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Nutrient leaching from soil amended with apple waste

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Abstract – Among the possibilities for disposing of overproduction of apple, land application is flexible and inexpensive. Six soil columns receiving 0, 200 or 500 Mg of apple waste·ha⁻¹ were studied in laboratory experiments with various irrigation depths and timing, and alternate irrigated and drying periods. Leaching solutions were collected at different times for chemical analyses. Organic matter input stimulated microbial activity that used O₂ and released CO₂, then reduction occurred. Major cations like Ca²⁺, Mg²⁺, and K⁺ involved in mineral dissolution or soil solution exchange were released. High N immobilization and possibly denitrification occurred, organic C was leached, while decreasing redox potential led to Mn dissolution and sulfate reduction. The reoxidation of the soil during drying helped to restore the soil to a condition which pollutes less. Quantities of apple waste deposition less than 200 Mg·ha⁻¹ are recommended to minimize environmental damage.

soil / apples / leaching / redox reactions / pollution

Résumé – Lessivage d'éléments d'un sol amendé par des pommes de retrait. Parmi les différentes possibilités pour résorber les excédents de production de pommes, l'épandage in situ est une solution flexible et bon marché. Six colonnes de sol ayant reçu 0, 200 ou 500 Mg·ha⁻¹ de pommes ont été suivies en laboratoire dans des conditions d'irrigation variant par les doses et le calendrier d'apport d'eau, et en imposant une alternance entre des périodes d'irrigation et des périodes sèches. Les solutions drainées à la base des colonnes ont été récupérées à différentes dates et analysées. L'apport de matière organique fraîche a stimulé l'activité microbienne, induisant une consommation de O₂ et une production de CO₂. En conséquence, le sol est devenu réducteur. Des cations mis en jeu par dissolution minérale et échanges cationiques tels Ca²⁺, Mg²⁺ et K⁺ sont lixiviés. L'immobilisation d'azote, et probablement la dénitrification, expliquent la disparition rapide du nitrate. Du carbone organique est lixivié, et l'intensité des conditions réductrices induit la mise en solution de Mn et la sulfato-réduction. La réoxydation du sol suite aux phases de dessèchement restaure des conditions oxydantes potentiellement moins polluantes. Des quantités de matière organique fraîches inférieures à 200 Mg·ha⁻¹ sont recommandées pour minimiser les risques de pollution environnementale par lixiviation.

sol / pommes / lixiviation / oxydo-réduction / pollution

1. INTRODUCTION

Overproduction of apple and the vagaries of the market can result in a significant surplus, which has to be used. Among the possibilities for disposing of this irregular overproduction (food for animals, apple juice, dona-

tion), land application of apple waste is flexible and inexpensive. In the Provence Alpes Côte d'Azur region (France), apple production varied from 430 000 to 600 000 Mg per year between 1986 and 1995, while apple destruction ranged from 0 to 230 000 Mg per year. Incorporating apple waste into the soil may eliminate

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surplus apples and also supply nutrients for plants, provided that no toxic concentrations of pollutants or environmental damage occur [15]. Addition of fresh organic matter to soil generally stimulates microbial activity, increasing nitrogen (N) immobilization due to assimilation in microbial biomass or increasing N losses due to denitrification [2, 6, 11, 12, 18, 22]. As NO_3^- rapidly disappears under anaerobic conditions, the manganese (Mn) and iron (Fe) redox systems become dominant [21] and favorable to Mn oxide solubility, increasing the risk of Mn toxicity [23]. In a recent study [5] the main geochemical consequences of apple waste deposition on soil under field conditions were described. Briefly, rapid pH and Eh decreases (from 7.0 to 5.5 for the pH and from +500 to -300 mV for the redox potential) were observed after incorporating large quantities of apples into the soil. The soil became reduced, thus causing the dissolution of Mn oxides, and the formation of organic anions complexed the metals and major cations. Data also suggested that the oxidation of the soil during drying created conditions which polluted less, emphasizing the importance of the choice of season for land application of organic waste and the effect of change in climatic conditions over a long period after apple waste is applied to soil (typically one year or more). Nevertheless, accurate nutrient leaching estimates for major elements, in relation with climatic conditions and drainage fluxes, were not available under field conditions [5]. More generally, data relative to fresh waste deposition like fruits or legumes is scarce in the literature. Furthermore, no accurate mass balances after soil deposition of fresh plant residues like apple were found, although it may affect groundwater quality. Consequently, the objective of this work was to identify and quantify more precisely the main environmental risks associated with leaching combined with biogeochemical transformations when apple waste is added to soil. This was performed using soil columns in laboratory conditions in the case of successive cycles of wetting and drying.

2. MATERIALS AND METHODS

2.1. Preparation of soil columns

Six plastic columns with an internal diameter of 0.094 m and 0.90 m high were first prepared in an identical manner. A plastic grid (porosity 200 μm) topped by a layer of glass beads (spherical particles 1 mm in diameter) was placed at the bottom of each column. Columns were then filled with dry soil aggregates (diameter between 0.63 and 2.00 mm), starting with the 0.60 m–0.90 m layer, then the 0.30 m–0.60 m layer, and ending with the 0–0.30 m top soil layer. Before filling

the 0–0.30 m top soil layer, thin crushed apple layers were inserted between dry aggregate layers, and after the soil columns were completely filled, a preliminary wetting was carried out using a capillary rise process starting from the bottom of the column.

The six columns were separated into two groups of three. For each group, the first column corresponded to 500 $\text{Mg}\cdot\text{ha}^{-1}$ of apples, the second column received 200 $\text{Mg}\cdot\text{ha}^{-1}$, and the last received none (0 $\text{Mg}\cdot\text{ha}^{-1}$). After complete filling and wetting of the soil column, the mean bulk density was 1038, 1051 and 1053 $\text{kg}\cdot\text{m}^{-3}$ for the 500 $\text{Mg}\cdot\text{ha}^{-1}$, 200 $\text{Mg}\cdot\text{ha}^{-1}$ and 0 $\text{Mg}\cdot\text{ha}^{-1}$ treatments, respectively. Soil was taken from a silt-sandy soil profile (Tab. I). The clay content decreased in the bottom layer of the profile and the C/N ratio varied between 10 and 11. Nitrate ($\text{N}\text{-NO}_3^-$), ammonium-N ($\text{N}\text{-NH}_4^+$), and sodium (Na^+) concentrations in the soil were low, but a significant quantity of Mn was present in the first and the second layers. The chemical composition of apples (Tab. II) indicated as expected that C is the main constituent (40.8% on a dry basis), whereas they were low in N (0.44%).

Table I. Physical and chemical characteristics of the soil.

Parameter	Depth (m)	
	0.20–0.40	0.70–1.00
Organic C/N ratio	9.9	10.9
pH (water)	8.5	8.7
	%	
Clay	22.7	12.8
Loam	37.4	24.4
Sand	39.9	62.8
CaCO_3	27.5	22.8
	$\text{g}\cdot\text{kg}^{-1}$	
Organic matter	13.2	4.0
Organic C	7.7	2.3
Organic N	0.78	0.21
	$\text{mg}\cdot\text{kg}^{-1}$	
$\text{N}\text{-NO}_3^-$	8.6	3.8
$\text{N}\text{-NH}_4^+$	1.15	0.7
	$\text{cmol}\cdot\text{kg}^{-1}$	
CEC	8.9	5.6
Mg (exchangeable)	1.35	0.97
K (exchangeable)	0.76	0.24
Na (exchangeable)	0.025	0.042

Table II. Apple composition on the basis of dry mass (water content is 900 g·kg⁻¹).

