

# Phosphorus behaviour in sediments from a small agricultural watershed under oxic and anoxic conditions

Danilo Rheinheimer dos Santos<sup>A</sup>, Maria Alice Santanna<sup>B</sup>, Ricardo Schenato<sup>A</sup>, João Kaminski<sup>A</sup>, Jaderson dos Anjos<sup>A</sup> and Tales Tiecher<sup>B</sup>

<sup>A</sup>Department of Soil Science, Federal University of Santa Maria, Santa Maria, Rio Grande do Sul, Brasil, Email danilor@smail.ufsm.br

<sup>B</sup>Department of Physical, Federal University of Santa Maria, Santa Maria, Rio Grande do Sul, Brasil.

## Abstract

The use of soil outside of its capacity generates great amount of sediments and can transfer phosphate to water courses, giving rise to eutrophication. The present work aims to estimate the phosphorus desorption capacity of sediments transferred in the small watershed of Arroio Lino brook, in Agudo town, Brazil, under oxic and anoxic conditions. Samples of water + sediments were collected at four points (two subwatersheds, upstream and downstream) in two pluviometric events (winter fallow and tobacco seedling transplanting). The concentration of sediments in suspension in the water courses is related to the rainfall characteristics and soil use. The amounts of bioavailable particulate phosphorus and potentially bioavailable particulate phosphorus desorbed from sediments are increased by anthropic activity. Under anoxic conditions, the bioavailability of phosphorus in the sediments increased, increasing its effect on the eutrophication of lentic water environments.

## Key Words

River sediments, phosphorus desorption, particulate phosphorus, tobacco production.

## Introduction

In the tobacco production systems performed under conventional tillage, inorganic fertilizer is usually added in excess. In the conventional tillage management, the potential for soil erosion increased by topsoil ploughing in preparation for seeding and erosion can be accelerated during run-off events. Substances dissolved and suspended in runoff, such as nitrogen and phosphorus, are transported from the soil to the water courses along three pathways: overland flow (surface run-off), leachate (sub-surface run-off) or sub-surface groundwater flow (Reynolds and Davies 2001). Surface run-off occurs during and immediately after an intense precipitation and promotes the transfer of dissolved, colloidal or fine-particulate phosphorus from the topsoil to the water streams, eventually leading to eutrophic conditions and decreasing biodiversity of the surrounding surface water. The transport of phosphorus-containing particulates is greater from cultivated ground than from grassland; the phosphorus losses from agricultural areas are mostly as particulate-P, that is, the sediments act as phosphorus carriers (Pietiläinen 1997). The amount and quality of P losses depend on the magnitude of point-source P discharges and the dominance of P pathways. Natural buffer zones (such as riparian zones) can act as a P trap along the agricultural fields. The impact of particulate-P input on the eutrophication of surface waters depends on the sediment-water interactions and the processes behind retention and release of P. Some fractions of phosphorus in sediments are virtually permanently bound in the solid particle, while others are potentially mobile, and under appropriate conditions can lead to P release to the solution. P in solution is the only one available for biological uptake. The size and composition of the particles and the redox conditions of the environment play a major role on the P release. In soils the importance of Fe- and Al-rich amorphous minerals as carrier phases of P is well known (Beauchemin *et al.* 1999). Clays are important P-carrier phases of the colloidal fractions on river sediments. Part of the clay-bound fraction of particulate-P may be in the form of iron oxides or organic coatings (Poulenard *et al.* 2008). Iron and aluminium oxides play a significant role in the phosphate buffer mechanism of fluvial sediments, as they can act as a sink for phosphorus, maintaining low equilibrium phosphate solution concentrations (Froelich 1988). However, under anaerobic conditions, reductive dissolution of ferric hydroxides carrying P is an important orthophosphate release mechanism, increasing P bioavailability (Shenker *et al.* 2005). In this study the sediments are submitted to phosphorus desorption under oxic and anoxic environments in the laboratory.

