Total organic carbon and nitrogen contents in surface sediments of Harima Nada, eastern Seto Inland Sea, Japan: a comparison under two different trophic states

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Abstract Phytoplankton abundance in the surface waters of Harima Nada, eastern Seto Inland Sea of Japan, decreased after around the late 1970s following a reduction of terrestrial phosphorous inputs, and relatively low levels persisted thereafter. This symptom of de-eutrophication in recent decades might have reduced organic matter storage in surficial sediments. To test this possibility, we examined total organic carbon (TOC) and nitrogen (TN) contents of Harima Nada sediments in 2011, and compared the results to past data from more eutrophic states. In 2011, the TOC and TN varied horizontally within the basin, in relation to physicochemical properties (water and mud content) and phytoplankton remnants (pheo-pigments) of the sediments. These horizontal patterns were fundamentally similar to those of the early 1980s (1982–1983), although discrepancies between the periods were observed in some areas. Differences of mean TOC and TN in the 0–2 cm layer at 63 stations from 1982–1983 to 2011 were consequently <10 %. Hence, the recent de-eutrophication in Harima Nada was associated with little overall change of TOC and TN storage in the sediment. In Harima Nada, changes in water clarity and particle size composition of the sediment seem to have occurred during recent decades. The aforementioned paradoxical phenomenon may therefore be explained by factors that are affected by these environmental changes. Such factors include the ratio of export flux to the seafloor to phytoplankton production, phytoplankton biomass and production in the entire euphotic zone, and accumulation rate of surface sediment.

1 Introduction

Nitrogen (N) and phosphorus (P) loadings into estuaries and coasts, where they undergo cultural eutrophication, have decreased during recent decades in developed countries (Boesch 2002; Carstensen et al. 2006; Cloern 2001). This is attributable to anthropogenic interventions such as the development of sewage treatment technologies and environmental legislation. This tendency is true for the Seto Inland Sea, the largest semi-enclosed sea in Japan. In that sea, terrestrial P loading declined after a peak in the mid-1970s, when the Japanese government enacted a special law to address eutrophic problems there. It has been estimated that terrestrial P loading into the sea in 2004, ~ 30 tP day^{-1}, declined to <50 % of its peak (International EMECS Center 2008). Likewise, terrestrial N loading has tended to decrease since the mid- to late 1990s (International EMECS Center 2008).

The Seto Inland Sea ecosystem responded sensitively to the reductions of N and P loadings, similar to areas like Chesapeake Bay (Kemp et al. 2005), Tampa Bay (Greening and Janicki 2006), Black Sea (Oguz and Velikova 2010), Wadden Sea, North Sea, and Baltic Sea (Duarte et al. 2009). The Fisheries Agency of Japan (2007) noted that the occurrence of red tides decreased to one-third its peak in 1976 (~ 300 cases year^{-1}). Nishikawa et al. (2010) reported that phytoplankton abundance at the sea surface of

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Harima Nada, a sub-basin in the eastern sea, decreased after the late 1970s, and low levels (200–1,000 cells ml^{-1}) persisted thereafter. Tada et al. (2010) stated that the aquacultural yield of red algae, *Porphyra* spp., decreased since the early 2000s in the sub-basin, owing to a lack of sea surface nutrients in winter. Thus, it is probable that the Seto Inland Sea has undergone de-eutrophication (i.e., oligotrophication; Stockner et al. 2000) since around the late 1970s (Yamamoto 2003). This symptom is particularly remarkable in the eastern part of the sea (Tada et al. 2010).

We believe that symptoms of de-eutrophication in recent decades altered both sediment and water quality in the eastern Seto Inland Sea. Previous sediment trap studies estimated that at least 20–30 % of phytoplanktonic production in shallow (<50 m) coastal areas, including the sea (Yamaguchi et al. 2003), is deposited on the seafloor (Bhaskar et al. 2000; Suess 1980; Taguchi 1982; Roden et al. 1995). Although major portions of organic matter are mineralized on a yearly time scale, relatively small but significant fractions of organic matter are buried in sediments (Jørgensen et al. 1990; Roden et al. 1995). Therefore, variations of phytoplankton biomass and/or production in overlying water should affect the accumulation of organic remnants in sediments. If so, it may be hypothesized that organic matter storage in surficial sediments of the eastern Seto Inland Sea decreased during recent decades in relation to the de-eutrophication.

To test the aforementioned hypothesis, we examined total organic carbon (TOC) and nitrogen (TN) contents in surface sediments of Harima Nada in 2011. We compared these measurements with some from the mid- 1970s and early 1980s, when Japan's economy grew rapidly and the sea was more eutrophic than at present. The objective is to clarify the effect of improvement in water quality on the storage of TOC and TN in surface sediments during recent decades.

2 Materials and methods

2.1 Study area

Harima Nada covers an area of 3,400 km^2, with average depth of 26 m (Fig. 1). Its basin is surrounded by populated areas, particularly on the northern coast, and is recognized as an area of maximum impact from cultural eutrophication in the sea (International EMECS Center 2008). The two main rivers, the Kakogawa and Ibogawa, deliver the majority of freshwater with terrestrial N and P into the basin from the northern coast. The northern basin thus has relatively high levels of phytoplankton biomass, whereas the southern part is less productive (e.g., Manabe et al. 1994; Tada et al. 1998). Typical values of surface salinity in Harima Nada are between 30 and 33. We visited 63 sites to collect sediments. As explained later, all site locations were the same as those of an earlier study by our research group (Montani et al. 1987).

2.2 Field sampling

We carried out sediment sampling on cruises during May–July 2011. Four replicate sediment cores were taken at each station using a K.K.-type gravity corer, which was equipped with a polycarbonate tube 50 cm in length and 4 cm in diameter (Kimata et al. 1960). The 0–1 and 1–2 cm layers of triplicate cores were immediately subsampled onboard
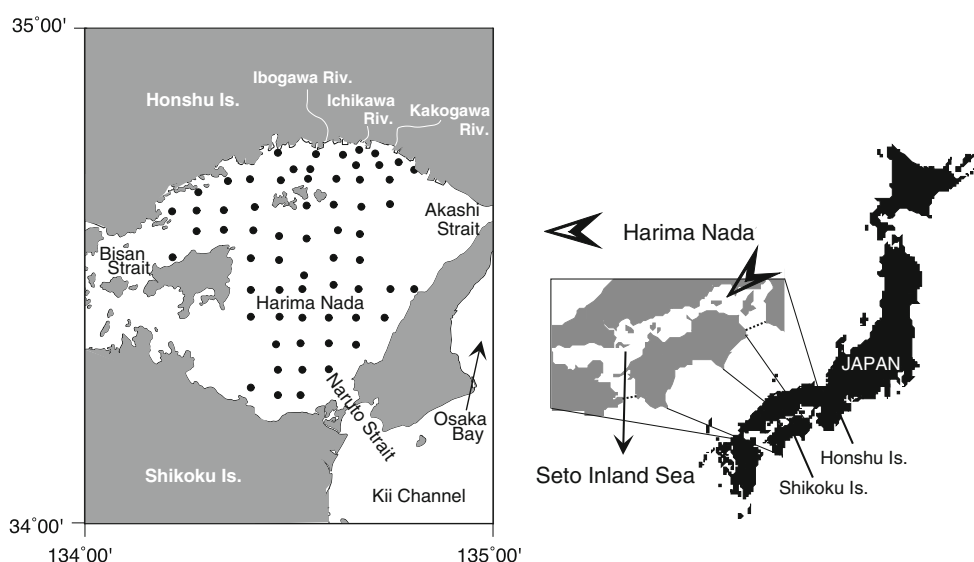
Fig. 1 Location of study area and sampling stations in Harima Nada, eastern Seto Inland Sea, Japan

