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Acidification of the interior of the Japan / East Sea

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Goal of this presentation:

To estimate rates of acidification in the Japan/East Sea for different depths.

Outline

I. Introduction (What's acidification)

II. Methods and Data

III. Data processing

IV. Results of Acidification

V. Linkage of acidification with temporal variability of nutrients concentrations and DO

VI. Preliminary explanations of interior JES acidification

(instead conclusions)

I. Introduction

Question: What is acidification?

Answer: Temporal decreasing of pH in natural or/and artificial water basins (oceans, seas, lakes and so on).

Main reasons of acidification:

a.Increasing events of acid rains ($SO_{2,}$ NO_2 atmospheric precipitations) as results acidification and decreasing of TA (Total Alkalinity);

b.Oxidation of sulfide ores (metallurgical tails) will give acidification and decreasing of TA;

c.Increasing of CO_2 partial pressure in atmosphere will result in acidification and no change in TA contents;

d. Intensification of decaying of organic matter will result in acidification and almost no change in TA contents when degradation of organic matter is occurred under aerobic conditions

II. Methods and Data

Acidification of interior of the JES was established as result of observations of carbonate system parameters during long period (1999 – 2014).

Measured parameters: pH and TA

Calculated parameters: DIC (Dissolved Inorganic Carbon) and pCO_2 (carbon dioxide partial pressure)

pH measurements were carried out by electromotive cell without liquid junction:

$$GE-Na^{+}\,|\,\text{test soution (standard solution)}\,|\,H^{+}-GE$$

T
PH measurements of seawater by means of cell without liquid junction //
Oceanology, 2001. v. 41. p. 849-859.

TA measurements were carried out by Bruevich method:

Pavlova G. Yu., Tishchenko P. Ya., Volkova T. I., Dickson A., Wallmann K.
The Intercalibration of Bruevich's Method for Determination of Total
Alkalinity in Seawater // Oceanology, 2008. v. 48. p. 477-483.

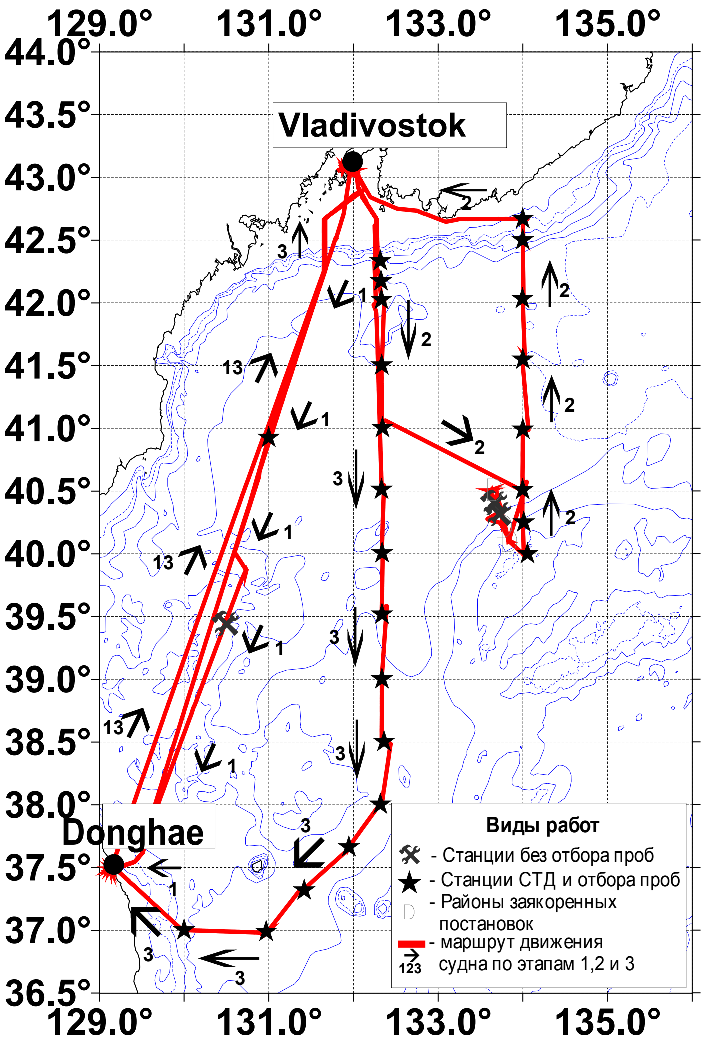
Additional parameters were collected:

-CTD-profiles;
-dissolved oxygen (Winkler method);
-nutrients (phosphates, silicates, nitrate).