## Methods

### Site description

The Lino stream watershed (480 ha) is located in the Nova Boêmia community, town of Agudo, Rio Grande do Sul state, Brazil, at coordinates Universal Transverse Mercator (UTM) 22 J 280000–283500 m/6733500–

6737000 m. This typical agricultural watershed is an important tributary of the Jacuí River. As concerning the geological aspects, the watershed belongs to the “Serra Geral Formation,” which presents basaltic hillsides and localized outcrops of Botucatu sandstone. The land altitude ranges from 100 to 500 m with long pendants and short slopes normally greater than 25°. The soils are classified as Mollisols and Inceptisols (Soil Survey Staff 1999) and the vegetation is composed by remnant seasonally deciduous forests in different stages of succession. The climate is humid subtropical, with an average annual rainfall of 1,600 mm and an average annual temperature of 19°C. Almost 25% of the watershed’s area is occupied by annual crops and more than 60% by native forest cover. Approximately 90% of the 36 farm production units are devoted to tobacco production. Tobacco is an intensively tilled crop, and its production system typically includes two to six cultivation operations per year (disk plow and disk harrowing 0.20 m soil disturbance depth). In addition to intensive tillage for weed control and preparation for tobacco transplanting, tobacco production employs many pesticides (insecticides, fungicides, and herbicides) to enhance leaf growth.

#### *Sediment sampling*

Water and suspended sediments were collected at the exit of four points (subwatersheds A and B; upstream and downstream). Subwatershed A (right stream) with a landscape conformation based on high sloped relief and high human activity. Agricultural fields are close to streams and with no protection by vegetation in stream-adjacent areas. Subwatershed B (left stream) with a landscape conformation based on highly sloping relief and high human activities. However, this subwatershed presented high soil cover by natural vegetation around stream areas; therefore, the agricultural fields are located far from streams in both collected points. Water and sediment samples were taken immediately after each of two rainfall events: fallow winter (average precipitation = 55 mm and maxima precipitation = 47 mm/h) and tobacco transplanting – seedling (average precipitation = 38 mm and maxima precipitation = 17 mm/h). The employed samplers are an adaptation of the model US U-59 (CEWEH-Y 1995), installed in pairs in the streambed of the watercourse. The suspended sediments of the two automatic samplers were mixed in a single sample.

#### *Physico-chemical analysis*

In laboratory, initial pH values were determined in water and sediment suspension samples. The soluble P was determined in water filtered a 0.45- $\mu$ m porous membrane (Murphy and Riley 1962). The soluble carbon was determinate by wet combustion and colorimetric analysis. After evaporation at 100°C, the sediment concentration was quantified. Iron was extracted by dithionite–citrate–sodium bicarbonate (Fed) and by oxalate (Loeppert and Inskeep 1996) and total organic carbon by dry combustion (Flash EA1112). P of sediment was extracted by acid digestion ( $H_2O_2 + H_2SO_4 + MgCl_2$  at 200°C), and this value was assumed as total P (Rheinheimer *et al.* 2003).

#### *Phosphorus desorption*

Phosphorus desorption capacity was estimated by successive extractions with an Anionic Exchange Resin (AER) membrane (Rheinheimer *et al.* 2003) in a water-jacketed glass reactor vessel. A constant suspension temperature of 25°C was achieved using a circulating water bath system. The desired Eh in the reactor suspensions were obtained by purging with  $N_2$  to induce reducing conditions (+20 $\pm$ 50 mV) or opening the vessel to air to achieve oxic environment (+420 $\pm$ 50 mV). A first-order kinetic model (McKean and Warren 1996) was employed to fit the desorption curves, allowing the estimate of the potentially bioavailable particulate P ( $\beta$ ), and the bioavailable particulate P, which is the P desorbed in the first extraction ( $\alpha$ ).

## **Results**

#### *Sediment concentration and physical and chemical properties of sediments*

In both rain events, the non-anthropized subwatershed released a much lower concentration of sediments than the others subwatersheds (Table 1), which highlight the important role of riparian zones in avoiding erosion by interception of drainage (Lowrence 1998). Sediments deriving from the non-anthropized watershed presented lower values of pH, soluble P, total P and Fe and higher contents of total organic carbon. In sediments of the anthropized subwatersheds, the amount of iron extracted by DCB was, approximately, 4 and 2 times those deriving from non-anthropized areas, for the two pluviometric events. This is a consequence of the low soil cover index, which facilitates soil disaggregation and, consequently, the dragging of sediments with the torrent of rain water. In the low precipitation event (tobacco seedlings transplanting) the sediment concentrations and the iron amounts extracted by DCB were lower than those corresponding to the winter fallow rainfall event. However, the forms of iron extracted by oxalate have not changed significantly, giving rise to the diminishing Fed/Feo ratio.

