

Original article

**Ionic adsorption of ammonium and nitrate on some  
animal litters and their role in ammonia volatilization.  
Laboratory results**

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**Abstract** — Two experiments were carried out to determine the adsorption of ammonium and nitrate on litters (Exp. 1) and the volatilization of ammonia in their presence (Exp. 2). In Exp. 1, glass tubes containing 15 ml of a buffered solution enriched with  $\text{NH}_4\text{Cl}$  calculated as  $10.59 \text{ mg}\cdot\text{l}^{-1}$  of  $\text{NH}_4^+$  or  $\text{KNO}_3$  calculated as  $50 \text{ mg}\cdot\text{l}^{-1}$  of  $\text{NO}_3^-$  were used. Graded amounts (0 [control], 25, 50, 100 mg) of litters (wheat straw, flax straw (Equi-lin<sup>®</sup>), zeolite (Zeolite Stall Fresh<sup>®</sup>), spruce sawdust and beech sawdust) were added to the tubes which were incubated for 24 h. Ammonium and nitrate concentrations, and pH, were checked on the supernatant. A preliminary experiment was carried out with zeolite to come to an ammonium balance. After adsorption of ammonium by graded amounts of zeolite, [0 (control), 0.25, 1, 2, 4 g], ammonium balance was assessed after two elutions with 1 N HCl. In Exp. 2, Woulff flasks were used and ammonia was trapped in a solution of 0.1 N HCl. The preliminary experiment showed that the ammonium added and adsorbed by different amounts of zeolite was completely recovered after 2 elutions. All litters, except beech sawdust, were effective in ammonium adsorption. Especially, the straws were required in very small amounts to immobilize the added ammonium or nitrate. Furthermore, with straws the pH value decreased from pH 7.50–7.60 to pH 6.90, and this effect was related to the amounts of material added. For each pH group, ammonia volatilization was significantly decreased ( $P < 0.05$ ) with straw (wheat straw, Equi-lin<sup>®</sup>) as compared with their blank pH group. However, no significant decrease was observed with sawdust (spruce, beech) and zeolite.

**ammonium / nitrate / adsorption / ammonia volatilization / litters**

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**Résumé — Adsorption des ions ammonium et nitrate sur quelques litières animales et leur rôle dans la volatilisation ammoniacale. Résultats de laboratoire.** Deux expériences en laboratoire ont été réalisées pour d'une part déterminer l'adsorption des ions ammonium ( $\text{NH}_4^+$ ) et nitrate ( $\text{NO}_3^-$ ) sur quelques litières animales à savoir la paille de froment, la paille de lin (Equi-lin<sup>®</sup>), la sciure d'épicéa, la sciure de hêtre ainsi que la zéolite (Zeolite Stall Fresh<sup>®</sup>), d'autre part, évaluer l'impact des mêmes litières sur la volatilisation de l'ammoniac en fonction du pH. Dans l'expérience 1 (Exp. 1), des tubes en verres (RN 19/26) d'une capacité de 15 ml contenant une solution tampon enrichie, soit d'une concentration en  $\text{NH}_4^+$  équivalente à  $10,59 \text{ mg}\cdot\text{l}^{-1}$  sous forme de  $\text{NH}_4\text{Cl}$ , soit d'une concentration en  $\text{NO}_3^-$  équivalente à  $50 \text{ mg}\cdot\text{l}^{-1}$  sous forme de  $\text{KNO}_3$  pendant une durée d'incubation de 24 heures, ont été utilisés. Des quantités croissantes (25, 50 et 100 mg) de litière broyée (particules < 4 mm) ont été soumises à l'adsorption et comparées aux témoins (0 mg de litières). Après centrifugation des tubes, les concentrations en ions ammonium et de nitrate, ainsi que le pH, ont été mesurés sur le surnageant. Une expérimentation préliminaire avec la zéolite a été mise au point. Après l'adsorption des ions ammonium par les quantités croissantes de zéolite (0 ; 0,25 ; 1 ; 2 ; 4 g), le bilan des ions ammonium a été effectué en procédant à deux désorptions à l'aide d'une solution HCl 1 N. Pour l'expérience 2 (Exp. 2), des flacons de Woulff contenant des solutions (300 ml) ajustées aux valeurs de pH : 1,15 ; 6,5 ; 7,5 et 8,5 ont été tour à tour utilisées pour 2 g de chaque litière. L'ammoniac volatilisé a été chaque fois piégé dans 50 ml d'une solution de HCl 0,1 N. Il ressort de cette étude que, à l'exception de la sciure de hêtre, toutes les autres litières adsorbent les ions ammonium dans des proportions variables. Particulièrement, la paille de froment et la paille de lin ont induit un effet prononcé même en présence d'une quantité de paille aussi faible que 25 mg. En effet, ces pailles adsorbent les ions ammonium et nitrate dans des proportions hautement significatives ( $P < 0,05$ ). Les résultats obtenus au cours de l'expérimentation préliminaire ont montré que les ions  $\text{NH}_4^+$  ajoutés ( $10,59 \text{ mg}\cdot\text{l}^{-1}$ ) ont été effectivement adsorbés sur la zéolite, à partir du moment où le recouvrement des ions ammonium a été entièrement obtenu après 2 désorptions. Ainsi, il n'a pas été possible d'établir une différence significative entre les témoins (0 g de zéolite) et les autres quantités (0,25 ; 1 ; 2 ; 4 g de zéolite) ( $P > 0,05$ ). Dans l'ensemble, la volatilisation de l'ammoniac (Exp. 2) a diminué avec les pailles d'une façon significative ( $P < 0,05$ ). Néanmoins, cette diminution est inversement proportionnelle aux valeurs du pH. En conclusion, les résultats obtenus au cours de cette étude suggèrent que des émissions ammoniacales pourraient être minimisées principalement par l'utilisation des pailles de froment et de lin (Equi-lin<sup>®</sup>) et accessoirement par la zéolite (Zeolite Stall Fresh<sup>®</sup>) et la sciure d'épicéa. Concomitamment, le lessivage des nitrates pourrait être maîtrisé par les pailles de froment et de lin. L'un des avantages de ces 2 pailles est celui de contribuer à l'acidification du milieu et ainsi réduire le risque de volatilisation ammoniacale.

