

Article

Characteristics of Nitrogen in Overlying Water and Sediment of Typical Agricultural Drainage Ditches during Different Periods in a Freezing-Thaw Area of China

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Abstract: In the Sanjiang Plain, agricultural drainage ditches effectively alleviate agricultural non-point source nitrogen pollution. However, limited information is known about the characteristics of bidirectional trans-ports of nitrogen between sediment and overlying and pore water in different patterns of ditches undergoing seasonal freezing-thawing cycles. It is vital to better understand nitrogen interception and purification by ecological ditches. In order to clarify the interception of ecological ditches on internal and external nitrogen, overlying water and sediment samples of two typical agricultural ditches were collected and analyzed in Sanjiang Plain during the growing seasons of 2015–2017. The results indicated that the N-NO_3^- in overlying water, which was higher than N-NH_4^+ , was the dominant inorganic nitrogen, whilst, in the sediment, N-NH_4^+ was much higher than N-NO_3^- , which should be attributed to the soil's adsorption of N-NH_4^+ . In contrast to the dryland ditch, the paddy ditch had a more significant amount of inorganic nitrogen both in overlying water and sediment, which means that the non-point source nitrogen pollution caused by paddy fields was more severe than that of drylands. Compared with dryland ditches, N-NH_4^+ in the sediment of paddy ditches seemed to be much easier to migrate to a deeper layer, which may cause a greater risk of nitrogen pollution to groundwater. Both in the overlying water and the sediment of ditches, nitrogen content fluctuated during different periods, and inter-annual variation was noticeable, which results means that estimation or prediction of the non-point source pollution output needs to extend the monitoring period and increase sampling frequency to reduce the great uncertainty. The findings may provide a foundation for forecasting agricultural nitrogen pollution and guide best management practices (BMPs) of non-point source nitrogen pollution control in seasonally frozen areas.

Keywords: freezing-thaw area; nitrogen; agricultural ditch; sediment; overlying water



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1. Introduction

The Sanjiang Plain is one of the main areas for the planning of ‘new 100 billion kilograms of grain’ of China. In the context of long-term high-intensity agricultural development, the application of a large amounts of pesticides and chemical fertilizers has promoted the movement of soil nitrogen into waters, resulting in continuous water environment deterioration [1–3]. As important facilities for hydroengineering, drainage ditches are buffer zones between agricultural pollution sources and waters, exhibiting characteristics of linear wetlands. They could diminish nutrients in receiving waters by multiple processes including soil adsorption, plant assimilation, and biodegradation. Drainage ditches have been widely used for interception and purification of nitrogen from agricultural non-point sources [4–6].

Improved nitrogen use efficiency, nitrogen removal by drainage ditches, and the best management practices are of high concern. In agricultural ditches, nitrogen forms and

distributions, hydrological conditions such as dry-wet alternation, meteorological conditions such as air temperature and freezing-thawing cycles, sediments, and vegetation cover play great roles in intercepting and purifying nitrogen [7–13]. When nitrogen concentration in pore water exceeded that in overlying water, dissolved nitrogen could be released into overlying water from sediments [14]. Dry-wet alternation remarkably affected the denitrification rate in ditch sediments, leading to alterations in nitrogen forms [4,15]. Freezing-thawing cycles promoted macroaggregate breakdown and disturbed the biological, physical, and chemical processes of soil, further exerting influences on nitrogen transport between sediment and overlying water and nutrient leakage [16]. Nitrogen processes in agricultural ditches consisted of mobilization between surface sediment and overlying water and between sediment layers with different depths, assimilation by plants, and degradation and release from plant litterfall. Sampling time and depth had great impacts on nitrogen concentration [17,18].

In recent years, the Sanjiang Plain has been experiencing policy-oriented land-use change from drylands to rice paddies for grain yield increase [19]. With these changes, nitrogen forms, vegetation, water flux, and sediment composition might greatly vary and conduct impacts on nitrogen interception and purification in ditches [20,21]. At mid-high latitudes with a frozen soil depth of 1.5 m in winter, seasonal freezing-thawing cycles regularly occur in the Sanjiang Plain, resulting in complicated spatial-temporal differentiation of nitrogen in ditches [22,23]. Mechanisms and factors of nitrogen interception and purification by ditches have been investigated in previous studies [24,25]; however, the pollutants were greatly emphasized other than the carbon:nitrogen ratio and carbon–nitrogen interactions. Compared studies on different seasons and disturbing intensities based on long-term datasets were seldom conducted in areas with freezing-thawing cycles.

Therefore, focusing on typical ditches in drylands and rice paddies in the Sanjiang Plain, through samples collected from overlying water and sediment in the growth period of crops in 2015–2017 and measurement of carbon and nitrogen concentrations, this study aimed (i) to characterize seasonal variations in concentrations of different nitrogen forms, and (ii) to compare nitrogen concentrations and distributions in ditches of drylands and rice paddies.

2. Materials and Methods

2.1. Study Site

This study was conducted in Bawujiu Farm (47°18′–47°50′ N, 133°50′–134°33′ E), a state-run farm in the eastern part of the Sanjiang Plain in Heilongjiang Province, northeast China. In the past several decades, numerous natural wetlands have been drained and converted to farmland and the project of drylands to rice paddies continues to be implemented. A cold temperate sub-humid climate characterizes the region, and the annual average temperature is 2.94 °C. The average precipitation is 583.18 mm, most falling in summer (from July to September). With an average frost-free period of 138 days, the frozen earth's mean annual maximum depth is 141 cm in the winter. Albic luvisols (luvisols with an albic E horizon) were widely distributed in this area. However, with the fertile but porous black soil on the surface and the impermeable clay horizon below, the soil is vulnerable to erosion and leaching, especially during the spring snowmelt and in the summer storm season [26]. In this area, fertilizers have generally been applied at very high rates, and the main types of nitrogen fertilizers are urea (accounts for 36.67% of the total nitrogen application), ammonium bicarbonate, and ammonium chloride (account for 63.33%).

The study area and sampling points are shown in Figure 1. Two typical ditches are selected randomly for investigation (Figure 2). The dryland ditch (47°25′5″ N, 134°06′32″ E) is located at the 19th operation station of Bawujiu Farm, with corn grown in the adjacent field from May to September. There were no anthropogenic drainage or irrigation processes in dryland, which depends on natural rainfall completely. The paddy field ditch (47°24′41″ N, 134°11′39″ E) is located at the 24th operation station of Bawujiu Farm, with rice grown in the adjacent field from the end of April to the beginning of October. There

were two large-scale anthropogenic drainage processes during this period, conducted in the middle of May and at the end of August, respectively. The fertilization period in the dryland field is the corn jointing stage (late May, late June, or early July). Fertilization period in the paddy field mainly includes the base fertilizer before sowing (late April or early May), foliar fertilizer when the leaf turns green (late May or early June), and top dressing at the jointing stage (late June or early July). Nearby the selected ditches, one ZENO Meteorological Station (Coastal, USA) was set in the field ($47^{\circ}24'20''$ N, $134^{\circ}07'12''$ E) in April 2010. General meteorological data were recorded at 30 min intervals. The daily mean temperature trends and rainfall distribution in the study area in 2015, 2016, and 2017 are presented in Figure 3.