**Table 1. Sediment concentration, soluble and total phosphorus, iron extracted by dithionite–citrate–sodium bicarbonate (Fe<sub>DCB</sub>) and by oxalate (Fe<sub>O</sub>), and ratio Fe<sub>DCB</sub> / Fe<sub>O</sub>, soluble and total organic carbon from sediment collected at four points in the two agricultural sub-watersheds during two rain events.**

| Subwatershed                    | Sediment concentration (g/l) | Soluble phosphorus (mg/l) | Total phosphorus (TP) (mg/kg) | Iron DCB (Fe <sub>DCB</sub> ) (g/kg) | Iron oxalate (Fe <sub>O</sub> ) (g/kg) | Ratio Fe <sub>DCB</sub> / Fe <sub>O</sub> | Soluble carbon (mg/l) | Total carbon (g/kg) |
|---------------------------------|------------------------------|---------------------------|-------------------------------|--------------------------------------|--|---|-----------------------|---------------------|
| Winter fallow                   |                              |                           |                               |                                      |  |   |                       |                     |
| Right stream                    |                              |                           |                               |                                      |  |   |                       |                     |
| Upstream (non-anthropized)      | 0.1                          | 0.04                      | 659.5                         | 19.5                                 | 0.8                                    | 24.4                                      | 4.72                  | 74.7                |
| Downstream                      | 12.8                         | 0.02                      | 916.4                         | 71.5                                 | 4.2                                    | 17.0                                      | 2.87                  | 18.3                |
| Left stream                     |                              |                           |                               |                                      |  |   |                       |                     |
| Upstream                        | 4.9                          | 0.20                      | 1011.0                        | 74.9                                 | 2.7                                    | 27.7                                      | 3.49                  | 24.1                |
| Downstream                      | 5.7                          | 0.08                      | 1037.0                        | 86.0                                 | 2.4                                    | 35.8                                      | 1.95                  | 15.9                |
| Tobacco seedlings transplanting |                              |                           |                               |                                      |  |   |                       |                     |
| Right stream                    |                              |                           |                               |                                      |  |   |                       |                     |
| Upstream (non-anthropized)      | 0.1                          | 0.01                      | 621.5                         | 12.3                                 | 0.6                                    | 20.5                                      | 4.62                  | 103.2               |
| Downstream                      | 2.3                          | 0.25                      | 963.5                         | 23.1                                 | 4.1                                    | 5.6                                       | 6.87                  | 21.7                |
| Left stream                     |                              |                           |                               |                                      |  |   |                       |                     |
| Upstream                        | 1.1                          | 0.18                      | 996.4                         | 22.6                                 | 5.7                                    | 4.0                                       | 6.00                  | 55.0                |
| Downstream                      | 0.9                          | 0.22                      | 1165.0                        | 20.1                                 | 5.3                                    | 3.8                                       | 5.59                  | 26.7                |

**Table 2. Phosphorus desorption from sediments collected in two rain events, winter fallow and seedlings transplanting, at different subwatersheds, submitted to oxic and anoxic conditions.**

| Subwatershed                    | Bioavailable particulate phosphorus (mg/kg) |        | Potentially bioavailable particulate phosphorus (mg/kg) |        |
|---------------------------------|---|--------|---|--------|
|                                 | Oxic  | Anoxic | Oxic  | Anoxic |
| Winter fallow                   |   |        |   |        |
| Ride stream                     |   |        |   |        |
| Upstream (non-anthropized)      | 0.9   | 28.7   | 38.9  | 58.4   |
| Downstream                      | 11.1  | 22.7   | 52.5  | 59.2   |
| Left stream                     |   |        |   |        |
| Upstream                        | 22.9  | 36.0   | 109.6   | 121.3  |
| Downstream                      | 28.3  | 44.7   | 113.0   | 128.7  |
| Tobacco seedlings transplanting |   |        |   |        |
| Ride stream                     |   |        |   |        |
| Upstream (non-anthropized)      | 0.3   | 31.6   | 19.9  | 80.8   |
| Downstream                      | 59.4  | 69.6   | 238.3   | 244.7  |
| Left stream                     |   |        |   |        |
| Upstream                        | 67.0  | 94.5   | 306.7   | 345.8  |
| Downstream                      | 83.0  | 84.1   | 234.3   | 243.8  |