II. Methods and Data

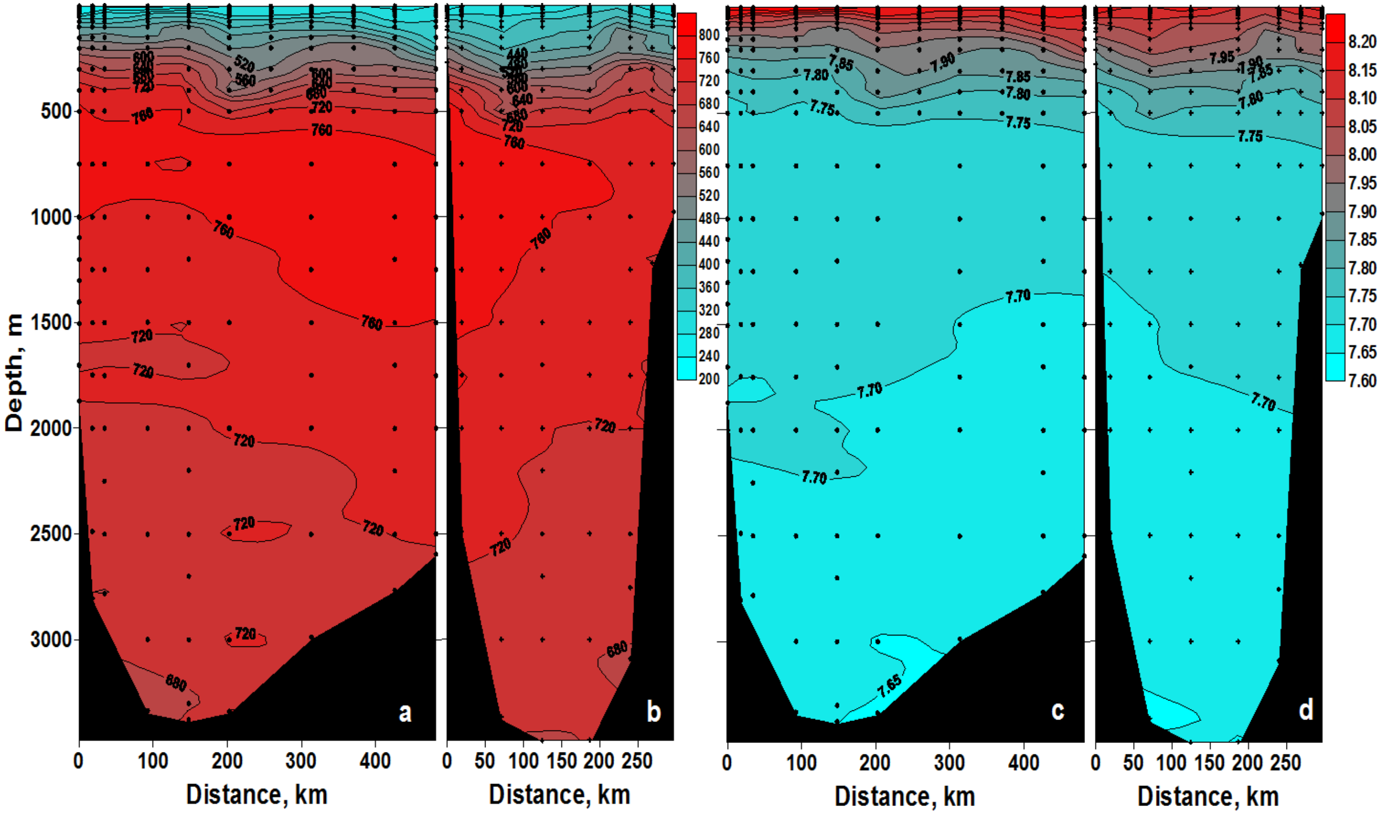
We have dataset more than 25 hydrochemical surveys of the JES since 1999 till present:

-1. April 1999 (R/V "Pavel Gordienko"),
-2. July 1999 (R/V "Revelle", "36-Professor Khromov"),
-3. February 2000 (R/V "38-Professor Khromov"),
-4. October 2000 (R/V "30-Professor Gagarinsky"),
-5. February 2001 (R/V "42-Professor Khromov"),
-6. April - May 2001 (R/V "31a-Professor Gagarinsky"),
-7. May 2001 (R/V "31b-Professor Gagarinsky"),
-8. April 2002 (R/V "34-Professor Gagarinsky"),
-9. February 2003 (R/V "30-Akademik M.A. Lavrentyev"),
-10. November 2003 (R/V "37-Professor Gagarinsky"),
-11. October 2003 (R/V "32-Akademik M.A. Lavrentyev"),
-12. May 2004 (R/V "33-Akademik M.A. Lavrentyev"),
-13. March 2005 (R/V "35-Akademik M.A. Lavrentyev"),
-14. October 2005 (R/V "38-Akademik M.A. Lavrentyev"),
-15. May 2007 (R/V "43-Professor Gagarinsky"),
-16. July 2009 (R/V "46-Akademik M.A. Lavrentyev"),
-17. November 2009 (R/V "44-Professor Gagarinsky"),
-18. May 2010 (R/V "47-Professor Gagarinsky"),
-19. June-July, 2010 (R/V "Hakuho Maru "),
-20. September 2011 (R/V "54-Professor Gagarinsky"),
-21. April 2012 (R/V "55-Professor Gagarinsky"),
-22. April 2014 (R/V "66-Akademik M.A. Lavrentyev"),
-23. May 2014 (R/V "62-Professor Gagarinsky"),
-24. May 2015 (R/V "65-Professor Gagarinsky"),
-25. October 2015 (R/V "68-Professor Gagarinsky"),
-26. December 2015 (R/V "72-Akademik M.A. Lavrentyev"),
-27. December 2016 (R/V "79-Akademik M.A. Lavrentyev").



II. Methods and Data

Distributions of the CO2 partial pressure and pH for 132.3 and 134 E which reveal mesoscale spatial dynamics for depths less than 500 m.



