Response to Discussion of "Atmospheric deposition as an important nitrogen load to a typical agro-ecosystem in the Huang-Huai-Hai Plain" by Huang et al. (2016)

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We thank Pan *et al.* (2016) for their comments and discussions to our work on the nitrogen (N) deposition in a typical agro-ecosystem in the Huang-Huai-Hai Plain using the water surrogate surface method (Huang *et al.*, 2016). We appreciate this opportunity to respond to their comments, and we hope it will further clarify the findings in our work as well.

To summarize, Pan *et al.* (2016) raised concerns about that the differences in the amount and species of N deposition between our results and the similar reports in the North China Plain (Pan *et al.*, 2012; Xu *et al.*, 2015) probably due to the uncertainties of the method we used for deposition sampling. The results of our paper (Huang *et al.*, 2016), and of a preceding paper (Huang *et al.*, 2011) that describes the validation of water surrogate surface method, monthly and inter-annual variations of N deposition, and the influencing factors of their temporal variations in detail, indicate that the four-year (2008-2012) data collected by the water surrogate surface method could be a robust reference for nutrient management in this region. As evidenced by our

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responses below, we maintain our initial conclusion that the water surrogate surface method should be applicable in collecting N deposition samples in the agro-ecosystem under the tested conditions. Generally, the major points raised by Pan *et al.* (2016) can be addressed as follows:

1. Location of the sampling sites

The sampling site in the present study is located in the remote rural area of Huang-Huai-Hai Plain (114°240' E, 35°00' N), hundreds of kilometers far away from the referred studies in Quzhou and Yucheng in North China Plain (NCP) (Pan *et al.*, 2012; Xu *et al.*, 2015), so we can imagine the spatial variations of N depositions. It should be noted that the annual N deposition amounts demonstrated highly spatial variation, ranging from 28.5 to 100.4 kg N ha⁻¹ yr⁻¹ even within the region of Northern China (Pan *et al.*, 2012).

2. Sampling method

As indicated by Pan *et al.* (2016), the method we used in N deposition sampling is suitable to monitor the atmospheric N input into long-term waterlogged surfaces, such as water bodies, wetlands and paddy fields. However, we cannot agree that it is unsuitable for dry land without sustained waterlogged conditions. In our previously published paper related to method validation (Huang *et al.*, 2011), we discussed the effect of surface conditions on sampling results. Although the physical, biological, and chemical properties of water surface were totally different from that of the farmland, the deposition velocities of major gaseous N compounds on water surface were generally similar to those on the farmland (Wesely and Hicks, 2000; Zhang *et al.*, 2004). Samplers with distilled water as the surrogate surface have been tested to be effective in the collection of dry deposition of water-soluble gaseous or aerosol species and coarse and fine particles (Yi *et al.*, 1997; Shahin *et al.*, 2002; Raymond *et al.*, 2004). Therefore, distilled water could be a promising surrogate surface for N deposition sampling.

In order to optimize the sampling conditions, we carried out systematic field trials and lab analysis to test the effects of sampling intervals and water volumes on potential N losses and transformation and thus the deposition results (Huang *et al.*, 2011). To minimize the possible effects of water evaporation and N transformation (i.e. nitrification, ammonia volatilization and denitrification) on N deposition sampling, appropriate water volumes and sampling intervals under different weather conditions and cropping seasons were determined by a series of field experiments. No biocide was used for sample conservation because of limited conversion of organic N to mineral N under such sampling and analyzing conditions (Chen and Mulder, 2007; Huang *et al.*, 2011). In addition, we estimated N deposition from the N balance of a long-term fertilization experiment (commenced from 1983) in the Field Station to validate the direct measurement using the water surrogate surface method. The results of N deposition from plots receiving no N fertilizers were in consistent with the direct measurement during the sampling period (Huang *et al.*, 2011). Therefore, the method we used was reliable for N deposition sampling in the current study.

