Deep-Sea Research II 97 (2013) 43–50

Contents lists available at ScienceDirect

Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Concentration, solubility and deposition flux of atmospheric particulate nutrients over the Yellow Sea

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ARTICLE INFO

Available online 20 May 2013

Keywords:
Asian dust
Atmospheric deposition
Nitrogen
Soluble iron
Yellow Sea

ABSTRACT

Satellite images showed that two large dust storms swept over the Yellow Sea from 31 Mach to 1 April 2007; both were accompanied by precipitation. Three to four days after the dust episodes, blooms occurred in the Yellow Sea. As an important and potential controlling factor of the bloom, nutrients in the total suspended particle (TSP) and size-segregated particle samples during the cruise campaign were measured and their atmospheric deposition fluxes of nutrients are reported in this paper. Concentrations of total P and TIN (NH_4^+, NO_2^- and NO_3^-) in TSP varied from 0.01 to 1.05 μg m^{-3}, and from 1.21 to 22.28 μg m^{-3}, with the maximum occurring concurrently with the dust storm events. In addition, the measured solubility of Fe in these particles varied from 1.0 to 20.1%, while it ranged from 0.8 to 15% for Al. The total deposition fluxes of Asian dust as well as the contained nutrients were estimated on the basis of an episodic increment of the measured concentration of dissolved Al in the surface ocean during the dust events. The estimated fluxes of atmospheric deposition of soluble Fe, P and inorganic nitrogen over the Yellow Sea during the dust episodes were 42.5 ± 10.9, 10.3 ± 2.6 and 772.0 ± 198.0 mg m^{-2}, respectively. The estimated fluxes of nutrients via dry atmospheric deposition accounted for only ~2% of the total fluxes. The deposition fluxes of particulate Fe and P during the two dust storm events associated with precipitation were about 500–1000 times of that daily averaged flux during non-dust days, indicating the importance of the episodic inputs to the annual budget of these metals deposited into the ocean.

1. Introduction

In the last decade, much attention has been paid to the impact of dust deposition on oceanic biological activity since dust deposition could provide micronutrient and/or trace metals (e.g. iron) to the ocean, enhancing the phytoplankton growth and primary productivity (Boyd et al., 1998; Bishop et al., 2002; Gabric et al., 2002; Yuan and Zhang, 2006; Cassar et al., 2007; Jo et al., 2007; Meskhidze et al., 2007; Mackie et al., 2008; Hung et al., 2009). Bishop et al. (2002) observed a doubling of biomass in the mixed layer in the subarctic North Pacific near Station PAPA (145°W, 50°N) after the passage of a dust storm in April 2001, and provided evidence of biotic response to natural iron fertilization associated with the input of dust particles. Natural iron fertilization was also reported at the oligotrophic time series station ESTOC (29°11′N, 15° 27′W) by Neuer et al. (2004). Jo et al. (2007) reported that Asian dust events could initiate early spring bloom in the northern East/Japan Sea, especially when accompanied by precipitation. In situ bioassay incubation experiments with Fe enrichments significantly stimulated phytoplankton growth in the central Yellow Sea (Zou et al., 2000), suggesting that Fe could limits or co-limits productivity of at least some of the phytoplankton species in this region. In addition, we recently investigate the relative importance of various origins of nutrients in a spring biogenic bloom event in the central Yellow Sea and found that Asian dust input can provide bioavailable Fe far exceeding the demand of the bloom event and was the major supplies of N and P to support the growth of phytoplankton (Shi et al., 2012). Zhang et al. (2007) also proposed that atmospheric deposition was a major source of nutrients and micronutrients in the Yellow Sea, especially in the central Southern Yellow Sea, which is far away from the direct influence of rivers.

Due to the difficulties in capturing episodic dust storms and their subsequent biological response, study of the impact of dust

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http://dx.doi.org/10.1016/j.dsr2.2013.05.004

supply on ocean biota based on direct monitoring is rare (Young et al., 1991). In the spring of 2007, we made a direct observation of dust episodes along with a subsequent bloom event in the Yellow Sea. The bloom and its potential triggering mechanisms are studied in this special issue. This paper focused on the atmospheric deposition and the objectives include: (1) to characterize the nutrients in atmospheric particles; (2) to determine the solubility of the metals in the atmospheric particles; (3) to compare the relative contribution of the dry and wet atmospheric depositions to the fluxes of nutrients.

2. Methods

2.1. Sample collection

During the period from 31 March to 24 April, 2007, a cruise campaign was launched to study the biogenic bloom over the south Yellow Sea. The bad weather interrupted the campaign three times, i.e., from 8:00pm on 1 to 10:00am on 3 April, from 4:00am on 11 to 10:00am on 14 April and from 5:00pm on 17 to 1:00pm on 22 April. In the campaign, two high volume aerosol samplers (KC-1000, Qingdao Laoshan Elec. Inc., China) were set up on the front deck of the R/V "BeiDou" for collection of the total suspended particle (TSP) in the ambient air. In one KC-1000 sampler, Whatman 41 cellulose filters were used. The collected samples were used for trace metal analysis. Whatman QM-A quartz fiber filters which were pre-combusted for 4 h at 500 °C in a muffle furnace were installed in another KC-1000 sampler. The collected samples were used to determine inorganic ions and organic components. The sampling duration was 15–20 h and the flow rate was about 1.0 m^3 min^{-1}. In addition, 60–90 h size-segregated particle samples were collected on Pallflex fiber-film T60A20 80 mm filters using a 9-stages low-volume Anderson cascade impacter (AN-200, Sibata Co. Inc., Japan). The 50% aerodynamic cut-off diameters for stages 0–8 were >11 μm, 7.0–11 μm, 4.7–7.0 μm, 3.3–4.7 μm, 2.1–3.3 μm, 1.1–2.1 μm, 0.65–1.1 μm, 0.43–0.65 μm, and≤0.43 μm, respectively. The flow rate of the AN-200 was 28.3 L min^{-1}. To avoid contamination from the ship's exhaust, samples were collected only when the ship was sailing and the relative wind direction ranged from −90° to 90° of the bow. The cruise track is shown in Fig. 1.