Parameter	Apple composition
	g·kg ⁻¹
CaCO ₃ (total)	< 2
Organic C	408.0
Organic N	4.45
Organic C/N ratio (dimensionless)	(91.7)
Ca ²⁺	0.5
Mg ²⁺	0.3
K ⁺	8.9
Na ⁺	< 0.2
Fe	< 0.2
P	0.6
Mn	< 0.010

2.2. Wetting and drying periods

Immediately after preparing the columns, three irrigation periods started, each being separated by drying periods. Each irrigation was made with a plastic grid topped by a layer of glass beads placed at the top of the soil column to obtain a homogeneous water distribution at the soil surface and the water inflow rate was 5 ml·min⁻¹. The irrigation timing and duration differed between the two groups of three columns. For the first group, the first irrigation period went from 28 April 1997 to 7 July 1997 (70 days). During this period, the columns were irrigated each week with a quantity of 72 mm. There were thus 11 irrigations and a cumulative quantity of 792 mm. Then the first drying period started from 8 July 1997 to 5 October 1997 (87 days). The second irrigation period started from 6 October 1997 to 3 November 1997 (28 days). As with the first irrigation period, the columns were irrigated each week, thus amounting to 5 irrigations and a cumulative quantity of 365 mm. The second drying period started from 4 November 1997 to 26 April 1998 (172 days), then followed by the third irrigation period from 27 April 1998 to 27 May 1998 (30 days), corresponding to a water amount of 292 mm in 5 irrigations. The total duration of the laboratory experiment including three wetting and two drying periods was more than one year (387 days), and the cumulative irrigation applied was 1449 mm. The second group of three columns was irrigated with a different program. First, irrigation events were separated by a period of two weeks instead of the period of one week for the first group. Consequently, the first and second groups will be called the “7-day” and

the “15-day” treatment, respectively. Second, only the first and longer irrigation period was investigated in the 15-day treatment, to focus particularly on the period just after waste deposition on the soil when biogeochemical processes are the most intensive. The total water amount in the 15-day treatment during the first irrigation period (396 mm) was half that of the 7-day treatment. The choice of irrigation quantity and timing in the 7-day and 15-day treatments was made to analyze leaching risks and their environmental consequences arising from the combination of both water fluxes and biogeochemical transformations under “extreme” (7-day treatment) or “high” (15-day treatment) drainage conditions, and to take into account the impact of drying periods separating drainage phases on biotransformations in soil. These experimental conditions, however, are similar to actual rain conditions existing in the Rhône valley (Drôme, France) as indicated in Table III which shows that a maximal cumulative rain of 1325 mm observed during a 21-year period is close to the cumulative irrigation of 1449 mm in the 7-day treatment.

2.3. Chemical analysis

The chemical characteristics of the irrigation water were controlled for major anions [Cl⁻ (3.5 mg·l⁻¹), S-SO₄²⁻ (18.0 mg·l⁻¹), C-CO₃²⁻ (12.1 mg·l⁻¹), N-NO₃⁻ (0.6 mg·l⁻¹), N-NO₂⁻ (0 mg·l⁻¹)], cations [N-NH₄⁺ (0 mg·l⁻¹), Ca²⁺ (21.8 mg·l⁻¹), Mg²⁺ (3.3 mg·l⁻¹), K⁺ (0.4 mg·l⁻¹), Na⁺ (3.1 mg·l⁻¹), Mn²⁺ (0 mg·l⁻¹)], and C-org. (1.2 mg·l⁻¹). The pH and redox potential (Eh) were rapidly measured in the leachate after the beginning of the drainage at the bottom of the column. Redox potentials were measured using Pt microelectrodes against a calomel reference electrode. For each sample, the leachate was collected for 4 h after the beginning of

Table III. Statistics of the rain distribution for the “May–November” and “December–April” periods over 21 years (Site “L’étoile”, Drôme, Rhône valley, France).

	Rain (mm)		Year
	May to November	December to April	
Min	275	126	456
Max	1037	382	1325
Median	627	263	867
Mean	623	265	888
Standard deviation	197	81	215
CV (%)	32	31	24

drainage, and then followed by a microfiltration at 0.45 μm . If necessary, the filtered solution was stored under dark conditions at a constant temperature (4 °C). A 0.50N HCl solution (10 μl) was added to a fraction of the filtered solution (20 ml) for major cations and metal analysis, and another fraction (30 ml) was used for organic and inorganic C analysis after adding 300 μl of NaN_3 at a 30 $\text{g}\cdot\text{l}^{-1}$ concentration. The last fraction (approximately 250 ml) was used for inorganic anion analysis, and chloride (Cl^-), sulfate (SO_4^{2-}), nitrite (NO_2^-), and nitrate (NO_3^-) were analyzed by capillary electrophoresis (CIA method) using an electrolyte made of chromate (4.6 mM), OFM-OH (0.5 mM) and boric acid to obtain a pH value of 8 [9, 27]. The Cl^- , SO_4^{2-} , NO_2^- and NO_3^- concentrations in the leachate were determined on the same or the following day of collection. The major cations (sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+})) were measured by capillary electrophoresis (CIA method), and total Mn was measured by atomic absorption [20]. The coefficients of variation provided by control replicates were less than 2% for major anion [Cl^- (1.4%), NO_3^- (1.6%), SO_4^{2-} (1.9%)] and cation [Ca^{2+} (1.3%), Mg^{2+} (1.0%), K^+ (1.3%), Na^+ (0.9%)] analysis, and less than 3.4% for organic C, 3.7% for inorganic C, and 2% for Mn. Total alkalinity (HCO_3^- , CO_3^{2-} , organic anions) was measured by titration (0.1N HCl), whereas carbonated alkalinity was determined by NaOH (0.1N) titration [3]. The last two parameters make it possible to estimate the non-carbonated alkalinity, which is mainly of organic origin. Initial organic N was analyzed with the Kjeldahl method, organic and inorganic C was analyzed by a carbon analyzer (TOC 5050 A, Shimadzu). The mean air temperature in the laboratory varied from 19.5 °C to 20.5 °C during the experiments.