Considerable attempts have been made to qualify dry N deposition (Wesely and Hicks, 2000; Liu *et al.*, 2011), but respective uncertainties of different sampling methods hampered the measuring results. Till now, there are no standard protocols for N deposition worldwide mainly due to the uncertainties of different sampling methods.

3. Magnitude of N deposition

Atmospheric N deposition greatly depends on the reactive N sources including their species and concentrations in the air. The results reported by Pan *et al.* (2012) and Xu *et al.* (2015) in neighboring agroecosystems were higher than our current studies, mainly due to their vicinity to megacities like Beijing, Shijiazhuang and Zhengzhou. With great impacts of high vehicle retentions, large livestock farms, or fossil-fueled industries in the surrounding areas, the atmospheric N deposition would be higher in these monitoring sites.

We also monitored ammonia volatilization and denitrification losses in the ambient

croplands around the sampling sites (Huang *et al.*, 2015), and the N deposition results agreed well with the gaseous N losses. Moreover, atmospheric N deposition estimated via N uptake by crops without any N fertilizers showed substantial annual variations (Huang *et al.*, 2011).

We have specified that direct foliar uptake of N compounds was excluded from the current study, and this portion of N deposition could be derived from the difference ($5.27 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in 2009) between N uptake by crops receiving no N fertilizers and total N deposition (Huang *et al.*, 2011), accounting for 9.4% of the estimated annual N deposition. Due to the influences of plant species, leaf surface and growth status, direct foliar uptake of N compounds is highly variable (He *et al.*, 2007).

Auto-samplers based on the water surrogate surface method were deployed in three urban areas of Chongqing to collect N deposition samples from October 2012 to September 2014. The results (Table 1) showed a higher value of annual N deposition ($> 100 \text{ kg N ha}^{-1}$) in urban Chongqing than that in a remote rural area of Huang-Huai-Hai Plain (Huang *et al.*, 2016). Main reactive N sources, such as high vehicle retentions, intensive infrastructure construction, and fossil-fueled heavy industries, were responsible for the high N deposition in Chongqing.

Table 1. Nitrogen deposition and its composition monitored by auto-samplers based on surrogate water surface method in urban areas of Chongqing from October 2012 to September 2014. Wet N deposition (Wet) and Dry N deposition (Dry) were automatically separated by rain sensors (0.02 mm) and sampled following the protocols described by Huang *et al.* (2011). Water samples were ultrasound oscillated for 30 min (25 °C) and filtered through 0.45 μm fiber membranes. Nitrate-N (NO_3^- -N), Nitrite-N (NO_2^- -N), and Ammonium-N (NH_4^+ -N) were measured by ion chromatograph (Dionex, ICS 1100). Total N and organic N (O-N) was determined by the methods described by Huang *et al.* (2011).

	2012-2013	Percentage	2013-2014	Percentage
	(kg N hm^{-2})	(%)	(kg N hm^{-2})	(%)
Wet	62.97	59.0	57.96	56.3
Dry	43.72	41.0	44.95	43.7

Total	106.69	100.0	102.91	100.0
NO ₃ ⁻ -N	53.05	49.7	58.68	57.0
NO ₂ ⁻ -N	3.41	3.2	3.58	3.5
NH ₄ ⁺ -N	5.58	5.2	8.04	7.8
O-N	44.65	41.9	32.61	31.7
Total	106.69	100.0	102.91	100.0

4. Composition of N deposition

We are grateful that Pan *et al.* (2016) have acknowledged that uncertainties widely existed in the dry deposition estimate among different sampling methods and monitoring sites. Furthermore, Pan *et al.* (2016) doubted our results of wet N deposition because of the difference in amount between different monitoring sites. As the sampling of wet N deposition species is not so challenging and uncertain as compared with dry species, the most probable reason for the relatively small amount of wet inorganic N deposition in our case (6.4-16.1 kg N ha⁻¹ yr⁻¹), in contrast to the results reported in agricultural areas of Shandong (24.8 kg N ha⁻¹ yr⁻¹) and Hebei (22.1 kg N ha⁻¹ yr⁻¹) during 2008-2010 (Pan *et al.*, 2012), is the relatively low concentrations of reactive N species for deposition in our present sampling site. In recent years, field management practices, such as improved fertilization techniques and balanced rates, deep placement of fertilizers, and irrigation right after fertilization, have been widely applied to mitigate N losses during crop production in the surrounding regions of our sampling site (Huang *et al.*, 2015), which significantly reduced the concentrations of reactive N species for deposition in such an agriculture-dominated agro-ecosystem.

