AMMONIUM ADSORPTION BY SURFACE SEDIMENTS IN THE LOUGHOR ESTUARY, UK

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ABSTRACT

Ammonium is a form of nitrogen that can be present in natural water systems due to various sources, including agricultural runoff, wastewater discharge, and decomposition of organic matter. High concentrations of ammonium in seawater can have several significant consequences for marine ecosystems such as harmful algal blooms, oxygen depletion, acidification, and changes in nutrient ratios. Therefore, monitoring and regulating nutrient inputs are essential for protecting marine ecosystems and maintaining the health and productivity of coastal and open ocean environments. In this study, adsorption isotherm experiments were used to study ammonium adsorption by surface bed sediments in the Loughor Estuary, South Wales, UK. The findings indicated that the adsorption isotherm was linear and fitted the Freundlich adsorption isotherm. The adsorption coefficient of ammonium in the study area ranged from 9.3 to 18 ml/g and the dimensionless ammonium adsorption coefficient was found to be ranged between 23.0 and 36.5. These values correlated well with the organic carbon content, of the sediments and can be considered as the main factors controlling ammonium sorption. The results also showed that salinity affected the adsorption of ammonium and the distribution of ammonium between the sediments and the water column. The amount of ammonium adsorption on the sediments was found to decrease gradually with the increment of the salinity levels.

Keywords: Adsorption Coefficients, Ammonium, Estuaries, Salinity, Surface Sediments

1.0 INTRODUCTION

Over the centuries the sub-aerial processes of erosion and deposition have led to the formation of river valleys and estuaries [1]. An estuary conveys marine conditions into a river valley potentially up to the tidal limit to form a semi-enclosed coastal body of water connected to the open sea at one end and to an influx of fresh river water at the other [1], [2]. When the sea level rise exceeds the peak filling level, then the estuary is regarded as well-developed and persists. Marine environments and estuaries have acted as filters for a range of constituents, with large quantities of materials such as fertilisers and organic materials from the land being deposited in the receiving estuarine/marine basin [3]. This organic matter is decomposed by various heterotrophic organisms and produces large amounts of ammonium ions [4], [5].

Ammonium ions can accumulate in pore water and can be re-incorporated into organisms, adsorbed onto sediment particles, or diffused out of the sediments and into the overlying water column [6], [7]. The ammonium ions can be adsorbed onto the sediments due to adsorption at the cation exchange sites [8], [9]. These sites are present on the surface of clay minerals and organic matter [10], [11]. Organic matter controls the behaviour of ammonium sorption on sediments with low clay content [12], [13]. The amount of ammonium adsorption depends on the ion exchange capacity of the sediment which is usually related to organic matter and clay content of the sediments [14]. Therefore, the adsorption of ammonium by the sediments has an important influence on nitrogen cycling [15], which affects not only the diffusive flux of ammonium into the overlying water column but also the coupled nitrification/ denitrification occurring in the sediments.

Fluctuating salinity in estuarine sediments plays a major role in controlling the ammonium ion adsorption of the sediments [16]. It was reported by Seitzinger *et al*. (1991) [17] that the amount of adsorbed ammonium was lower in estuarine sediments as compared to freshwater sediments. Salinity can influence the ammonium ion adsorption rate when freshwater mixes with seawater in estuaries. Sea water cations (e.g. Mg^{++}, Na^{+}, K^{+}) compete with the NH_4^{+} ions on the surface of clay particles and the adsorption rate decreases with increasing salinity [17], [18], [19]. Increasing the ammonium ion desorption rate, as well as increasing the salinity in an estuarine system, can potentially affect the nitrification rate due to the decreasing residence time of ammonium on the surface of the clay [20], [21].

The Loughor Estuary, located in the Bristol Channel in the UK, has a land-sea transitional area which is a typical environmentally vulnerable zone. The changes in the environmental factors, particularly salinity, are very intense and can influence the ammonium adsorption rate as a result of the interaction between the fresh and seawater. The authors have measured the ammonium and nitrate concentrations in the Loughor Estuary waters and found that concentrations were between 0.08 to 4.12 mg/l for ammonia and 2.65 to 8.31 mg/l for nitrate. The ammonium adsorption rate by the sediments from the Loughor Estuary has not previously been reported in the literature. The objectives of the present study have therefore been to determine the adsorption coefficients for ammonium at the Loughor Estuary sediments and to establish the effect of salinity on this ammonium adsorption coefficient.

2.0 MATERIALS AND METHODS

2.1 Study Area and Sample Collection

Samples were obtained from two sites in the Loughor Estuary as shown in Figure 1. The Loughor Estuary is located in Southwest Wales and is one of the main tributaries discharging into Carmarthen Bay and the Bristol Channel. The Bristol Channel is located on the west coast of the UK, is a funnel-shaped estuary, and has the second-highest tidal range in the world (up to 14.5m). As for most macro tidal estuaries, the tides in the Bristol Channel and Carmarthen Bay play a major role in mixing fresh and saltwater and in re-suspending sediments from the bed and transporting the suspended sediments landward or seaward. During spring tides, the suspended sediments in the Loughor Estuary are transported into the outer bay and deposited in the near shore region just beyond the river mouth. Human activity, including agricultural practices, sewage treatment works, and disused mine discharges all arising along the Loughor River basin, generally have a negative influence on the receiving basin water quality.

