# Chemical analysis of metals and essential nutrients in wetland dew Y. Xu<sup>1, 2\*</sup>, B. Yan<sup>3</sup>, J. Tang<sup>2</sup>, Y. Lin<sup>1</sup>

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In order to discuss the ecological efficiency of dew and reveal the air status of surface layer, pH and the concentrations of 25 metals including K, Na, Ca, Mg and essential nutrients (ammonium nitrogen (NH<sub>4</sub><sup>+</sup>-N), nitrogen (NO<sub>3</sub><sup>-</sup>-N) and phosphate (P)) in dew samples from the wetland of the Sanjiang Plain were monitored. Carex lasiocarpa dew was collected from mid July to mid September from 2008 to 2012. The results showed that the mean pH of Carex lasiocarpa dew was 6.41 and the acid dew did not occur in the research area during the monitoring period, therefore dew cannot damage protective surfaces on leaves. Carex lasiocarpa dew contained various types of metals, which can provide nutrient and trace elements to the plant. Dry deposition was the main source of elements in dew. The contents of main metals (K, Ca, Na, Mg, Mn, Fe, Zn) in *Carex lasiocarpa* dew were higher than those in rain (P<0.05). The trace amounts of Pb, Ba, Se, As, Co, Cr, Cu in *Carex lasiocarpa* dew implied that there was no significant contamination by automobile exhaust, coal combustion or industrial pollution in this area. The deposition amounts of NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and PO<sub>4</sub><sup>3-</sup>-P from July to October in wetland dew were 0.065, 0.14 and 0.007 kg/ha, respectively. In addition, dew condenses on both sides of the leaf and can be taken up by rice more effectively. Therefore, nitrogen (N) and phosphorus (P) in wetland dew are another nutrition source. Dew is an important pathway for the nutrient transfer within a wetland. In consequence, dew can reveal the air pollution status and it is significant to monitor the chemical character of dew. Analyzing the metal content of dew is a simple and useful method to reveal the status of the surface layer. This method can provide foundation and reference of the air pollution and quality assessment.

Key words: wetland dew, metals, dry deposition, wetland surface water, dew chemical character.

#### **INTRODUCTION**

Particles and gases can be removed from the atmosphere by wet deposition (rain, fog and dew) and by dry deposition. The wet deposition process is a major pathway for the transport of acidic pollutants from the atmosphere to the biosphere [1]. Dew, which is an important part of wet deposition, occurs when the air temperature reaches to the dew point temperature, further it can indicate the quality of the near-surface atmosphere. Sanjiang Plain was the largest concentrated area of freshwater wetlands in China in the 1960s, and marsh vegetation here was distributed densely. Dew plays a crucial role in the water balance of a wetland ecosystem. As a form of wet deposition, dew is a major pathway for the transport of acidic pollutants from the atmosphere to the biosphere [2], furthermore, the acidity or alkalinity of dew can also influence plant growth [3]. Formation of acidic dew is critical to assess corrosion process. For example, acidic dew is

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damage to surface structures. Acidic dew damages the protective surfaces of leaves, interferes with guard cells, and poisons plant cells [4]. Moreover, some metals from dry deposition on leaves can dissolve in dew. Some metals in dew are helpful to plants, such as K, Mg, Ca, Zn, Na, Fe which can be assimilated by leaves [5]. However, other metals (As, Pb, Cr) are harmful to the plants [6, 7]. Therefore, identifying the relative character of dew is necessary to determine the significance of dew to the plants in the wetland. On the other hand, dew formation is a local phenomenon, significantly influenced by microclimatic ambiance, land profile, and favorable meteorological conditions. Analyzing the chemistry of dew can also provide information of the quality of air. The dew amount has attracted great interest and has been extensively studied, but few studies have focused on the chemical characterization of dew [8, 9]. Consequently, the objectives of the present study are to (a) determine the pH, and the concentrations of some elements in dew; (b) identify the source of the nutrients; (c) compare the dew with the drinking water.

potentially more effective than acid rain in causing

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## MATERIALS AND METHODS

The experiment was organized at the Sanjiang Wetland Experimental Station (47°35'N, 133°31'E), Chinese Academy of Sciences, in Tongjiang, Heilongjiang Province, Northeast China. The elevation is about 56 m above sea level. An average annual temperature of 1.9°C can be expected. The annual precipitation which is in the range of 550 to 600 mm accounts for over 65% precipitation from June to September [10]. The annual dewfall in the wetland is about 10 mm [11]. *Carex lasiocarpa* is the dominant plant, and it was selected as the typical experiment plot.

