Estuarine, Coastal and Shelf Science 121-122 (2013) 1–7

Contents lists available at SciVerse ScienceDirect

Estuarine, Coastal and Shelf Science

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

Ionised silica in the estuary of a river as supply to seawater: Identification and ionization efficiency of silica species by FAB-MS

Miho Tanaka[a,*], Kazuya Takahashi[b]

[a] Tokyo University of Marine Science and Technology, Konan, Minato-ku, Tokyo 108-8477, Japan
[b] RIKEN, Hirosawa, Wako, Saitama 351-0198, Japan

ARTICLE INFO

Article history:
Received 6 May 2012
Accepted 11 February 2013
Available online 27 February 2013

Keywords:
FAB-MS
silica species
ionic form
river estuary
electrolyte

ABSTRACT

Measurement of the dissolution state of silicic acid is difficult. In river water, silica exists in particle form, but silica particles with a diameter of less than approximately 0.45 μm are considered as dissolved silica. In seawater, silica exists in two forms: ionic silica and particle silica. In this study, we focused on ionic silica. Using fast atom bombardment mass spectrometry (FAB-MS), the silica species in river water and seawater were detected as ionic forms. Ionic silica forms various chemical species in aquatic solutions, including the monomer ($[Si(OH)_3O^-]$) and dimer ($[Si_2(OH)_5O_2{}^-]$). The relative abundances of these species in aquatic solutions depend on the chemical and physical conditions. Silica species such as $[Si(OH)_2O_2Na]^-$ ($[monomer\text{-}Na^+]^-$), $[Si_2(OH)_5O_2]^-$ ($[dimer]^-$), $[Si_2(OH)_4O_3Na]^-$($[dimer\text{-}Na^+]^-$), $[Si_4(OH)_7O_5]^-$ ([cyclic tetramer]$^-$), $[Si_4(OH)_6O_6Na]^-$ ([cyclic tetramer-Na$^+$]$^-$), $[Si_4(OH)_9O_4]^-$ ([linear tetramer]$^-$) and $[Si_4(OH)_8O_5Na]^-$ ([linear tetramer-Na$^+$]$^-$) were directly observed by FAB-MS in river water and seawater. Some of these ionic silica species are expected to serve as "nutrients" for diatoms in seawater. Large silica particles are transported in river water, whereas in estuaries, a large amount of silica is precipitated and a small amount of silica is dissolved as ionic forms in sodium chloride solution. In river water, the concentration of silica was high, but the ionic silica species were hardly ionised by FAB-MS. In seawater, the concentration of silica was low, but the ionic silica species were well ionised. Thus, the ionization efficiency of silica species by FAB-MS indicates the type of silica species. The filtration process of silicic acid and the ionization of silicic acid to dissolve the silica species in seawater, which is an electrolyte (sodium chloride), occur in the estuary of a river. Thus, the estuary of a river plays an important role in the restructuring of silica from particle form to ionic form.

1. Introduction

Silicic acid is generally used to represent silicon oxide. Silicic acid is regarded as $Si(OH)_4$ in aquatic solutions in geochemical studies (Ning, 2002; Cornelis et al., 2011). It is well known that the silica in seawater is mainly supplied from river water in coastal regions. Silica is used as a "nutrient" by diatoms in seawater, and several studies on silica and diatom cell wall interactions have been reported (Kröger et al., 1994, 1999; Brabdriss et al., 1998; Poulsen and Kröger, 2004). River water plays an important role in the supply of silica to seawater. The silicon and oxygen isotopic distributions of marine diatoms have been studied (De La Rocha et al., 1997, 1998, 2000; Schmidt et al., 1997a,b). In these studies, changes in the silicon and oxygen isotopes with the biogenic concentration were observed, implying an effect of the marine environment. The identification of silica species is a key problem in elucidating the role and circulation of silica in seawater. Generally, silica is considered to be supplied to surface seawater from river water. Moreover, changes in the chemical forms of silica species during their passage from river water to seawater may be expected.

For the chemical speciation of silica, we have employed fast atomic bombardment mass spectrometry (FAB-MS) (Tanaka and Takahashi, 1999, 2000a,b,c, 2001, 2002, 2005, 2007; Tanaka et al., 2009). In these studies, the silica species in seawater were able to be observed directly by FAB-MS and the elucidation of the role of the estuary of a river in the formation of silicic acid has become possible.

Silica has been reported to form several types of complexes and chemical forms in solution, such as the monomer $[Si(OH)_3O]^-$, dimer $[Si_2(OH)_5O_2]^-$ and cyclic tetramer $[Si_4(OH)_7O_5]^-$, according to the results of ^{29}Si-NMR studies on samples containing high concentrations of silica of above 0.1 mol dm^{-3} (M) (Harris et al., 1981; Harris and Knight, 1983a,b). Moreover, the monomer, dimer, trimer,

* Corresponding author.
E-mail addresses: mihotnk@kaiyodai.ac.jp, mihotnk@annie.ne.jp (M. Tanaka).