The Loughor Estuary is of particular interest in studying the transport pathways and the adsorption and desorption behaviour of nutrients associated with the sediments; eutrophication problems are not uncommon, and this has economic implications for the coastal waters in West Wales, particularly in connection with the fishing and tourism industries. A study by Abdulgawad *et al*. (2008) [22] indicated that high concentrations of all nutrients were found to occur in the Loughor Estuary and both the Loughor Estuary and the receiving coastal water body were affected regularly by algal blooms.

Bed sediment samples were taken close to the water's edge (at depths of 0-3 cm along the Loughor Estuary. These samples were taken as part of a project that was sponsored by the Environment Agency (EA) Wales and the samples were used for laboratory analysis. Three sediment samples were taken at each site and at hourly intervals. Samples $1b_1$, $1b_2$, $1b_3$, and 2_1, 2_2, 2_3 were collected at times of 1 pm, 2 pm, and 3 pm, respectively. The tidal predictions for 14th December show that the tide was above neap tide with tides ranging between 7.9 m at 8:48 am and 2.1 at 3:12 pm. Plastic bags were used for collecting the surface sediments, with the samples being stored in a refrigerator at 4 ºC for the next day (or night) for a series of adsorption experiments.

2.2 Determination of Sediment Physio-Chemical Parameters

The sediment-water content was measured by determining the weight loss of a known amount of wet sediment, dried at 105 ºC for 48 hr. The sediment particle density was measured as a mass of a known volume of the solid sediment. The sediment porosity was determined by use of the following formula [23]:

$$\phi = W / \{(100 - W)/\rho_s + W\} \quad (1)$$

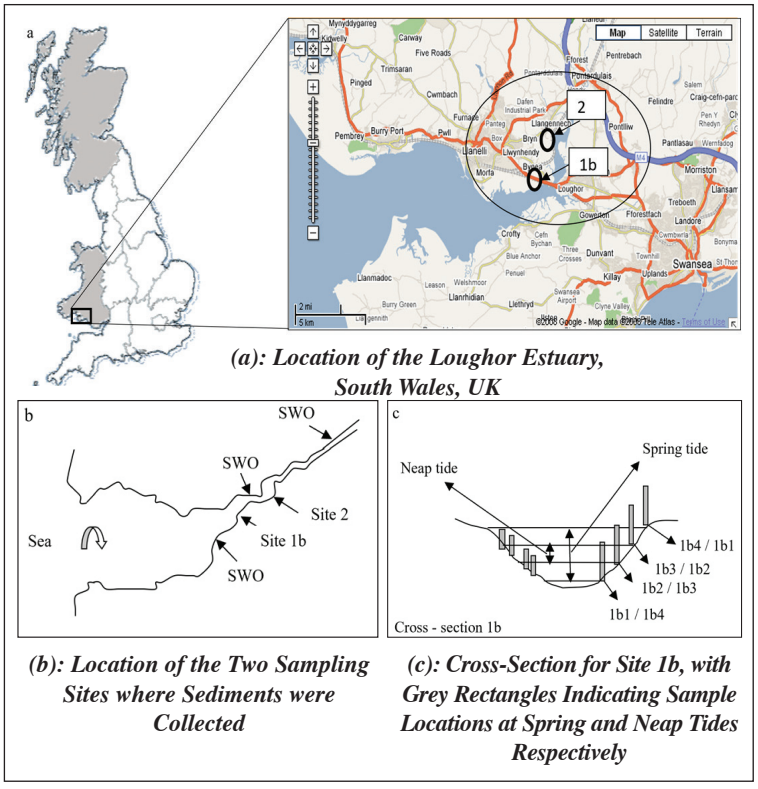
Where;

ϕ = sediment porosity; W (%) = sediment water content and ρ_s (g /cm^3) = sediment particle density.

The organic carbon (OC) content was determined after acidification with phosphoric acid and was obtained using a SHIMADZU analyser. The particle size distribution of the sediments was determined by using a laser particle size instrument, namely a Malvern Master sizer. Dry samples were measured and dispersed in distilled water and ultrasound was used to prevent flocculation. The corresponding results are given in table (1).

2.3 Fixed Ammonium on the Sediment

Measurement of the level of fixed ammonium on the sediments was obtained by KCl extraction. In this procedure, the slurry was made by adding 50 ml 2 M KCl solution to the centrifuge tubes containing a portion of the wet sediments. The slurries were shaken for 2 hr, centrifuged at 3,000 rpm for 20 min, and the supernatant was removed for analysis. The ammonium concentration in the supernatant was determined using a spectrophotometer, together with a HACH reagent. The spectrophotometer and the HACH



(a): Location of the Loughor Estuary, South Wales, UK

(b): Location of the Two Sampling Sites where Sediments were Collected

(c): Cross-Section for Site 1b, with Grey Rectangles Indicating Sample Locations at Spring and Neap Tides Respectively

Figure 1: Sewage Treatment Station Outfall (SWO)

meter (i.e., a colour meter) employed a similar concept of measurement which depends on the light wavelength absorbed by the sample. The wavelength of ammonium is 640 nm. The reagents used in both methods were identified as being roughly similar, which is used in the Phenate method [24]. All the measurements were made on wet sediments within 24 hours of collection.