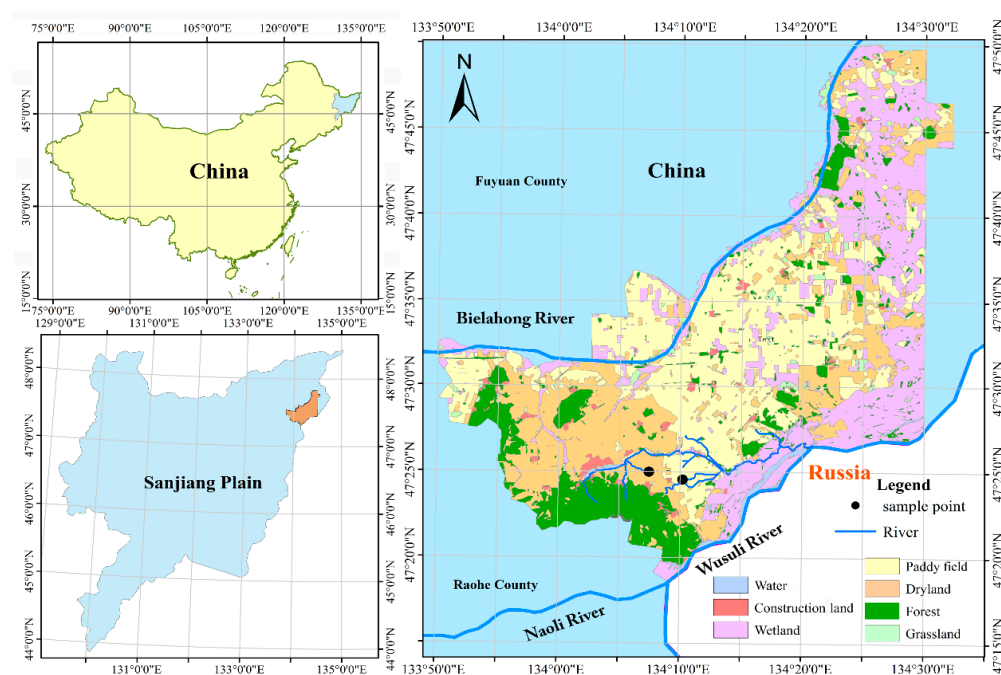


Figure 1. Study area and sampling points.



Figure 2. The two types of typical farmlands and adjacent ditches in the study area.

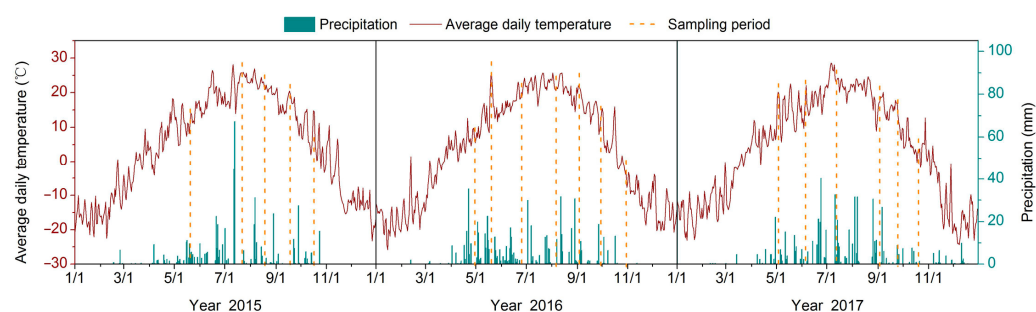


Figure 3. Daily average temperature, precipitation, and sampling date in the study area in 2015, 2016, and 2017.

2.2. Sampling and Laboratory Analysis

Considering that the freeze–thaw process may aggravate the nitrogen leakage loss and the absorption of nitrogen by plants varied during different growth stages [27,28], the sampling time was set to the crop growth period, from late April to late October. The sampling time was divided into five periods: the thawing period, early growth stage, vigorous growth period, harvest period, and early freezing period. Overlying water and sediment samples were collected from 2015 to 2017, approximately once a month, and the specific sampling date and corresponding period are shown in Table 1.

Table 1. Sampling date and corresponding periods.

Year	Period				
	Thawing	Early Growth	Vigorous Growth	Harvest	Early Freezing
2015		20/5	23/7 and 20/8	20/9	20/10
2016	30/4	18/5	25/6, 6/8 and 3/9	29/9	30/10
2017	3/5	5/6	13/7 and 3/9	25/9	20/10

At each site, sediment cores of 6.5 cm diameter were sampled at six individual points randomly scattered in the drainage ditches using a stainless-steel cylinder with 20 cm intervals of 0–60 cm depth (0–20, 20–40, and 40–60 cm). They were correspondingly intermixed to composite a representative sample for each interval, sealed in identifiable polyvinyl chloride bags. Simultaneously overlying water was collected in mid-depth, and triplicate samples were collected using polypropylene containers (AS ONE CORPORATION, Tokyo, Japan) in each site of ditches. Then all the samples were taken to the laboratory, and the water was stored at 4 °C after being purified with a 0.45 µm filter and measured as soon as possible. The moist sediment was sub-sampled for determination of moisture content by oven-drying at 105 °C for 24 h, another part of the sediment samples was sub-sampled and air-dried at 25 °C, freed of plant residues, grounded, and passed through 2 mm sieves for pH measurement, and the rest of sediment samples were freeze-dried at −20 °C and ground through 100-mesh (0.145 mm) sieves and then stored for later determination.

The sediment's pH was determined by pH 400 m (Thermo Fisher Scientific, Rockford, IL, USA) at a soil/deionized water ratio of 1:2.5 (*w/v*). The N-NO_3^- and N-NH_4^+ were extracted using CaCl_2 solution before being determined with the AA3 Continuous Flow Analytical System, and the SOC and TN contents (as % dry weight of the sediment) were measured with a C/H/N elemental analyzer (EuroVector S.P.A. EA3000, Milan, Italy). The pH was detected using pH 400 m at the sites for water samples. The N-NH_4^+ concentrations were determined using an ion chromatograph (CS-2100 and DX-600, Thermo Fisher Scientific, Waltham, MA, USA) and the TOC was measured using a Total Organic Carbon Analyzer (TOC-VCSH, Shimadzu, Japan). All of the above instrumental measurements were taken at the Analytical and Testing Center of BNU.

2.3. Statistical Analysis

All statistical analyses were performed using PASW Statistics (IBM SPSS Cor. Released 2013. IBM SPSS Statistics for Windows, Version 22.0. Armonk, NY, USA). After testing for normality (Shapiro–Wilk test) and homogeneity of variances (Levene test), analysis of variance (ANOVA) was operated with a multivariate general linear model (GLM) on contents of SOC, TN, C/N ratio, N-NO_3^- and N-NH_4^+ as dependent variables, while ditch-type layers and sampling periods were molded as independent variables. In analyses where $p < 0.05$, the factor tested and the comparisons were considered statistically significant. OriginLab Corporation (Northampton, MA, USA). Released 2010. Computer software for Windows, Version 8.5 was used to map figures.