the ship. Sediments from the same layer were combined, homogenized, and treated as a single sample, to reduce lateral sample inhomogeneity (cf. Krom and Berner 1981; Montani et al. 1987). The remaining core was scraped off the top 5 cm layer to retain sufficient volume of sediment. All sediment samples were stored in a cool and dark location until transported to the laboratory.

2.3 Analytical methods

Both the 0–1 and 1–2 cm sediment layers were used for water content, TOC, TN, and pheo-pigments analysis. Water contents were determined by oven drying a known volume of wet sediment at 60 °C, for approximately 48 h. We then determined the proportion of sediment dry mass and porosity, to calculate values of water content, TOC, TN, and pheo-pigments within the 0–2 cm layer. For the TOC and TN analysis, the sediments were freeze-dried and ground into powder using an agate mortar and pestle. The powdered sediments were treated with approximately 1 N hydrochloric acid to remove carbonates, and freeze-dried again. TOC and TN in the sediments were then determined by a dry combustion method using a CHN elemental analyzer (Micro Corder JM-10; J-Science Lab.). For determination of pheo-pigments, freeze-dried sediments were soaked in 90 % acetone and stored in darkness for approximately 24 h. Following this, supersonic treatment was performed to promote pigment extractability. Acetone extracts were passed through PTFE Ekicrodisk filters (0.45 μm pore size) and thereafter determined by the method of Lorenzen (1967) using a spectrophotometer (V-630; Jasco Analytical Instruments). To compare the present results with earlier ones, salt correction for dried sediment was not applied, so dry weight-based TOC, TN, and pheo-pigments without salt corrections are presented here.

The top 5 cm of sediments was used for grain size analysis. Grain size composition was analyzed by a standard wet sieving method (e.g., Mudroch and MacKnight 1991), using a series of nested sieves. We present mass percentages of sediment finer than 63 μm in diameter (silt and clay).

2.4 Comparison with previous data

In the past, when eutrophic conditions were severe, Shiozawa et al. (1979) and Montani et al. (1987) examined TOC and TN contents in superficial sediments (uppermost 1 and 2 cm layers, respectively) over the entire area of Harima Nada. We thus compare the present results with those of these two studies.

Montani et al. (1987) established 72 stations in the basin, and collected the top 2 cm layer of sediment at each station on cruises during October–December 1982 and 1983. They used a K.K.-type gravity corer for sampling and, after sediment pretreatment with 0.5 N hydrochloric acid, determined TOC and TN by a dry combustion method using a CN elemental analyzer (MT-500; Yanagimoto). The sampling method and sample processing by Montani et al. (1987) were thus similar to those in the present study. We obtained TOC and TN records from 63 of the 72 sites. These sites (Fig. 1) were therefore established as the sampling stations. This made possible the evaluation of temporal changes in TOC and TN contents between 2011 and the early 1980s (1982–1983) at the stations.

Montani et al. (1987) also measured pheo-pigments in the early 1980s, but there was a difference in sample processing between our study and theirs. We analyzed pheo-pigments soon after sample collection, whereas the timing was delayed in the 1980s (K. Tada, second author of Montani et al. 1987, personal communication). We were concerned that comparison of the present measurements with earlier ones could yield inaccurate estimates of changes in the absolute values, in relation to the methodological difference. Thus, we focus here only on the relationships between pheo-pigments and both TOC and TN in the 1980s.

Shiozawa et al. (1979) collected the 0–1 cm sediment layer for TOC and TN analysis at 90 stations between September and October 1975. These sediments were collected by a Smith-McIntyre grab sampler. They determined TOC content in the sediment by a slightly modified Tyurin method (Mizuno 1968) (a wet digestion method), using potassium dichromate solution in sulfuric acid as an oxidant. For the determination of TN, the Kjeldahl method with a Kjelfoss automatic analyzer (N. Foss Electric) was used. Unfortunately, we were unable to obtain the raw TOC and TN data of Shiozawa et al. (1979), because they were likely lost. Given this restriction, we used mean values of TOC and TN from 1975, which were given in the literature.

According to Hoshika et al. (1983) and Nagafuchi et al. (1998), sedimentation rates of bottom sediments in Harima Nada were in the range of 0.27–1.00 cm year^{-1}, with a mean of 0.59 cm year^{-1}. This indicates that the first few centimeters (top 1 or 2 cm) of the sediments reflect the history of a few years. In contrast to Japanese subarctic coasts such as Funka Bay (e.g., Kudo and Matsunaga 1999), there is no intense spring phytoplankton bloom in Harima Nada (e.g., Tada et al. 2004). Therefore, it is often assumed that there is little seasonal variation of TOC and TN contents in the surface sediments of the Seto Inland Sea, including Harima Nada (Yamaguchi et al. 2011). For this reason, we did not consider differences in seasonality of sediment sampling between the present study and the prior two.

3 Results

3.1 Water, mud, and pheo-pigments content

Water content in the 0–2 cm layer showed horizontal variations (Fig. 2a) in the range of 22.5–78.8 %, with a mean 63.4 % ($n = 63$). Higher values (>70 %) were recorded in the northern part of Harima Nada and central through the southeast parts. Conversely, lower values (<50 %) were near straits connected to neighboring areas (Osaka Bay, Kii Channel, and Bisan Strait).

Weight percentage of mud (silt and clay) content of sediment showed strong variation, with minimum 2.8 % and maximum 94.9 % (Fig. 2b). However, 62 % (39 of 63 stations) of the measurements showed contents >50 %, indicating that sediments in the study area were mainly composed of mud. The horizontal distribution of mud content in the 0–5 cm layer strongly coincided with that of water content in the 0–2 cm layer. Linear regression indicated significant correlation between these two variables ($r = 0.827$, $p < 0.01$).