3. RESULTS

3.1. Transport properties and Eh-pH evolution

Figure 1 shows the cumulative fluxes of Cl^- leached at the bottom of the soil column during the first irrigation period for three apple treatments (0 $\text{Mg}\cdot\text{ha}^{-1}$, 200 $\text{Mg}\cdot\text{ha}^{-1}$, 500 $\text{Mg}\cdot\text{ha}^{-1}$) and two water supply intervals (7-day and 15-day). For each water supply interval, the control and the two treatments had similar results. Because Cl^- is a chemical tracer for water, this indicated that each group of three soil columns was similar from a physical point of view, and consequently, possible differences in leaching for organic or inorganic elements could be explained by differences in biogeochemical processes according to each treatment. This point was confirmed by the second and third irrigation periods

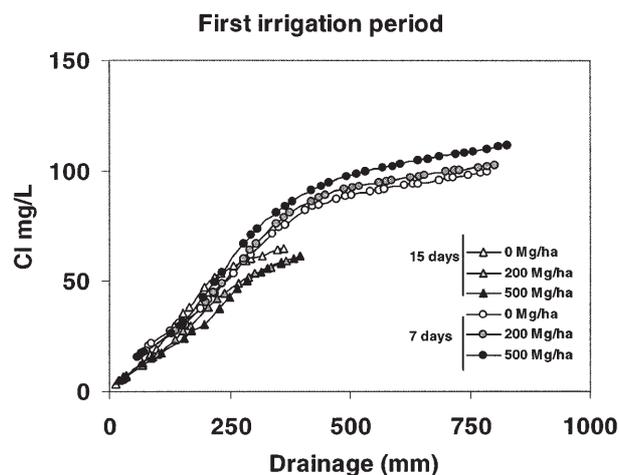


Figure 1. Relationships between cumulative leached Cl^- and cumulative drainage depth during the first irrigation period for three apple deposition (0 $\text{Mg}\cdot\text{ha}^{-1}$, 200 $\text{Mg}\cdot\text{ha}^{-1}$, 500 $\text{Mg}\cdot\text{ha}^{-1}$) and two water supply interval (7-day and 15-day) treatments on soil.

which exhibited the same Cl^- leaching curves for the 0 $\text{Mg}\cdot\text{ha}^{-1}$, 200 $\text{Mg}\cdot\text{ha}^{-1}$, 500 $\text{Mg}\cdot\text{ha}^{-1}$ and 7-day water supply treatment, respectively.

During the first irrigation period, pH values of the leachate remained around 7.5–8.0 for the untreated soils, 7.0–7.5 for the 200 $\text{Mg}\cdot\text{ha}^{-1}$ treatment, whereas the pH slightly decreased reaching 6.5–7.0 for the 500 $\text{Mg}\cdot\text{ha}^{-1}$ treatment (Fig. 2). Eh values remained around +300 and +500 mV for the untreated soils and 200 $\text{Mg}\cdot\text{ha}^{-1}$ treatment, respectively, indicating continuous oxidizing conditions in the soil column (Fig. 2). The redox potential decreased progressively and reached +150 to +250 mV for the 500 $\text{Mg}\cdot\text{ha}^{-1}$ treatments. After the soil profile dried out, the redox potential increased in the 500 $\text{Mg}\cdot\text{ha}^{-1}$ treatment. During the second irrigation period (results not shown), pH values of each treatment in the 7-day water supply treatments were close to the values of the control, indicating that the soil returned to conditions similar before apple deposition, while reducing conditions did not occur again.

3.2. Nitrate, sulfate and organic carbon

For the 7-day water supply interval, large differences occurred between the treatments (Fig. 3). During the first irrigation period, the control underwent a continuous NO_3^- leaching. The 500 $\text{Mg}\cdot\text{ha}^{-1}$ treatment provided no

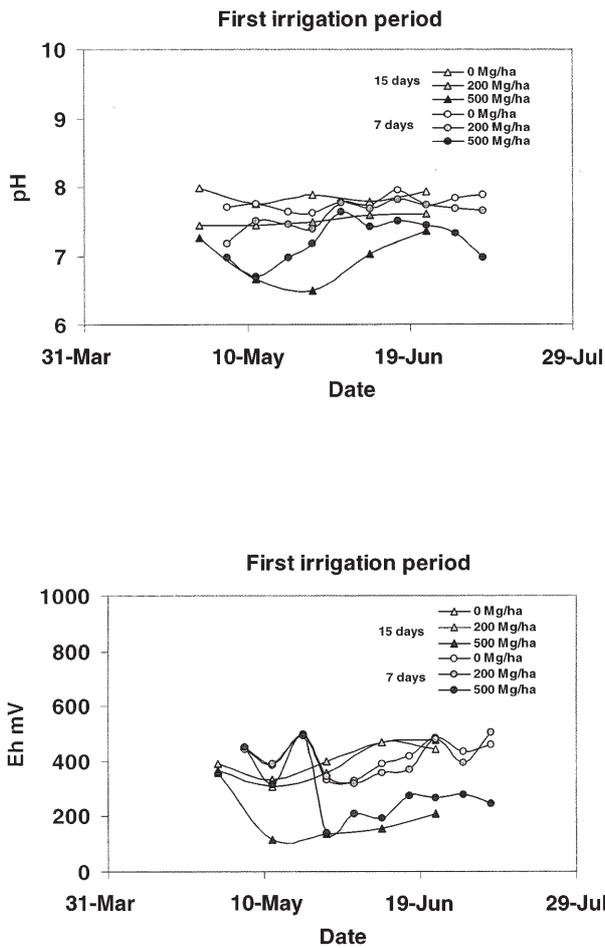


Figure 2. Leachate pH and Eh versus time during the first irrigation period for three apple deposition ($0 \text{ Mg}\cdot\text{ha}^{-1}$, $200 \text{ Mg}\cdot\text{ha}^{-1}$, $500 \text{ Mg}\cdot\text{ha}^{-1}$) and two water supply interval (7-day and 15-day) treatments on soil.

NO_3^- , while the $200 \text{ Mg}\cdot\text{ha}^{-1}$ treatment had an intermediate position. Moreover, results of the 7-day and 15-day treatments had a similar pattern. During the second irrigation period, the higher treatments produced higher NO_3^- leaching, while during the last irrigation period, the quantities of NO_3^- leached were close to each other for the three treatments. Similarly, results indicated a SO_4^{2-} depletion for both the 7-day and 15-day experiments in the higher treatment during the first irrigation period, while continuous and decreasing SO_4^{2-} leaching occurred in the control and $200 \text{ Mg}\cdot\text{ha}^{-1}$ treatments (Fig. 4). Release of SO_4^{2-} was high for the higher treatment in the second irrigation period. Similar SO_4^{2-}

