surface soil slope on these P forms was observed in sand soil ($P < 0.05$). Major P losses occurred as DOP (< 90%) and PP (< 35%) forms in leachate of sand whereas DRP constituted < 25 %. Similarly in clay soil, DRP and DOP loads ranged from 0.02-2.00 mg (3-27% of TP) and 0.07-3.20 mg (26-70% of TP), respectively, and P load increased significantly with P rate ($P < 0.05$). Greater relative P loss occurred in throughflow as DOP (< 68%) and PP (< 84%) compared to DRP (< 34%, data not shown).

Phosphorus concentration in leachate
Dissolved OP (1.2-53 mg/l) was a major fraction of TDP in the leachate followed by DRP (0.05-6.7 mg/l) in sand. Although similar trends were observed with clay and loam, the TDP concentration was low compared

to sand ($P < 0.05$) and the values varied from 0.2-9.5 mg/l and 1.4-23 mg/l, respectively. The leachate obtained from clay and loam soils was highly turbid unlike in sand. Columns of clay generating turbidity with leaching events often became blocked after the 7th event. A higher percent of P was leached and a lower percent was retained in sand (18.6 %) and loam (14.8 %) compared to clay (7.1%) at the higher P application rate.

Leaching losses
Initially soil solution without P application (control) had a DRP of <2 mg/l but with increased P application an increase in P concentration was found regardless of soil type ($P < 0.05$). With the increase in time of contact of fertilizer with soil, P concentration decreased in sand soil and to a lesser extent in clay and loam soil. Dissolved OP constituted the main proportion of TDP in soil solution at depth after application of inorganic P. Significant increase in DOP concentrations occurred with higher rates of P application at 5 cm (533 mg/l and 400 mg/l) compared to DRP ($P < 0.05$) in sand and clay soil of the box study

Discussion
Runoff losses of P
The high proportion of TP lost as DOP and its stronger relationship with TDP compared to DRP ($P < 0.01$, $R^2_{sand} = 0.81$, $R^2_{clay} = 0.79$) suggest that the DOP fraction was the major dissolved P form lost in runoff. Runoff TP concentrations were linearly related with PP ($P < 0.01$, $R^2_{sand} = 49$, $R^2_{clay} = 0.35$) in both soil types in the box study reflecting the important contribution of PP to TP concentration in runoff which is consistent with the findings of Kleinman *et al.* (2004). The concentration of P in the runoff was increased after P application as observed in the field simulation but was higher with broadcast P application than drilled P ($P < 0.05$). Hence, the conventional practise of broadcasting P fertilizer on the soil surface during the summer months appears to be inherently more risky in terms of run-off P transport to streams than P application by drilling for crop production.

Throughflow P losses
The throughflow volume generally depends on topsoil texture and the degree of porosity contrast between topsoil and subsoil (Stevens *et al.* 1999). Sediment can be readily transported below the soil surface as dispersed particles. Higher ESP of the subsoil and increased turbidity of throughflow with rain events for the clay soil indicate that dispersion is contributing to PP transport in throughflow. The throughflow samples collected from the clay soil were highly turbid for initial rain events, which most likely was due to the higher internal erosion in macropores. A higher proportion of PP was found for the clay soil at depth in comparison to the sand, therefore subsurface lateral flow along the interface with dispersive clay might be a source of P mobility in the clay soil. The hydraulic behaviour below 10 cm in clay soil largely depends on the amounts and nature of the clay minerals present, soil structure and the levels of exchangeable Na and ESP.

Phosphorus leaching losses
The rate of applied P fertilizer was the major factor influencing P leaching losses from sand and clay soils under leaching conditions both in field and box studies ($P <0.05$). Below 5 cm, P leaching was slow in the clay soil, which might be due to slow water movement, reduced macro porosity and increased sorption of DRP. The concentration and total amount of P moving in DOP form in the leachate was significantly larger than DRP in the column leaching, field run-off plots and the packed box. The runoff, throughflow and leachate were dominated by colloidal organic materials (DOP). The DOP fraction may contain fine (< 0.45 μm in filtered samples and <0.1 μm in soil solutions) quartz, mica, kaolinite and chlorite minerals which are potential inorganic carriers for DRP. On the other hand, DOP in soil solution (< 0.1 m) might be associated with fine colloidal compounds such as silicates, metal hydroxides, humic acids, polysaccharides, fulvic acids and proteins. It was evident from the dark colour of soil solution and its high SOC concentration at depth in the soils that a potential organic carrier of P exists in mobile water, even though the exact composition of it remains unresolved. In addition to DP, P bound to suspended particles and colloids contributes to P leaching from agricultural soils (Motoshita *et al.* 2003). Phosphorus may be bound to mineral colloids, such as Fe and Al oxides, or to organic or organo–mineral colloids (Hens and Merckx 2002). Colloidal P in soil solution accounted for about 13 to 95% of TP, but its relevance for P leaching and the processes governing its release from soils are not fully understood.

Conclusion

The P load in mobile P forms increased with increasing P rate in column leaching, packed box and field studies. Under field conditions, higher P loss occurred with broadcast P application compared to drill placement. A high proportion of TDP was in the form of DOP in runoff and throughflow (at 10 and 30 cm depths). The significant correlation between DOP and SOC in soil solution of sand and clay soils at 0-5 cm depth suggests that the amount of organic matter dissolved in soil solution influences P sorption and mobility. The relatively higher affinity of soil for DRP compared to DOP might allow soluble organic P (DOP) to be more mobile through the profile in association with colloidal compounds <0.1 μm. Overall, DRP comprised <35% of TP in runoff while about 90% or more of relative P losses via runoff and leachate were in DOP and PP forms. The higher PP concentration for the clay soil at the interface of clay and sandy layers indicates subsurface lateral flow is exacerbated by dispersive clay which might be an additional concern regarding P mobility in clay and duplex soils of the catchment.

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