**ammonium / nitrate / adsorption / volatilisation ammoniacale / litières**

## 1. INTRODUCTION

Since ammonia volatilization from animal manure and slurries represents the most important source of atmospheric ammonia in Europe (80%) [9]; the control of ammonia emissions and nitrate water pollution from animal husbandry and industrial activities is one of the major environmental preoccupations of many European and North-American countries.

To avoid ammonia emissions, a large number of reduction measures have been put forward. For example, Kitai and Arakawa

[19] suggested the sterilization of excreta from broiler chickens or the incubation of fresh excreta with the antibiotic thiopeptin. Ammonia release can be also prevented by slurry acidification [15, 25, 27, 28, 32, 43]. For example, Stevens et al. [41] reported that at least 80% of the ammonia release from pig and cow slurries could be prevented by acidifying the slurry to pH 6.0 and 5.5, respectively. Nevertheless, acidification remains very hazardous when handling and requires substantial quantities to be effective, and therefore this treatment is expensive.

Addition of substances such as *Yucca schidigera* extract to the slurry or to the animal feed in order to reduce the release of ammonia from the manure has resulted in contradictory findings. Positive results were obtained in laboratory tests, but were not confirmed when used in pig slurry pits [24]. These positive results were in agreement with those obtained by Rowland et al. [34], and Headon and Dawson [17]. Indeed, *Yucca schidigera* extract may have a significant benefit in reducing ammonia levels from poultry house. In contrast, Johnston et al. [20] demonstrated that the *Yucca* extract did not effectively suppress ammonia release from poultry manure.

Since the proportion of protein in the feed is responsible for the N content of the excreta [40], it has become increasingly clear that excess protein in the feed should be avoided.

Many studies have focused on the influence of factors such as temperature, wind speed, humidity, pH and dry matter content on the ammonia volatilization from animal slurries [26, 39] or manure [12]. However, there is little information about the potential for ammonium/nitrate adsorption by animal litter materials. In general, it is considered that the greater the cation exchange capacity, the less is the amount of ammonia volatilized [42, 45]. Moreover, it has been shown that particles in the dung can immobilize some nitrogen from the urine [45]. Therefore, choosing bedding materials with

low cost and good efficacy in reducing ammonia emissions from animal slurry appears very important.

The present study was then designed, to compare under laboratory conditions, the ability of some animal litters [wheat straw, flax straw (Equi-lin<sup>®</sup>), zeolite (Zeolite Stall Fresh<sup>®</sup>), spruce sawdust and beech sawdust] to adsorb ammonium and nitrate (Exp. 1). Ammonia volatilization in the presence of each litter was also investigated as a function of pH (Exp. 2).

## 2. MATERIALS AND METHODS

### 2.1. Materials

Five bedding materials were used in the present study: chopped wheat straw, flax straw (Equi-lin<sup>®</sup>), Zeolite Stall Fresh<sup>®</sup>, spruce sawdust and beech sawdust.

