Responses to reviewer #1 comments

Interactive comment on "A 12 year observation of water-soluble inorganic ions in TSP aerosols collected at a remote marine location in the western North Pacific: an outflow region of Asian dust" by S. K. R. Boreddy and K. Kawamura

Anonymous Referee #1
Received and published: 13 April 2015

This is an interesting manuscript presenting 12 years of inorganics ions (TSP) measured at the remote location of Chichijima Island (western North Pacific) which I consider as suitable for publication in ACP after minor revisions.
Response: Thank you for the careful reading and valuable suggestions to improve the scientific content of our paper.

Main comments:

1) A comparison with similar measurements performed at other remote locations is missing. I suggest to add a short review of previous studies presenting inorganic ions aerosol measurements performed at other remote sites in order to compare them with the values reported in this manuscript. This kind of comparison could be interesting especially for the ratios (i.e. MSA/nss-SO_4^{2-});
Response: Based on the reviewer's comment, we added a short review on comparison of major inorganic ions over the North Pacific and results are summarized in Table 4. Thanks for the helpful suggestion.

Table 4. Mean concentrations of major ions at Chichijima Island from 2001-2012 and those at several other remote marine locations in the Pacific

Location (data set)	NO_3^-	nss-SO_4^{2-}	MSA^-	References
		Present study		
Chichijima (2001-2012)	0.58±0.07	2.12±0.42	0.02±0.00	
		Other remote marine locations		
Fanning Island (1981-86)	0.16±0.08	0.67±0.27	0.04±0.01	Savoie et al., (1989)
Nauru	0.16±0.09			Savoie et al., (1989)
Funafuti	0.10±0.07			Savoie et al., (1989)
American Samoa (1983-87)	0.11±0.05	0.34±0.14	0.02±0.01	Savoie et al., (1989)
Rarotonga	0.12±0.08			Savoie et al., (1989)
Midway (1981-2000)	0.29±0.16	0.56±0.45	0.02±0.01	Prospero and Savoie (2003)
N. Caledonia (1983-85)		0.42	0.02	Savoie and Prospero (1989)

We added the following sentences in the revised manuscript. Please see lines 517-546 and Table 4.

"The mean concentrations of NO_3^-, nss-SO_4^{2-}, and MSA^- at Chichijima during the period 2001-2012 are compared with those from several other remote marine sites in the Pacific as summarized in Table 4. Results from the Chichijima data show that mean concentrations of NO_3^- and nss-SO_4^{2-} are higher than those from other remote marine locations. The mean concentration of nitrate (0.58 μgm^{-3}) at Chichijima is more than 4 times higher than those from other remote marine sites (Fanning, Nauru, Funafuti, American Samoa, Rarotonga, and N. Caledonia) and more than twice higher than those from Midway. Whereas concentrations of nss-sulfate at Chichijima (2.12 μgm^{-3}) is 4 times higher than at Fanning, Midway, and N. Caledonia and more than 7 times higher than those from American Samoa and Norfolk. The mean concentration of MSA^- (0.02 μgm^{-3}) at Chichijima is comparable to those from other remote marine locations (see Table 4). These results suggest a similarity to that of the oceanic biological productivity in the North Pacific. In contrast, the mean MSA^- concentration at Fanning in the equatorial Pacific is about twice higher (0.044 μgm^{-3}) than Chichijima. Savoie and Prospero (1989) have found high biological productivity associated with the upwelling of nutrient rich water near the equatorial divergence with mean DMS levels of 3.8 nmol/l in the surface ocean. They also documented that in the oligotrophic regions, the mean concentrations of MSA in the air and DMS in the seawater vary over the narrow range from 0.02-0.03 μgm^{-3} and 1.4-1.7 nmol/l, respectively.

The mean concentration ratio (MSA^-/nss-SO_4^{2-}) at Chichijima is 0.02, which is lower than those of other remote marine locations by a factor of 5-7, indicating a substantial impact from continentally derived sulfate. At the tropical stations, American Samoa and Fanning Islands, MSA/nss-SO_4^{2-} ratios exhibit similar values with mean ratios of 0.07 and 0.06, respectively, indicating a cleanest locations regarding to the continental inputs (Arimoto et al., 1987). This result further supports our assumption that Asian dusts can act as an important source of nutrients that stimulate the DMS production in the ocean surface followed the emission to the marine atmosphere over the western North Pacific. However, it is rather less important that yield of MSA from DMS oxidation is enhanced as a function of temperature (Hyens et al., 1996)."