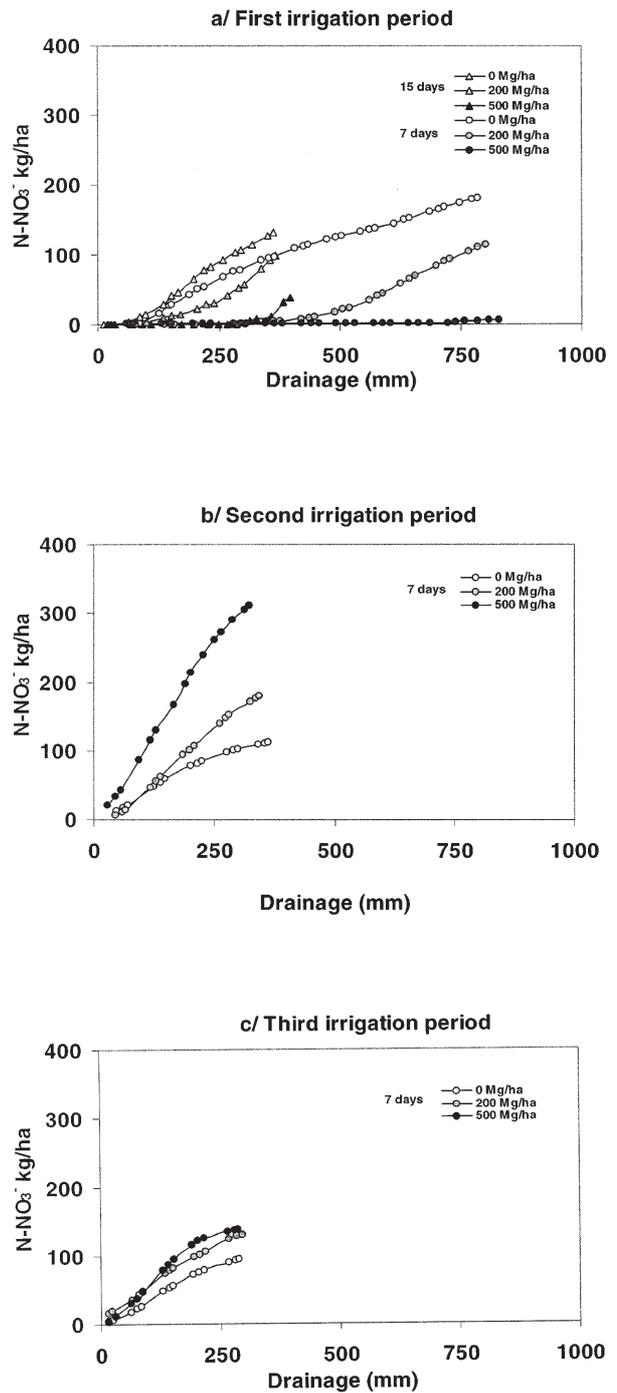


Figure 3. Relationships between cumulative leached N-NO_3^- fluxes and cumulative drainage depth during three successive irrigation periods for three apple deposition ($0 \text{ Mg}\cdot\text{ha}^{-1}$, $200 \text{ Mg}\cdot\text{ha}^{-1}$, $500 \text{ Mg}\cdot\text{ha}^{-1}$) and two water supply interval (7-day and 15-day) treatments on soil. a: first period; b: second period; c: third period.

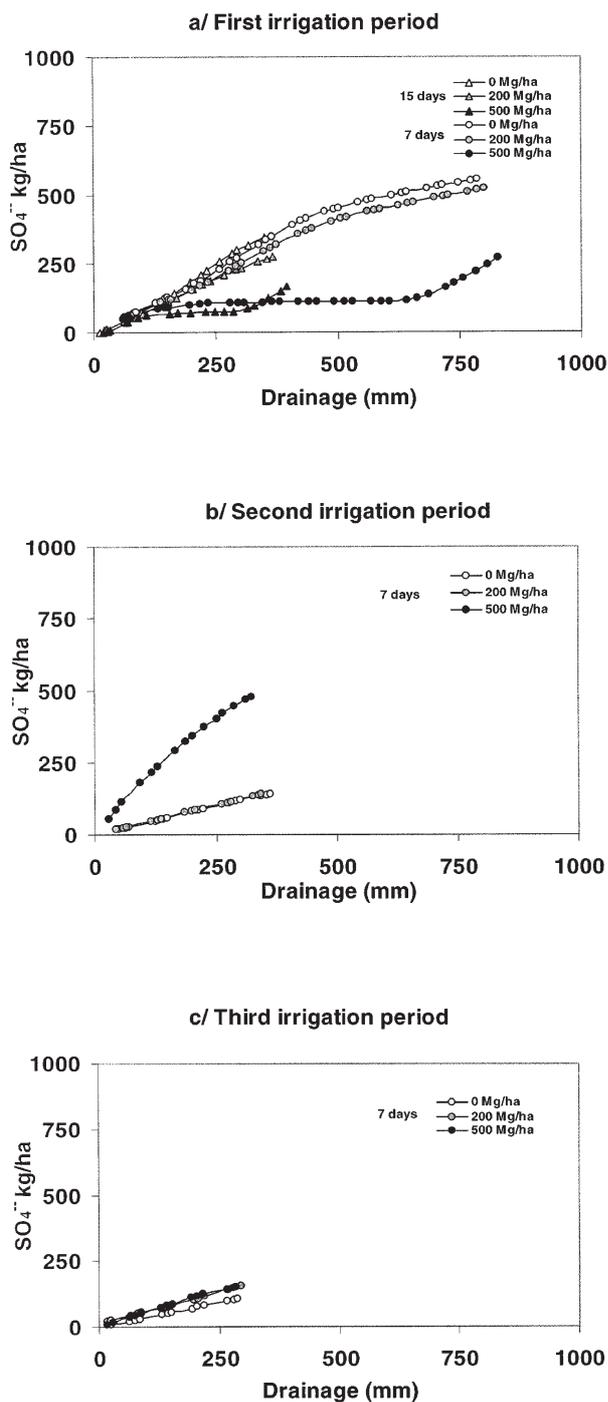


Figure 4. Relationships between cumulative leached SO_4^{2-} fluxes and cumulative drainage depth during three successive irrigation periods for three apple deposition ($0 \text{ Mg}\cdot\text{ha}^{-1}$, $200 \text{ Mg}\cdot\text{ha}^{-1}$, $500 \text{ Mg}\cdot\text{ha}^{-1}$) and two water supply interval (7-day and 15-day) treatments on soil. **a:** first period; **b:** second period; **c:** third period.

production and leaching were observed for the three treatments in the last irrigation period. No transport of dissolved organic C outside the soil column was observed for the control and the $200 \text{ Mg}\cdot\text{ha}^{-1}$ treatment, while high fluxes of dissolved organic C in the leachate occurred in the $500 \text{ Mg}\cdot\text{ha}^{-1}$ for both the 7-day and 15-day treatments (Fig. 5). This indicates that NO_3^- was probably limiting for complete C use by microorganisms in the higher treatment, as confirmed by NO_3^- analysis. In the subsequent irrigation periods, all 7-day treatments exhibited no organic C at the bottom of the soil column (results not shown).

3.3. Ca, Mg, K and Mn evolution

Large quantities of Ca^{2+} were found in the leachate for the $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment in the first irrigation period for both the 7-day and 15-day interval treatments (Fig. 6a), while smaller quantities were released in the second (Fig. 6b) and third irrigation period (results not shown). The results of the control and the $200 \text{ Mg}\cdot\text{ha}^{-1}$ were similar whatever the water supply interval, and during the last irrigation period, similar quantities were found for the control and the treatments, indicating that the main geochemical processes in the treatments reverted to a situation similar to the conditions before apple deposition. Similar trends were found for K^+ (Figs. 6a and 6b) and Mg^{2+} (results not shown), however the quantities of K^+ released were much smaller than for Ca^{2+} and Mg^{2+} . In the $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment, reducing conditions favored the solubilization of Mn oxides in the first

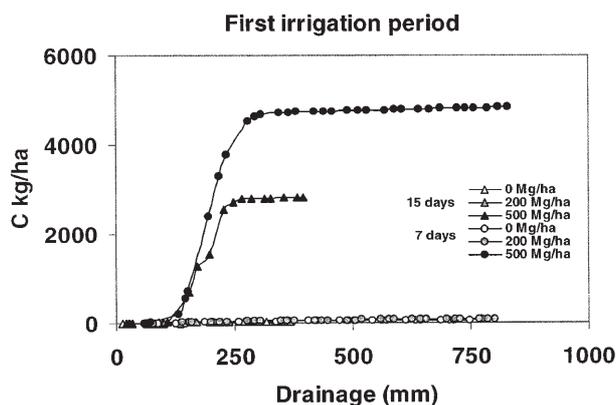


Figure 5. Relationship between cumulative leached dissolved organic C and cumulative drainage depth during the first irrigation period for three apple deposition ($0 \text{ Mg}\cdot\text{ha}^{-1}$, $200 \text{ Mg}\cdot\text{ha}^{-1}$, $500 \text{ Mg}\cdot\text{ha}^{-1}$) and two water supply interval (7-day and 15-day) treatments on soil.