### *Phosphorus desorption*

In oxic condition, the bioavailable particulate P ( $\alpha$ ) and the potentially bioavailable particulate P ( $\beta$ ) from sediments collected at the non-anthropized subwatershed were very low (< 1 mg/kg and < 40 mg/kg, respectively). Sediments collected during tobacco seedling transplanting, in the anthropized subwatersheds, showed higher bioavailable particulate P than those of the winter fallow rain. For example, in the seedlings transplanting event, the  $\beta$  value was 306.7 mg/kg in the upstream point of the left stream, but it changed to 109.6 mg/kg in the winter fallow rainfall (Table 2). This result is not explained by the sediment concentration, since lower losses of sediments were observed for the seedlings transplanting rainfall, as a consequence of the lower total and average precipitation intensity. Probably, this difference can be attributed to the phosphate originating from the soluble phosphate fertilizers added before tobacco seedlings transplanting.

When the sediments were submitted to anoxic conditions, there was an increase in P desorption, especially in non-anthropized watershed (Table 2) because there are the highest amount of carbon organic total (Table 1). In oxic environments, the microorganisms promote the oxidation of organic carbon and the electrons generated by the oxidation are accepted by oxygen dissolved in the water, therefore being reduced to water. Under lower redox potential, in absence of dissolved O<sub>2</sub>, the oxidation of organic carbon occurs only if another electron acceptor is present. For sediments and soil particles, a possible electron acceptor is the Fe III present in the iron oxides structure, which is reduced to Fe II and dissolves in the water phase, along with its iron oxide-bound phosphate, increasing P bioavailability (Shenker *et al.* 2005).

## Conclusion

The biggest amounts of bioavailable particulate phosphorus were obtained in sediments collected in the anthropized area during tobacco seedlings transplanting. Phosphorus desorption was higher when sediments were submitted to anoxic conditions, especially for those derived from non-anthropized areas, have larger total organic carbon contents.

## References

- Reynolds CS, Davies PS (2001) Sources and bioavailability of phosphorus fractions in freshwaters: a British perspective. *Biology Review* **76**, 27-64.
- Pietiläinen OP (1997) Agricultural phosphorus load and phosphorus as a limiting factor for algal growth in Finnish lakes and rivers. In 'Phosphorus loss from soil to water' (Eds Tunney H, Carton OT, Brookes PC, Johnston AE) pp.354-356. (CAB International: Wallingford).
- Murphy J, Riley JF (1962) A modified single solution method for the determination of phosphate in natural waters. *Analitica Chimica Acta* **27**, 31-36.
- Loeppert RH, Inskeep WP (1996) Iron. In 'Methods of Soil Analysis Part 3 – Chemical Methods' 3<sup>rd</sup> ed. (Eds DL Sparks *et al.*) pp.639-664. (SSSA: Madison).
- Shenker M, Seitelbach S, Brand S, Haim A, Litaor MI (2005) Redox reactions and phosphorus release in reflooded soils of an altered wetland. *European Journal of Soil Science* **56**, 515-525.
- Poulenard J, Dorioz JM, Elsass F (2008) Analytical electron-microscopy fractionation of fine and colloidal particulate-phosphorus in riverbed and suspended sediments. *Aquatic Geochemistry* **14**, 193-210.
- Froelich PN (1988) Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. *Limnology Oceanographic* **33**, 649-668.
- Beauchemin S, Simard RR (1999) Soil phosphorus saturation degree: review of some indices and their suitability for P management in Québec, Canada. *Canadian Journal of Soil Science* **79**, 615-625.
- Rheinheimer DS, Anghinoni I, Conte E (2003) Sorção de fósforo em função do teor inicial e de sistemas de manejo de solos. *Revista Brasileira de Ciência do Solo* **27**, 41-49.
- McKean SJ, Warren GP (1996) Determination of phosphate desorption characteristics in soils using successive resin extractions. *Communication in Soil Science and Plant Analysis* **27**, 2397-2417.
- Lowrence R (1998) The Riparian Ecosystem Management Model: simulator for ecological processes in riparian zones. In 'Proceedings of the first Federal Interagency Hydrologic Modeling Conference', (Las Vegas).
- CEW-EH-Y (1995) Engineering and design: sedimentation investigations of rivers and reservoirs. In 'Department of the Army' (Ed US Army Corps of Engineers: Washington).
- Soil Survey Staff (1999) 'Keys to soil taxonomy' (U.S. Gov. Print.Office: Washington).