Sections of the carbon dioxide partial pressure (**a, b**) and pH $_{\text{in situ}}$ (**c, d**) along 132.3 ^{o}E (**a, c**) and 134 ^{o}E (**b, d**) Longitude. April, 2014.

II. Methods and Data

After examination of all our data on seasonal and mesoscale dynamics, we used hydrochemical data obtained for **warm** period only for two sections of the JES, along 132.3° and 134° E .

Analyzed data were obtained in international cruises:
-July 1999 (R/V “36-Professor Khromov”),
-April - May 2001 (R/V “31a-Professor Gagarinsky”),
-May 2001 (R/V “31b-Professor Gagarinsky”),
-May 2004 (R/V “33-Akademik M.A. Lavrentyev”),
-March 2005 (R/V “35-Akademik M.A. Lavrentyev”),
-May 2007 (R/V “43-Professor Gagarinsky”),
-July 2009 (R/V “46-Akademik M.A. Lavrentyev”),
-May 2010 (R/V “47-Professor Gagarinsky”),
-April 2014 (R/V “66-Akademik M.A. Lavrentyev”).

III. Data processing

i) All data for levels shallower than 500 m were discarded;

ii) Other data were grouped into five depth intervals - 500-1000, 1000-1500, 1500-2000, 2000-2500, 2500-3400;

iii) Average values of each hydrochemical parameter and each depth interval were obtained by means of relationship:

$$\overline{m_i} = \frac{\sum_j m_{ij} \cdot Z_j}{\sum_j Z_j}$$

Here m_i is concentration of i parameter; Z_j is depth for j level

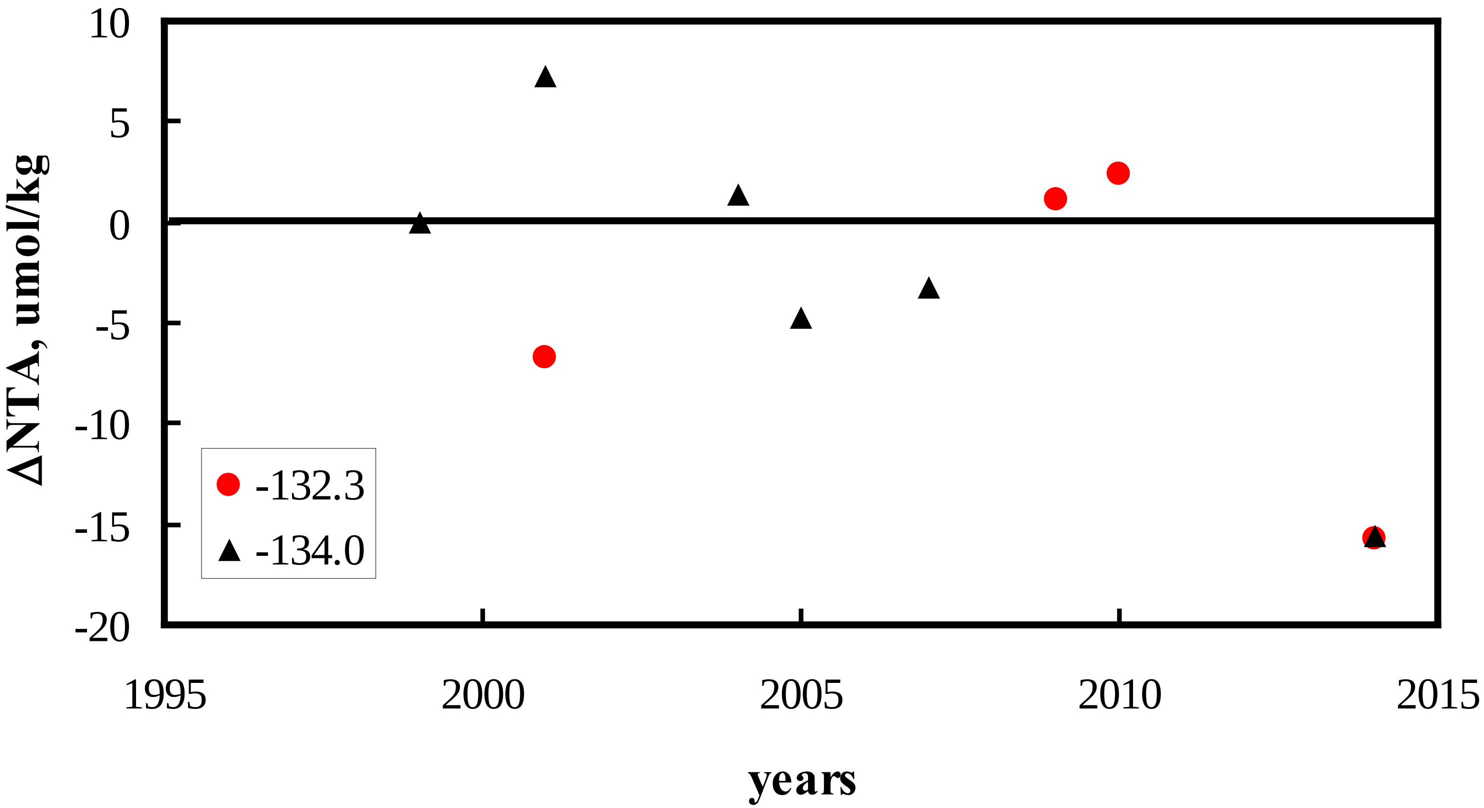
Average depth is determined by

$$\overline{Z_k} = (\sum_j Z_j) / N$$

iv) Average values were corrected to average depths: 750, 1250, 1750, 2250 and 3000 m.