3. Results

3.1. Nitrogen Concentrations in Overlying Water

During the crop growth period of 2015–2017, the pH of the overlying water in the ditches fluctuated, ranging between 6.30–8.64 and 7.29–10.12 for dryland ditch and paddy ditch, respectively (Figure 4a). The inter-annual variability was largely different. However, the pH variation trends of the overlying water in the two types of ditches were approximately synchronized.

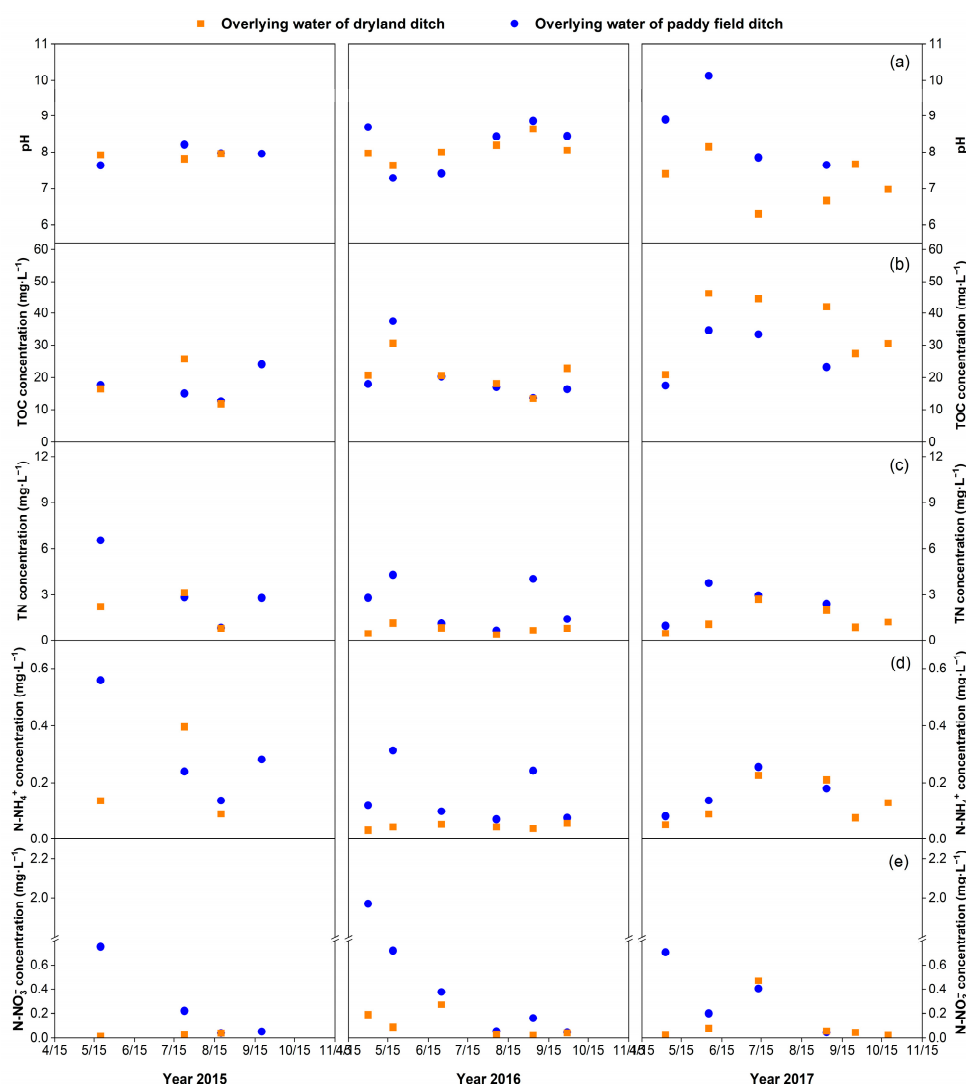


Figure 4. Variation of pH, TOC, TN, N-NH_4^+ and N-NO_3^- concentration in overlying water of two ditches, (a): pH, (b): TOC, (c): TN, (d) N-NH_4^+ , (e): N-NO_3^- .

The seasonal variation characteristics of TOC and nitrogen concentration in the overlying water of the ditches are shown in Figure 4b–e. Evidently, the TOC, TN, N-NH_4^+ and N-NO_3^- in the overlying water of dryland and paddy ditches fluctuated with the seasons, and the inter-annual differences were obvious. A similar seasonal variation trend of N-NH_4^+ and TN was observed, and the N-NO_3^- concentration was generally higher than N-NH_4^+ . In the overlying water of dryland and paddy ditch, the NH_4^+ concentration ranged within 0.03–0.40 mg N L⁻¹ and 0.07–0.56 mg N L⁻¹, respectively; the N-NO_3^- concentration ranged within 0.01–0.47 and 0.04–1.97 mg N L⁻¹, respectively; the TN concentration ranged within 0.40–3.14 mg N L⁻¹ and 0.68–6.54 mg N L⁻¹, respectively; and the TOC concentration ranged within 11.76–46.10 mg L⁻¹ and 12.70–37.47 mg L⁻¹, respectively.

3.2. Nitrogen Contents in Sediment

The pH of the sediment (0–60 cm) from the ditches is presented in Table 2. For 0–20 cm, 20–40 cm, and 40–60 cm sediment, pH ranged within 5.19–6.45, 5.41–6.29, and 5.48–6.20, respectively, in dryland ditch and between 5.40–6.29, 5.16–6.10, and 5.01–5.90, respectively, in paddy ditch, all of which were slightly acidic. In addition, although the sediment pH fluctuated following the seasons in both ditches, the overall variation was relatively small compared with the overlying water's pH (Figure 4a).

Table 2. Variation of pH in different sediment layers of two ditches. All values based on three replicates.

Year	Date	Period *	Dryland Ditch			Paddy Ditch		
			0–20 cm	20–40 cm	40–60 cm	0–20 cm	20–40 cm	40–60 cm
2015	05.20	2	5.30	5.41	5.66	5.94	5.63	5.59
	07.23	3	5.44	5.57	5.72	5.65	5.16	5.90
	08.20	3	5.76	5.52	5.79	6.10	5.61	5.45
	09.20	4	5.97	5.81	5.74	6.28	5.78	5.01
	10.20	5	6.45	6.29	6.20	5.75	5.69	5.71
2016	04.30	1	5.59	5.48	5.58	6.04	5.80	5.58
	05.18	2	5.56	5.64	5.80	6.29	6.10	5.61
	06.25	3	5.19	5.50	5.49	6.03	5.56	5.61
	08.06	3	5.58	5.73	5.62	5.96	5.76	5.48
	09.03	3	5.86	5.54	5.48	5.63	5.52	5.25
	09.29	4	5.91	5.64	5.72	6.27	5.57	5.39
	10.30	5	6.05	5.66	5.64	6.07	5.78	5.44
2017	05.03	1	5.66	5.49	5.78	5.40	5.29	5.28
	06.05	2	5.99	5.63	5.76	6.23	6.00	5.71
	07.13	3	5.51	5.69	5.57	5.68	5.53	5.50
	09.03	3	5.71	5.68	5.62	5.48	5.40	5.48
	09.25	4	5.69	5.64	5.66	5.95	5.56	5.66
	10.20	5	5.76	5.67	5.78	5.85	5.57	5.66

Note: * Period: 1 = Thawing; 2 = Early growth; 3 = Vigorous growth; 4 = Harvest; 5 = Early freezing.