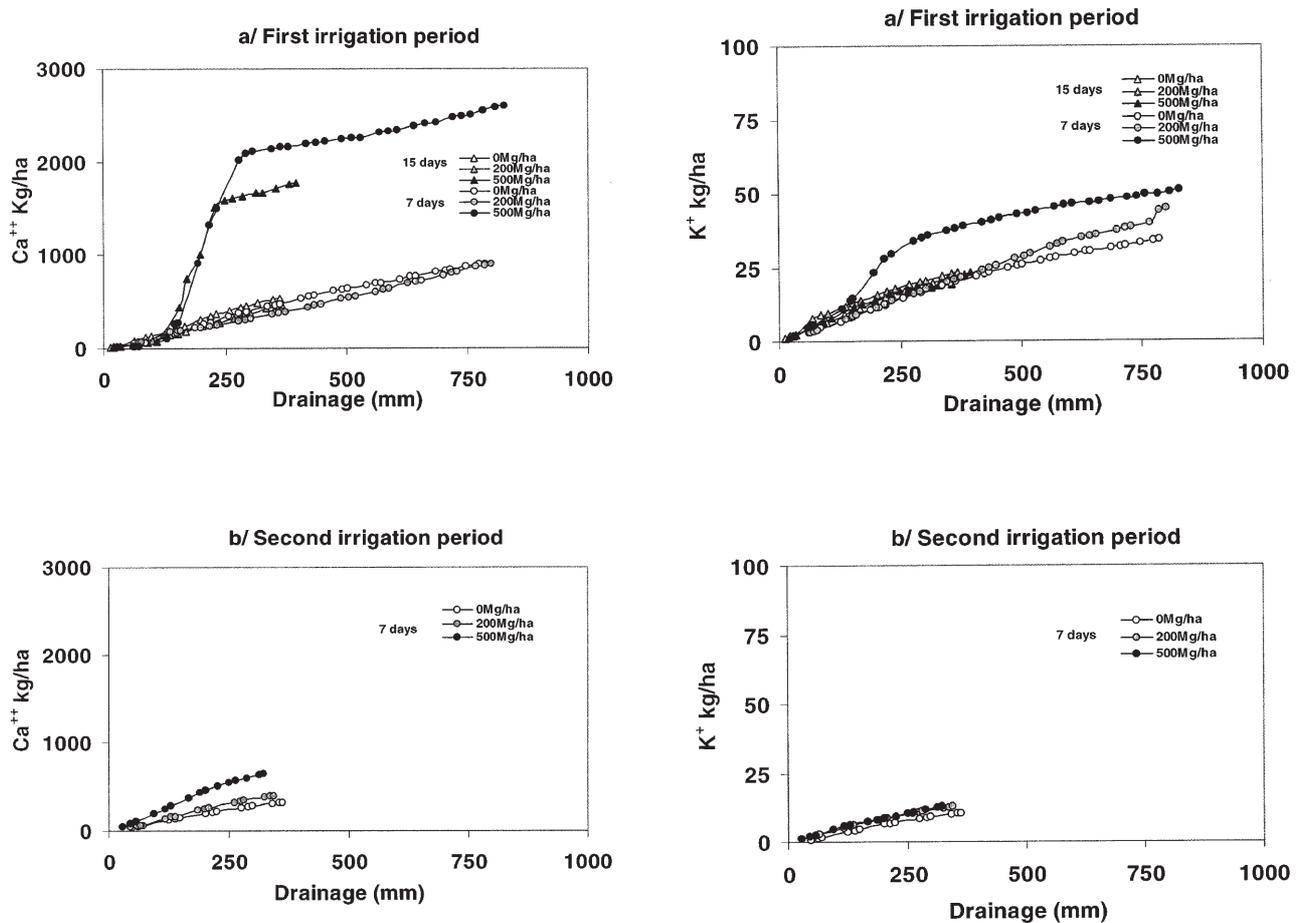


Figure 6. Relationship between cumulative leached Ca^{2+} , K^{+} fluxes and cumulative drainage depth during two successive irrigation periods for three apple deposition ($0 \text{ Mg}\cdot\text{ha}^{-1}$, $200 \text{ Mg}\cdot\text{ha}^{-1}$, $500 \text{ Mg}\cdot\text{ha}^{-1}$) and two water supply interval (7-day and 15-day) treatments on soil. **a:** first period; **b:** second period.

irrigation period (Fig. 7), and Mn^{2+} concentration increased to values higher than the norm for potability ($50 \mu\text{g}\cdot\text{l}^{-1}$). Results of the $200 \text{ Mg}\cdot\text{ha}^{-1}$ treatment were close to the results of the control, indicating that the effect of the application rate on Mn solubilization was not significant. Soluble Mn strongly decreased in the second and third irrigation period after the soil profile dried and became reoxygenated (results not shown).

3.4. Mass balance

Table IV gives the nutrient leaching for each irrigation period in the 7-day and $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment,

while Table V compares the cumulative nutrient leaching in the 7-day experiment during the three irrigation periods for the 0, 200 or $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment, respectively. Results show that in the high input treatment (Tab. IV), nutrients may be separated into two groups: one having a maximum leaching in the second irrigation period after a first phase of active biogeochemical transformation (NO_3^- , SO_4^{2-}), and the second one (other elements) having a continuous decreasing leaching versus time until complete disappearing in some cases (Mn, or organic C). As indicated in Table V, leaching was not proportional to apple doses. In some cases (Cl^- , K^+ , or Na^+ for example), leaching was more or less independent of apple treatment, whereas in other cases (C, Ca^{2+} ,

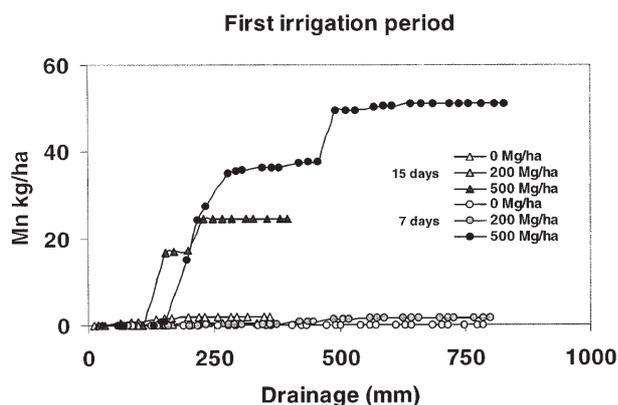


Figure 7. Relationship between cumulative leached Mn^{2+} and cumulative drainage depth during the first irrigation period for three apple deposition ($0 \text{ Mg}\cdot\text{ha}^{-1}$, $200 \text{ Mg}\cdot\text{ha}^{-1}$, $500 \text{ Mg}\cdot\text{ha}^{-1}$) and two water supply interval (7-day and 15-day) treatments on soil.