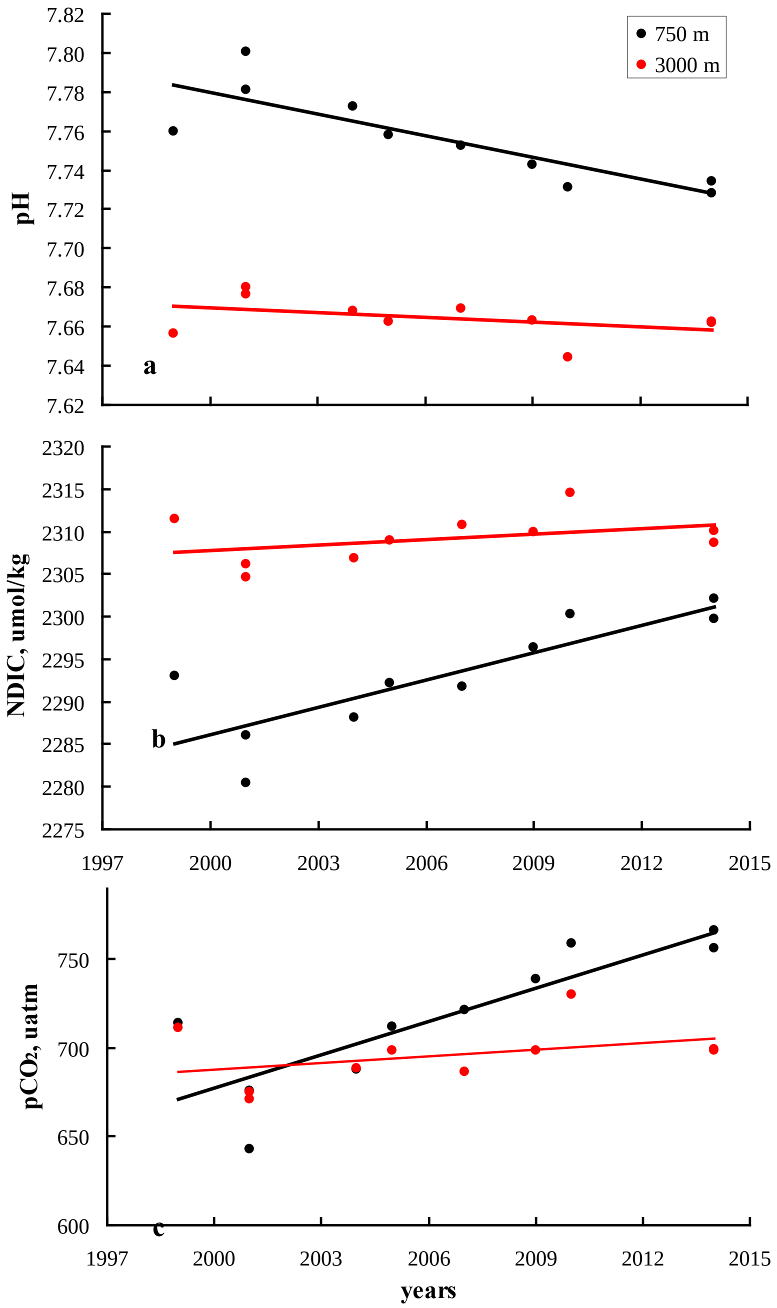
III. Data processing

Average differences of NTA between given year and 1999 (DNTA = NTA(year) – NTA(1999)).



It was accepted that NTA does not have temporal variability and equals NTA (1999). TA values for given year were corrected regarding TA obtained in 1999 when Dickson's CRM was used as standard.