For dryland ditch, SOC and TN contents virtually decreased with depth, ranging within 10.91–24.7, 6.08–18.25, and 4.1–15.57 g kg⁻¹ and 0.81–1.84, 0.69–1.50, and 0.50–1.35 g kg⁻¹ for 0–20 cm, 20–40 cm, and 40–60 cm sediment, respectively (Figure 5a,b). For paddy ditch, SOC and TN contents decreased with depth overall, ranging within 10.98–17.81, 9.67–19.51, and 7.99–16.81 g kg⁻¹ and 0.83–1.69, 0.66–1.88, and 0.68–1.38 g kg⁻¹ for 0–20 cm, 20–40 cm, and 40–60 cm sediment, respectively. However, among adjacent layers only subtle changes were observed (Figure 5a,b). For 0–20 cm, 20–40 cm, and 40–60 cm sediment, the C:N ratio ranged between 9.32–18.27, 7.90–17.70, and 7.52–17.20, respectively, in dryland ditch and within 9.09–16.14, 9.36–17.29 and 9.10–16.58, respectively in paddy ditch. In both ditches, SOC, TN, and C:N ratios of each layer fluctuated with seasons but were stable in general.

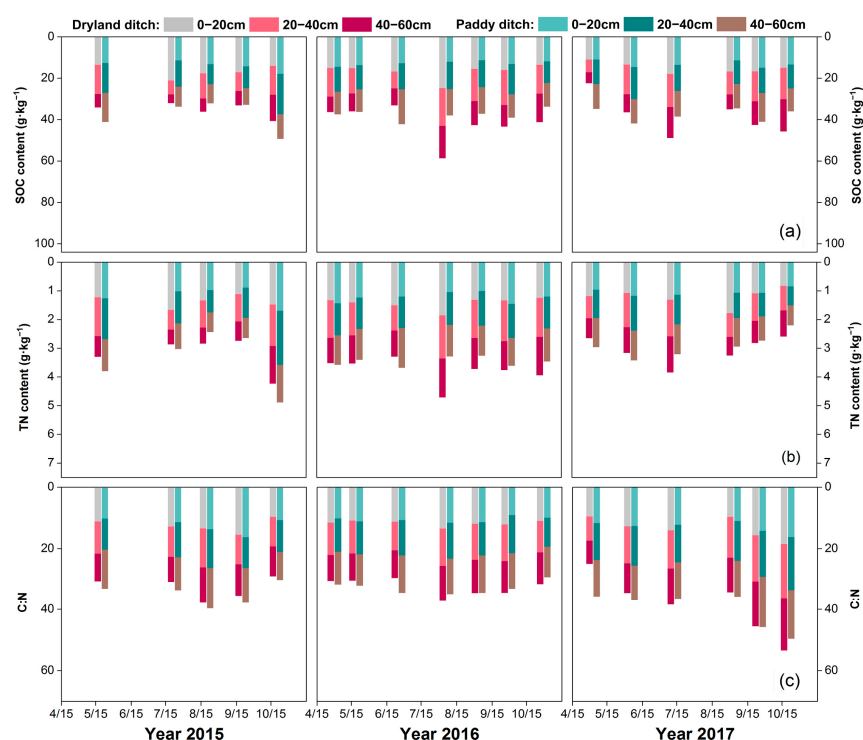


Figure 5. Variation of SOC, TN, and C:N ratio in different sediment layers of two ditches, (a): SOC, (b): TN, (c): C:N ratio.

The N-NH_4^+ and N-NO_3^- contents of the sediment from the ditches are shown in Figure 6. It was obvious that N-NH_4^+ and N-NO_3^- contents of the sediment in both ditches fluctuated strongly with the seasons, and the inter-annual characteristics changed remarkably. For 0–20 cm, 20–40 cm, and 40–60 cm sediment, N-NH_4^+ contents ranged within 2.95–22.38, 2.71–22.92, and 2.43–33.37 mg kg^{-1} , respectively, in dryland ditch and within 3.92–15.11, 5.67–39.83, and 5.04–25.23 mg kg^{-1} , respectively, in paddy ditch (Figure 6a). In a similar manner, N-NO_3^- contents ranged within 0.40–11.55, 0.30–8.78, and 0.28–3.35 mg kg^{-1} , respectively, in dryland ditch and within 0.72–9.17, 0.53–5.03, and 0.27–4.13 mg kg^{-1} , respectively, in paddy ditch (Figure 6b).

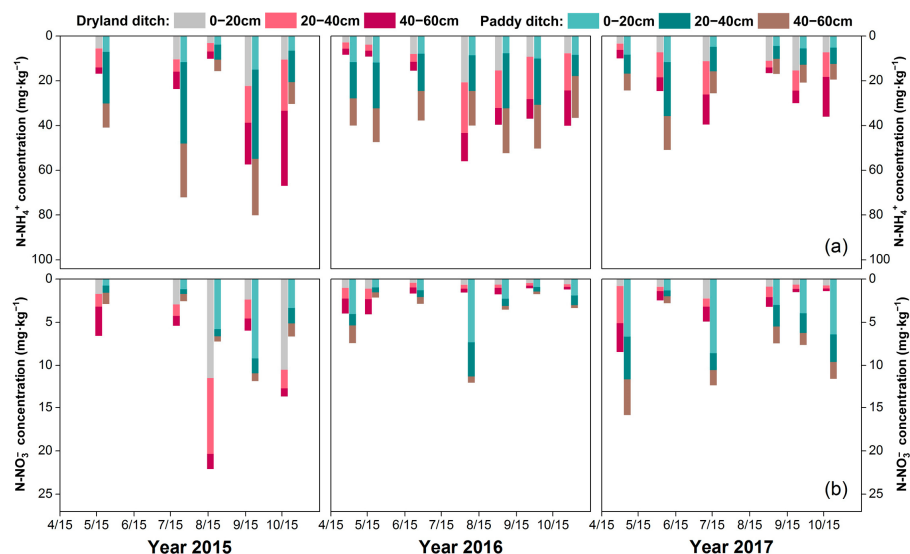


Figure 6. Variation of N-NH_4^+ and N-NO_3^- contents in different sediment layers of two ditches, (a): N-NH_4^+ , (b): N-NO_3^- .