Horizontal distribution of pheo-pigments reflected water and mud contents at each sampling station (Fig. 2c). There were significant linear relationships between pheo-pigments and water ($r = 0.883$, $p < 0.01$) and mud ($r = 0.819$, $p < 0.01$) contents. Since the water and mud contents had higher values in the northern and central parts through the southeast areas, pheo-pigments had high values (>40 μg g^{-1}) there. By contrast, lower values were often observed around the straits. The mean of all pheo-pigments data was 36.6 μg g^{-1} ($n = 63$).

3.2 Current sedimentary TOC and TN contents

TOC in the 0–2 cm layer was in the range of 1.1–22.8 mgC g^{-1} (Fig. 3a). High contents, from 15.0 to 22.8 mgC g^{-1}, were recorded in the north. High TOC contents were also observed in the central and southeast, but they decreased toward the straits. The distribution of TN content in the 0–2 cm layer was similar to that of TOC (Fig. 3b). Stations with TN contents >2.0 mgN g^{-1} were nearly identical to stations with TOC contents in excess of 15.0 mgC g^{-1}. Low TN contents, e.g., those <1.0 mgN g^{-1} around the straits, were a consequence of lower TOC contents.

There were no large differences in horizontal distribution of either TOC or TN content between the 0–2 cm (Fig. 3a, b) and 0–1 cm (Fig. 3c, d) layers. Although differences were significant (paired t test, $p < 0.01$), mean TOC and TN in the 0–2 cm (13.4 ± 5.9 mgC g^{-1} and 1.68 ± 0.76 mgN g^{-1}, respectively) and 0–1 cm (13.7 ± 5.9 mgC g^{-1} and 1.72 ± 0.76 mgN g^{-1}) layers had similar values.
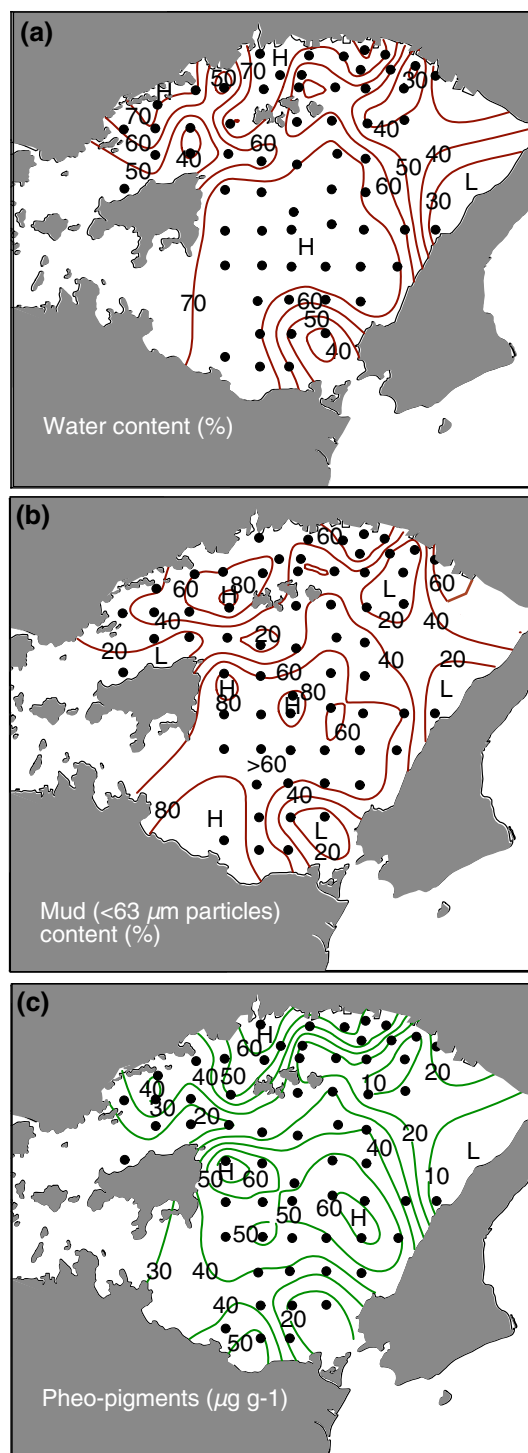
Fig. 2 Horizontal contour maps of **a** water content in the 0–2 cm layer, **b** mud content in the 0–5 cm layer, and **c** pheo-pigments in the 0–2 cm layer in Harima Nada sediments during 2011