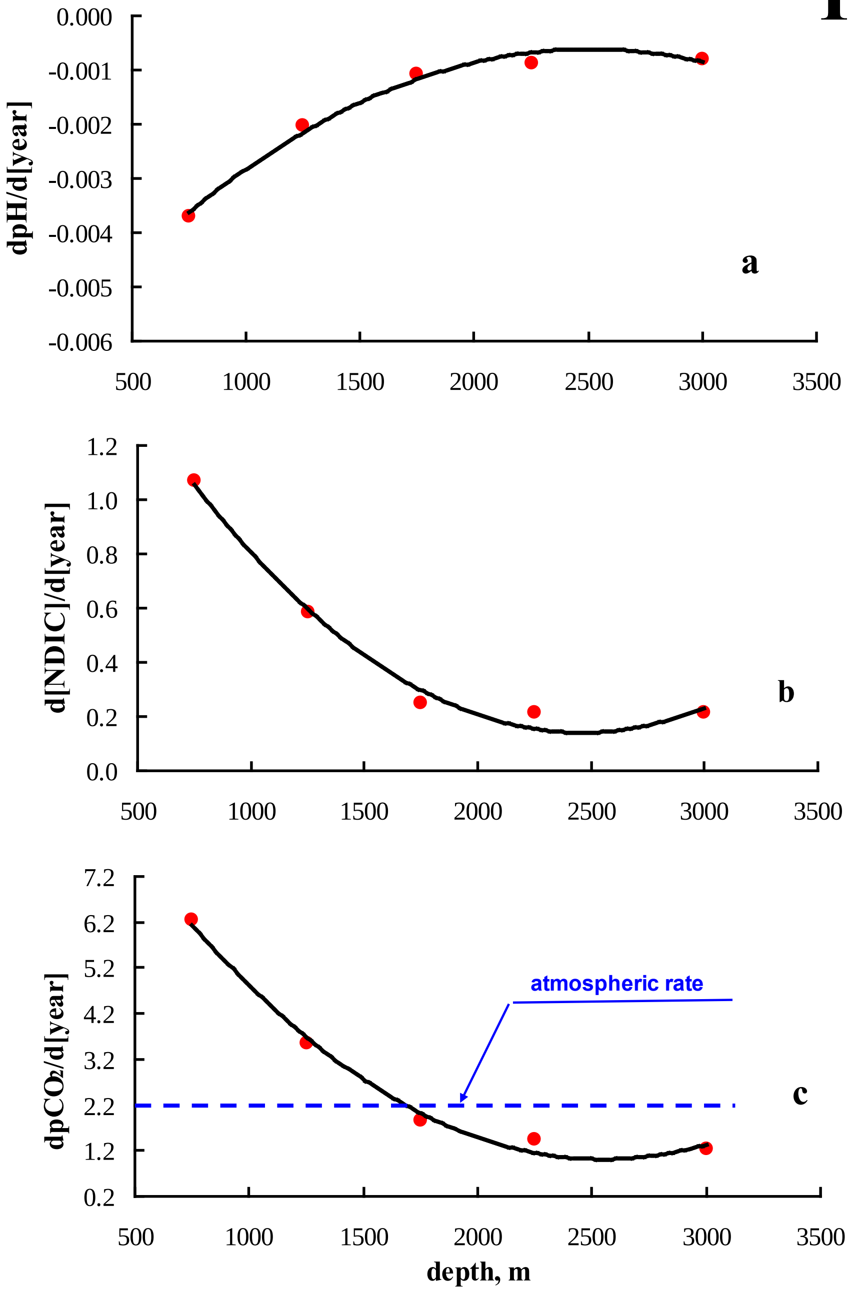
IV. Results of Acidification



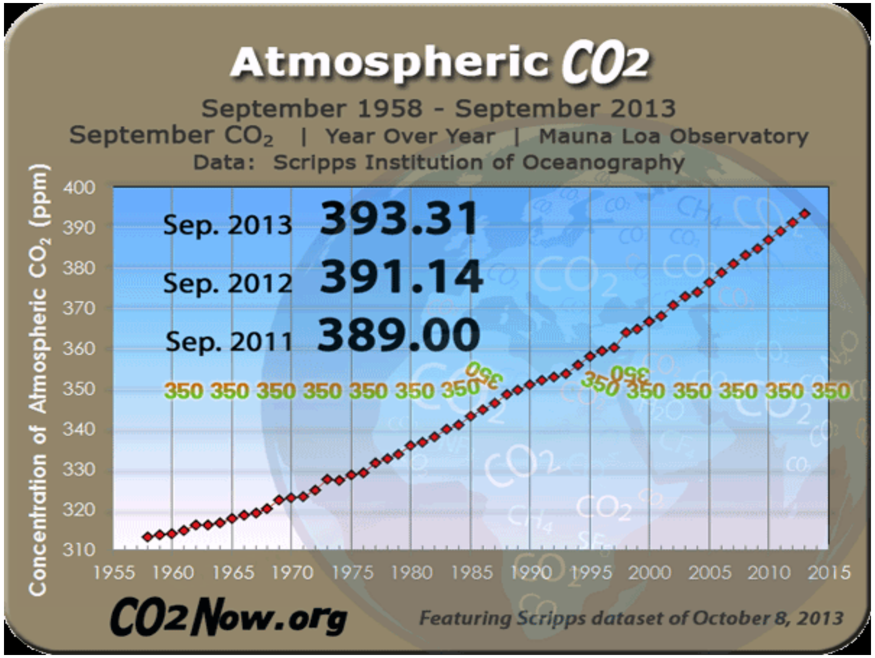
Using corrected TA data for different years and measured pH data temporal variability of carbonate system was established.

The temporal variability of the averaged carbonate system parameters in the JES in depths 750 m (black color) and 3000 m (red color). a – pH (in situ); b – Normalized Dissolved Inorganic Carbon; c – carbon dioxide partial pressure.