4. Discussion

4.1. Nitrogen Content of Ditch Systems during Different Periods

According to the statistical analysis results, there was no significant difference among different periods for all variables of the overlying water in the dryland ditches (Table 3). Correspondingly, in the overlying water of the paddy ditch, TOC, TN, and N-NH_4^+ concentrations were significantly higher during the period of Early growth than in other periods, and N-NO_3^- concentration was significantly higher during the period of Thawing than in other periods. On the one hand, it could be explained by applying base fertilizer and artificial drainage in paddy fields during these two periods. On the other hand, freezing and thawing will also increase the risk of soil nitrogen loss [22]. It means that the Thawing period and Early growth period should be paid more attention to control the loss of non-point source nitrogen in paddy fields. However, in both dryland ditch and paddy ditch, there were significant inter-annual differences for all variables of the overlying water (Figure 4), which may be related to the sampling time and interval. Our previous study found that fertilization significantly influenced the nitrogen concentration of the overlying water in drainage ditches. Simultaneously, during the drainage period, the nitrogen concentration of the overlying water in the paddy ditch was monitored for six days. The results revealed that TN and N-NH_4^+ concentrations decreased by 21.5% and 46.3% [29]. Therefore, farmland situations at the time of sample collection, such as whether it has been fertilized, whether it is in the drainage period, at the initial or the end of the drainage period, and so on, would impact the results greatly.

Table 3. Analysis of variance of various indexes in overlying water of two ditches in different sampling periods.

Variable	Type *	Period				
		Thawing	Early Growth	Vigorous Growth	Harvest	Early Freezing
pH	DLD	$7.69 \pm 0.40^{\text{a} \dagger}$	$7.90 \pm 0.26^{\text{a}}$	$7.65 \pm 0.84^{\text{a}}$	$7.85 \pm 0.27^{\text{a}}$	$6.97 \pm /^{\text{a}}$
	PDD	$8.79 \pm 0.15^{\text{a}}$	$8.35 \pm 1.55^{\text{a}}$	$8.05 \pm 0.49^{\text{a}}$	$8.20 \pm 0.34^{\text{a}}$	/
TOC (mg L^{-1})	DLD	$20.78 \pm 0.12^{\text{a}}$	$31.04 \pm 14.82^{\text{a}}$	$25.13 \pm 13.16^{\text{a}}$	$25.12 \pm 3.28^{\text{a}}$	$30.45 \pm /^{\text{a}}$
	PDD	$17.72 \pm 0.35^{\text{b}}$	$29.90 \pm 10.69^{\text{a}}$	$19.33 \pm 7.21^{\text{b}}$	$20.22 \pm 5.44^{\text{ab}}$	/
TN (mg L^{-1})	DLD	$0.48 \pm 0.01^{\text{a}}$	$1.49 \pm 0.65^{\text{a}}$	$1.51 \pm 1.10^{\text{a}}$	$0.85 \pm 0.06^{\text{a}}$	$1.24 \pm /^{\text{a}}$
	PDD	$1.90 \pm 1.29^{\text{b}}$	$4.87 \pm 1.47^{\text{a}}$	$2.13 \pm 1.27^{\text{b}}$	$2.11 \pm 0.97^{\text{b}}$	/
N-NH_4^+ (mg L^{-1})	DLD	$0.04 \pm 0.01^{\text{a}}$	$0.09 \pm 0.05^{\text{a}}$	$0.15 \pm 0.13^{\text{a}}$	$0.06 \pm 0.01^{\text{a}}$	$0.13 \pm /^{\text{a}}$
	PDD	$0.10 \pm 0.03^{\text{b}}$	$0.34 \pm 0.21^{\text{a}}$	$0.17 \pm 0.07^{\text{b}}$	$0.18 \pm 0.15^{\text{ab}}$	/
N-NO_3^- (mg L^{-1})	DLD	$0.11 \pm 0.11^{\text{a}}$	$0.06 \pm 0.04^{\text{a}}$	$0.13 \pm 0.17^{\text{a}}$	$0.04 \pm 0.00^{\text{a}}$	$0.03 \pm /^{\text{a}}$
	PDD	$1.34 \pm 0.90^{\text{a}}$	$0.56 \pm 0.31^{\text{b}}$	$0.19 \pm 0.15^{\text{b}}$	$0.05 \pm 0.00^{\text{b}}$	/

Notes: * DLD = dryland ditch; PDD = paddy ditch. [†] Within each variable, different lowercase letters following means in the same rows indicate significant differences among periods at $p < 0.05$.

Following the change in seasons, variation trends of carbon and nitrogen contents and the C:N ratio in sediment were not precisely the same (Figures 5 and 6). In the dryland ditch, sediment pH, SOC contents, C:N ratio, and N-NH_4^+ contents exhibited ascent tendencies from the period of Thawing and reached the maximum at the period of Harvest and Early freezing, concurrently sediment TN contents and N-NO_3^- presented no significant differences among periods (Table 3). In the paddy ditch, sediment SOC and TN contents and C:N ratio showed no significant differences among periods, concomitantly with fluctuant changes of sediment pH, N-NH_4^+ , and N-NO_3^- contents (Table 4). Different variation characteristics between dryland and paddy ditch may be related to vegetation abundance and coverage. In consideration of drainage needs, the paddy ditches were cleaned regularly in this area, which caused low vegetation coverage and subsequent little vegetation litter, combined with long-term flooding conditions, which led to difficulty for litter return to sediment, resulting in no noticeable seasonal changes in soil organic carbon.

Table 4. Analysis of variance of various indexes in sediment of two ditches in different sampling periods.

Variable	Type *	Period				
		Thawing	Early Growth	Vigorous Growth	Harvest	Early Freezing
pH	DLD	5.60 ± 0.11 ^{bc†}	5.64 ± 0.20 ^{bc}	5.60 ± 0.15 ^c	5.75 ± 0.12 ^b	5.94 ± 0.31 ^a
	PDD	5.57 ± 0.31 ^b	5.90 ± 0.27 ^a	5.61 ± 0.24 ^b	5.72 ± 0.41 ^{ab}	5.72 ± 0.18 ^{ab}
SOC (g kg ^{−1})	DLD	9.73 ± 4.12 ^b	11.79 ± 3.11 ^{ab}	13.59 ± 5.36 ^a	13.17 ± 3.84 ^a	14.13 ± 0.90 ^a
	PDD	12.02 ± 1.31 ^a	13.22 ± 1.57 ^a	12.16 ± 1.63 ^a	12.51 ± 2.30 ^a	13.18 ± 3.24 ^a
TN (g kg ^{−1})	DLD	1.02 ± 0.28 ^a	1.10 ± 0.22 ^a	1.16 ± 0.39 ^a	1.03 ± 0.24 ^a	1.19 ± 0.26 ^a
	PDD	1.08 ± 0.18 ^a	1.18 ± 0.12 ^a	1.04 ± 0.15 ^a	0.99 ± 0.23 ^a	1.17 ± 0.42 ^a
C:N ratio	DLD	9.19 ± 1.55 ^c	10.55 ± 1.26 ^{bc}	11.49 ± 1.58 ^{ab}	12.75 ± 2.42 ^a	12.60 ± 3.87 ^a
	PDD	11.17 ± 0.75 ^a	11.28 ± 1.16 ^a	11.80 ± 0.81 ^a	12.90 ± 2.66 ^a	12.07 ± 3.35 ^a
N-NH ₄ ⁺ (mg kg ^{−1})	DLD	3.04 ± 0.43 ^d	5.63 ± 2.79 ^{cd}	9.57 ± 6.11 ^{bc}	13.81 ± 5.81 ^{ab}	15.89 ± 8.29 ^a
	PDD	10.71 ± 3.26 ^{ab}	15.46 ± 5.82 ^a	12.39 ± 8.26 ^{ab}	16.80 ± 10.97 ^a	9.60 ± 4.20 ^b
N-NO ₃ [−] (mg kg ^{−1})	DLD	2.01 ± 1.43 ^a	1.44 ± 0.82 ^a	1.92 ± 2.85 ^a	0.93 ± 0.83 ^a	1.79 ± 3.32 ^a
	PDD	3.70 ± 2.19 ^a	0.85 ± 0.29 ^b	2.28 ± 2.31 ^a	2.35 ± 2.79 ^{ab}	2.39 ± 1.78 ^a