The wheat straw is classically used as bedding material. The Equi-lin<sup>®</sup> is marketed by the Groupe Lamerant SA, Neubourg, France. The spruce and beech sawdusts were purchased from the woodworker. The Zeolite Stall Fresh<sup>®</sup> is an additive material and is marketed by the American Absorbents, Inc. Austin, Texas.

Before experiments, the amounts of ammonium and nitrate eventually fixed on the different materials were determined (Tab. I). The pH was also measured. The

**Table I.** Ammonium, nitrate concentrations and pH of each animal litter material. The materials (0.1 g each) were incubated in a buffered solution (0.02 M; initial pH 7.50) with permanent shaking for 1 h for measuring  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , and for 24 h for pH measurement. The results are expressed as mean  $\pm$  SEM ( $n = 3$ ). \* ( $P < 0.05$ ); \*\* ( $P < 0.01$ ); \*\*\* ( $P < 0.001$ ) indicates a value different from other litter materials (Zeolite Stall Fresh<sup>®</sup>, spruce sawdust and beech sawdust).

Litter materials	Concentration of $\text{NH}_4^+$ (mg·l <sup>-1</sup> )	Concentration of $\text{NO}_3^-$ (mg·l <sup>-1</sup> )	Changes from initial pH (pH 7.50)
Equi-lin <sup>®</sup>	0.33 $\pm$ 0.03 *	8.61 $\pm$ 0.39 ***	7.25 $\pm$ 0.04 *
Wheat straw	1.02 $\pm$ 0.13 **	7.85 $\pm$ 0.52 ***	6.90 $\pm$ 0.11 *
Zeolite Stall Fresh <sup>®</sup>	0.16 $\pm$ 0.04	1.43 $\pm$ 0.15	7.45 $\pm$ 0.01
Spruce sawdust	0.17 $\pm$ 0.02	2.33 $\pm$ 0.04	7.46 $\pm$ 0.01
Beech sawdust	0.18 $\pm$ 0.02	2.45 $\pm$ 0.46	7.50 $\pm$ 0.01

**Table II.** The granulometry and the dry matter content of the animal litter materials.

Granulometry	Litter or additive materials														
	Equi-lin <sup>®</sup>			Wheat straw			Zeolite Stall Fresh <sup>®</sup>			Spruce sawdust			Beech sawdust		
Size range (mm)	≤ 2	2–4	≥ 4	≤ 2	2–4	≥ 4	≤ 2	2–4	≥ 4	≤ 2	2–4	≥ 4	≤ 2	2–4	≥ 4
(%) of total weight	63.9	32.7	3.4	61.2	37.1	1.7	100	0	0	85.0	10.7	4.3	98.9	0.9	0.2
Dry matter (%)	96.3			97.0			98.0			90.9			93.3		

granulometry was measured by a screen (Din 4188, Fritsch analysette, Germany). The method was used for particle size distribution of the litter amendments and the screen sizes were given on Table II. Dry matter (%) was determined by drying at 105 °C for 24 h (Tab. II). The sawdust (spruce, beech), the zeolite and Equi-lin<sup>®</sup> are used in their usual commercial size particles and granulometry distribution. The wheat straw has been finely chopped.

## 2.2. Experimental design

In Exp. 1, different amounts of litter materials (0 (control), 25, 50, 100 mg) were placed inside glass tubes (RN 19/26). The tubes were filled with 15 ml of buffered solution containing NH<sub>4</sub>Cl calculated as 10.59 mg·l<sup>-1</sup> of NH<sub>4</sub><sup>+</sup> or KNO<sub>3</sub> calculated as 50 mg·l<sup>-1</sup> of NO<sub>3</sub><sup>-</sup>. Each treatment was performed in triplicate.

The buffered solution (0.02 M; pH 7.50) consisted of 2.97 g·l<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>·2 H<sub>2</sub>O and 0.452 g·l<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>. The tubes, closed to avoid volatilization, were incubated for 24 h at room temperature, and mixed continuously on a rotatory shaker (Rotamix Heto, High Technology of Scandinavia). After the incubation, the tubes were centrifuged at 1000 rotations per minute for 3 min, and samples were taken from the supernatant for measurements of ammonium and nitrate concentrations and pH.