Both TOC and TN contents were positively correlated with those of water (Fig. 4a, d), mud (Fig. 4b, e), and pheo-pigments (Fig. 4c, f). Consequently, higher TOC and TN tended to occur with increasing water, mud, and pheo-pigments contents in the sediment.
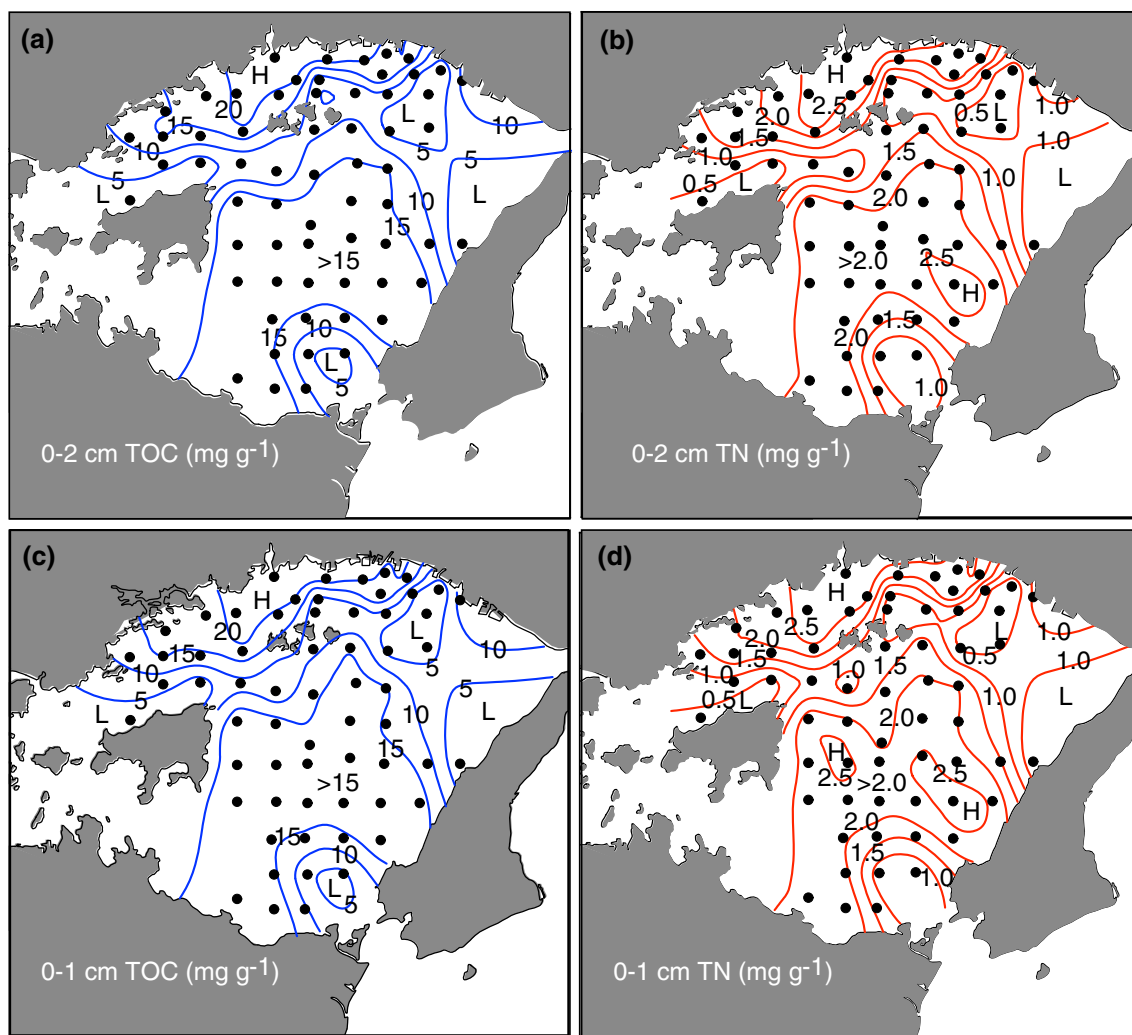
Fig. 3 Horizontal contour maps of **a** TOC and **b** TN content in the 0–2 cm layer, and **c** TOC and **d** TN content in the 0–1 cm layer in Harima Nada sediments during 2011

3.3 Comparison between present and past

We compared the 2011 TOC and TN measurements in the 0–2 cm layer with those in the early 1980s at each station (Figs. 5, 6). Extremely high values of TOC and TN (≥ 25 mgC g^{-1} and >3 mgN g^{-1}, respectively) were observed near the river mouths of the Ichikawa and Kakogawa in the early 1980s, but such values were never recorded in 2011. Including these river-mouth areas, substantial decreases of TOC and TN (<-2.5 mgC g^{-1} and <-0.3 mgN g^{-1}, respectively) were found in the northeast (Fig. 6). On the other hand, both TOC and TN tended to increase substantially (>2.5 mgC g^{-1} and >0.3 mgN g^{-1}) in the north-central area and at some stations in the south. Thus, present and past distributions of both TOC and TN contents did not necessarily coincide.

Nevertheless, distributions of both TOC and TN in 2011 were highly and significantly correlated with those in the early 1980s ($r = 0.757$ and 0.706, respectively; $n = 63$, both $p < 0.01$) (Fig. 5). This indicates that fundamental patterns in the horizontal plane were similar between the two ages, because large numbers of stations showed small changes in TOC and TN contents (Fig. 6).

Percent differences of TOC and TN contents in the 0–2 cm layer between 2011 and 1982–1983 were obtained by dividing station measurements in 2011 by those of 1982–1983 (Fig. 7). The frequency histograms showed unimodal patterns, and neither were significantly different from normal distributions (Shapiro–Wilk test, both $p > 0.05$).

The mean 2011 TOC content in the 0–2 cm layer for the 63 stations, 13.4 ± 5.9 mgC g^{-1}, was significantly (paired t test, $p < 0.05$) higher than that of 1982–1983, 12.1 ± 5.0 mgC g^{-1} (Table 1). However, this difference was slight (by 9 %). There was no significant difference of mean TN content in the aforementioned layer and period
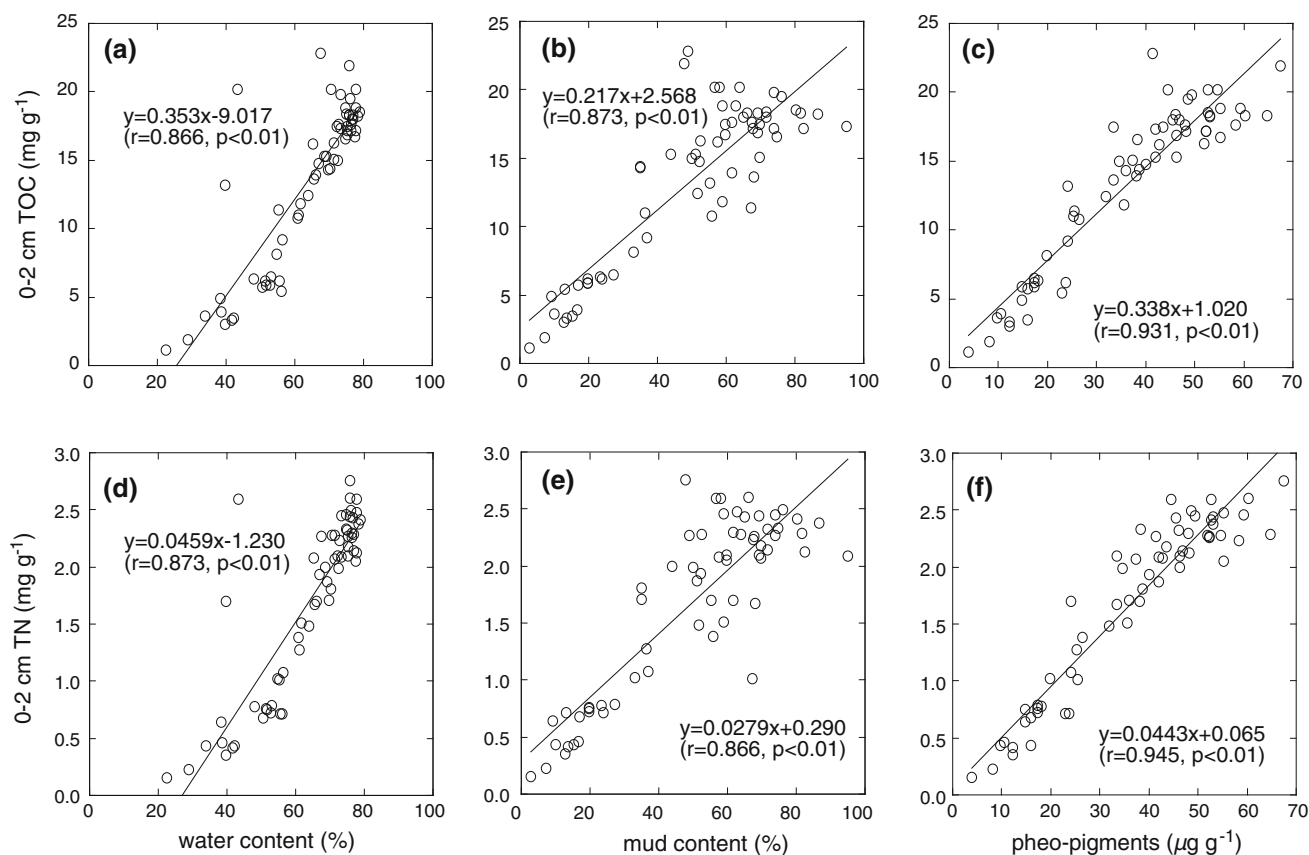
Fig. 4 Relationships of TOC in 0–2 cm layer with **a** water content, **b** mud content, and **c** pheo-pigments, plus TN in the 0–2 cm layer with **d** water content, **e** mud content, and **f** pheo-pigments in Harima Nada sediments during 2011