Notes: * DLD = dryland ditch; PDD = paddy ditch. † Within each variable, different lowercase letters following means in the same rows indicate significant differences among periods at $p < 0.05$.

In contrast, plants in dryland ditches were generally not interfered with, causing higher vegetation abundance and coverage and, subsequently, much litter. Field investigations in the study area revealed that vegetation in ditches generally germinated in early May, then thrived from June to July, and the biomass on the ground reached the maximum in mid-August. Little litter in ditches began to appear from June to July, then increased rapidly in August, and the plants almost all died [30,31]. The number of plant residues, litter, and root exudates reached the maximum at the end of October, resulting in an increment of sediment organic carbon. Furthermore, soil enzyme activities had significant seasonal variations [32]. A previous study focusing on the *Calamagrostis angustifolia* wetland of Sanjiang Plain, which was similar to ditch systems to some extent, found that Urease, Sucrase, and Cellulase activities, which were positively correlated with SOC content, and Amylase activity which was positively correlated with TN content, reached the maximum at the end of the growth period (September) [33]. In other words, higher SOC and TN contents and corresponding enzyme activities at the Harvest and Early freezing period may be one reason for the increase in C:N ratio and N-NH₄⁺ contents in dryland ditch sediment. Moreover, from the period of Harvest, the temperate continental climate led to less precipitation in the study area, accompanied by a decrease in soil temperature, which weakened the dilution effect of rainfall on the N-NH₄⁺ concentration in the sediment, together with less plant uptake, which made it was not easy to reduce the concentration of N-NH₄⁺, thus presenting higher concentration characteristics [34,35].

From our results, no matter the overlying water or the sediment of the ditch, different collection periods may cause variations in nitrogen contents. To assess the nitrogen pollution of the ditch system, only sampling once or several times during a short period may cause significant uncertainty. In this study, samples were collected over three years, and the results showed that inter-annual differences existed, which may be related to climate, rainfall, management of farmland and ditches, etc. Nevertheless, we could not determine the exact causes of the inter-annual differences due to the sampling frequency and monitoring indicators needing to be improved.

4.2. Characteristics of Nitrogen Content in Sediment Profiles

Although there were period fluctuation and inter-annual variation for the indicators of ditch sediment, SOC and TN contents were higher in upper layers as compared to deeper layers generally (Table 5), which were closely related to the distribution characteristics of

organic matter and following the soil of adjacent farmlands [16] (Table 6). On the one hand, soil erosion caused by rainfall and drainage are important sources of organic carbon in the sediment of ditches. This led to changes in SOC content and distribution of the ditch sediment following the land use types [36–38]. On the other hand, the decomposition of plants, which mainly depends on the activity of microbes in the root zone of the soil, is another important source of organic carbon and total nitrogen to the sediment of ditches [39,40]. Consequently, the vertical distribution of SOC and TN contents is generally closely related to the distribution of plant roots. As the root zone of the ditch plants is mainly located in the layer of 0–40 cm, especially the surface layer 0–20 cm is a concentrated area of the root, the SOC and TN contents of sediment descended from the surface layer to the deeper layers.

Table 5. Analysis of variance of various indexes among different sediment layers in two ditches.

Variable	Type *	Layer		
		0–20 cm	20–40 cm	40–60 cm
pH	DLD	5.72 ± 0.30 ^{aB} †	5.64 ± 0.19 ^{aA}	5.70 ± 0.16 ^{aA}
	PDD	5.92 ± 0.27 ^{aA}	5.63 ± 0.23 ^{bA}	5.52 ± 0.20 ^{bB}
SOC (g kg ^{−1})	DLD	16.07 ± 3.10 ^{aA}	12.90 ± 3.44 ^{bA}	9.67 ± 3.63 ^{cB}
	PDD	13.20 ± 1.68 ^{aB}	12.68 ± 2.26 ^{abA}	11.77 ± 1.98 ^{bA}
TN (g kg ^{−1})	DLD	1.32 ± 0.26 ^{aA}	1.12 ± 0.26 ^{bA}	0.91 ± 0.27 ^{cA}
	PDD	1.14 ± 0.22 ^{aB}	1.10 ± 0.27 ^{abA}	1.00 ± 0.19 ^{bA}
C:N ratio	DLD	12.35 ± 2.33 ^{aA}	11.51 ± 2.30 ^{abA}	10.56 ± 2.37 ^{bB}
	PDD	11.81 ± 1.99 ^{aA}	11.85 ± 1.89 ^{aA}	11.95 ± 1.89 ^{aA}
N-NH ₄ ⁺ (mg kg ^{−1})	DLD	9.82 ± 5.69 ^{aA}	10.66 ± 7.15 ^{aB}	9.37 ± 8.05 ^{aA}
	PDD	8.48 ± 3.10 ^{bA}	17.03 ± 9.90 ^{aA}	13.45 ± 6.08 ^{aA}
N-NO ₃ [−] (mg kg ^{−1})	DLD	2.21 ± 3.29 ^{aA}	1.57 ± 2.06 ^{aA}	1.23 ± 0.93 ^{aA}
	PDD	3.82 ± 2.83 ^{aA}	1.68 ± 1.30 ^{bA}	1.19 ± 0.91 ^{bA}

Notes: * DLD = dryland ditch; PDD = paddy ditch. † Within each variable, different lowercase letters following means in the same rows indicate significant differences among layers at $p < 0.05$; different capital letters following means in the same columns indicate significant differences between ditch types at $p < 0.05$.

Table 6. Analysis of variance of various indexes among different soil layers in two land-use types.