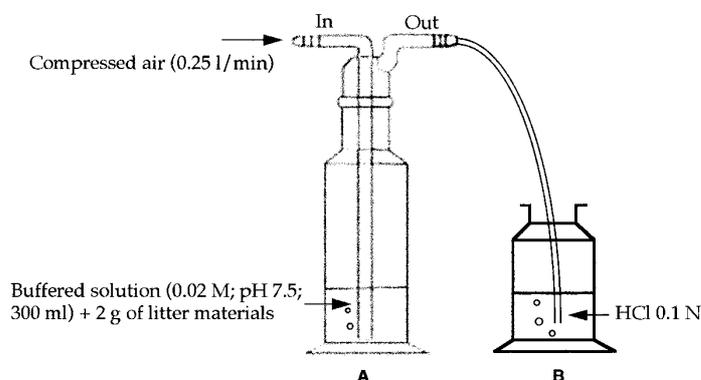
In Exp. 2, Woulff flasks (Fig. 1) were used to measure the ammonia volatilization as a function of pH and litter material. These

flasks were filled with only one amount of each litter (2 g in 300 ml of a solution containing ammonium; *n* = 3 for each pH and each litter). Each Woulff flask was continuously flushed with compressed air at a rate of 0.25 l·min<sup>-1</sup>, and the flow was controlled by a flow meter. Ammonia in effluent air was trapped in a flask containing 50 ml of 0.1 N HCl. Ammonia volatilized from the Woulff flasks were measured in the 0.1 N HCl flask. Results were expressed as percentages of the initial input of ammonium (10.59 mg·l<sup>-1</sup>).

## 2.3. Ammonium balance (preliminary experiment)

The basic procedure presented above was used to investigate the ammonium balance after ammonium adsorption on graded amounts of Zeolite Stall Fresh<sup>®</sup> [0 (control), 0.25, 1, 2, 4 g; *n* = 3 for each amount]. Ammonium adsorption on Zeolite Stall Fresh<sup>®</sup> was calculated after incubation for 24 h. After centrifugation, the ammonium concentrations were determined in the clear supernatant. The remainder of the aqueous layer was siphoned off and discarded. Fifteen ml of 1 N HCl were added to the precipitate and the tubes were reincubated for 1 h on the rotatory shaker, after which the samples were again centrifuged. This operation was repeated once. Ammonium concentrations were determined on the supernatant after each centrifugation. For each amount of Zeolite Stall Fresh<sup>®</sup>, the ammonium balance was calculated by adding the

**Figure 1.** Wouff flask (A) and 0.1 N HCl flask (B) for investigation of ammonia volatilization.



concentration of ammonium measured after the first centrifugation to the concentrations derived from each supernatant of the two extractions.

#### 2.4. Experimental measurements

Ammonium was measured colorimetrically by using the phenol-hypochlorite method of Berthelot at 640 nm [11] (spectrophotometer Coulter<sup>®</sup> Mini-Ke<sup>™</sup>). Nitrate was monitored using a nitrate electrode (Orion Research, Expandable ion Analyzer EA 920). The pH was monitored using a digital pH meter (Beckman<sup>®</sup> model 3550).

#### 2.5. Statistical analysis

Data are expressed as means  $\pm$  SEM. Statistical evaluation was performed using one-way analysis (Anova) for repeated measures and followed when required by Dunnett's test. The significance level was declared at  $P < 0.05$ .

### 3. RESULTS

#### 3.1. Characteristics of the different litter materials

Table I shows ammonium and nitrate concentrations and pH of each material prior to the adsorption experiments. In the results pre-

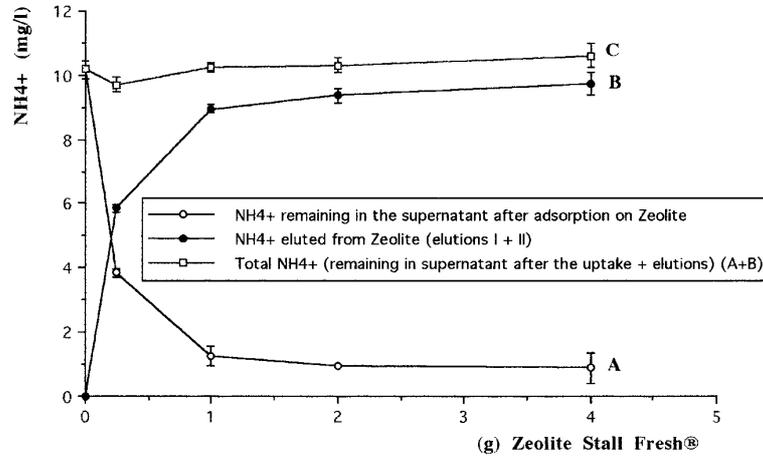
sented here, ammonium contents were initially higher ( $P < 0.05$ ) for wheat straw and ( $P < 0.01$ ) for Equi-lin<sup>®</sup> in comparison with other litters. Additionally, nitrate content was also higher ( $P < 0.001$ ) for wheat straw and Equi-lin<sup>®</sup>, in comparison with other litter materials. Similarly, these materials also decreased ( $P < 0.05$ ) the initial pH (7.50) from the buffered solution. The granulometry and the dry matter content (%) of the 5 different litters are presented in Table II.