The aerosol samples were stored in polyethylene bags and kept in a −80 °C refrigerator for land laboratory chemical analysis.

The temperature and salinity profiles in the water columns at the grid stations were measured using a Sea−Bird CTD 11plus. Discrete water samples for Al analysis were collected using 5-L Niskin bottles attached to the CTD rosette. The pre-cleaned 0.45 μm pore size cellulose filters were used to filter the water samples immediately after collection for chemical analysis as reported in Ren et al. (2011).

2.2. Sample analysis

2.2.1. Element analysis

The method of aerosol measurement for elements was referenced to Zhuang et al. (2001). Briefly, the sample filters were digested at 170 °C for 4 h in a high pressure Teflon digestion vessel with a 5 mL mixture of HNO_3, $HClO_4$, and HF (volume ratio 3:1:1). After digestion, the solutions were evaporated to nearly dryness at 60 °C, the residue was re-dissolved in 1 mL HCl and then diluted to 10 mL with deionized water. A total of 21 elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sr, Ti, V, Zn and S) were analyzed using a inductively coupled plasma spectroscopy and atomic emission spectroscopy (ICP-AES) (Model: ULTIMA, JOBIN-YVON Company, France). Moreover, procedural and field blanks were also analyzed. The averaged concentrations of total Fe, Al and P in the samples were 10–385 times, 12–210 times and 7–914 times higher than the corresponding field blank, respectively. The field blank has been deducted in the later analysis.

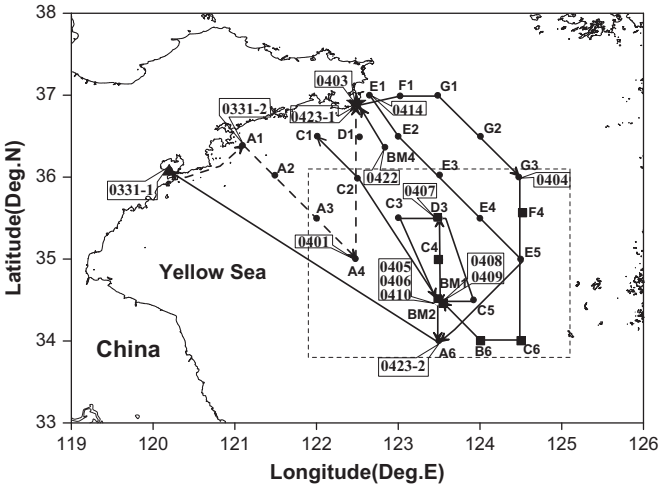

Fig. 1. Sampling locations and cruise track in the Yellow Sea, spring, 2007. The aerosol sample identifications in bold numbers (mmdd) indicate the starting dates of sampling for each sample and the arrows indicate the end location of sampling. The dash line cruise track indicates the observation during the Asian dust event. Seawater samples were collected at grid stations (labeled as letter and number, e.g. C2) and at a 25 h anchor station (BM1). Several repeated observations were conducted along section of A6-BM1-C4-D3 on 5–11 of April. The square symbols represent the stations in which the bloom was observed. The triangle and the star represent the anchorages of Jiaozhou Bay and Shi Island, respectively. In the dash line rectangle region, the aerosol index was 2-3.5 and the precipitation was 12.6–14.2 mm d^{-1} during the dust events associated with precipitation.

2.2.2. Soluble metal analysis

Water-soluble metals such as Fe^{3+} (Fe^{3+} or Fe^{3+}+Fe^{2+}) and Al^{3+} were extracted using an ammonium acetate leach at a pH of 4.7 on a reciprocating shaker for 1 h (Sarthou et al., 2003; Hsu et al., 2005). The extract was filtered through pre-cleaned 0.45 μm cellulose filters and then analyzed using ICP-AES. The pH chosen to simulate the dissolution processes affecting the aerosols occurred during rainwater scavenging. Zhang et al. (2000) reported the pH of rainwater collected from Qianliyan island within the Yellow Sea averaged 4.64 in 1997 and 4.76 in 1998, respectively. Under the acidic condition, iron dissolution rate could reach up the maximum potential to mimic the longer term dissolution (Boyd et al., 2010). The longer term dissolution reflected a slow but continuous dissolution of the aerosol iron during its residence time in the surface mixed layer (Boyd et al., 2010). Although the pH of seawater is much higher than the pH chosen, Boyd et al. (2010) proposed that the dissolution schemes adopted to quantify the magnitude of metal elements released from dust should take into account the longer term dissolution of these metals. They also summarized a few recent growing evidences of the longer term dissolution of metals and the longer term dissolution may be both biologically and photochemically mediated.

2.2.3. Ion analysis

A quarter of the filters was extracted by purified water (>18.2 MΩ cm) for 40 min of ultrasonic agitation at 0 °C. The extract was analyzed using a Dionex ICS-3000 ion chromatograph. An AS11 column was used to analyze anions (NO_3^-, NO_2^-, F^-, Cl^-, Br^-, SO_4^{2-}) while a CS12A column was used to determine cations (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}). The eluents used were 30 mmol L^{-1} KOH for the anions and 30 mmol L^{-1} methanesulfonic acid (MSA) for cations, respectively. In general at least one replicate injection