Variable	Type	Layer		
		0–20 cm	20–40 cm	40–60 cm
pH	Dryland	5.23 ± 0.12 ^{aB} *	5.28 ± 0.11 ^{aB}	5.27 ± 0.01 ^{aA}
	Paddy field	5.64 ± 0.19 ^{aA}	5.41 ± 0.20 ^{bA}	5.38 ± 0.20 ^{bA}
TC (g kg ^{−1})	Dryland	24.51 ± 1.71 ^{aA}	24.57 ± 1.96 ^{aA}	11.52 ± 1.30 ^{bA}
	Paddy field	12.96 ± 3.47 ^{aB}	13.84 ± 5.83 ^{aB}	13.45 ± 4.89 ^{aA}
TN (g kg ^{−1})	Dryland	1.97 ± 0.27 ^{aA}	1.92 ± 0.30 ^{aA}	1.03 ± 0.01 ^{bA}
	Paddy field	1.04 ± 0.23 ^{aB}	1.08 ± 0.40 ^{aB}	1.13 ± 0.21 ^{aA}
C/N	Dryland	12.61 ± 1.52 ^{aA}	12.96 ± 1.68 ^{aA}	11.24 ± 1.35 ^{bA}
	Paddy field	12.41 ± 1.64 ^{abA}	12.92 ± 2.17 ^{aA}	11.47 ± 1.79 ^{bA}
N-NH ₄ ⁺ (mg kg ^{−1})	Dryland	7.97 ± 2.64 ^{aB}	7.65 ± 1.78 ^{aA}	4.46 ± 0.05 ^{bA}
	Paddy field	12.02 ± 6.61 ^{aA}	10.11 ± 6.43 ^{aA}	11.03 ± 6.72 ^{aA}
N-NO ₃ [−] (mg kg ^{−1})	Dryland	14.60 ± 9.89 ^{aA}	10.66 ± 5.42 ^{abA}	2.05 ± 0.06 ^{bA}
	Paddy field	2.52 ± 2.64 ^{aB}	1.62 ± 1.21 ^{aB}	2.84 ± 3.77 ^{aA}

Notes: * Within each variable, different lowercase letters following means in the same rows indicate significant differences among layers at $p < 0.05$; different capital letters following means in the same columns indicate significant differences between land use types at $p < 0.05$.

Comparing dryland ditch and paddy ditch, SOC and TN contents and C:N ratio of dryland ditch sediment were significantly higher in the upper layers than in deeper

layers, while the above indicators of paddy ditch sediment were not always like this (Figure 5, Table 5). In other words, the varying amplitudes of SOC and TN contents and C:N ratio were larger in sediment profiles of dryland ditch than in paddy ditch, which was consistent with the characteristics of SOC and TN in corresponding adjacent farmlands [22] (Table 6). One interpretation was very different water regimes. In the crop growing season, paddy fields needed to be artificially irrigated /drained so that adjacent paddy ditches kept flooding for more time. At the same time, drylands had no artificial irrigation, and adjacent dryland ditches were kept dry until rainfall. Thus, compared with episodic rewetting in dryland ditch, intensive water mobility under oversaturation in paddy ditch contributed to SOC and TN movement to and accumulation in deep layers [40,41]. Moreover, while Feo penetrated at a lower velocity and only ephemerally occurred during rainstorm events for dryland ditch [22], relative long-term submergence for paddy ditch is conducive to the formation and redistribution of poorly crystalline Feo oxides along the soil profile, which favors SOM stabilization through promoting soil aggregation or directly surface interacting with the highly reactive surface [42,43]. C:N ratio of soil is always regarded as a sensitive indicator of soil quality and its carbon/nitrogen balance and as a soil nitrogen mineralization rate guide. It is generally considered that a lower C:N ratio could promote microbial decomposition and nitrogen mineralization rate, and a higher C:N ratio is beneficial for the accumulation of carbon and nitrogen [44,45]. In this study, the C:N ratio of dryland ditch sediment decreased significantly with the depth of layers (Table 5), indicating that the surface sediment had higher C and N storage capacity than deeper layers, and the nitrogen decomposition rate may be the opposite. While the C:N ratio of paddy ditch sediment was almost stable among different layers, indicating equivalent C and N storage capacity and nitrogen decomposition rate.

Irrespective of ditch types, the N-NH_4^+ content of the sediment was higher than N-NO_3^- (Table 5). It may be related to not only the mineralization of soil organic nitrogen but also the types of fertilizers applied, of which urea, ammonium bicarbonate, and chlorination accounted for the central part and resulting in higher N-NH_4^+ concentrations than N-NO_3^- discharged into the ditch. Especially, N-NH_4^+ prefers to be adsorbed by soil rather than leaches, while N-NO_3^- is highly prone to leaching during irrigation and precipitation [35]. In ditch systems, sediment could adsorb N-NH_4^+ or make it nitrify, and the adsorption plays a dominant role in the interception of nitrogen pollution [46].

For paddy ditch, N-NH_4^+ contents in the surface layer (0–20 cm) were significantly lower than that in the deeper layer (20–60cm), and N-NO_3^- content presented the opposite trend, i.e., it was significantly higher in the surface layer than the deeper layer (Figure 6, Table 5). While for dryland ditches, there was no noticeable difference in inorganic nitrogen (N-NH_4^+ and N-NO_3^-) contents among layers (Figure 6, Table 5). We conjecture that in a paddy ditch, N-NH_4^+ may be more likely to migrate to the deeper layer or be converted to N-NO_3^- by nitrification, thereby increasing the risk of inorganic nitrogen pollution to the groundwater, which deserves to be paid more attention. However, there were other possible interpretations. Lu (2015) analyzed the inorganic nitrogen composition of groundwater in different land-use types in the study area and found that N-NO_3^- dominated the groundwater of urban, dryland, and forest, while N-NH_4^+ dominated in the groundwater of paddy fields, which was consistent with the results of this study. He thought that in the paddy field, the anaerobic environment was beneficial for denitrification and thus increased the N-NH_4^+ concentration, and higher iron ion content in the groundwater may lead to the reduction of N-NO_3^- concentration [1].

4.3. Comparison of Nitrogen Content in Dryland and Paddy Ditches

Although there were inter-annual variations for the indicators, the results of statistical analysis revealed that the nitrogen content of overlying water in the paddy ditch was higher than that in the dryland ditch (Table 7), which means the nitrogen output of the paddy field was larger than the dry land. This is consistent with the previous study about the non-point source pollution output of different land use types in this region, in which it was concluded

that the non-point source nitrogen pollution discharged from dryland sub-basins was approximately 50% lower than that from paddy field using model simulation methods [14]. Therefore, “changing from dryland to paddy field” may aggravate the non-point source pollution in this intensive agricultural area.

Table 7. Analysis of variance of various indexes in overlying water of two ditches.

Type *	Variable				
	pH	TOC (mg L ⁻¹)	TN (mg L ⁻¹)	N-NH ₄ (mg L ⁻¹)	N-NO ₃ (mg L ⁻¹)
DLD	7.69 ± 0.62	26.09 ± 10.84	1.26 ± 0.85	0.11 ± 0.10	0.10 ± 0.13
PDD	8.24 ± 0.75	21.49 ± 8.07	2.68 ± 1.64	0.20 ± 0.13	0.41 ± 0.52
Sig.	0.034	0.181	0.000	0.022	0.006

Notes: * DLD = dryland ditch; PDD = paddy ditch.