for the stations (1.68 ± 0.76 mgN g^{-1} in 2011 and 1.61 ± 0.69 mgN g^{-1} in 1982–1983) (paired t test, $p > 0.05$).

The mean TOC content of the 0–1 cm layer in 2011 (13.7 mgC g^{-1}, $n = 63$) was 18 % less than that in 1975 (16.7 mgC g^{-1}, $n = 90$). Considering significant digits, however, mean TN content in that layer was the same in 2011 and 1975 (1.7 mg g^{-1}).

4 Discussion

4.1 Present and past states of organic matter in sediment

We determined TOC and TN contents in Harima Nada sediments during 2011 and compared the results with those reported for the more eutrophic states of 1975 (Shiozawa et al. 1979) and 1982–1983 (Montani et al. 1987). We found no temporal decrease of mean TOC content with comparison of the 2011 value and that of 1982–1983, though the former content was considerably less (18 %) than that of 1975. There was no difference of mean TN

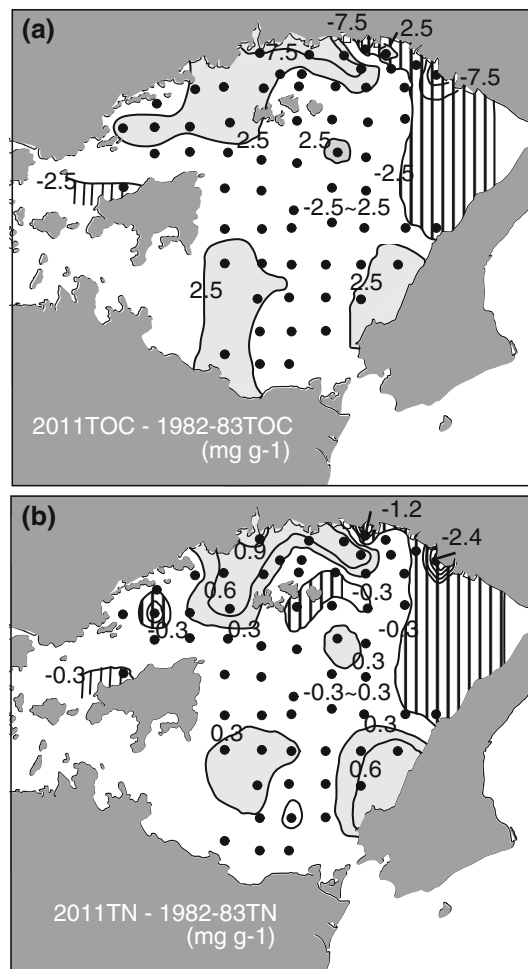content between present and past (either 1975 or 1982–1983).

For the data comparison and compilation, we must consider the effect of method differences on the measurements. The analysis of TOC and TN from 1975 samples was based on the modified Tyurin method (Mizuno 1968) and Kjeldahl method, respectively. In the two later studies, the dry combustion method was used for TOC and TN determination. For terrestrial soil samples, TOC measured by Tyurin dichromatic oxidation does not always coincide with TOC measured by the dry combustion method (Heczko et al. 2011). Furthermore, chloride and ferrous ions can interfere with TOC measurements using dichromatic methods under certain situations (Nelson and Sommer 1982). Hence, the difference of TOC between 2011 and 1975 may be attributed in part to the methodology, and it is difficult to compare the result of 1975 directly with the later two studies. Conversely, TN measured by the Kjeldahl and dry combustion methods can be compared without any correction, because the former can recover nearly 100 % of sedimentary TN from coastal samples (Craft et al. 1991). It is therefore probable that mean organic matter contents (both TOC and TN), at least in the surface
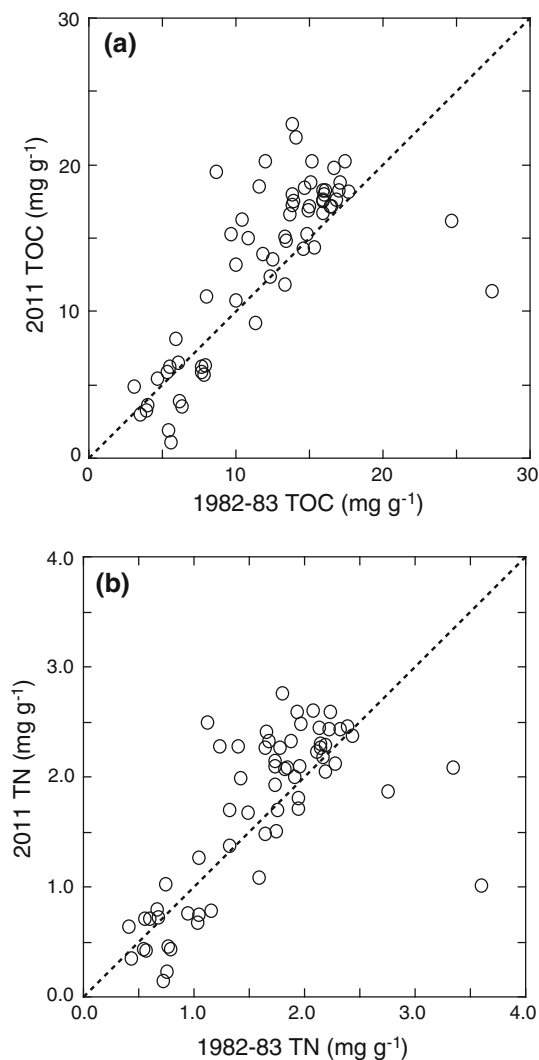
Fig. 5 Plots of 2011 measurements against 1982–1983 measurements of **a** TOC and **b** TN in the 0–2 cm layer in Harima Nada sediments. *Dashed lines* indicate $y = x$, where the two measurements are identical. Linear regression analysis indicate significant correlation between 2011 TOC and 1982–1983 TOC ($r = 0.757$, $n = 63$, $p < 0.01$), and between 2011 TN and 1982–1983 TN ($r = 0.706$, $n = 63$, $p < 0.01$)

Fig. 6 Change maps of **a** TOC and **b** TN in the 0–2 cm layer in Harima Nada sediments, from 1982–1983 to 2011. Differences were calculated subtracting 2011 measurements from those of 1982–1983

sediment of Harima Nada, have not decreased drastically during recent decades.