2.4 Ammonium Adsorption Isotherm

Ammonium adsorption studies were undertaken using sediments again taken from the surface and between depths of 0 to 3 cm. Wet homogenised sediments were taken at each site, weighed, and placed in a centrifuge tube containing 40ml of NH_4^+Cl, at varying concentrations of NH_4^+. These sediment samples gave concentrations of 2, 6, and 10 mg/l NH_4^+. The centrifuge tube was placed on a shaker with continuous agitation for 24 hours, at a temperature of 20 °C +/- 2 °C. The samples were then centrifuged at 3000 rpm for 15 min. The supernatant was collected, filtered through a 0.45 µm cellulose filter paper, and then analysed for NH_4^+. The determination of ammonium concentration in the supernatant was undertaken using a Spectrophotometer Lambda EZ150, set at 640 nm [[24]. The ammonium concentration in the supernatant was considered to be the equilibrium concentration for the water. The adsorption isotherm experiments were followed by an adsorption procedure, in order to remove ammonium ions from the solids. 40ml of 2 M KCl solution was added to the sediments remaining in the centrifuge tubes and these sediments were then used to replace those on the shaker. After 2 hours of agitation, the solutions were centrifuged at 3000 rpm for 15 min. The supernatant was removed and analysed using the spectrophotometer. This procedure was repeated until all of the NH_4^+ was removed from the sediments.

2.5 Salinity Effect on Ammonium Adsorption

To study the effects of the salinity on ammonium adsorption, four different concentrations of artificial seawater were prepared including 1, 2, 3, and 4 parts per thousand (ppt). Artificial seawater was prepared according to the Scottish Association for Marine Science procedure [25](MASM, 2007), with the pH value of the artificial seawater being set to 8. The same methodology was used as that outlined for the above-mentioned isotherm adsorption experiments.

3.0 RESULTS

3.1 Sediment Characteristics

The sediments in the Loughor Estuary at the two sampling sites constituted fine sand with mean particle sizes (D_{50}) of 83 to 130 µm and 130 to 170 µm respectively (see Figure 2), samples were collected when the tidal range was greater than neap tide on 14th December. Sample 1b1 had the largest mean particle size of 130µm at site 1b. The mean particle diameter for site 1b samples (i.e., 1b1, 1b2, 1b3) decreased, declining gradually in cross-sectional area and with diameters of the order of 130, 100, and 83 µm, respectively. In addition, the mean grain diameter decreased during the outgoing tide. Sample 2_2 had the largest particle size among the samples for both sites (170 µm) and was collected in the middle of the cross-sectional area. At 2_3, i.e., the position furthest going down along the cross-section, sediment samples had the lowest mean particle size at 130 µm among the samples of site 2. Site 1b was located closer to the sea along the Loughor estuary, and was typically the area most affected by the interaction of seawater and freshwater along the estuary and further from the sea, as shown in Figure 1. The channel width at site 2 was larger than at site 1b, thus typically the water velocity at site 1b was generally higher than that at site 2. Samples collected from site 2 had a measured particle size higher than site 1b due to the water velocity being higher at site 2. The sediment porosity is ranged between 0.43 and 0.58. Sample 1b1 had the highest porosity value of 58% attributed to the amount of organic carbon contained in the sample. Sediments from site 1b were high in carbon content, constituting typically 1.53% – 3.74 % when compared to the sediment samples taken from site 2, which ranged from 1.29% to 4.81%. Sample 21 had the highest amount of organic carbon (4.81%), among the samples for both sites 1b and 2. This sample was collected at high tide. In contrast, sample 2_3 had the lowest amount of organic carbon at 1.29% which was collected at low tide compared to other samples from sites 1b and 2. The particle and the bulk density typically ranged from 1.0 to 1.6 mg/m^3 and 2.60 to 2.70 mg/m^3 respectively. The particle and bulk density are influenced by the mineralogy of the sediments and the organic matter content. The density of organic matter is much lower than the mineral solids density. Sediments high in organic matter and also some clay minerals have low bulk density. The particle density for sediments from both sites 1b and 2 ranged between, 2.63 to 2.69 mg/m^3, see Table 1. The Particle density for a quartz-dominated sediment is normally expected to

Table 1: Sediment Characteristics for Sites 1b and 2 of the Loughor Estuary

Sample	Sample Number	Porosity	Median Grain Size (µm)	Organic Carbon (%)	Particle Density (g cm^{-3})
$1b_1$	1	0.58	130	3.74	2.65
$1b_2$	2	0.51	100	2.82	2.67
$1b_3$	3	0.52	83	1.53	2.69
2_1	1	0.43	160	4.81	2.65
2_2	2	0.51	170	1.39	2.68
2_3	3	0.54	130	1.29	2.63

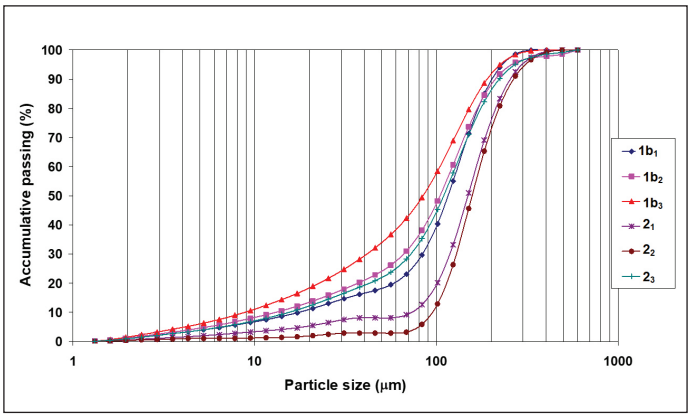


Figure 2: Particle Size Distribution of the Loughor Estuary Sediment Samples at Sites 1b and 2 (The subscript numbers refer to the Sampling Time)

be close to 2.65 mg/m^3 the slight variation of the particle density between the samples was believed to be due to the organic carbon and clay minerals content for both sites ranging from 2.63 to 2.69 g cm^{-3}. The sediment characteristics are summarised in Table (1). The results of X-ray diffraction (XRD) for the sediment samples collected at sites 1b and 2 indicated that the sediments from both sites mostly comprise quartz (66.1 to 88.3%), followed by calcite (9.9 to 17.5%), with minor amount of halloysite (0.1 to 8.4%), and Kaolinite (0.7 to 7.9%).