IV. Results of Acidification

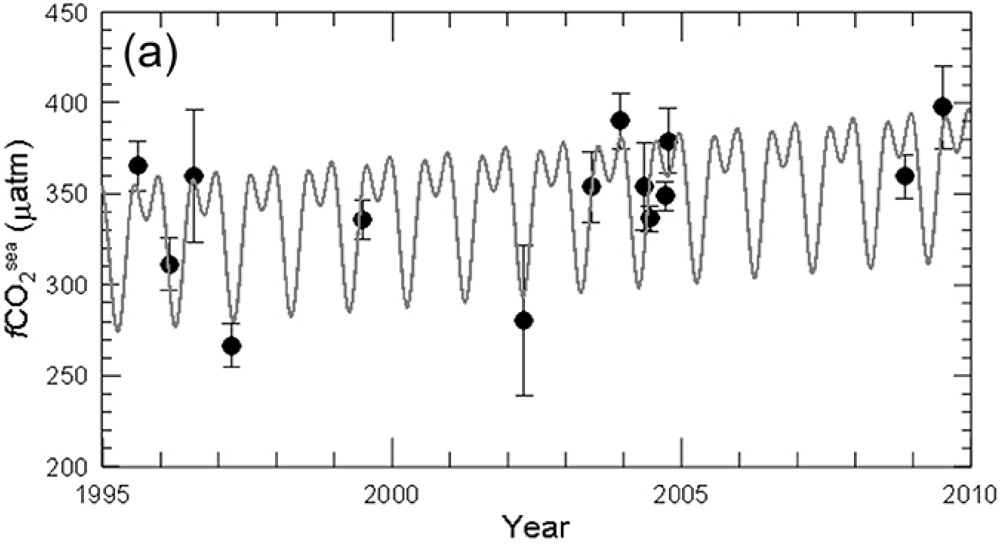


Rates of the temporal variability of carbonate system parameters in the JES as function of depths. **a** – for pH (in situ), “pH_unit/year”; **b** – for Dissolved Inorganic Carbon,” umol/kg)/year”; **c** – for Carbon Dioxide partial pressure, “uatm/year”.



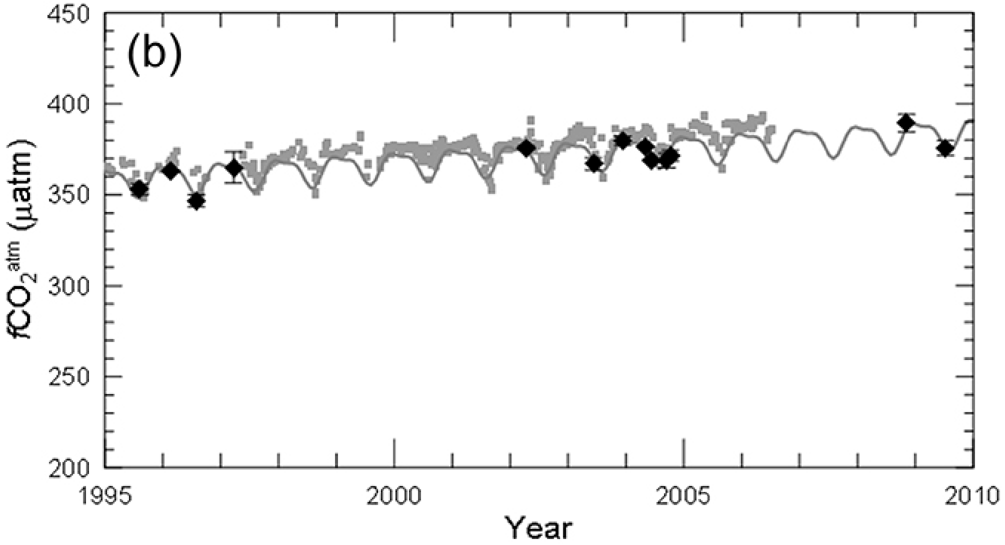
IV. Results of Acidification

Temporal variability of CO2 fugacity in surface seawater (a) and atmosphere (b) at the Ulleung Basin from 1995 to 2009.