According to a report by AECSIS (2006), mean TOC and TN in the upper 5 cm of Harima Nada sediments did not differ significantly, with little overall change between 1981, 1991, and 2001 (Table 1). Nagafuchi et al. (1998) discussed the possibility that the thick sediment interval (5 cm depth) used in the AECSIS survey might obscure differences in characteristics of the surface sediment between 1981 and 1991. Nevertheless, the present study analyzed a relatively thin sediment column (upper 1 and 2 cm), and also found no large change of TOC and TN. Thus, with support from the earlier works (AECSIS 2006;

Nagafuchi et al. 1998), there appears to have been no drastic decrease of sedimentary TOC and TN in the study area.

In the eastern Seto Inland Sea, both terrestrial and marine organic materials are sources of sedimentary organic matter. Mishima et al. (1999) investigated distributions of terrestrial and marine organic matter in Osaka Bay, which is in the eastern Seto Inland Sea near Harima Nada. Based on carbon and nitrogen stable isotopic analysis, they noted that a relatively small portion of sedimentary TOC (21 % on average) in the bay was composed of terrigenous materials. They also indicated that most terrestrial organic carbon was deposited within 10 km of the river mouth. This suggests that TOC in the eastern Seto Inland Sea was composed almost entirely of marine organic matter.

As calculated from data in Table 1, the mean sedimentary C/N atomic ratio in Harima Nada over the last three decades was estimated at around 9 (between 8.8 and 9.3),
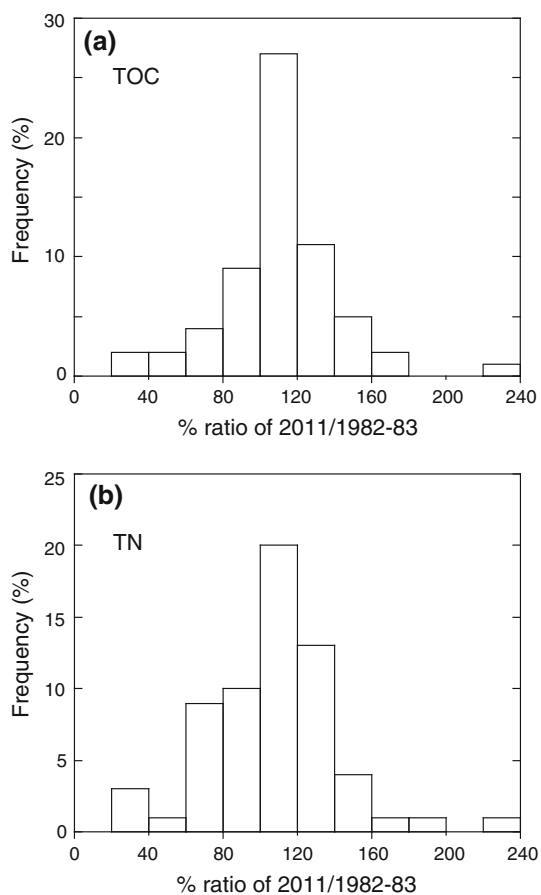
Fig. 7 Frequency histograms of **a** TOC and **b** TN ratios of 2011 to 1982–1983. Percentages are from dividing 2011 measurements by those of 1982–1983

irrespective of period (except for 1975, when TOC was determined by the dichromatic method). This mean is considerably less than the typical C/N ratio of terrestrial materials and higher plants (Müller and Mathesius 1999). Furthermore, there were strong linear relationships

between pheo-pigments and both TOC and TN in the 0–2 cm layer during 2011 (Fig. 4c, f). Similar regression analysis (cf. Fig. 4c, f) was done by Montani et al. (1987) in Harima Nada in the 1980s. Like the present study, they reported the significant relationships between pheo-pigments and TOC (TOC = 0.304 pheo-pigments + 2.44, $r = 0.894$) and TN (TN = 0.0395 pheo-pigments + 0.35, $r = 0.841$) in the 0–2 cm layer during 1982–1983. For these four linear regression lines, values of y-intercepts (1.02 mgC g^{-1} and 0.07 mgN g^{-1} in 2011, and 2.44 mgC g^{-1} and 0.35 mgN g^{-1} in 1982–1983) were roughly one order of magnitude less than the mean TOC and TN for all measurements (13.4 mgC g^{-1} and 1.68 mgN g^{-1} in 2011, and 12.1 mgC g^{-1} and 1.61 mgN g^{-1} in 1982–1983). The y-intercepts are often regarded as TOC and/or TN values that were not originally from pheo-pigments (Montani et al. 1987). These findings therefore indicate that phytoplankton, the predominant producer of marine organic matter, is mainly composed of TOC and TN in the surface sediment of Harima Nada, at least during recent decades. In contrast to the relatively stable values of mean sedimentary C/N ratios over the last three decades (~ 9; Table 1), estimated C/N ratios from the y intercepts were different between the 1980s (8.1) and the 2010s (18.4). This difference may be explained by changes of the environment in Harima Nada, such as those of quality of riverine input, benthic activities, and others.