0272-7714/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ecss.2013.02.010

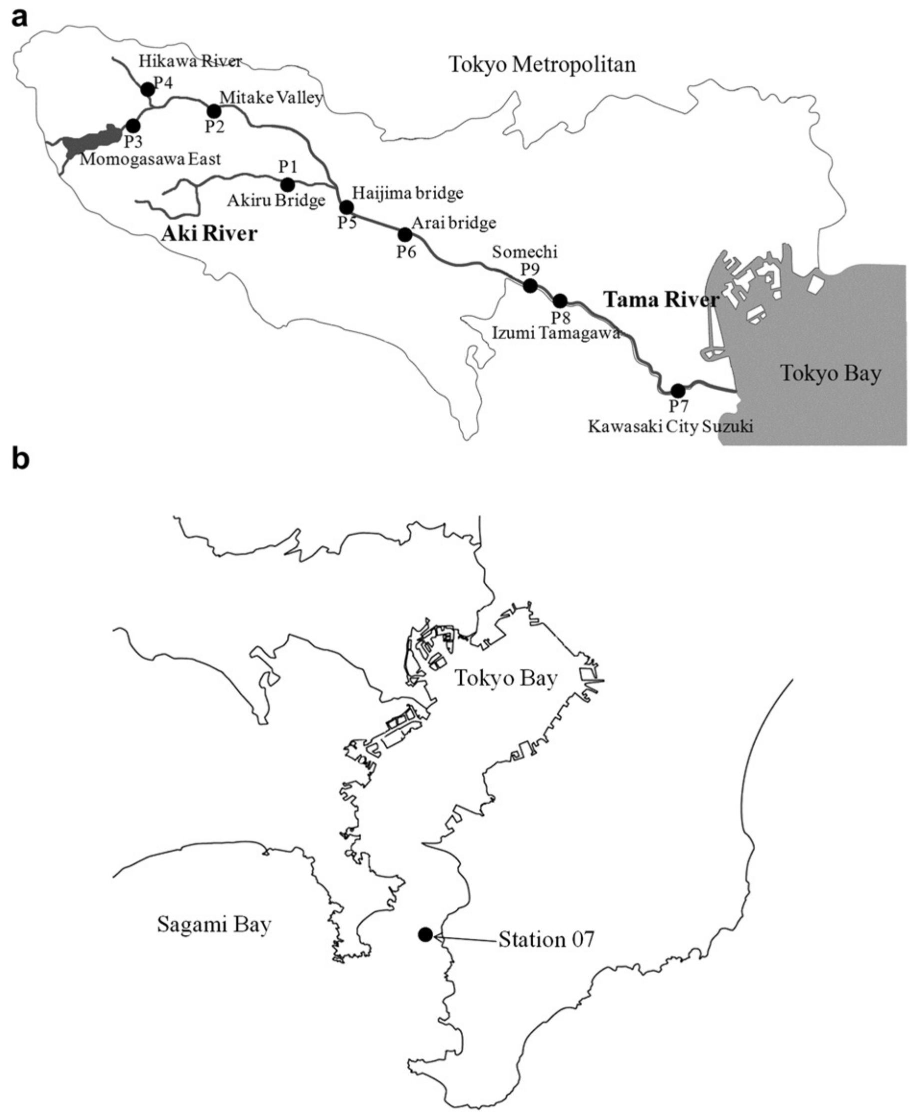

Fig. 1. Locations of sampling sites. a) The Tama River samples were collected in Sep. 2001. P9 was collected from Somechi in Sep. 2007. b) Station 7 in Tokyo Bay.

tetramer and octamer exist in sulphuric aqueous solution at pH 3, which were formed by the dissolution of silicate and silica in minerals, as clarified by the simulation of silicomolybdic acid formation and measurement by spectrophotometry (Dietzel, 2000). We have studied silica species and their roles in several systems (Tanaka and Takahashi, 1999, 2000a,b,c, 2001, 2002, 2005, 2007; Tanaka et al., 2009). We identified the monomer, dimer, trimer, linear and cyclic tetramers, and linear and cyclic pentamers, linear and cyclic hexamers in sodium chloride solution containing silica gel and natural water. For both high and low concentrations of silica, the silica species observed by FAB-MS (monomer, dimer, trimer, and tetramers) are in good agreement with those observed by Harris et al. using ^{29}Si-NMR, and those observed by Dietzel by spectrophotometry in extracted silica solution. In addition, the structures of silica complexes, such as cyclic tetramer, linear tetramer, and linear and cyclic pentamers, linear and cyclic hexamers could be observed by FAB-MS.

Studies on urban rivers have been reported (González-López et al., 2005; García-Gil et al., 2011). In the case of the Tama River, an urban river that flows through the south of the Tokyo Metropolitan Area in Japan, the silica concentrations in the upper river and lower river are approximately 0.2 mmol dm^{-3} (mM) and 0.3 mM, respectively. Because the density of river water is lower than that of seawater,

Table 1
Concentrations of cations and silica and the pH of samples from the Tama River and Tokyo Bay.

Point	Na (mg/l)	K (mg/l)	Mg (mg/l)	Ca (mg/l)	Sr (mg/l)	Si (μmol/l)	pH
P3 Momogasawa East	3.96	1.21	2.39	27.87	0.1032	220	8.32
P4 Nippara River	2.38	0.55	1.01	21.05	0.0448	211	8.15
P2 Mitake	2.93	0.34	2.96	13.78	0.0272	269	8.04
P5 Aki River	3.82	0.79	1.65	17.12	0.0441	113	8.21
P9 Somechi	16.50	3.74	3.40	20.95	0.0688	334	7.93
P8 Izumitamagawa	14.94	3.29	3.44	21.66	0.0587	319	8.13
P7 Kawasaki	425.60	203.30	48.52	37.91	0.4044	326	7.68
P1 Akiru Bridge	4.28	1.00	1.75	13.72	0.0378	302	7.99
P6 Asakawa	15.29	3.48	5.09	19.59	0.0796	413	7.25

	Na (g/l)	K (mg/l)	Mg (g/l)	Ca (mg/l)	pH	Si (μmol/l)
Tokyo Bay St7 (0 m)	10.3	237	1.27	367	8.64	19.5
Tokyo Bay St7 (300 m)	11.0	299	1.33	387	8.27	60