The method of monitoring dewfall was validated. The woodstick as the collector on monitoring dewfall was weighed daily at sunset and sunrise with an electronic balance (accuracy is within 0.001 g). The collectors were kept in the experimental plot until the next sunrise. These collectors were gathered half an hour before sunrise and weighed again. Dew intensity and dewfall was calculated with the following formula:

$$I = 10 \times (W_r - W_s) / S \tag{1}$$

Where, *I* is the dew intensity (mm);  $W_r$  is the weight of woodstick before sunrise (g);  $W_s$  is the weight of woodstick after sunset (g); *S* is the surface area of woodstick (cm<sup>2</sup>)

$$DF = \sum_{i=1}^{n} DF_i \tag{2}$$

$$DF_i = 2 \times LAI_i \times I_i \times D_i \tag{3}$$

Where, *DF* is the total dewfall (mm); *DF<sub>i</sub>* is the dewfall in a particular period (mm); *LAI<sub>i</sub>* is the *LAI* in a particular period (cm<sup>2</sup>/cm<sup>2</sup>);  $\overline{I_i}$  is the average *I* in a particular period (mm); *D<sub>i</sub>* is the *D* in a particular period (days); 2 is the coefficient of a leaf side; *n* is the time of measuring *LAI*.

It is convenient to collect dew samples in July and August since the dewfall is high [11]. The leaf dew samples were collected 30 min before sunrise in the heavy-dew days. A total of 47 leaf dew samples were collected during the growth season from 2008 to 2012 in the current study. After washing with distilled water and drying, a polyethylene basin was used to collect dew water. All samples were then placed into polyethylene bottles (50 mL) [12]. To avoid contamination during the collection process, dew water was collected in situ. The collector was placed close to the root of the Carex lasiocarpa, and the Carex lasiocarpa stem was slightly shaken until the dew dropped into the collector. The dew was then poured from the collector into the polyethylene bottle. The steps were repeated until the polyethylene bottle was full. The Carex lasiocarpa were distributed in the four corners of a 20 m  $\times$  20 m 1096

field. Surface water was collected using a polyethylene bottle (100 mL) when the leaf dew was collected. Rainwater was collected from the same site using polyethylene containers during the experimental period. Surface water and rain were collected in three parallel samples each time. In total, 141 surface water and 63 rain samples were collected.

The analyses were carried out in a laboratory at the Sanjiang Experimental Station, Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences. The pH was immediately determined after collecting the samples. The samples were filtered through a 0.45  $\mu$ m pore membrane. The concentrations of K, Zn, Ca, Mn, Na, Fe, Mg in each sample were immediately measured using ICP-MS (Agilent 7500a, USA). The samples were filtered through a 0.45  $\mu$ m pore size membrane. Then NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and PO<sub>4</sub><sup>3-</sup>-P were measured by a Discrete Auto Analyzer (Smartchem 200, Italy).

The statistical analyses were carried out by SPSS software version 16.0. To test the normal distribution of metal concentrations, Q-Q probability plots were employed. The data of metal concentrations in the rain, surface water, and dew were all with normal distribution. The ANOVA of metal concentrations was performed using one-way ANOVA, and the significance limit was set to P<0.05. The Least Significant Difference or Tamhane's T2 procedure was used to determine the significant differences between each group of concentrations. The mean separation of pH among rain, surface water, and leaf dew was performed according to the t-test at  $\alpha$ =0.05 level. The data of dew, rain and surface water are the mean of three replicates.

## **RESULTS AND DISCUSSION**

## pH of dew

The pH is an important aspect of the assessment of ecological effects of dew in wetland. As displayed in Table 1 and Fig. 1, dew pH varied between 5.84 and 6.95, with an average of 6.41, whereas pH of rain was higher compared with dew and surface water. Even though the dew pH was below 7, the dew cannot endanger leaves in the wetland (the pH of acid rain is around 3.0 [13]). Data for acidic dew were reported in different references, e.g., the average dew pH in the farmland in the Sanjaing Plain was 6.3 [14]. In Zadar, Croatia, the dew pH was between 5.5 and 7.8, with a mean value of 6.7 [8]. In Bordeaux, France, the average dew pH was 6.3 [15]. The pH of dew in Indianapolis was between 6.0 and 7.2 [15], whereas in north-central India, it varied between 6.0 and 7.7, with an average of 6.8 [3]. The dews in these areas are acidic. Dew acidity is derived from the  $CO_2$  absorption and the acidic aerosol dissolution during droplet growth. However, the rain pH in these areas is lower than dew pH because of the various quantities of acidic species (SO<sub>2</sub>, NO<sub>x</sub>) influenced by human activities, such as fluctuating pollutant production and wind dispersion, or preceding rain events that clear out the aerosols in these areas. In the Sanjiang Plain, no automobile exhaust, coal combustion, or industrial pollution was detected; thus, its rain pH is higher than in other areas. It can be explained that dew can absorb  $CO_2$  and the acidic aerosol dissolution during droplet growth [8].

