TRANSFER OF NUTRIENTS AND MAJOR IONS OF AN AGRICULTURAL CATCHMENT TO RUNOFF WATERS: ANALYSIS OF THEIR SPATIAL DISTRIBUTION

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Abstract
The increase in agricultural production over the last five decades has resulted in nutrient surpluses in some areas. Among the factors that control nutrients and major ion loss from the agricultural soils to surface waters are anthropogenic activities.

In this work we analyze the influence of soil use and soil management practices on the variation of electrical conductivity and concentrations of nitrates, ammonium, phosphates, calcium, magnesium, sodium, potassium, chlorides, and sulfates in runoff waters collected at three points from a small agricultural catchment (NW Spain) treated with slurries. The concentrations of ammonium and nitrate follow opposite spatial distribution patterns. As the distance to the uppermost part of the catchment increases, where the highest amounts of slurry are found, the concentration of ammonium declines while that of nitrates rises. The concentrations of phosphates, calcium, magnesium, potassium, chlorides, sulfates and also the electrical conductivity values follow distribution patterns that are similar to those of ammonium, whose origin is related to both the dilution effect of the slurry contaminating load and to factors related with the configuration of the catchment.

Additional Keywords: ionic species, nitrogen, phosphorus, NW Spain.

Introduction
The principal contaminants associated with agriculture include sediments, nutrients, pesticides, pathogens and certain heavy metals (Novotny and Olem, 1994; Haygarth and Jarvis, 2002). These contaminants are generally leached or eroded into streams by stormflows and infiltration waters (Diéguez-Villar *et al*., 2002). The most dangerous consequence of an increase in nutrients (especially P and N) in surface and underground waters is its contribution toward the eutrophication of rivers and lakes (Meybeck, 1996). Nitrogen is leached from agricultural soils mainly as nitrate. Much of the P transported from cultivation lands is generally in particulate form (Sharpley *et al*., 1992).

Surface waters contain other ionic species (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, etc.) that may be present at high concentrations and contribute to the salinity and hardness of the water. Moreover, some of these major ions can be used effectively as indicators of contaminating processes. Among the factors that govern the transport of these constituents as well N and P from the agricultural soils to surface waters are climate, topography and hydrology (Jarvie *et al*., 1997; Jordan *et al*., 1997), and the characteristics of the soil. These factors can be altered by anthropogenic activities, among them being: (i) soil uses and crop rotation (Giupponi and Rosato, 1999), (ii) type of land tillage and silage practices (Schreiber *et al*., 2001) (iii) addition of slurry and other fertilizers including amounts and methods of application, (iv) erosion control (Moreau *et al*., 1998), and (v) drainage.

An agricultural practice that is commonly used in Galicia (NW Spain) in recent decades is slurry addition to cultivation fields. However, its indiscriminate use and lack of information on its varied chemical composition (Carballas and Díaz-Fierros, 1990; Danes and Boixadera, 2001) can have serious repercussions on the quality of the waters (López-Periago *et al*., 1994; Diéguez-Villar *et al*., 2002; Taboada-Castro *et al*., 2002, 2003).

In this work the spatial variation of the concentrations of nutrients (NO_3^-, NH_4^+ and PO_4^{3-}–P), major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, and SO_4^{2-}) and electrical conductivity in runoff waters of a small agricultural catchment that received large amounts of slurries is shown. Finally, factors regulating losses of nutrients and other constituents from agricultural lands receiving waters are discussed.

Materials and Methods
Study area
This study was carried out on surface waters of a small catchment used for agriculture (10.7 ha) located in the province of A Coruña (NW Spain). The characterisctics of the catchment have been described in previous works (Dafonte *et al*., 1999). This catchment has a moderate slope mean (6.9%) and annual rainfall of about 1400 mm.

The parent material is basic schist and the soil is acid. The organic matter range is variable (1.64-23.84 %) and the texture is loam and silt-loam.

The study period was from November 1997 to June 1998. This period was characterized by massive additions of slurries (bovine and porcine) to the catchment. Slurry addition was carried out basically by means of a high-pressure hose that was connected to a pipe located at the uppermost part of the catchment. During this period heavy crusting was produced on the surface of the land in the part of the catchment that remains fallow. This crusting favors water runoff and leads to the creation of a preferential path for the transport of the slurries to the recipient stream, where one of the sampling sites (point A1) is located. The sampling was carried out at the catchment scale at the outlet of the main stream (A3), which flows continuously during the winter, and at the subcatchment scale in ephemeral streams (point A1 received runoff from the fallow land comprising up 2.4 ha and point A2 received runoff from grassland occupying 3.3 ha) whose existence is linked to the occurrence of heavy precipitation events.

Analytical techniques
Manual sampling was performed. Samples were filtered through a 0.45 micron pore filter. Concentrations of PO_4^{3-} and SO_4^{2-} were determined by capillary electrophoresis and electrical conductivity, NH_4^+, Ca^{2+}, Na^+, K^+, Cl^-, and NO_3^- were measured with a Hydrion-10 Multiparametric Probe equipped with ion-selective electrodes.

Statistical analysis was performed using spreadsheet software. Nonparametric (median and interquartile range) statistical methods were used.

Results and Discussion
Table 1 presents a statistical summary of the NO_3^-, NH_4^+ and PO_4^{3-}-P results obtained at the three sampling points of the catchment. Although the highest recorded NO_3^- value was found at point A1, which is closest to the point of slurry application, overall NO_3^- levels were highest at point A3 in the lowest part of the catchment. The opposite case was found with ammonium.