#### 3.2. Ammonium balance (preliminary experiment)

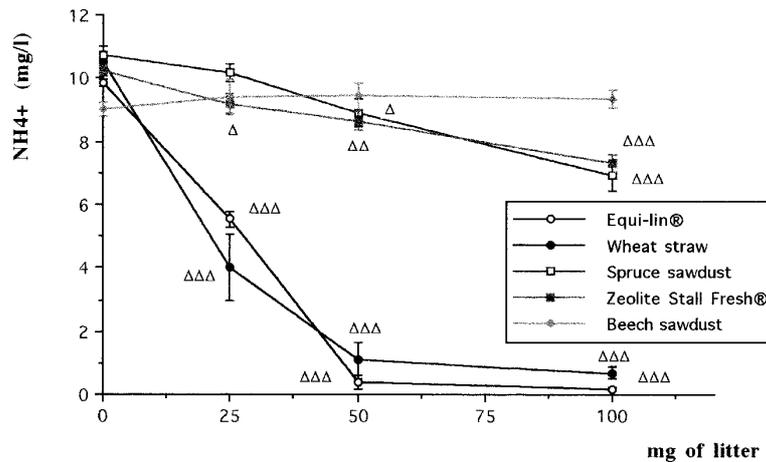
Figure 2 illustrates the ammonium balance (C) after adsorption of  $10.59 \text{ mg}\cdot\text{l}^{-1}$  ammonium on graded amounts of Zeolite Stall Fresh<sup>®</sup> [0 (control), 0.25, 1, 2, 4 g] (A) and two extractions (elutions) with 1 N HCl (B). The different recoveries calculated for 0.25, 1, 2 and 4 g of Zeolite Stall Fresh<sup>®</sup> did not significantly differ from the control group (0 g of Zeolite Stall Fresh<sup>®</sup>;  $P > 0.05$ ).

#### 3.3. Ammonium and nitrate adsorption in function of the amount of materials used (Exp. 1)

Figure 3 shows the ammonium adsorption ( $10.59 \text{ mg}\cdot\text{l}^{-1}$ ) and Figure 4 the nitrate adsorption on different amounts of litter



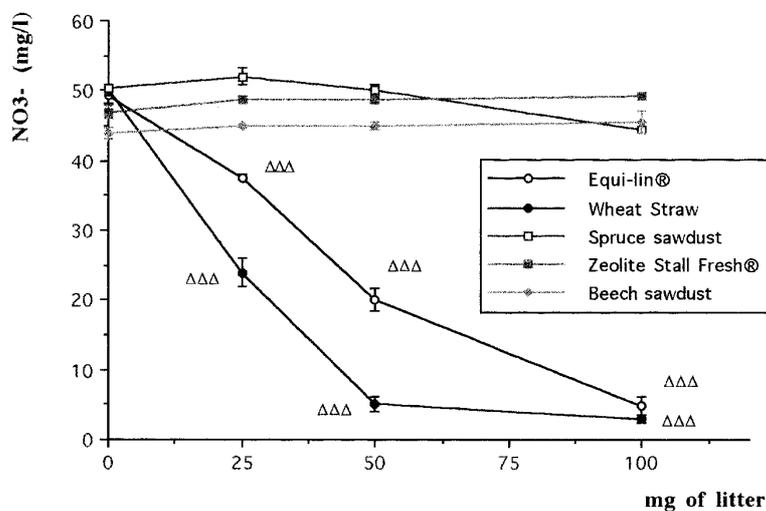
**Figure 2.** Ammonium balance after adsorption of  $10.59 \text{ mg}\cdot\text{l}^{-1}$  of ammonium on graded amounts of Zeolite Stall Fresh® (0, 0.25, 1, 2, 4 g) and two extractions. For each amount of Zeolite Stall Fresh® used, values of ammonium concentrations (expressed as  $\text{mg}\cdot\text{l}^{-1}$ ) were means  $\pm$  SEM ( $n = 3$ ).