**Table 1.** The pH of dew, rain, and surface water by type during the experimental period from 2008 to 2012 in the Sanjiang Plain



**Fig. 1**. Seasonal variability of pH in dew, rain, and surface water from 2008 to 2012 in the Sanjiang Plain.

# Metal of dew

As the results showed, the mean concentrations of Cd, Be, Co, Se, Mo, Th, U and Tl were below 1.0  $\mu$ g/L. The mean concentrations of Pb, As, Ni, Cr, V, Ag, Cu and Zn were between 1.0  $\mu$ g/L and 100  $\mu$ g/L. The mean concentrations of Na, Al, Fe and Ba were between 100  $\mu$ g/L and 1000  $\mu$ g/L. The mean concentrations of K, Mg, Ca and Mn were higher than 1000  $\mu$ g/L (Table 2).

Some nutrient elements (K, Mg, Ca), trace elements (Mn, Cu, Cr, Zn, Na, Mo, V, As, Fe, Ni) [16] and heavy metals which are harmful to the plants (Cd, Pb, Al) [17] were detected in the dew. The results indicate that dew can provide various elements to the plants in the wetland ecosystem. But the process of plant assimilation is ambiguous, for instance, some elements such as As with a low concentration can stimulate plants growth, but constrain it when it is in high concentration.

The trace amounts of Pb, Ba, Se, As, Co, Cr, Cu in wetland dew implied that there is no automobile exhaust, coal combustion or industrial pollution in this area [18, 19]. Therefore, dew can reveal the air pollution status and it is significant to monitor the chemical character of dew.

Table 2. Concentrations of different metals in wetlan	ıd
dew from 2008 to 2012.	

	Mean±SD	Max	Max Min	
	$(\mu g/L)$	$(\mu g/L)$	$(\mu g/L)$	
Cu	11.72±5.34	26.42	2.28	
Pb	8.56±1.38	14.09	5.08	
Zn	90.56±35.71	252.00	4.00	
Cd	0.17±0.03	0.19	0.09	
As	2.57±0.75	4.41	1.35	
Be	0.03±0.01	0.05	0.01	
Κ	32521±15646	149200	1089	
Na	955±470	2591	52	
Ca	12082±9458	55400	287	
Mg	4876±2456	27360	578	
Al	$181.57 \pm 148.71$	255.56	24.10	
Mn	1956.48±1075.73	6507.00	572.00	
Fe	276.04±196.35	1148.00	22.00	
Co	0.81±0.09	1.520	0.35	
Ni	3.53±0.87	4.29	1.36	
Cr	$4.74 \pm 1.82$	8.25	2.31	
Se	0.87±0.33	1.61	0.23	
V	2.62±1.01	4.24	1.12	
Mo	0.95±0.215	1.86	0.31	
Ag	0.01±0.01	0.01	0.00	
Sb	2.13±0.47	4.38	1.18	
Ba	195.75±59.50	398.00	65.16	
Th	$0.03 \pm 0.02$	0.07	0.01	
U	$0.02 \pm 0.01$	0.03	0.01	
Tl	0.02±0.01	0.04	0.01	

#### $NH_4^+$ -N, $NO_3^-$ -N and P in dew

The diffusion of  $NH_3$  from surface water contributes some N to the wetland dew. In this N cycle process, the first step is  $NH_3$  conversion to  $NH_4^+$ . Dew condenses under aerobic conditions.  $NH_4^+$ -N is prone to convert to  $NO_3^-$ -N by the following steps:

 $\begin{array}{c} NH_{4}^{+}+1.5O_{2}\rightarrow NO_{2}^{-}+2H^{+}+H_{2}O,\ (4)\\ NO_{2}^{-}+0.5O_{2}\rightarrow NO_{3}^{-}\ (5)\\ NH_{3}+1.32NO_{2}^{-}+H^{+}\rightarrow 1.02N_{2}+0.26NO_{3}^{-}+2H_{2}O,\ (6)\\ NH_{3}+0.85O_{2}\rightarrow 0.11NO_{3}^{-}\\ +0.44N_{2}+0.14H^{+}+1.43H_{2}O,\ (7)\\ \end{array}$ 