3.2 Adsorption Isotherm of Ammonium on Sediments

During out-going tides over a period of 3 hours at sites 1b and 2 samples were collected at regular intervals (i.e., samples $1b_1$, $1b_2$, $1b_3$, and 2_1, 2_2, 2_3), as shown in Figure (1). Figure (3) shows comparisons between the experimental or field data and the theoretical results, using Langmuir and Freundlich adsorption isotherm equations. In general, the results show good agreement between the experimental or field data and theoretical results. The Langmuir model fits the data particularly well for all the samples tested, according to the error analysis that was performed for all samples. The Langmuir adsorption equations have the following forms:

$$qe = x/m = \overline{Q}bC_e/(1+bC_e) \quad (2)$$

$$C/q_e = 1/\overline{Q}b + C/\overline{Q} \quad (3)$$

where, $\overline{Q}$ is Langmuir constants related to adsorption capacity, b is a constant related to; the energy of adsorption and the Langmuir adsorption coefficient (K_L), q_e is the ion adsorption amount (µg/g dry wt), C_e is the equilibrium concentration of the solute remaining in solute [26].

Freundlich equation has the following form [26], [27]:

$$q_e = x/m = K^* C^{1/n} \quad (4)$$

Where qe is the ion adsorption amount (µg/g dry wt), x is the amount of the adsorbate, m is the mass of the adsorbent, C is the ion equilibrium concentration in water (mg/l), K* and n are constants and n is almost equivalent to 1, i.e., the ion adsorption is linear [28]. In these experiments n 1. The equation is more useful in its logarithmic form, as expressed by Martin *et al*., 1979.

Table 2 shows the error analysis for the Langmuir and Freundlich adsorption isotherms. The Chi-squared test (X^2) and nonlinear regression (R^2) were used to evaluate the fit of the theoretical data with the experimental data. The error analysis was applied to all of the samples using deionised water. The Chi-squared test for the Langmuir isotherm has lower values compared to the Freundlich isotherm for all sampling sites, showing that the Langmuir isotherm better fits the sample data. Sample $1b_1$ had the highest value of X^2 for all of the samples, with a value of 31.10. In contrast, sample $1b_2$ had the lowest X^2 of 8.93, in comparison with the other samples at both sites. The R^2 test also resulted in higher values for Langmuir isotherm data for all samples at both sites (1b and 2) in comparison with the Freundlich isotherm data. These results also illustrate that the Langumuir isotherm better fits the data of the ammonium adsorption for the Loughor Estuary samples.

Table 2: Error Analysis for Langmuir and Freundlich Adsorption Isotherms using Chi-squared Test (X^2) and Nonlinear Regression (R^2)

Samples	Langmuir Isotherm		Freundlich Isotherm	
	X^2	R^2	X^2	R^2
$1b_1$	9.30	0.94	31.10	0.75
$1b_2$	2.87	0.97	8.93	0.88
$1b_3$	4.99	0.94	13.17	0.81
2_1	7.86	0.95	15.65	0.80
2_2	6.30	0.95	14.15	0.86
2_3	7.80	0.94	15.65	0.84

The adsorption coefficient for ammonium is an important factor in calculating the concentration of nitrogen in the sediments. The formula of the ammonium adsorption coefficient of the sediment for the Loughor Estuary has the following form:

$$Q = K^*C + q \quad (5)$$

Where, Q (µg/g dry wt) is the amount of ammonium adsorbed on the sediment of the Loughor Estuary, K* is the slope of the regression line (adsorption coefficient), C (mg/l) is the ammonium ion equilibrium concentration in water, q is the fixed ammonium content in the sediments being zero.

The ammonium adsorption coefficient of the sediments for the Loughor Estuary was calculated according to the following formula.

$$K = [(1-\Phi)/\Phi]\,\rho K^* \quad (6)$$

Where K is the dimensionless ammonium adsorption coefficient; Φ is the porosity of the sediments; ρ is the density of the sediment (g cm^{-3}); and K* is the slope of the regression line or the Adsorption coefficient (ml g^{-1}).