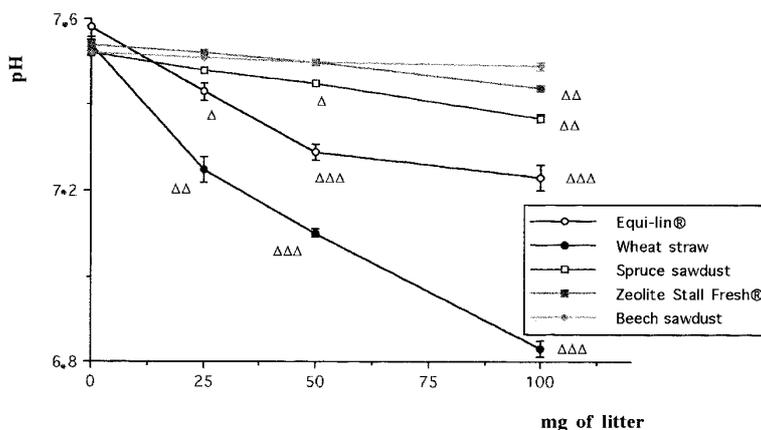
**Figure 3.** Ammonium adsorption on different amounts of litter materials (0, 25, 50, 100 mg) after 24 h of incubation. Each point is the mean  $\pm$  SEM ( $n = 3$ ).  $\Delta$  ( $P < 0.05$ );  $\Delta\Delta$  ( $P < 0.01$ );  $\Delta\Delta\Delta$  ( $P < 0.001$ ) indicates a value different from the control point (0 g of litter material).

materials [0 (control), 25, 50, 100 mg] after 24 h of incubation time. The wheat straw and the Equi-lin® induced a significant decrease of both ammonium and nitrate. The zeolite and the spruce sawdust induced only a decrease of ammonium while the

beech sawdust had no effect. However, the most pronounced effect was observed for the wheat straw and Equi-lin®. Indeed, for both materials this adsorbent effect was extremely significant ( $P < 0.001$ ) even at the lowest amount of litter (25 mg).



**Figure 4.** Nitrate adsorption on different amounts of litter materials (0, 25, 50, 100 mg). Each point is the mean  $\pm$  SEM ( $n = 3$ ).  $\Delta\Delta\Delta$  ( $P < 0.001$ ) indicates a value different from the control point (0 g of litter material).



**Figure 5.** pH changes during ammonium or nitrate adsorption on different amounts of litter materials (0, 25, 50, 100 mg). Each point is the mean  $\pm$  SEM ( $n = 3$ ).  $\Delta$  ( $P < 0.05$ );  $\Delta\Delta$  ( $P < 0.01$ );  $\Delta\Delta\Delta$  ( $P < 0.001$ ) indicates a value different from the control point (initial pH). For clarity of the figure, the pH origin on the y-axis began at 6.8.

### 3.4. The pH changes

As shown by Figure 5, the wheat straw and the Equi-lin® induced a significant

decrease in pH following ammonium and nitrate adsorption. By contrast, the three other materials had less influence on the pH values.

### 3.5. Ammonia volatilization as a function of the pH and of the different litters (Exp. 2)

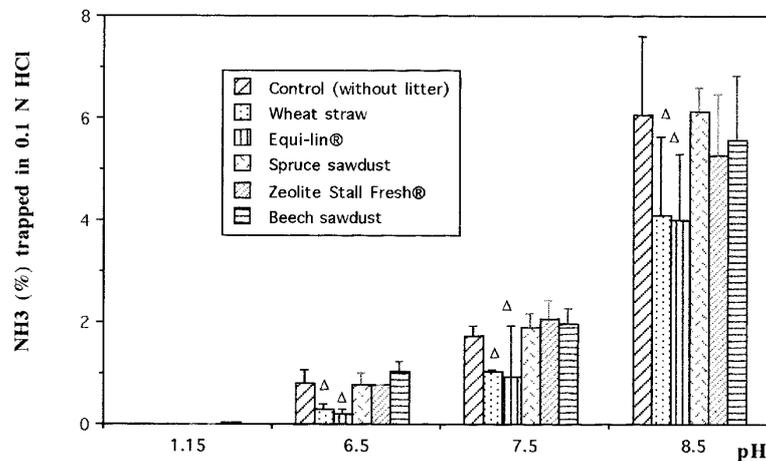
Results from Figure 6 show that at pH 1.15, no ammonia volatilization was observed. However, from pH 6.5 to 8.5, ammonia volatilization progressively increased for all materials ( $P < 0.05$ ) including the controls. But, at each pH group value (6.5, 7.5, 8.5), ammonia volatilization was significantly lower for the wheat straw and the Equi-lin<sup>®</sup> than for the other materials and the controls ( $P < 0.05$ ).

## 4. DISCUSSION AND CONCLUSION

It is well known that nitrogen compounds are excreted by animals as free ammonia (for most fish species), uric acid (for birds and terrestrials reptiles) or urea (for terrestrials mammals and adult amphibia). Mammals can also directly excrete ammonia into their urine [46].