Therefore,  $NO_3^{-}N$  concentration is greater than  $NH_4^+$ -N. Meanwhile,  $H^+$  is produced in this process. This phenomenon leads to the pH of dew being lower than that of surface water and rain. Maria noticed that the concentration of nitrite strongly correlates with the pH of dew [20].  $NH_4^+$ -N and  $NO_3^-$ -N concentrations may have a relationship with pH. In order to assess the nutrient concentrations in dew and to compare them with rain, the  $NH_4^+$ -N,  $NO_3^-$ -N and P concentrations were analyzed (Fig. 2). It was found that the  $NO_3^-$ -N concentration is significantly

higher than that of  $NH_4^+$ -N and P (P<0.05) in dew. The trend of  $NH_4^+$ -N,  $NO_3^-$ -N and P concentrations in dew and rain is fluctuating and irregular.

Ammonia is oxidized to nitrite by ammoniaoxidizing bacteria, and nitrite is further oxidized to nitrate by nitrite-oxidizing bacteria. The concentration of nitrite is strongly correlated with the pH of dew.  $NH_4^+$ -N and  $NO_3^-$ -N concentrations may have a relationship with pH. Dew samples contained many suspended solids because of the method of collecting dew. The absorbability of P is weaker under the acidic condition. This fact will lead to increased P concentrations when the pH is less than 7.0. Moreover, under alkaline conditions,  $NH_4^+$ is prone to convert to  $NH_3$ , and the  $NH_4^+$ -N concentration declined with  $NH_3$  diffusion. Therefore,  $NH_4^+$ -N condensation was higher under acidic conditions. Although through statistical analysis, P and  $NH_4^+$ -N condensations did not correlate with pH (*P*>0.05), as presented in Fig. 3, P and  $NH_4^+$ -N condensations increased markedly on 25 July and 8 August with a lower pH. The pH can affect P and  $NH_4^+$ -N condensations to some extent.



Fig. 2. Monthly variation of NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and P concentrations in dew and rain in 2010 in the Sanjiang Plain.



**Fig. 3.** Variation of pH and NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and P concentrations of wetland dew in 2010 in the Sanjiang Plain.



**Fig. 4.** Average concentrations (in ppb) of major metals in dew, rain, and surface water from 2008 to 2012 in the Sanjiang Plain.



Fig.5 Variation of dewfall, *LAI* and dew intensity of wetland.

#### Dew and rain

As shown in Fig. 2, K, Ca, Na, Mg, Mn, Fe and Zn concentrations in dew and surface water are significantly higher than those in rain (P < 0.05). Therefore, leaf dew can offer more nutrients to plant than rain. Similar results have been reported in south-western Morocco [22], Santiago City, Chile [20], and Amman, Jordan [23], where the concentrations of chemical species in dew were much higher than in rainwater. For instance, the concentrations of K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and  $SO_4^{2-}$  in dew were 6-9 times as much as in the rain in north-central India [3]. The high values in dew may be due to the dry deposition on a wet surface [22] and the variations in the composition of high altitude (cloud level) and low altitude (ground level) aerosols and gases, to which dew and rain are exposed [24].

## Deposition amount

Fig. 5 presents the daily dew intensity and the monthly dewfall. The concentration and the deposition of  $NH_4^+$ -N,  $NO_3^-$ -N and  $PO_4^{3^-}$ -P in dew are displayed in Table 3. Because part of N in dew was from NH<sub>3</sub> diffusion, the concentration of N was dependent on the amount in surface water. However, it was hard to collect the dew during wetland plant shoot. Therefore, the deposition of  $NH_4^+$ -N and  $NO_3^-$ -N of dew which was calculated, was below the real value. Table 3 sketches the deposition amount of  $NH_4^+$ -N,  $NO_3^-$ -N and  $PO_4^{3^-}$ -P from July to October 2010 in wetland dew as 0.065, 0.14 and 0.007 kg/ha, respectively.

**Table 3.** Concentration and deposition of  $NH_4^+$ -N,  $NO_3^-$ -N and P of wetland dew

Concentration(mg/L)			Deposition(kg/ha)		
NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	Р	NH4 <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	Р
0.37	0.82	0.14	0.065	0.14	0.007

Timing of applying foliar fertilizer

The foliar fertilizer should be applied from 15:00

to 17:00 in a fine afternoon. From 5:00 to 8:00, the dewdrops are still clinging on the wetland and the foliar fertilizer would drop down easily. From 8:00 to 14:00, the sunshine is intense. The nutrients in the foliar fertilizer decrease because of  $NH_3$  diffusion if this part of N does not return to the farmland ecosystem with rain, but as an input to river. This phenomenon accelerates the environment pollution. If the foliar fertilizer is applied from 15:00 to 17:00, the diffuse  $NH_3$  would return to the leave with the condensed vapour in the night. Therefore, foliar fertilizer spayed in this period can cling on the leave more tightly. Besides, the efficiency of the fertilizer will improve and avoid polluting environment.