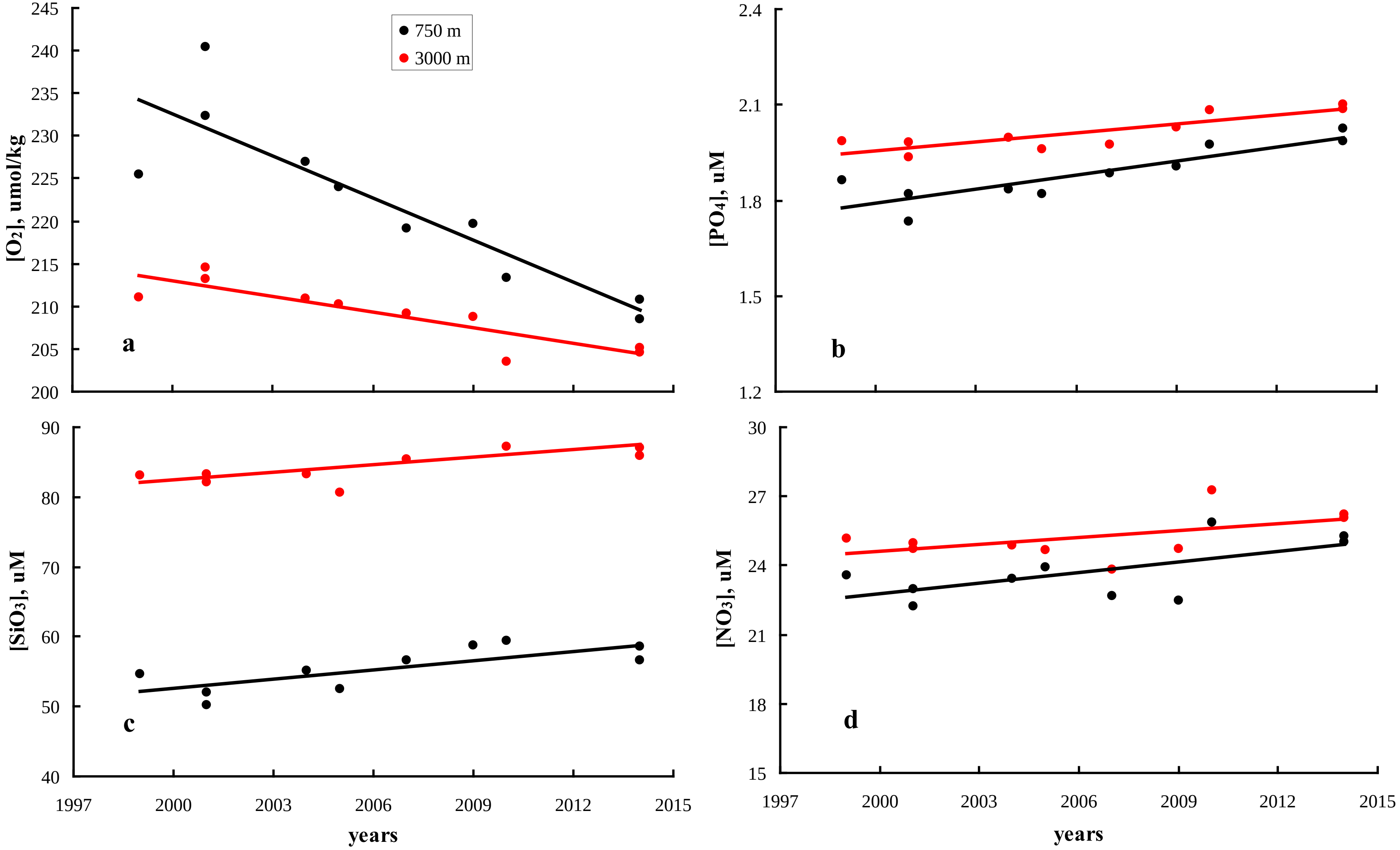


The fCO_{2sw} shows an increasing trend by 3.36 ± 2.7 µatm yr^{-1} and 1.97±2.92 µatm yr^{-1}

Dong-Jin Kang, Jae-Yeon Kim // PICES Report, 2016.