From each type of animal excreta, ammonia is formed by the action of enzymes and released into the atmosphere, where it may contribute to cause damage to the respiratory tract in pigs [14, 44], in poultry [2] and in farm laborers [13]. Ammonia also has negative effects on animal performance and leads to a greater degree of susceptibility to a variety of infectious diseases [17]. Furthermore, ammonia volatilization in the atmosphere plays an important role in the formation of acid rain [3]. Ammonia has a direct effect on the vegetation in the areas surrounding animal husbandries, causing also corrosion of buildings and noxious odors [31]. Transported over long distances through the air, the ammonium causes eutrophication and acidification of water and soil [16] and imbalances in soil nutrients [31].

A large number of methods have been proposed to reduce ammonia emissions from animal husbandries, such as acidification of slurry or addition of substances such as



**Figure 6.** Ammonia volatilization from a buffered solution ( $10.59 \text{ mg}\cdot\text{l}^{-1}$  of ammonium) as a function of different pHs (1.15, 6.50, 7.50, 8.50) in the absence (control) and the presence of animal litter materials (2 g per 300 ml of ammonium buffered solution). Released ammonia was measured after 24 h and effects are expressed as percentage of the initial ammonium added in the solution. Values are given as means  $\pm$  SEM ( $n = 3$ ).  $\Delta$  ( $P < 0.05$ ) indicates a value different from the control in the same pH group.

Yucca extract. However, these suggestions are often expensive and sometimes hazardous. Moreover, contradictory findings were obtained about their efficacy [17, 20, 24, 34].

The aim of our study was to investigate the capacity of 5 different animal litters to adsorb ammonium and nitrate, and to reduce ammonia volatilization in an in vitro model.

Previously, ammonia volatilization from animal husbandries has been assessed by micrometeorological mass balance methods [6, 32] and by wind tunnels [23, 38]. The in vitro model described in the present work had the advantage to be more simple, fast and cost-effective than both micrometeorological techniques and wind tunnels. However, the experimental system used in this report is far more artificial than those which have been studied with micrometeorological methods and wind tunnels. But, the method is a preliminary step in understanding the fundamental principles which underlie environmental protection related to ammonia and nitrate from manures and slurries. Moreover, litter materials used in the present study were cheaper than the chemical agents used by Moore et al. [27, 28] and Martinez et al. [25] to reduce ammonia emissions.

The results from the present study showed that important ammonium adsorption occurred on wheat straw, Equi-lin<sup>®</sup>, Zeolite Stall Fresh<sup>®</sup> and spruce sawdust during a 24-h incubation (Fig. 3). In particular, the wheat straw and the Equi-lin<sup>®</sup> exhibited pronounced adsorbent effects and significantly reduced ammonia volatilization (Fig. 6). This is in line with results consistently obtained by other authors. Indeed, Bernal et al. [5] showed that ammonia emissions were reduced when pig slurry was composted with chopped straw. This finding was in agreement with investigations of Bonazzi et al. [7], who suggested that ammonia emissions could be minimized by increasing the amount of straw per head of pig. This also agreed with the results of Dewes [12],

showing that ammonia emissions declined while increasing the amounts of litter (2.5, 5.0 and 15.0 kg straw per large animal unit (LAU) per day), both in abiotic and biotic conditions. Our results, obtained in an in vitro model, confirm these studies and show the efficacy of straws in reducing ammonia emissions (Fig. 6), due to a direct adsorption on these materials.

Other straws can contribute to reduce ammonia volatilization. Morisaki et al. [29] indicated that ammonia volatilization during sewage-sludge composting could be reduced by increasing the amount of rice husks. In this sense, Li et al. [22], who studied the effect of controlling odor emissions from manure surfaces by covering them with low cost materials, suggested that wheat straw and corn stalk covers may be an alternative cheap solution. Similar results have been reported by Sommer [39]. Indeed, the volatilization of ammonia from slurry has been reduced by covering it with straw. Although the odor emissions were not investigated in the present study, it is possible that wheat straw can be used as ammonia trapper and, thus, odor trapper.

The reduction of ammonia volatilization has been also reported by Nicks et al. [30], using deep litter for pigs. Indeed, it has been found that ammonia emissions were greater from sawdust litter than from a mixture of straw and sawdust following the aeration of the deep litter. In addition, NO emissions were only observed with the sawdust litter [30]. In this sense, the use of sawdust as bedding material may improve animal welfare but increase ammonia volatilization and airborne dust concentrations [1].