### Advantage of dew

The research revealed that grain yield can improve when foliar fertilizer is used over time. The NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and PO<sub>4</sub><sup>3-</sup>-P in the fertilizer cannot be ignored. Compared to foliar fertilizer, on one hand, dew does not cost money or manpower. On the other hand, the foliar fertilizer should be sprayed on both sides of the leaves, because the effect will be more obvious when fertilizer is sprayed on the underside of leaves. The foliar fertilizer was not sprayed on the back side of leaves, in fact. Dew naturally condenses on both sides of the leaves and is more efficient. If the foliar fertilizer concentration is high, it will not be taken up by the plant and could even burn or damage the leaves. The low concentration of nutrients in the dew can be taken up by the plant more efficiently. In a word, dew is a natural and potential fertilizer, and it is safe, efficient and convenient.

## CONCLUISIONS

The mean pH of Carex lasiocarpa dew was 6.41 and no acid dew occurred in the research area. The metals in Carex lasiocarpa dew were abundant. NO<sub>3</sub><sup>-</sup>-N concentration in the dew was significantly higheer than that of NH4<sup>+</sup>-N and P. Nutrient elements and trace elements were detected in the dew. The metals in the dry bulk deposition were the main sources of metals in dew. The contents of K, Ca, Na, Mg, Mn, Fe, Zn in Carex lasiocarpa dew were obviously higher than those in rain (P < 0.05) which demonstrated that dew can offer more nutrient elements than rain. The trace amounts of Pb, Ba, Se, As, Co, Cr, Cu in Carex lasiocarpa dew implied that there is no significant pollution by automobile exhaust, coal combustion or industry in this area. The deposition of NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and PO<sub>4</sub><sup>3-</sup>-P of dew was 0.065, 0.14 and 0.007 kg/ha from July to October, respectively. Dew is a crucial input for nutrient cycling of farmland ecosystems. With dew acting as a sort of surfactant adhering nutrients to the leaves, recognition of dew as a factor in nutrient uptake is important. The quantity of nutrients evaporating with the dew each morning seems to be an interesting question to be dealt with in further research.

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# ХИМИЧЕН АНАЛИЗ НА МЕТАЛИ И НЕОБХОДИМИ НУТРИЕНТИ ПРИ РОСА ВЪВ ВЛАЖНИ ЗОНИ

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#### (Резюме)

Изследвани са екологичната ефективност на росата и състоянието на въздуха при повърхностния слой над влажната зона в равнината Санджиянг. Изследвани са pH, концентрациите на 25 метала(вкл.К, Na, Ca, Mg и др.) и необходими нутриенти – амониев азот (NH4+-N), нитратен азот (NO3-N) и фосфати (P) в росата. Събирана е росата върху*Carexlasiocarpa*от средата на м. юли до средата на м. септември от 2008 до 2012 г.Резултатите показват, че средната стойност на pH за росата на Carexlasiocarpa е била 6.41, като роса с кисела реакция не е била наблюдавана през изследвания период. Поради това росата не може да навреди на листата на растението.Росата върху Carexlasiocarpaсъдържа йони на различни метали, които предоставят хранителни съставки за растението. Елементите в сухите отлагания са от същия произход, както и в росата. Съдържанието на основните метали (K, Ca, Na, Mg, Mn, Fe, Zn)в росата на Carexlasiocarpae по-шисоко, отколкото в дъждовните капки (P<0.05).Следите отРb, Ba, Se, As, Co, Cr, Cu в росата на Carexlasio carpa показват, че няма значимо замърсяване от автомобилни газове, изгаряне на въглища или от промишлени източници.Отлаганите количества от NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N и PO<sub>4</sub><sup>3-</sup>-P от юли до октомври в росата са били съответно 0.065, 0.14и 0.007 kg/ha.Освен това росата кондензира и по двете повърхности на листата и мове да се асимилира ефективно. Затова азотът (N) и фосфорът (Р) в росата на влажните зони са друг хранителен източник за растенията.Росата е важен способ за пренасянето на хранителни вещества във влавните зони. Освен това росата може да разкрива степента на замъррсяване на въздуха, поради което важно да се следи химическия й състав.

Анализът на съдържанието на метални йони в росата е прост и полезен метод за определяне на състоянието на повърхността. Това дава основа за преденка за замърсяването и качеството на въздуха.