Mg^{2+} , or Mn^{2+} for example), leaching strongly increased in the higher treatment. This was due to threshold effects in developing reducing conditions after apple deposition on the soil.

4. DISCUSSION

4.1. Transport properties and Eh-pH evolution

The concentration of Cl^- in leached water after one pore volume (the volume corresponding to the total porosity of the soil column) equaled approximately $5 \text{ mg}\cdot\text{l}^{-1}$, which was close to the initial concentration of the irrigation water (approximately $4 \text{ mg}\cdot\text{l}^{-1}$). This indicates that there was low dispersion in the soil column. This low dispersion was in agreement with the low bulk density of the soil in the columns, which corresponded to a high and homogeneous porosity available for water transport (approximately 60%), and possible rapid flow with low dispersion. Results relative to Eh-pH variations are in agreement with the field experiments [5] which showed a pH of between 7.0 to 8.0, and 6.0 to 7.5 for the untreated soil and the $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment, respectively. Two main reasons explain the pH decrease for the higher treatment. First, the availability of the added C from residue material increases CO_2 -C production resulting from high respiratory O_2 consumption in the vicinity of the organic material [1, 2]. This decreased the pH of the soil solution, although the decrease in pH is moderated by calcite dissolution. Second, during apple fermentation, malic acid ($\text{C}_4\text{H}_6\text{O}_5$) has been shown to contribute

Table IV. Nutrient leaching determined for the main chemical elements in the 7-day and $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment during the three successive irrigation periods.

Parameter	Leached during the irrigation periods			
	First period	Second period	Third period	Total
	$\text{kg}\cdot\text{ha}^{-1}$			
Cl^-	161	23	17	201
$\text{N}\text{-NO}_3^-$	6	311	139	456
SO_4^{2-}	268	478	151	897
Inorganic C	692	94	76	862
Organic C	4844	14	11	4869
Ca^{2+}	2599	645	340	3584
Mg^{2+}	458	74	32	564
K^+	51	13	8	72
Na^+	98	27	14	139
Mn^{2+}	51	0	0	51

Table V. Cumulative nutrient leaching determined for three apple deposition ($0 \text{ Mg}\cdot\text{ha}^{-1}$, $200 \text{ Mg}\cdot\text{ha}^{-1}$, $500 \text{ Mg}\cdot\text{ha}^{-1}$) and a 7-day water supply interval treatments during the three irrigation periods.

Parameter	Treatments (7-day experiments)		
	$0 \text{ Mg}\cdot\text{ha}^{-1}$	$200 \text{ Mg}\cdot\text{ha}^{-1}$	$500 \text{ Mg}\cdot\text{ha}^{-1}$
	$\text{kg}\cdot\text{ha}^{-1}$		
Cl^-	181	185	201
$\text{N}\text{-NO}_3^-$	388	425	456
SO_4^{2-}	806	820	897
Inorganic C	565	788	862
Organic C	104	120	4869
Ca^{2+}	1501	1630	3584
Mg^{2+}	187	232	564
K^+	53	67	72
Na^+	142	153	139
Mn^{2+}	0.1	1.7	51

up to 90% of the total acidity [19], while other organic acids derived from apples may also contribute to soil acidification. Redox potential measurements indicated reducing conditions in the high input treatment ($500 \text{ Mg}\cdot\text{ha}^{-1}$). Nevertheless, these measurements must be carefully considered, because they assume that chemical reactions have attained equilibrium. Requirements for obtaining rapid equilibrium are a high concentration of a dominant redox-couple and stable conditions at the time of measurement [24]. Different reactions may occur more or less independently of each other [16] and complex formation may alter redox equilibrium between inorganic ions [21]. Other difficulties for interpreting redox data may come from the fact that O_2 could be

introduced to the system when electrodes are inserted in water, or that measurements in leached and mobile water may be different from soil measurements with immobile water within small regions. Nevertheless, the reduction of O_2 and the other inorganic redox components is generally sequential, with O_2 being reduced first, followed in turn by NO_3^- , Mn-, Fe-oxides, SO_4^{2-} and CO_2 [26].

4.2. Nitrate, sulfate and organic carbon

During the first irrigation period, the control showed the leaching of mineralized N present in the soil profile (Tab. I) or derived from mineralization of organic matter. Continuous wetting and high temperatures under laboratory conditions provided favorable conditions for both mineralization and leaching. On the other hand, NO_3^- depletion in the $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment may be attributed to intensive N immobilization after adding large quantities of soluble C, and second, by denitrification in wet conditions due to irrigation. It has been suggested that for a high C/N ratio in residual organic matter, like apples ($C/N = 92$), the amount of residue N recovered in the soil is high because N immobilization is stimulated, although the nature of the organic material may modify or regulate the microbial processes under similar conditions [2, 12]. These results were supported by the C/N ratio variation versus time for the three treatments as observed under field conditions [5]. After incorporating apple in the 0–0.30 m soil layer, the C/N ratio increased to 40, resulting from a mixture of the C/N ratio of the soil organic matter ($C/N = 10$ to 11) and of the C/N ratio of apple waste ($C/N = 92$). Then, due to CO_2 -C production by the microbial biomass, the C/N ratio of the remaining organic residues progressively decreases, and at some point N is no longer limiting to microbial biomass. Critical values of C/N for equilibrium between mineralization and immobilization have been reported to be in the 20–25 range [6]. On the other hand [12] it was found that between 41% and 86% of the existing NO_3^- was immobilized during a 5-d aerobic incubation experiment in soil without added NO_3^- , and that intense stimulation of microbial immobilization could limit the amount of NO_3^- available for denitrification during a subsequent anaerobic phase. Denitrification possibly exists, however. Critical Eh for N_2O production is considered to occur at +200 to +250 mV [6], and this range coincides with the experimental data for the $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment, as shown in the Eh-pH diagram (Fig. 8). The availability of NO_3^- combined with limited gas diffusion from the atmosphere leads to the formation of anaerobic zones around the organic residues [11, 12, 14, 25]. By comparing the effects of adding dry residue with the similar effects of water-soluble extracts of the

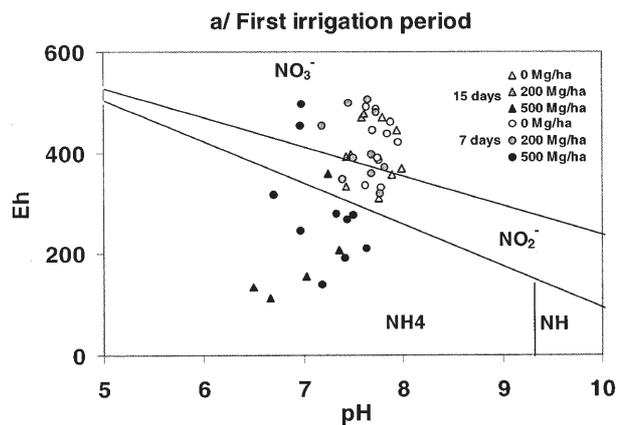


Figure 8. Eh-pH diagram for N during the first irrigation period for three apple deposition ($0 \text{ Mg}\cdot\text{ha}^{-1}$, $200 \text{ Mg}\cdot\text{ha}^{-1}$, $500 \text{ Mg}\cdot\text{ha}^{-1}$) and two water supply interval (7-day and 15-day) treatments on soil.