Table 3: Ammonium Adsorption Coefficients of the Loughor Estuary, its Relative Parameters, and Total Organic Carbon Content (TOC)

Parameters	Sampling Sites					
	$1b^1$	$1b^2$	$1b^3$	2^1	2^2	2^3
K	34.5	26.2	23.0	36.5	25.7	23.0
Φ	0.58	0.51	0.52	0.43	0.51	0.54
K*(ml/ g)	18	10.20	9.3	10.4	10	10.3
ρ_s (g /cm^3)	2.65	2.67	2.69	2.65	2.68	2.63
TOC (%)	3.74	2.82	1.53	4.81	1.39	1.29

Table 3 summarises the relative parameters of the ammonium adsorption coefficient, such as the porosity, particle density total organic carbon, and the adsorption coefficient of ammonium. These parameters are important to calculate the dimensionless adsorption coefficient of ammonium (K) for the sediments of the Loughor Estuary. The table shows that the values of the dimensionless adsorption coefficient for ammonium ranged from 23.0 to 36.5. The highest dimensionless adsorption coefficient was found in the sediment containing the highest amount of total organic carbon, which was in sample 2_1 and with

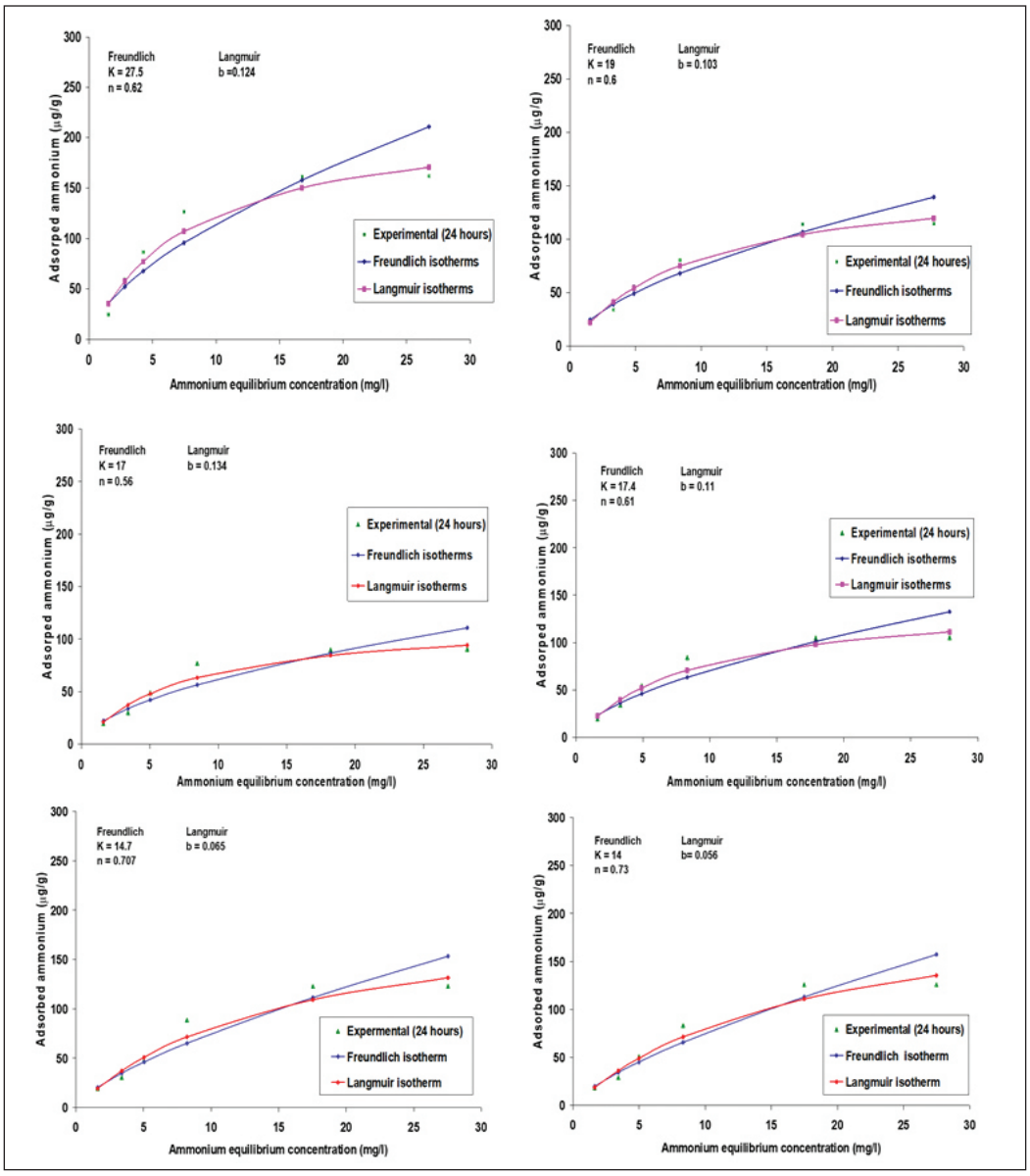


Figure 3: Experimental Results and Theoretical (Langmuir and Freundlich) Adsorption Isotherms of Ammonium for Samples in Distilled Water. b is the Langmuir Constant and Adsorption Coefficient, K is the Freundlich Adsorption Coefficient, and n is the Freundlich Constant

values of 36.5 and 4.81(%) respectively. In contrast, the lowest dimensionless adsorption coefficient was found in the sediment samples $1b_3$ and 2_3 which contained the smallest amounts of total organic carbon. The corresponding adsorption coefficient and TOC values were 23, 23, and 1.53 (%). 1.29 (%) respectively. These results indicate that total organic carbon is an important factor affecting the adsorption of ammonium onto the sediments in the Loughor Estuary. However, the results did not show any influence for other parameters namely Φ and ρ_s.

K is dimensionless adsorption; Φ is the sediment porosity; coefficient K*(ml g^{-1}) is the slope of the regression line (Adsorption coefficient); ρ_s (g cm^{-3}) is sediment density; TOC (%) is organic carbon.