Shen *et al.* (2009) investigated dry N deposition at two sites in the North China Plain, and they discussed and estimated a very large proportion of dry deposition in their sampling sites as well. Pan *et al.* (2012) also reported that dry N deposition accounted for 60% of the annual total deposition, which was parallel with our published results on the composition of N deposition (Huang *et al.*, 2016).

For our current sampling method, if rains occurred in the night without any predictable signs, the manual discrimination of wet and dry deposition was not so strict as designed (Huang *et al.*, 2011). Auto-samplers with a water surrogate surface and rain sensors was designed for the collection of N deposition based on the manual sampling protocols, and such measures could strictly differentiate the wet deposition and dry deposition (Huang *et al.*, 2016), which addressed the uncertainty from the manual discrimination of wet and dry deposition (Fig. 1).

Fig. 1 Atmospheric N deposition as monitored by auto-samples in Chongqing.

5. Species of N deposition

The ratio of ammonium to nitrate greatly depends on the sampling locations and dominant reactive N sources. There are two plausible explanations, which could explain the difference in the ratio of ammonium to nitrate between the current study and the results observed at five agricultural sites in NCP (Xu *et al.*, 2015). On the one hand, the sources of ammonium deposition mostly originated from ammonia volatilization in the current agriculture-dominated sampling site. On the other hand, nitrate deposition relied very little on the NO_x fluxes because of their small proportion in N losses from the rural farmlands (Huang *et al.*, 2015) and almost free of urban interference and point source pollution, such as large-sized livestock breeding farms and heavy pollutant-emitting manufactures in a 50 km radius of the sampling site

(Huang *et al.*, 2016). The nearest megacity, Zhengzhou, is 130 km from our sampling site. Therefore, the influence of fossil-fueled industries and vehicle exhausts on the N deposition was much lower than that in the urban areas.

Fig. 2 Species of N deposition in three urban areas of Chongqing from October 2012 to September 2014.

In the urban areas of Chongqing, the composition and species of N deposition (Fig.2) were quite different from those in the rural areas of Huang-Huai-Hai Plain (Huang *et al.*, 2016). NO₃⁻-N was the dominant species in N deposition, and the proportion of NO₃⁻-N in total deposition was significantly higher than that for NH₄⁺-N (Table 1).

The statement in our paper, “even with the impact of N fertilization in the agriculture-dominated sites of north and east China, nitrate was the dominant species in N deposition”, at first reflection may be interpreted ambiguously from the single sentence, but from the context, we clearly specified that “In the agriculture-dominated sites of north and east China, nitrate was reported to be the dominant species in atmospheric N deposition”, due to their vicinity with megacities, such as Beijing, Shijiazhuang (Liu *et al.*, 2011), or point sources of N pollution, such as large livestock farms, or fossil-fueled industries (Yang *et al.*, 2010). We intended to find the differences between our current work and similar studies and tried to figure out the

possible underlying causes. Anyway, we are regretful to bring such unexpected misunderstandings from the expressions for the readers of our paper.

Finally, it should also be emphasized that results for N deposition, especially for the dry classes, varied significantly with different sampling methods, crop types and growth status, soil water regime, field management, et al. in the agro-ecosystem (Wesely and Hicks, 2000; He *et al.*, 2007). However, we need to provide more data collected by different methods and techniques as references to obtain reliable results due to the lack of standard protocols for N deposition sampling in such intensively managed agroecosystems.

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