2) Some Figures need to be re-edited: y-axis missing in Fig. 2 and 3; Fig. 5: S+/S- is presented in the Figure 5, but S-/S+ is described in the text; Figure 6h;

Response: We re-edited the two figures. Please see Figures 2 and 3 in the revised manuscript and also see lines 232, 234, and 235.

3) Paragraph 3.8. : Here the possible relationship between MSA- and nss-Ca2+ is discussed comparing monthly averages. Are there any intense Ca episodes during the study period which can be related with variations in MSA? For example Ca episodes of few days accompanied by statistically significant variations in MSA?. This could help in identifying any MSA-nssCa2+ relationship.

Response: Following the referee's suggestion, we revisited the data of Ca and MSA during the study period in which we found some relation in the variations of Ca and MSA. We added

few sentences in the revised MS. Please see Figure 12 and lines 498-515 in the revised manuscript. Thanks for the helpful suggestion.

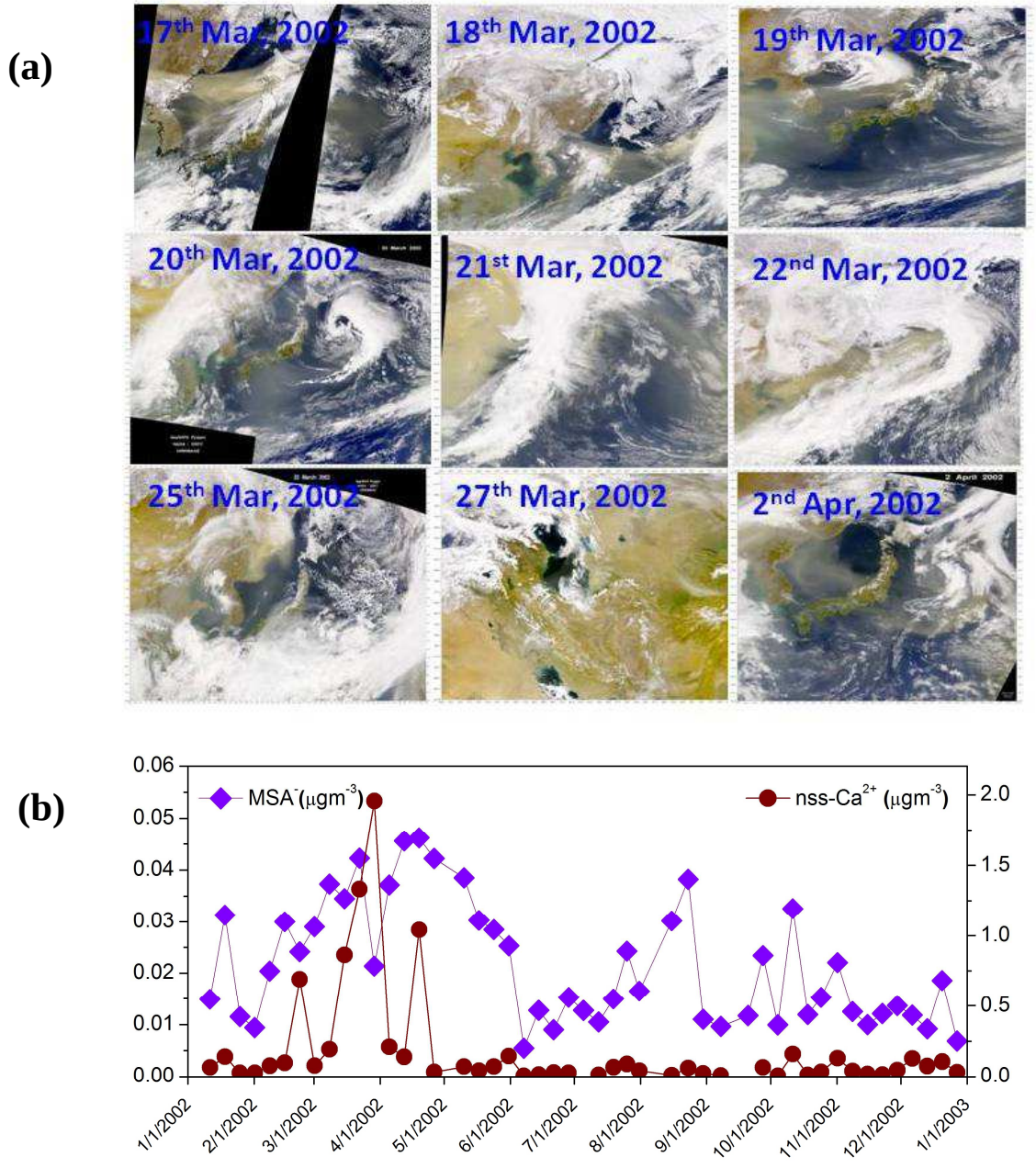

Figure 12. (a) The Sea-viewing Wide Field-of-view Sensor (SeaWiFS) images that captured the large Asian dust storm visible over the Sea of Japan and North Pacific Ocean during March 17-April 2, 2002, (b) temporal variations of MSA^- and nss-Ca^{2+} concentrations during 2002 over the western North Pacific. The black regions in Figure 12a are the gaps between consecutive SeaWiFS' viewing swaths and represent areas where no data were collected.

"To further clarify the relations between MSA^- and nss-Ca^{2+}, we examined the intense nss-Ca^{2+} episodes during the study period (March 2002), which can be related with variations

in MSA^- as shown in Figure 12 as a typical example. Figure 12a shows the SeaWiFS (Sea-viewing Wide Field-of-view Sensor, flying aboard Orbview-2) images, which captured the large Asian dust storms over the North Pacific during March 17-April 2, 2002. Dust storms originate in the deserts of North China and Mongolia. The East Asian dust storm appears to have diminished somewhat on March 20, 2002, as compared to previous days. However, there seemed a new batch of dust rising toward the left side of this image. This scene spans from eastern Asia across Japan and over the western North Pacific, where the dust was partly entrained by a low-pressure system. On the other hand, the possible variations of MSA^- concentrations related to the East Asian dusts are shown in Figure 12b. Interestingly, we found higher levels of MSA^- after the Asian