3.3 Salinity Effects on Ammonium Adsorption

Site 1b was located in the mouth of the Loughor Estuary and in the region most affected by the interaction of seawater with riverine freshwater. Site 2 is located more towards the middle of the estuary. The salinity in the water column between low and high tides ranged from 0.02 to 26.90 ppt at site 1b and from 0.32 ppt to 17.21 ppt at site 2 (low to high tides) respectively. Sites 1b and 2 were therefore regarded as being ideal example sites for studying the salinity effects on the adsorption of ammonium by sediments for the Loughor Estuary. The results are shown in Figure 4, which indicates the salinity effect on the adsorption coefficient (K*) and the dimensionless adsorption coefficient for samples from sites 1b and 2. The results shown in the figure indicate that the adsorption coefficients (K* and K) for ammonium at both sites 1b and 2 were highest for zero salinity conditions and continuously dropped with increasing salinity up to 25 ppt. This result was as expected, caused by the sediment cation exchange sites being increasingly occupied by seawater cations and decreasingly by ammonium ions as salinity rose. The adsorption coefficients for ammonium were found to be higher for samples from site $1b_1$ compared to samples from site 2_1 for all salinity conditions. This was thought to be done in sample $1b_1$ containing a higher amount of organic matter than sample 2_1, which resulted in more exchange sites for ammonium being present. Thus, there was found to be a correlation between the level of organic matter in the bed sediments and the amount of ammonium adsorbed onto the sediments.

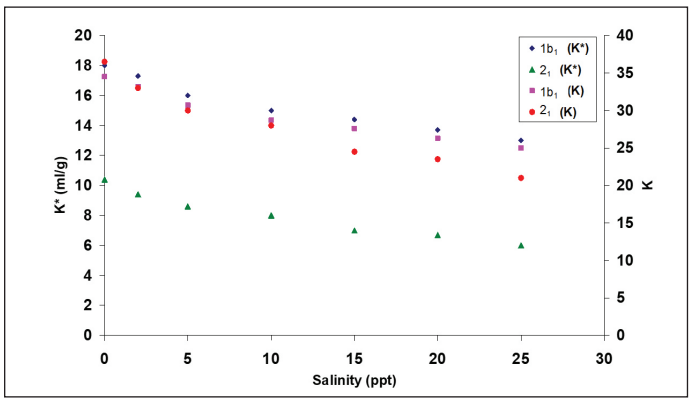


Figure 4: Ammonium Adsorption for Samples from Sites $1b_1$ and 2 under Varying Salinity Concentrations

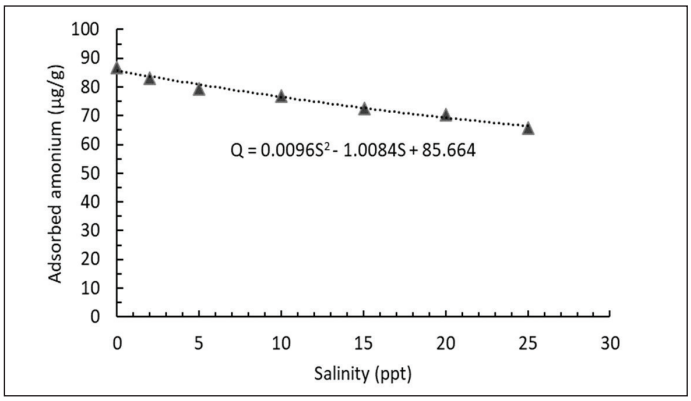


Figure 5: Salinity-Dependent Ammonium Adsorption in the Sediments for Sample $1b_1$, Q (µg/ g dry wt); S (ppt)

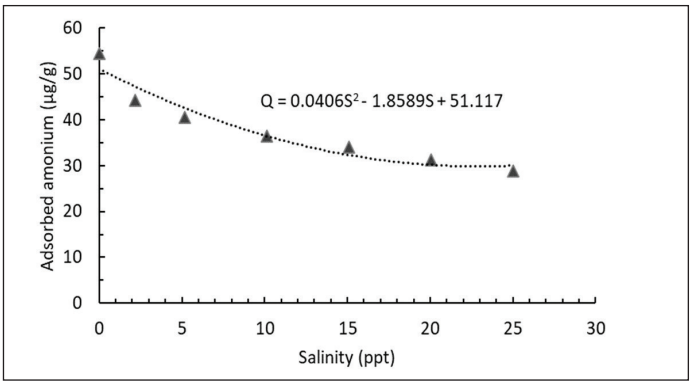


Figure 6: Salinity-Dependent Ammonium Adsorption in the Sediments for Sample 2_1, Q (µg/ G Dry Wt); S (Ppt)

Figures 5 and 6 show the difference in the ammonium adsorption under different salinity conditions and based on the same initial ammonium concentration (of 6 mg/l) in the water column for samples from sites 1b and 2. Equation 9 relates to site 1b for sample $1b_1$ and Equation 10 refers to site 2 for sample 2_1. The ammonium adsorption value in the sediments for samples $1b_1$ and 2_1 gradually decreased with increasing salinity levels, varying from 86.5 mg/g at 0 ppt to 64 mg/g at 25 ppt and 45.5 mg/g at 0 ppt to 28.5 mg/g at 25 ppt respectively, and was found to be best represented by the following equations:

Equation for sample $1b_1$:

$$Q = 0.0098\ S^2 - 1.0756\ S + 85.477 \quad (7)$$

The equation for sample 2_1:

$$Q = 0.0393\ S^2 - 1.8321\ S + 50.916 \quad (8)$$

Where, Q is the ion adsorption quantity (µg/ g dry wt); and S is salinity in the water column (ppt).