Concerning sawdust, these results were in agreement with our findings and demonstrated that spruce sawdust and more particularly the beech sawdust did not satisfactorily adsorb ammonia or nitrate, such as did the straws. Consequently, from our study, ammonia volatilization was not inhibited with the sawdusts (Fig. 6).

There is no report about the utilization of flax straw as an animal litter. Sahi and Leitch [35] only reported that linseed straw could be a potential alternative source of paper pulp or geotextiles, a biodegradable product offering temporary protection to slopes prior to vegetation establishment.

The results obtained in the preliminary experiment with Zeolite Stall Fresh<sup>®</sup> show that ammonium is really adsorbed by the material, since the ammonium in our system was entirely recovered through two elutions with 1 N HCl from the zeolite (Fig. 2).

Zeolites are a group of minerals with a very open structure and high cation-exchange capacity (CEC value) allowing specific exchange of sodium or calcium ions for ammonium ions [18]. Zeolite, as clinoptilolite, and as zeolite-like sepiolite minerals, has been used for the reduction of ammonia emissions during the composting of organic wastes [4, 5]. Furthermore and in accordance with our findings, clinoptilolite seems to have the highest ammonium removal capacity by the ion exchange phenomenon [21].

In the present work, a significant nitrate adsorption on wheat straw and Equi-lin<sup>®</sup>, was observed (Fig. 4). Indeed, our results were in accordance with those of Catt et al. [10] who showed that straw incorporation in soil with manure decreased nitrate leaching. Similarly, Saviozzi et al. [36] reported that the wheat straw-treated soil showed a constant decrease in nitrate and a slight lowering of pH in comparison with the control.

The lowering of pH values during ammonium and nitrate adsorption was also demonstrated, especially with straws (Fig. 5). Indeed, a marked decline of pH has been observed after the application of wheat straw in rice-wheat cropping [37]. It was presumed that the presence of silicic acid was responsible of this pH decrease [37]. Moreover, it has been long known that the pH of aqueous systems has a marked effect on the volatilization of ammonia, due to its effect on the ratio of ammonia to ammonium. Our

results were also in good agreement with these findings (Fig. 6), since ammonia volatilization was higher when the pH increased.

In the present work, when compared to Zeolite Stall Fresh<sup>®</sup>, spruce sawdust, beech sawdust and acidifying products, the major advantage of wheat straw and Equi-lin<sup>®</sup> was that they adsorbed ammonium and nitrate, but also significantly diminished the pH to low levels (Fig. 5). Indeed, Reece et al. [33] reported that the maintenance of litter at pH below 7 is an important aspect of ammonia control, because ammonia release increases above 7. In this sense, additions of acidifying chemicals have been used to control ammonia emissions. Indeed, Moore et al. [28] indicated that the addition of phosphoric acid ( $H_3PO_4$ ) to poultry litter, greatly reduces ammonia volatilization. Similarly, Martinez et al. [25] showed that the emissions from slurries treated with Biosuper [powder:  $H_2SO_4 + H_3PO_4 + Ca(H_2PO_4)_2$ ] were reduced by approximately 40 to 50% in comparison to emissions from untreated slurries.

According to Buckman and Brady [8], clay and humus act as centres of activity around which chemical reactions and nutrient exchange occur. The experiments described in the present work indicated that some litter materials led to the same exchange. Therefore, they may temporarily protect ammonia and nitrate from volatilization and leaching, and then release them slowly for growing plants. Consequently, by decreasing ammonia and nitrate losses, the use of wheat straw and Equi-lin<sup>®</sup> as animal litter material should result in higher total nitrogen concentrations in the litter material, thus increasing manure value as fertilizer.

In conclusion, the main objective of the present report was to investigate how to limit ammonium or nitrate which could be leached into slurry from animal housing with litter. In fact, animal slurries are responsible for large losses of nitrogen after spreading. Our

preliminary postulate consisted of adding 10.59 mg·l<sup>-1</sup> of ammonium or 50 mg·l<sup>-1</sup> of nitrate to a certain amount of litter. After that, further studies were devoted to quantify the amount of litter for ammonium or nitrate adsorption which effectively takes place in breeding reality. From our results, it was concluded that wheat straw and Equi-lin<sup>®</sup> would be preferred over spruce and beech sawdusts due to the fact that the straws adsorb larger amounts of ammonium and nitrate and also lower the pH. However, it has been demonstrated that Zeolite Stall Fresh<sup>®</sup> was also a good adsorbent when used in high amounts, but unfortunately it did not contribute to lowering the pH. Further experiments are also required to establish ammonium and nitrate balances in the presence of the straws. Moreover, the specific surface for adsorption on our experimental model needs to be investigated.

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