dust deposition over the ocean surface. This evidence strongly reveals that Ca episodes supply the nutrients to significantly stimulate plankton blooms accompanied by statistically significant variations in MSA concentrations in the atmosphere few days after the episodes. This result also demonstrates that Asian dusts can act as an important source of macro and micro nutrient including iron for phytoplankton and thus sea-to-air emission of DMS over the western North Pacific."

4) Tables 1 and 2. Are the presented differences statistically significant between each pair of variables (seasons or year)? Please, clarify which differences are statistically significant.

Response: Considering the comment, we removed the result of t-test and applied new statistical approach for checking the annual and seasonal differences. The results are reported in Table 1 and Table 2. Please see Tables 1 and 2 in the revised manuscript.

5) The presence of any trend should be demonstrated by applying tests such as Mann-Kendall (for annual averages) or Theil-Sen (also for monthly averages).

Response: Based on the reviewer's comment, we demonstrated annual and monthly trends using Mann-Kendall and Theil-Sen slope, respectively. The result of these tests are reported in Tables 1 and 2 in the revised manuscript and also given below for the reviewer reference.

"Monthly or seasonal mean concentrations of major inorganic ions (mean±SD) during 2001-2012 at Chichijima Island in the western North Pacific are reported in Table 1. The presence of monthly averaged trend is demonstrated by Theil-Sen Slope test (Sen, 1968; Theil, 1950). The results show that these differences are statistically significant with Theil-Sen slope values of less than 0.01."

"Annual mean concentrations of major inorganic ions (mean±SD) for different seasons during 2001-2012 are reported in Table 2. The presence of annual averages trend is demonstrated by Mann-Kendall nonparametric test for each season during study period and the results are also reported in Table 2. The Mann–Kendall trend test (Mann, 1945 and Kendall, 1975) is one of the widely used non-parametric tests to detect significant trends in time series. In this test, the absolute value of Z is compared to the standard normal cumulative distribution to define if there is a trend or not at the selected level α (=0.01) of significance. A positive (negative) value of Z indicates an upward (downward) trend."

Please see lines 263-267 and 319-326 in the revised manuscript.