3.4 Organic Carbon and Grain Size Effect on Ammonium Adsorption

Sediments at Site 1b were found to be higher in carbon content when compared to the sediment samples taken from Site 2. It was found that the organic carbon content had a significant effect on the ammonium adsorption and this result agreed well with previous studies, such as those of de Lange, (1992); and Raaphorst and Malschaert, (1996) [29], [30]. The samples from Site 1b were found to have higher ammonium adsorption values than those at Site 2. It was also found that the samples taken from Site 1b, with a higher content of organic carbon, had a higher ammonium adsorption than those taken from the same site but with a lower organic carbon content. This finding was attributed to the fact that Site 1b was rich in organic carbon in comparison with Site 2. Studies published by other authors have indicated that sediments with a high ammonium adsorption rate also have a relatively large amount of organic matter, with this result being compatible with the studies of [12], [18]. The corresponding results are shown in Figure 7.

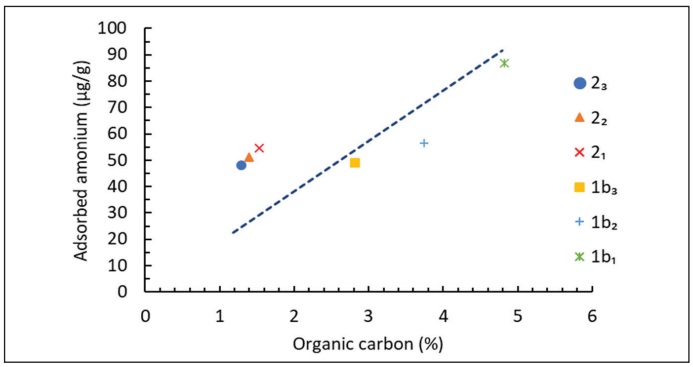


Figure 7: Correlation of Ammonium Adsorption with Organic Carbon Content for the Loughor Estuary Sediment Samples at Sites 1b and 2

4.0 DISCUSSION

The ammonium ion adsorption level in the sediments was found to obey the Langmuir isotherm equation, in particular, the study showed that the rate of adsorption by the sediments was found to be linear and fitted the Langmuir adsorption equation within the controlled range of ammonium concentrations in the water column. Figure 3 indicated that the experimental data fitted well with the theoretical data of adsorption (Langmuir isotherm) than (Freundlich isotherm) and there was found to be good agreement between the values for ammonium adsorption using both methods. The error analysis (Chi-squared and nonlinear regression) confirmed that ammonium adsorption data fits the Langmuir isotherm well. There was found to be good agreement between the values for ammonium adsorption using both error analysis methods.

The ammonium adsorption coefficient, defined as the ratio of the concentration of adsorbed ammonium and the equilibrium ammonium, was found to be important in highlighting the characteristics of ammonium adsorption on the sediments. K is the dimensionless equivalent of K*, with K being larger than K*, which is due to the sediment physio-chemical parameters. The sediment physio-chemical parameters are known to have a significant influence on the behaviour of ammonium adsorption [31]. The particle size of the sediments was also found to have a significant influence on the amount of ammonium adsorption. Samples with a small mean particle size have a larger overall surface area per unit diameter and therefore will have a high ammonium adsorption coefficient. The present study shows that samples with a 65 µm grain size, had the highest ammonium adsorption coefficient when compared to the other samples with a larger mean grain size; this result agrees with the findings of Raaphorst and Malschaert (1996) [29].

The present study showed that the ammonium adsorption coefficient did not appear to have any significant correlation with the sediment porosity. However, the adsorption coefficient was found to be highest in the sediments with comparatively higher

amounts of organic carbon. Availability of organic matter was therefore considered to be one of the important factors controlling the degree of ammonium adsorption in the Loughor Estuary (see Figure 7); as can be seen, the adsorption coefficients were higher at Site1b when compared to the corresponding values measured at Site 2. This finding was attributed to the fact that Site 1b was rich in organic carbon in comparison with it 2. Studies published by other authors have indicated that sediments with a high ammonium adsorption rate also have a relatively large amount of organic matter, with this result being comparable with the studies of Hou *et al* (2003); Boatman and Murray (1982); and Mackin and Aller (1984) [12], [18], [28].

The difference in the adsorption isotherm of ammonium for the Loughor Estuary sediments, particularly at Sites 1b and 2, for different salinity concentrations showed that salinity affected the distribution of ammonium between the sediments and the water column. The ammonium adsorption coefficient was found to decrease with increasing salinity concentrations; meaning that lower salinity levels were found to be more favourable to ammonium adsorption by the sediments. The ammonium adsorption levels detected in the Loughor Estuary sediments, as taken from Site 1b and 2 when linked to the salinity levels were fitted to Equations 9 and 10, with the first derivative of this equation being given as:

$$dQ/dS = 0.0196\ S - 1.0756 \quad (9)$$

$$dQ/dS = 0.0786\ S - 1.8321 \quad (10)$$

Where, dQ/dS is the rate of change of the quantity of ammonium (µg g^{-1} ppt); and S - the salinity -ranged from 0 to 25 ppt. From the above first-order derivative equations, it is possible to calculate the rate of change of ammonium adsorption in the sediments with respect to increasing salinity. The rate of change is higher within the lower range of salinity, thereby reflecting the fact that a small variation in the salinity at the start of the incoming tide has a relatively large effect on the rate of ammonium adsorption. One of the obvious challenges in analysing such processes in estuarine and coastal waters is the huge variation in the salinity levels during the mixing region between the freshwater and seawater flows.