The difference in the concentrations of these two ions between points A1 and A2 could be due to various factors. One could be the distinct use of the soil (point A1 collects waters from a fallow cultivation field, while the waters of point A2 come mainly from grassland), that can bring on differential retention of the compounds contained in the slurries. Other factors to consider are the topography or simply the selection of a point for slurry addition that is more or less close to one of the two sampling points.

Between points A1, A2 and A3, dilution of the concentrations of NH_4^+ coming from the manure at the highest areas of the catchment is produced by entrance into the stream of clean waters not influenced by massive applications of slurry. Nevertheless, in all probability the decrease in ammonium concentrations along with the increase in nitrate concentrations throughout the catchment may be due to the composition of the slurry and to nitrogen cycle processes. Novotny and Olem (1994) found that the greatest rates of nitrification in water courses take place in small streams of solid bottom. These characteristics coincide with those of small streams that collect waters from the catchment studied.

Table 1. Statistical summary of the concentrations (mg L^{-1}) of NO_3^-, NH_4^+ and PO_4^{3-}-P at three points in the catchment

	NO_3^-			NH_4^+			PO_4^{3-}-P		
	A1	**A2**	**A3**	**A1**	**A2**	**A3**	**A1**	**A2**	**A3**
Median	5.99	21.83	30.39	9.45	3.18	2.93	6.95	1.26	0.62
Minimum	1.07	0.7	7.26	0.04	0.10	0.05	0.04	0.04	0.04
Maximum	144.74	57.35	61.68	350	261	31	28.59	21.44	11.98
Interquartile range	18.4	18.72	13.72	42.49	10.45	6.97	17.51	3.48	3.43
N	21	21	21	21	21	21	16	16	16

The lowest P concentrations were found in samples taken at point A3, while the highest were found at point A1 (Table 1). The decrease in P concentrations from point A1 to A3 may be attributed to dilution of the contaminating load since less contaminated waters from lower areas of the catchment enter the stream. In addition, transformations among different P fractions and reaction with stream sediments may also alter dissolved P concentrations in the stream.

The causes for the striking difference between points A1 and A2 may result from processes similar to those mentioned for NO_3^-. There are factors related to configuration of the catchment, such as topography and hydrology (Lennox *et al*., 1997) that must be considered apart from factors related to spatial variability of the structure and composition of the soil (Dafonte *et al*., 1999). The possible influence of the different uses of the soil should be noted as well as the presence of grazing animals. Different authors showed that greater P losses were found in runoff from cultivation fields than from grasslands (Lennox *et al*., 1997; Sharpley and Rekolainen, 1997).

Table 2 shows the statistical results of electrical conductivity (EC) and of the anions Cl^- and SO_4^{2-} and table 3 those of the cations Ca^{2+}, K^+, Na^+ and Mg^{2+} measured at the three sampling points of the catchment. The median values of EC and the ions Cl^-, SO_4^{2-}, Ca^{2+} and K^+ decreased in the direction of A1 to A2 to A3. The difference between points A1 and A2 always being greater than that between A2 and A3. The case of Na is slightly different. Median values do not show great differences, and those that do appear are oriented in the opposite direction (Table 3). Median Mg concentrations do not present significant differences between samples of points A2 and A3, although a big jump exists between these values and those recorded at point A1. In reference to variability, in all cases, the interquartile range results at point A1 being the highest, followed by those of point A2 and lastly, those of A3.

Table 2. Statistical summary of the results of electrical conductivity (EC: $\mu S\ cm^{-1}$), Cl^- and SO_4^{2-} (mg L^{-1}) at three points in the catchment

	EC			Cl^-			SO_4^{2-}		
	A1	A2	A3	A1	A2	A3	A1	A2	A3
Median	362	134	141	24.66	14.84	13.84	5.25	3.17	2.05
Minimum	78	75	117	3.26	7.97	11.57	1.47	1.45	1.12
Maximum	2834	2725	2043	169.24	129.36	96.05	55.81	22.72	16.62
Interquartile range	1414	314	194	61.00	10.59	8.22	6.64	2.23	2.18
N	21	21	21	22	22	22	20	20	20

Table 3. Statistical summary of the concentrations (mg L^{-1}) of Ca^{2+}, K^+, Na^+, and Mg^{2+} at the tree points in the catchment

	Ca^{2+}			K^+			Na^+			Mg^{2+}		
	A1	A2	A3	A1	A2	A3	A1	A2	A3	A1	A2	A3
Median	17.49	5.85	5.67	27.35	5.35	4.96	9.03	9.61	9.91	11.68	5.30	5.60
Minimum	0.92	2.65	4.42	0.17	1.39	2.99	1.57	5.04	5.44	0.38	2.67	4.05
Maximum	76.40	69.20	30.20	224.6	111.9	96.93	85.99	68.20	10.56	40.70	38.10	12.42
Interquartile range	27.24	6.38	3.22	122.4	18.60	10.29	17.44	5.05	3.41	10.20	4.76	1.90
N	22	22	22	22	22	22	22	22	22	19	19	19

Conclusions

The concentrations of ammonium and nitrate measured in surface waters of three sampling points of an agricultural catchment follow opposite spatial distribution patterns. As the distance to the uppermost part of the catchment, where the highest amounts of slurry are found, increases, the concentration of ammonium declines while that of nitrate rises. This behavior is the result of a mixture of processes involved in the nitrogen cycle and dilution of the contaminating load provided by entrance into stream of less contaminated waters in the lower part of the catchment.

The concentrations of phosphates, calcium, magnesium, potassium, chlorides, sulfates and also the electrical conductivity values follow distribution patterns that are similar to those of ammonium, whose origin is related to both the dilution effect of the slurry contaminating load and to factors related with the configuration of the catchment.

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