Responses to reviewer #2 comments

Anonymous Referee #2
Received and published: 13 April 2015

General Comments

The manuscript explores the chemical composition of water-soluble inorganic ion over a remote marine atmosphere in the western North Pacific. TSP aerosol samples are collected from Chichijima Island and analyzed for water-soluble ions such as Na+, NH4+, K+, Mg2+, Ca2+, Cl-, NO3-, SO42- and MSA-. The manuscript covers a 12-year observation and focuses on the impact of long range transport from East Asia on water-soluble ionic composition. Furthermore, the study identifies the decadal variability in nitrate, sulfate and nssK+ particularly considering anthropogenic emissions and biomass burning originating from East Asia. In this respect, it may be the interest of scientific community. Consequently I suggest acceptance of the manuscript. However, before that the manuscript should be revised.

Response: Thanks for the helpful comments on our manuscript, which improve the original scientific content.

Specific Comments

Title: I suggest modification of the title. Although the title implies that the water-soluble inorganic ions are of interest, the organic water-soluble methane sulfonic is also discussed in the text. For example, whole section (3.7) is dedicated to methane-sulfonic acid. It would be misleading to retain' inorganic' before ions. The discussion about the dust transport from the Asia is particularly limited (see comments below). Unlike the 'the title' (as it implies), the manuscript mainly focuses on the pollution transport from Asian continent. To illustrate, the impact of pollutants originating from Asia on the annual variability of chemical species is discussed in detail (in section 3.5). Thus, please modify the title according to the abovementioned statement.

Response: Based on the referee's suggestion, we modified the title by deleting the term of "inorganic". Thanks for the helpful suggestion.

Experimental

2.1. Sampling site and aerosol sampling: Please give more information about the sampling. Was the aerosol sampling carried out daily or weekly? What was the degree of blank contributions to water-soluble ions?

Response: Aerosol sampling was carried out on a weekly basis. Contributions from the field blanks varied between 0-8% and 0-2% of real samples for anions and cations, respectively, during the sampling period. These points have already been noted in the manuscript. Please see lines 122 and 147-149 in the revised manuscript.

2.2. Analysis of chemical species: In order to determine the concentrations of the water-soluble ions a punch of 2mm diameter from each filter was extracted. Was a punch of 2mm diameter representative for the collected aerosol sample when one considers the area of the filter? Please specify this issue.

Response: It seems that the reviewer might have confused with used filter area. We used a punch of 20 mm in diameter (not 2 mm) to determine the concentrations of the water-soluble ions. Please see line 133 in the revised manuscript.

Results and Discussion

3.1. Evaluation of Non Sea Salt Analysis: Please move this section to Experimental section, since this section simply defined the calculation of non-salt fractions.

Response: Following referee's suggestion, we moved this section to Experimental section. Please see section 2.5 in the revised manuscript.

3.3. Temporal Variation of Major Inorganic Species, MSA-/nssSO42- and S+/S-
3.4. Monthly Variations of Major Inorganic Species, MSA-/nssSO42-:

Please supply a table that shows relationship between the water-soluble species. Such an application would be useful to determine the (a) similar sources, (b) similar generation and/or removal mechanism and/or (c) similar transport patterns.

(Page 10, lines 286-289): It is claimed that drastic increase in the concentration of nssCa during spring was associated with dust transport originated from Asian continent. However, this claim should be supported by using dust episode. It would be useful to identify at least one dust event and discuss the episode in detail by applying ground measurements, back trajectories and satellite images.

Response: Regarding to the relation between water-soluble species, we added correlation coefficient matrix in the revised manuscript. Concerning the dust event, we discussed Ca episodes during the study period (in the year 2002) which can be related with variations in MSA. Please see lines 492-508 in the revised manuscript.

3.6. Percent Contribution of Major Ions to Total WSIM

The depletion of the Cl was ascribed to reaction between the alkaline sea-salt particles and the acidic species namely, sulfuric acid, nitric acid and oxalic acid (page 12, lines 349-367). Considering the written text, it is not clear which acid or acids responsible for the depletion of Cl. This claim should be clarified. For instance, the relationship between Cl depletion and acid species might be useful to address this issue.

Response: Following referee's suggestion, we have discussed the relations between chloride depletion and acidic species as given below.