Nishikawa et al. (2010) visited 19 sites in Harima Nada, examining temporal changes in annual means of phytoplankton abundance of the sea surface during 1973–2007. They revealed that mean abundance in a recent decade (1998–2007), ~ 600 cells ml^{-1}, was a third that of 1973–1982 ($\sim 1,800$ cells ml^{-1}). The substantial reduction of phytoplankton in the surface waters of Harima Nada after the latter period was also suggested by a halving of annual red tide occurrence (AECSIS 2013). Therefore, we

Table 1 Summary of mean reported TOC and TN contents in Harima Nada, eastern Seto Inland Sea

Years	TOC (mg g^{-1})			TN (mg g^{-1})			References
	0–1 cm Mean	0–2 cm Mean	0–5 cm Mean	0–1 cm Mean	0–2 cm Mean	0–5 cm Mean	
1975	16.7			1.7			Shiozawa et al. (1979)
1981			12.6 ± 7.2			1.65 ± 0.95	AECSIS (2006)
1982-1983		12.1 ± 5.0[a]			1.61 ± 0.69[a]		Montani et al. (1987)
		14.0[b]			1.80[b]		
1991			12.7 ± 7.4			1.6 ± 1.0	AECSIS (2006)
2001			11.7 ± 7.3			1.5 ± 0.9	AECSIS (2006)
2011	13.7 ± 5.9	13.4 ± 5.9		1.72 ± 0.76	1.68 ± 0.76		This study

Differences in significant digits depend on the references. ± value indicates standard deviation

[a] Mean value of 63 cites of Harima Nada (see text)

[b] Mean value of sedimentation area of Harima Nada

conclude that such substantial improvement of water quality has not been clearly reflected by TOC and TN storage in the sediments of Harima Nada.

4.2 Possible explanations for slight change of sedimentary TOC and TN contents

De-eutrophication is believed to reduce phytoplankton abundance in overlying water. Therefore, the exported amount of organic matter from the water column to the seafloor is usually assumed to decrease with the progress of de-eutrophication (e.g., Takeoka and Murao 1997). Under the same physicochemical characteristics of sediment, a decrease of organic matter supply to sediments tends to oxygenate the water–sediment interface in coastal areas. Once surface sediments become more aerobic and redox potential increases, the decomposition rate of sedimentary organic matter may increase (e.g., Uyeno et al. 2000; Kuwae et al. 2007). This is partly because oxygenation can affect the decomposition rate of organic matter when it is accompanied by an increase of benthic fauna and bioturbation. According to Kristensen and Blackburn (1987), bioturbation of benthic fauna increases rates of organic matter mineralization more than that by oxygenation, mainly by enhancing microbial activities in the sediment. As a consequence of the synergistic effect of the water and sediment processes, organic matter storage in the surficial sediments is expected to decrease with time during the de-eutrophication phase. However, despite the improvement of water quality (e.g., AECSIS 2013; Nishikawa et al. 2010), TOC and TN in the sediment did not drastically decrease in Harima Nada. There are several potential explanations of this paradoxical phenomenon.

## 4.3 Possible impact of export ratio from water column to sediment

A possible explanation for the aforementioned paradox is the change of ratio between export production from the water column to the seafloor and primary production by phytoplankton in the overlying water. It is estimated that the export production is approximately 10–30 % of the primary production in the eastern Seto Inland Sea (Handa et al. 1984; Montani et al. 1991). However, the percentages are affected by different factors, and are highly variable.

With a smaller distance between euphotic depth and the seafloor, higher ratios of export to primary production are expected. This is because of a decrease in the aphotic layer, which occurs solely with organic matter decomposition. Temporal variation of light attenuation in the water column of Harima Nada is largely influenced by changes of phytoplankton abundance (Yamaguchi et al. 2013). Therefore, the recent reduction of sea surface phytoplankton in this

basin appears to have increased the euphotic depth. There are several long-term monitoring programs of Secchi depth (transparency), an index of water clarity, in the Seto Inland Sea (including Harima Nada). The Comprehensive Water Quality Survey in the Seto Inland Sea is one such program, which is accessible for research use. According to the program data, the annual harmonic mean of transparency has increased with time, by ~ 3 m from 1983 to 2011 (Fig. 8). Euphotic depth is generally estimated to be three times the transparency. This indicates that aphotic depth in Harima Nada (mean depth = 26 m) decreased an average 9 m during a 29-year period. We should keep in mind that temporal variation of transparency in Harima Nada does not necessarily coincide among the monitoring programs. However, if such a trend was real, the ratio between export production from the water column to the seafloor and primary production by phytoplankton in the overlying water should have increased during the last three decades. If so, TOC and TN contents in the sediments might not clearly reflect the reduction of sea surface phytoplankton.

4.4 Possible impact of phytoplankton biomass and production

We must also examine the magnitude of change in phytoplankton abundance and production in Harima Nada. As

$$y = 0.11(x-1983) - 1.4$$
$$(r=0.827, p<0.01)$$
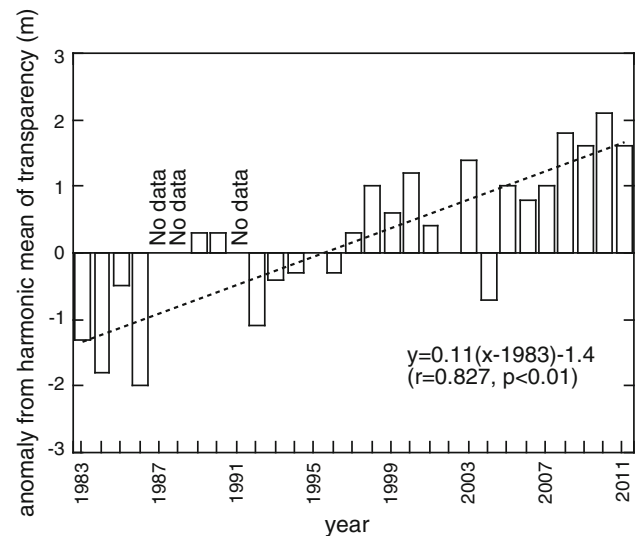
Fig. 8 Variations in transparency in Harima Nada from 1983 to 2011. Results are shown as an anomaly from the harmonic mean (=4.6 m), temporally averaged from 1983 to 2011. Original data are based on the Comprehensive Water Quality Survey in the Seto Inland Sea, cited from http://www.pa.cgr.mlit.go.jp/chiki/suishitu/index.html. Based on results of a four-season survey in a year, each season's data were harmonically averaged over all sampling stations (basically 37 stations). The four seasonal values were used to calculate an annual harmonic mean. Results of 1987, 1988, and 1991 were excluded from the analysis, because sampling was not done four times per year

mentioned earlier, the drastic decrease of phytoplankton at the sea surface was evidenced by other studies (Fisheries Agency of Japan 2007; AECSIS 2013; Nishikawa et al. 2010). By contrast, because of a lack of continuous monitoring data, there is no information on long-term changes in standing stock and production rate of phytoplankton over the entire euphotic zone.

Tada et al. (1998) studied chlorophyll-a (Chl-a) concentrations in nine sub-basins of the Seto Inland Sea, obtaining average euphotic-layer thicknesses between about 15 and 35 m. They revealed that, in contrast to the sea surface Chl-a ($\sim$1–5 mg m^{-3}), differences in means of Chl-a stocks in the euphotic zones ($\sim$30–70 mg m^{-3}) were not remarkable between the sub-basins. This finding suggests that, although de-eutrophication is proceeding in Harima Nada, changes of phytoplankton abundance and production are smaller than generally expected, in relation to euphotic depth increase. This may be an explanation for the relatively small changes in sedimentary TOC and TN contents relative to those observed for phytoplankton abundance at the sea surface.