Past studies by other authors of ammonium adsorption for Montmorillonite, Kaolinite, and fine and coarse sand, for different salinity concentrations, have indicated that the adsorption coefficient of ammonium was higher for distilled water and lower for artificial seawater conditions for Montmorilonite, Kaolinite and fine and coarse sand, respectively. For the current samples, Montmorilonite was found to have the highest adsorption coefficient, both for distilled water and artificial seawater [22]. This result led to further studies being undertaken to compare further the results between the field data and the modelled results, with both clay and sand being used. Figure 8 shows the adsorption coefficient for the field data, taken at both Sites 1b and 2 for clean clays (i.e., Montmorillonite and Kaolinite) and sand both (fine and coarse) under different salinity conditions. For all samples, it can be seen that the adsorption coefficients decreased gradually with increasing salinity concentrations. Also, the results indicated that Montmorillonite had much higher adsorption coefficients for all salinities than the field samples ($1b_1$ and 2_1), the clays, and the sand samples. The adsorption coefficients for Montmorillonite, at 0 and 25 ppt salinity ranged from 126 ml/g to 34 ml/g respectively. Kaolinite had the second highest adsorption coefficient ranging from 19.3 ml/g at 0 ppt salinity, to 8.5 ml/g at 25 ppt. Sample $1b_1$ at 25 ppt had a higher adsorption coefficient than Kaolinite with a value of 13 ml/g compared to 8.5 ml/g. Furthermore, the adsorption coefficients for sample $1b_1$ were higher than for fine sand, coarse sand, and sample 2_1 for all saline concentrations.

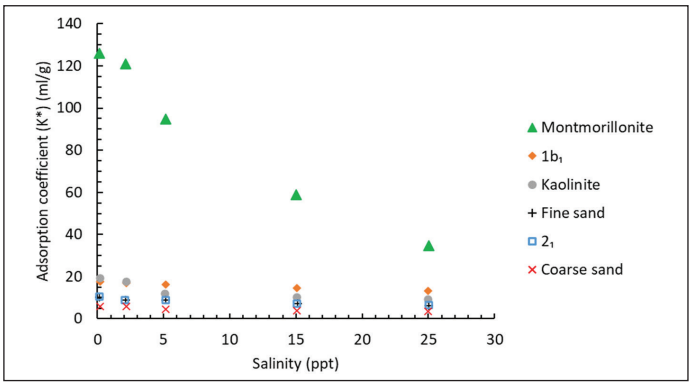


Figure 8: Comparison of Adsorption Coefficient of Field Samples $1b_1$ & 2_1 and Clean Clays (Montmorillonite and Kaolinite) and Sand (Fine and Coarse)

The fixed ammonium levels in the sediments for the Loughor Estuary were zero, as indicated earlier. This was attributed to the constant exchange of ammonium being adsorbed by the sediments, with large quantities of seawater cations such as Na^+, K^+, and Ca^{2+} from the area controlled by seawater (Sites 1b and 2). The salinity was found to have a significant influence on the fixed ammonium levels in the sediments. In addition, the ammonium levels were also thought to have been influenced by the nitrification process, which was relatively high in the estuary. This high of ammonium could be due to the agricultural activities along this section of the river (next to the farms) or due to a SWO outfall future upstream or have come with the river. This nitrification process is due to the level of inorganic carbon and dissolved oxygen, both of which are readily available as a result of the ammonium produced in the sediments and was rapidly converted to nitrate.

5.0 CONCLUSIONS

Ammonium adsorption isotherms for the sediments have been analysed for the Loughor Estuary, in the U.K. These analyses showed that the adsorption of ammonium by the sediments was almost linear and fitted to the Langmuir adsorption isotherm equation. The ammonium adsorption coefficient K* for the Loughor Estuary sediments ranged from 9.3 to 18 ml/g and the dimensionless ammonium adsorption coefficient, K, ranged from 23.0 to 36.5. These results showed a close affinity with the total organic carbon content and the types of sediments analysed indicated that the organic matter and mineralogy of the sediments were the main factors controlling the adsorption of ammonium. The main parameter found to affect the adsorption of ammonium by the sediments was salinity. Low salinity levels resulted in more ammonium adsorption on the sediments, in comparison with the levels of adsorption measured for higher levels. The fixed amount of ammonium measured on the Loughor sediments was zero, which was thought to be due to the competition of seawater cations to replace the ammonium on the surface of the sediment particles. Also, nitrification was

anticipated to be higher in the estuary sediments as a result of the ammonium produced within the sediments being rapidly converted to nitrate. However, the adsorption of ammonium by surface bed sediments in aquatic environments is complex and influenced by several factors. Understanding these factors is essential for managing water quality and the fate of ammonium in natural systems. Future studies should in-depth investigate the effects of sediment composition, pH of the water, ionic strength, and sediment depth on the ammonium adsorption rate by the surface sediments.

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