residues, it has been suggested that introducing fresh organic matter or dry residue to the soil quickly promotes denitrification by supplying available C [11]. For apples, probably a high release of labile C occurred rapidly and this dependence of denitrifying microorganisms on fermentation has already been suggested or supported through experimental data by several authors [18, 22]. Following immobilization, limiting soluble C in the soil solution leads to biomass death and degradation, and then NO_3^- release in the soil column. This starts first in the $200 \text{ Mg}\cdot\text{ha}^{-1}$ treatment during the first irrigation period, and later in the $500 \text{ Mg}\cdot\text{ha}^{-1}$ treatment during the second irrigation period, whereas continuous mineralization and leaching are observed for the control. The timing of NO_3^- release in the soil after immobilization corresponds to the timing of limiting available C in the soil solution, which depends on the quantity of apple waste incorporated. Similar results showing the more reducing conditions for the higher treatment were provided by SO_4^{2-} analysis, and decreasing the reducing conditions after drying the soil reoxidized the soil solution and provided SO_4^{2-} leaching again. Thus, intensive microbial activity, in which the N and S biogeochemical cycles were involved, led to considerable disturbance in N and S transport as compared with a non-interactive tracer of water and solute movement like Cl^- , until complete reoxidation of the soil occurred.

4.3. Ca, Mg, K and Mn release

The production of CO₂ and organic acids results in a decrease in pH and a dissolution of minerals with an increase in Ca²⁺, Mg²⁺, and carbonated alkalinity content as well. Thus, most Ca²⁺ and Mg²⁺ transport was likely to have come from mineral dissolution, whereas K⁺ was released from soil - solution exchange processes. Results relating to Mn dissolution under reducing conditions agree with those obtained under field conditions [5] which showed that reduction of Mn takes place at redox potentials in the +200 to +300 mV range at pH between 6.0 and 8.0, and that soluble Mn was found down to the 0.50 m depth approximately. This suggested simultaneous local reducing biochemical conditions and/or Mn transport in the soil solution. After reduction, part of the Mn could thereafter precipitate or be adsorbed on the clay complex as the soil solution moves. In the same

way, an increase in soil solution pH as it moves downward would result in precipitation of Mn under less reducing conditions [4, 23]. Drying periods contributed to decreasing soil water content and to increasing soil air content, whereas wetting periods had the opposite effects especially with high quantities of organic matter, and consequently, the reactions may be reversed [17]. Mn oxidation-reduction reactions are also partly regulated by chelation of manganese by organic compounds produced in soil by microbiological activity (Fig. 9), especially when the decomposition of the soluble organic matter becomes incomplete and organic anions appear which facilitate metal solubilization [5, 10]. Similar results were found for Ca²⁺, Mg²⁺ and K⁺ (Fig. 9), and these results are in agreement with the previous field study [5] in which the formation of organo-metallic complexes was supported by the correlation between Ca or Mn concentration and non-carbonated alkalinity. Indeed, several

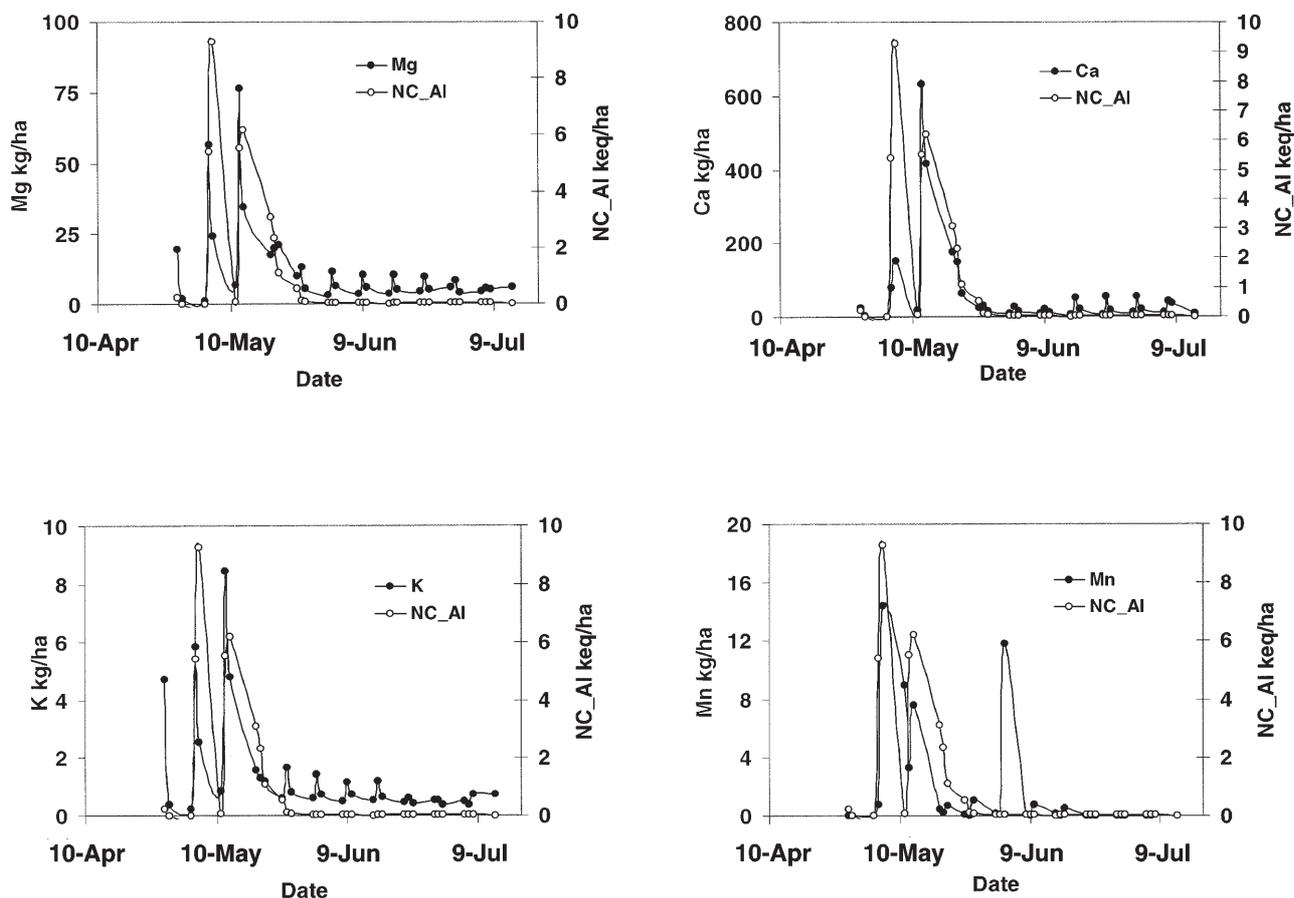


Figure 9. Instantaneous leached Ca²⁺, Mg²⁺, K⁺, Mn²⁺ fluxes and non-carbonated alkalinity versus time during the first irrigation period for the 500 Mg·ha⁻¹ apple deposition and 7-day water supply treatment.

investigations have shown that soil organic matter is capable of complexing metals by ion-exchange, surface absorption and chelation mechanisms, in a complex mixture of various fractions of soil organic matter which are pH and redox potential dependent [7, 8, 13].