Measurements of phytoplanktonic production in Harima Nada are scarce. A few studies have reported the production rate after the 1980s (e.g., Uye et al. 1987; Tada et al. 1998). Although there are some methodological differences between the studies, we found no temporal decrease of production with comparison of the 1990s (Tada et al. 1998) and 1980s (Uye et al. 1987) values. This may support the aforementioned explanation.

4.5 Possible impact of sedimentation and decomposition processes in sediment

As indicated in Fig. 4, sedimentary organic matter content is affected not only by the amount of phytoplankton remnants but also by physicochemical characteristics of the sediment. This means that, if particle size composition of the sediment changed, it would have impacted sedimentary TOC and TN contents in surface sediments. According to the report by AECSIS (2006), particle size composition of Harima Nada sediments in 2001 was significantly different from those of the past (both 1981 and 1991). We therefore reanalyzed the original data reported by AECSIS (2006), and estimated changes in the horizontal distribution of mud content in Harima Nada between present and past. Because the horizontal distribution of mud content in 1991 (but not 1981) was similar to those of TOC and TN reported by Montani et al. (1987), we focused on the 1991 content as the past state. Mud content increased in the north-central and northwest during 1991–2001 (Fig. 9). Some stations in the south also showed increasing mud content. Such horizontal patterns were qualitatively consistent with changes in TOC and TN between the early 1980s and 2001 (Figs. 6,
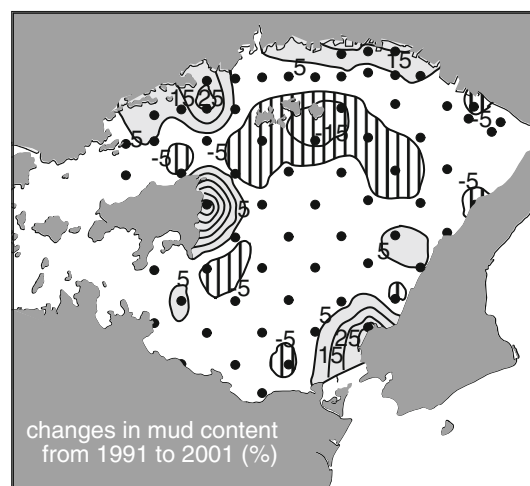
Fig. 9 Change maps of mud content in the 0–5 cm layer in Harima Nada sediments, from 1991 to 2001. Differences were calculated subtracting 2001 measurements from those of 1991. Original data of mud contents were cited from the Basic Survey for the Environmental Conservation of the Seto Inland Sea, published by the Ministry of the Environment, Japan

9), and both TOC and TN contents appeared to increase at stations where sediments became muddy. This tendency suggests that the lack of a decreasing trend of mean TOC and TN on a basin-wide scale in Harima Nada might also be attributable to changes of sedimentation processes.

As shown in Figs. 6 and 9, temporal changes in sedimentary organic matter and mud contents were especially pronounced in the northern part of Harima Nada. Judging from the distribution of sea surface salinity (Manabe et al. 1994), this part can be regarded as the estuarine area of the two main rivers, Kakogawa and Ibogawa. These two rivers deliver large amounts of freshwater to Harima Nada (approximately 60–80 m^3 s^{-1} on average; Japan River Association 1999), but the discharge varies temporally. The magnitude of freshwater discharge affects physicochemical characteristics of estuarine sediments through changes of erosion/deposition balance (Lesourd et al. 2003; Yokoyama 2005) as well as the supply rate of suspended terrigenous sediments of a river (Kurashige 1996; Yokoyama 2005). To our knowledge, there is no direct information on temporal variations of erosion/deposition balance of estuarine sediments and supply of terrigenous sediments in Harima Nada. Nevertheless, based on flow regime analysis, discharge of the Kakogawa River has tended to decrease gradually since the mid-1970s (Kinki Regional Development Bureau 2011). Furthermore, sand-mining activities in this river during that period decreased with time (Kinki Regional Development Bureau 2011). Hence, such changes in river environments and related factors might impact sediment characteristics in the northern part of Harima Nada.

In general, muddy sediments have higher sedimentation rates than sandier ones. Therefore, changes in particle size composition of the sediment may accompany changes of sedimentation rate over the last three decades. This rate in Harima Nada was extensively examined in the early 1980s via the constant initial concentration model of ^{210}Pb dating (Hoshika et al. 1983; Montani and Okaichi 1984), and was estimated at an average of 0.59 cm year^{-1} (Nagafuchi et al. 1998). However, to our knowledge, there have been few studies since. Therefore, there are many uncertainties regarding recent sedimentation rates. It may be worthwhile tackling these uncertainties in the future, to address the aforementioned possibility.

As mentioned above, the decomposition rate of sedimentary organic matter, which appears partly controlled by redox potential, is also a determinant of organic matter content in sediments. The sediments collected in the early 1980s tended to have a darker color than those in the 2010s (K. Tada, personal communication), probably owing to the presence of iron sulfate. This suggests that redox potential was lower in the early 1980s than in the 2010s, and the decomposition rate in 2011 would not be the same as in the past. Recently, Yanagi and Yamada (2014) reported variations in sediment chemistry of a hypereutrophic embayment, Dokai Bay, a neighboring area of the Seto Inland Sea. According to these authors, despite a drastic decrease in mean content of acid-volatile sulfide between 1994 (1.5 mgS g^{-1}) and 2011 (0.4 mgS g^{-1}), there were no corresponding changes of TOC and TN over this period. Taking the above into consideration, it is likely that there was little change of sedimentary organic matter between the present and past in Harima Nada, though the decomposition rate of organic matter changed.

5 Conclusions

The de-eutrophication during recent decades in Harima Nada may have reduced organic matter storage in surficial sediments. To test this possibility, we compared TOC and TN contents in 2011 with those in earlier, more eutrophic states. We conclude that the recent de-eutrophication was associated with little overall change of organic matter storage in the sediment. In Harima Nada, changes in water clarity and particle size composition of the sediment appear to have occurred during recent decades. The aforementioned paradoxical phenomenon may therefore be largely explained by factors that are affected by these environmental changes. Such factors include the ratio of export flux to the seafloor to phytoplankton production, phytoplankton biomass and production in the entire euphotic zone, and accumulation rate of surface sediment. However, the reality is certainly more complex. Quantitative evaluations of the possible explanations are needed.

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