"In order to investigate which acids are responsible for the depletion of chloride, we performed regression analysis between the Cl^-/Na^+ mass ratio and acidic species, nss-SO_4^{2-}, NO_3^-, MSA^- and oxalic acid for different seasons during 2001-2012 as shown in Figure 10. The regression analysis was verified by *t*-test. The results show that the differences between Cl^-/Na^+ mass ratio and acidic species are statistically significant with two tailed P value <

0.001 for each season during the study period. For all seasons, nss-SO_4^{2-} moderately correlated with Cl^-/Na^+ mass ratios with negative correlation coefficients (R^2) of 0.38, 0.29, 0.35 and 0.45 for winter, spring, summer, and autumn, respectively, whereas NO_3^- moderately correlated during winter (R^2= -0.30), weakly correlated in autumn (R^2= -0.22) and has no correlation in spring and summer. These results suggest that sulfate has more responsibility for the chloride depletion than nitrate. On the other hand, the biogenic tracer, MSA^-, moderately correlated during summer (R^2= -0.29) and has weak correlation in winter and spring. Freshly emitted MSA and H_2SO_4 (from oceanic biological productivity associated with the upwelling of nutrient rich water) are also little contribute to the chloride depletion by coating with sea salts, especially in summer. Interestingly, during spring, the Cl^-/Na^+ mass ratio did not correlate with NO_3^-, MSA^- but weakly correlated with nss-SO_4^{2-}. These results suggest that some other organic acids such as oxalic acid (because of its high abundance during spring) are responsible for the chloride depletion during spring. In fact, we found that oxalic acid significantly correlate with the chlorine loss in winter (R^2=-0.30), spring (-0.28) and autumn (-0.36) (see Figure 10d). These results confirm that oxalic acid plays an important role in a chlorine loss."

The above lines are briefly noted in the revised manuscript. Please see lines 419-439.

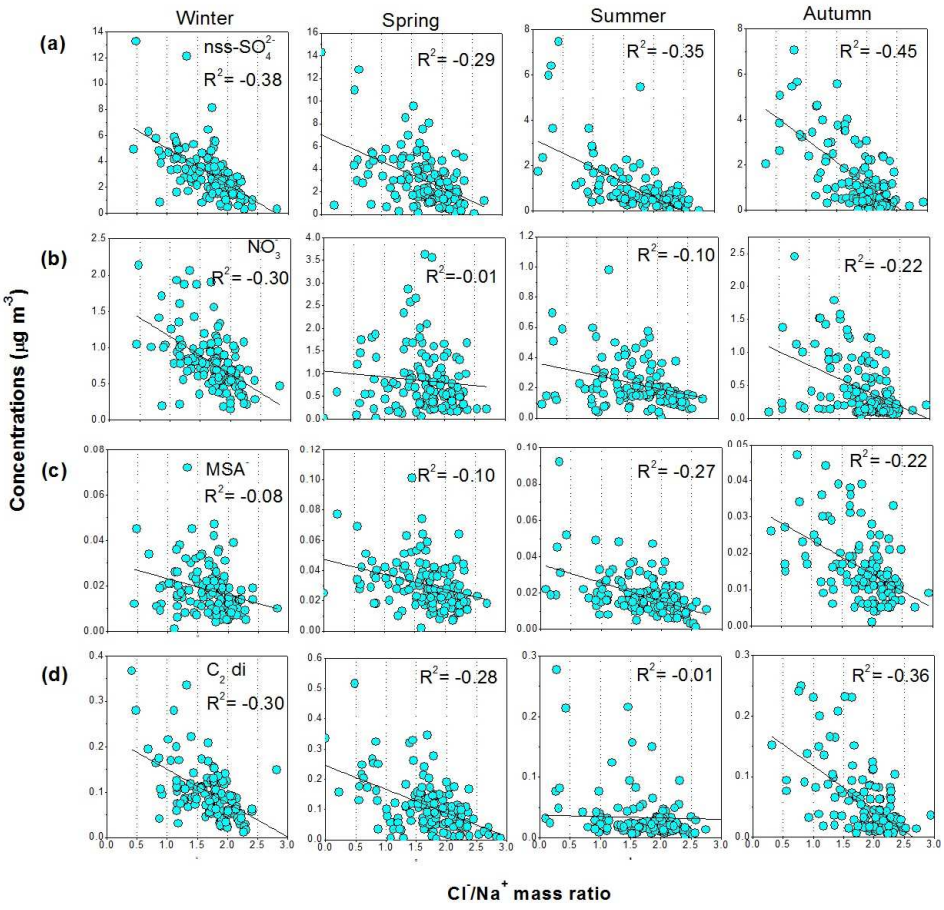

Figure 10. Relations between chloride depletion (Cl^-/Na^+ mass ratio) and acidic species (a) nss-SO_4^{2-}, (b) NO_3^-, (c) MSA^- and (d) oxalic acid (C_2di) for different seasons over the western North Pacific.