5. CONCLUSION

Various biogeochemical processes are involved after apple waste deposition on soil but they all derive from the intense biological activity brought about by the addition of highly fermentable material that leads to soil reduction. Both reoxidation periods and the decrease of available C for microbial biomass with time simultaneously favor the oxidizing properties of the soil, and limit the environmental damage after organic waste deposition. Some possible middle-term effects are demonstrated, like movement of labile C and NO_3^- following mineralization of microbial biomass after a preliminary intensive N immobilization, which could provide organic and inorganic compounds for subsequent denitrification in the water table. The results obtained under laboratory conditions confirm that the $200 \text{ Mg}\cdot\text{ha}^{-1}$ treatment has no dramatic environmental consequence, and that threshold effects exist [5]. Moreover, they show that the interactions between the transport process and the biogeochemical interactions determine the mass fluxes that could drain to the water table, and this underlines the importance of the choice of season for land application of fresh organic waste. From a practical aspect, fresh quantities less than $200 \text{ Mg}\cdot\text{ha}^{-1}$ are recommended to minimize the environmental damage during organic waste deposition on land, while calcareous soils are preferable because they limit the pH decrease due to calcite dissolution. Waste application must be made under dry climatic conditions to limit the soil chemical reducing conditions, and reoxygenated periods help to limit or stop the negative consequences of a low redox potential in the soil.

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REFERENCES

- [1] Anderson G.K., Donnelly T., Anaerobic digestion of high strength industrial wastewaters, *Public. Health Eng. 5* (1977) 64–71.
- [2] Aulakh M.S., Doran J.W., Walters D.T., Mosier A.R., Francis D.D., Crop residue type and placement effects on denitrification and mineralization, *Soil Sci. Soc. Am. J.* 55 (1991) 1020–1025.
- [3] Bourrié G., Relation entre le pH, l'alcalinité, le pouvoir tampon et les équilibres du CO_2 dans les eaux naturelles, *Bulletin "Association Française pour l'Étude du Sol"*, 1976, n° 3, pp. 141–159.
- [4] Collins J.F., Buo S.W., Patterns of iron and manganese precipitation under specified Eh-pH conditions, *Soil Sci.* 110 (1970) 157–162.
- [5] de Cockborne A.M., Vallès V., Bruckler L., Sévenier G., Cabibel B., Bertuzzi P., Bouisson V., Environmental consequences of apple waste deposition on soil, *J. Environ. Qual.* 28 (1999) 1031–1037.
- [6] Flessa H., Beese F., Effects of sugarbeet residues on soil redox potential and nitrous oxide emission, *Soil Sci. Soc. Am. J.* 59 (1995) 1044–1051.
- [7] Gotoh S., Patrick W.H. Jr., Transformation of manganese in a waterlogged soil as affected by redox potential and pH, *Soil Sci. Soc. Am. Proc.* 36 (1972) 738–742.
- [8] Gotoh S., Patrick W.H. Jr., Transformation of iron in a waterlogged soil as influenced by redox potential and pH, *Soil Sci. Soc. Am. Proc.* 38 (1974) 66–71.
- [9] Jandik P., Bonn G., *Capillary electrophoresis of small molecules and ions*, VCH Publishers, Inc., New-York (USA), 1993.
- [10] Marshall K.C., Biogeochemistry of manganese minerals, in: Trudinger P.A., Swaine D.J. (Eds.), *Biogeochemical cycling of mineral-forming elements*, 1979, pp. 253–292.
- [11] McKenney D.J., Wang S.W., Drury C.F., Findlay W.I., Denitrification and mineralization in soil amended with legume, grass, and corn residues, *Soil Sci. Soc. Am. J.* 57 (1993) 1013–1020.
- [12] McKenney D.J., Wang S.W., Drury C.F., Findlay W.I., Denitrification, immobilization and mineralization in nitrate limited and nonlimited residue-amended soil, *Soil Sci. Am. J.* 59 (1995) 118–124.
- [13] Mortensen J.L., Complexing of metals by soil organic matter, *Soil Sci. Soc. Proc.* (1963) 179–186.
- [14] Neeteson J.J., VanVeen J.A., Mechanistic and practical modelling of nitrogen mineralization-immobilization in soils, in: Wilson J.R. (Ed.), *Advances in nitrogen cycling in agricultural ecosystems*, CAB International, Wallingford, England, 1987, pp. 145–155.
- [15] Noodharmcho A., Flocker W.J., Marginal land as an acceptor for cannery waste, *J. Am. Soc. Hort. Sci.* 100 (1975) 682–684.
- [16] Norrström A.C., Field-measured redox potentials in soils at the groundwater-surface-water interface, *Eur. J. Soil Sci.* 45 (1994) 31–36.
- [17] Patrick W.H. Jr., Henderson R.E., Reduction and reoxydation cycles of manganese and iron in flooded soil and in water solution, *Soil Sci. Soc. Am. J.* 45 (1981) 855–859.

- [18] Paul J.W., Beauchamp E.G., Denitrification and fermentation in plant-residue amended soil, *Biol. Fer. Soils* 7 (1989) 303–309.
- [19] Philips J.D., Pollard A., Whiting G.C., Organic acid metabolism in cider and perry fermentations. I. A preliminary study, *J. Sci. Food Agric.* 7 (1956) 31–40.
- [20] Pinta M., Barroin G., Baudin G., Bellanger J., Spectrométrie d'absorption atomique. Volume 2 : Application à l'analyse chimique, Masson et Cie, ORSTOM (Ed.), Paris (France), 1971, 793 p.
- [21] Ponnamperna F.N., Tianco E.M., Loy T., Redox equilibria in flooded soils: I. The iron hydroxide systems, *Soil Sci.* 103 (1967) 374–382.
- [22] Schipper L.A., Harfoot C.G., McFarlane P.N., Cooper A.B., Anaerobic decomposition and denitrification during plant decomposition in an organic soil, *J. Environ. Qual.* 23 (1994) 923–928.
- [23] Sloan J.J., Basta N.T., Remediation of acid soils by using alkaline biosolids, *J. Environ. Qual.* 24 (1995) 1097–1103.
- [24] Stumm W., Morgan J.J., *Aquatic chemistry*, John Wiley, New York, 1981.
- [25] Tiedje J.M., Sextone A.J., Myrold D.D., Robinson J.A., Denitrification: Ecological niches, competition and survival, *Antonie van Leeuwenhoek*, 1982, Vol. 48, pp. 569–583.
- [26] Turner F.T., Patrick W.H. Jr., Chemical changes in waterlogged soils as a result of oxygen depletion, in: Holmes J.W. (Ed.), *Int. Congr. Soil Sci.* 9th, Adelaide, Vol. 4, Elsevier, New York, 1968, pp. 53–56.
- [27] Waters Capillary Ion analyzer, Operator's manual. Millipore, Waters Chromatography, Manual number 153-02TP, 1993.