For both ditches, SOC and TN contents of the sediment were not changeless at 0–60 cm depth. From the mean value, at 0–20 cm depth, the sediment SOC and TN of the dryland ditch was higher than that of the paddy ditch; at 20–40 cm depth, sediment SOC and TN of dryland ditch were equivalent to that of paddy ditch; at 40–60 cm depth, sediment SOC of dryland ditch was lower than that of paddy ditch while sediment TN of dryland ditch was equivalent to that of paddy ditch (Table 5). Generally, the mineralization rate of organic matter under flooding conditions is lower than that under drought conditions, and alternation of drying and wetting will be beneficial to the decomposition of organic matter [47]. As the paddy ditch was subjected to flooding for a longer time than the dryland ditch while the latter alternated drying and wetting more frequently, it can be inferred that the mineralization rate of organic matter in the dryland ditch was higher than that in the paddy ditch and subsequently leading to lower carbon contents of surface sediment in dryland ditch than that in paddy ditch. However, the results of this study were the opposite, which could be ascribed to the following possible reasons. First, the surface SOC and TN content of dryland, which was adjacent to the dryland ditch, was higher than that of the paddy field, which was adjacent to the paddy ditch (Table 6), and soil discharge is an essential source of ditch sediment. Second, the vegetation abundance and coverage of dryland ditch in the study area was much higher than that of paddy ditch, and the decomposition of plants is an essential source of sediment, carbon, and nitrogen [48]. The above two reasons led to higher SOC and TN content in the surface sediment of the dryland ditch than paddy ditch. Nevertheless, the SOC and TN contents in the sediment of ditches were not changeless among different periods. In this study, during the periods of Thawing and Early growth, the sediment SOC of the paddy ditch was higher than that of the dryland ditch, but the opposite was confirmed during the other three periods. The hypothesis of this study, i.e., the sampling time and depth of the soil greatly influence the SOC and TN contents, has been verified by previous studies [22,46].

There was no significant difference in the inorganic nitrogen content of surface sediment (0–20 cm) between the two types of ditches, but the NH₄⁺ content in the deeper sediment (20–40 cm) of the paddy ditch was significantly higher than that of the dryland ditch (Table 5), which difference was mainly manifested in the early stage of crop growth (April–June) (Figure 6). It may be affected by fertilization and drainage of paddy fields and associated with higher vegetation abundance and coverage in dryland ditches. In 2016 and 2017, N-NO₃⁻ content in the surface sediment (0–20 cm) of the dryland ditch was significantly lower than that of the paddy ditch (Figure 6), for which there were no significant differences in 2015. This might be because the study area experienced a rainstorm on 13 and 14 July 2015, on which two days the 24 h rainfall reached 44.70 mm and 67.31 mm, respectively (Figure 3). As drylands in the study area were generally not irrigated or drained artificially. No ridges had been set, and a rainstorm of this scale was likely to cause the discharge of dryland soil into the ditch [49], which would increase N-NO₃⁻ content in the surface sediment of the dryland ditch owing to the high N-NO₃⁻ content of

dryland surface soil [50,51] (Table 5). On the one hand, there were ridges set for irrigation and drainage for paddy fields, which limited the discharge of paddy soil to ditch under rainstorms partly. On the other hand, even if a certain amount of paddy soil transferred to the ditch, N-NO_3^- content in the surface sediment would not be impacted significantly owing to the equivalent N-NO_3^- content of paddy surface soil with paddy ditch surface sediment (Table 5). Generally, inorganic nitrogen, especially N-NH_4^+ , in the sediment of the paddy ditch was higher than that of the dryland ditch, which was consistent with that the inorganic nitrogen in the overlying water of the paddy ditch was higher than that of the dryland ditch.

In summary, on the one hand, N-NO_3^- and N-NH_4^+ contents in the overlying water and sediment of the paddy ditch were higher than that of the dryland ditch, which should be attributed to the following three aspects: First, the paddy ditch had lower vegetation coverage due to the regular cutting of ditch plants for drainage, and then the absorption of inorganic nitrogen by plants was reduced. Second, the paddy fields underwent several large-scale artificial drainage events, which increased nitrogen loss from fields to ditches while nitrogen discharge from drylands was limited unless there was heavy rainfall. Third, the paddy fields had much more extended water storage periods than drylands, which enlarged the risk of inorganic nitrogen loss through lateral seepage. Based on the results and the above points, from the perspective of nitrogen loss from farmland, the non-point source nitrogen pollution caused by paddy fields may be more severe than that of dry lands. On the other hand, compared with paddy ditch, dryland ditch had more frequent drying and wetting alternation, which could impact the sediment microenvironment and its structure of the microbial community and then organic matter decomposition and material circulation. Previous studies indicated that dry-wet alternating could promote the mineralization of organic carbon and nitrogen and then increase inorganic nitrogen concentration in the ditch system. Meanwhile, the alternation of dry and wet can promote alternate nitrification and denitrification, which was beneficial to the self-depuration of the ditch systems [49,52,53].

Therefore, from the perspective of ditch drainage function and non-point source nitrogen pollution control, the risk of nitrogen pollution caused by paddy ditches may be greater than that of dryland ditches. BMPs of paddy ditch should be paid more attention to reduce the non-point source nitrogen pollution from farmlands when implementing policy-oriented conversion of dryland to paddy.

5. Conclusions

Focusing on typical ditches in drylands and rice paddies, this study revealed the nitrogen contents and distribution characteristics during different periods in seasonally freezing-thaw zones of Northeast China. In the overlying water, N-NO_3^- concentration was higher than N-NH_4^+ , while in the sediment, N-NH_4^+ was much higher than N-NO_3^- , which should be attributed to the soil's adsorption of N-NH_4^+ . SOC and TN contents in the surface sediment of dryland ditch were significantly higher than that of paddy ditch. There were significant differences among layers in dryland ditch sediment but no significant differences among layers in paddy ditch sediment, which characteristics may be related to the SOC and TN contents of their respective adjacent farmlands, vegetation abundance and coverage of the ditches, the retention time of ditch water. Whether in the overlying water or the sediment of the ditch, the inorganic nitrogen contents of paddy ditch were generally higher than that of dryland ditch, which means that the non-point source nitrogen pollution caused by paddy fields was more severe than that of drylands. Compared with dryland ditch, N-NH_4^+ in the sediment of paddy ditch seemed to be much easier to migrate to a deeper layer, which may cause a greater risk of nitrogen pollution to groundwater, so effective BMPs are needed to purify the nitrogen in the ditch systems and control the nitrogen loss from the farmlands. From the results of this three-year experimental study, nitrogen contents, whether in the overlying water or in the sediment of the ditches, fluctuated during different periods, and inter-annual variation was evident.

From this aspect, to estimate or predict the non-point source pollution output needs to consider the impacts of precipitation, artificial drainage, vegetation, and other factors, and extending the monitoring period and increasing sampling frequency is essential. Otherwise, there will be great uncertainty. Similarly, BMPs for intercepting or purifying nitrogen from farmlands using drainage ditches should also consider the effects of sediment depth and seasonal periods.

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