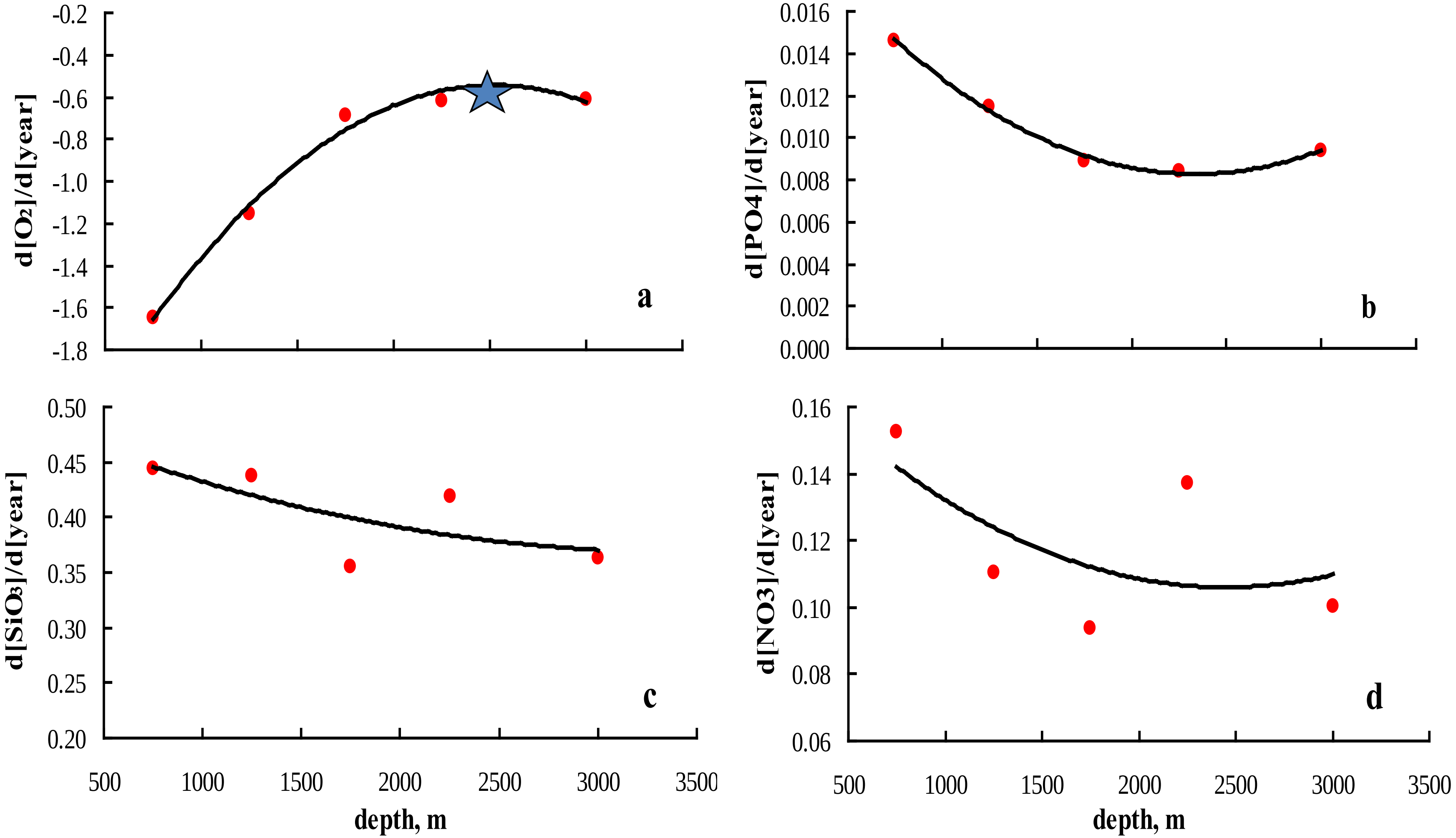


V. Linkage of acidification with temporal variability of nutrients concentrations and DO



Temporal variability of the averaged hydrochemical parameters in the JES in depths 750 m (black color) and 3000 m (red color). a – dissolved oxygen concentration; b – phosphates concentration; c – silicates concentration; d – nitrate concentration.

V. Linkage of acidification with temporal variability of nutrients concentrations and DO



Rates of the temporal variability of hydrochemical parameters in the JES as function of depths. a – for dissolved oxygen concentration; b – for phosphates concentration; c – for silicates concentration; d – for nitrate concentration.

V. Linkage of acidification with temporal variability of nutrients concentrations and DO

We suggest that observed acidification of interior JES is result non-stationary process of the aerobic degradation of organic matter according to reaction:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138 \cdot O_2 \rightarrow$$
$$106 \cdot CO_2 + 122 \cdot H_2O + 16 \cdot HNO_3 + H_3PO_4 \qquad \textbf{(A)}$$

	O:C	C:N	C:P	N:P
Average Rate ratios	-2.0	3.9	44.2	11.3
Redfield ratios	-1.3	6.6	106.0	16.0

Maximum rate of variability of the reaction (A) corresponds 750 m.

VI. Preliminary explanations of interior JES acidification

There are two explanations of non-stationary degradation of organic matter:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138 \cdot O_2 \rightarrow$$
$$106 \cdot CO_2 + 122 \cdot H_2O + 16 \cdot HNO_3 + H_3PO_4$$

1) **Cessation of the supply of the new bottom water** in the JES (generally accepted point of view for explanation decreasing DO concentration in JES). In this case:

- *residual time of nutrients is increasing,*
- *supplying of nutrients into photic layer is reduced and*
- *primary production is reducing in time.*
- *JES becomes more oligotrophic basin despite on increasing of nutrient concentrations.*

VI. Preliminary explanations of interior JES acidification (instead conclusions)

Alternative explanation is:

2) Vertical mixing processes are mostly stationary in time. Observed non-stationary process oxidation of organic matter can be explained by **the increasing of falling organic materials.**

In this case:

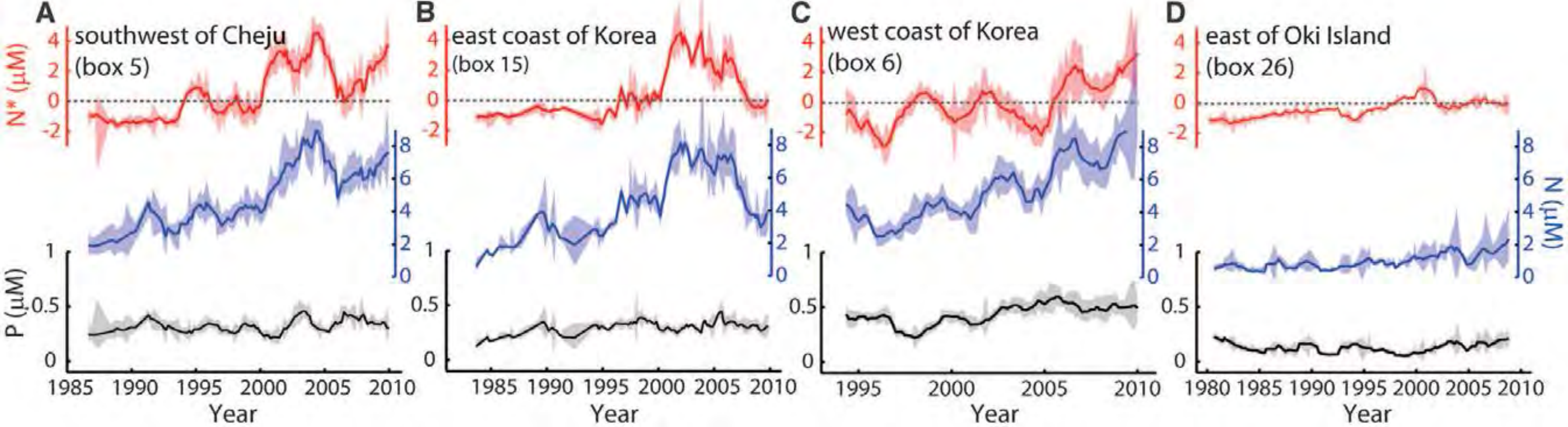
- *primary production is increasing with time and*
- *JES becomes more eutrophic basin.*

It is should be noted that both explanations gave Prof. Gamo-san with colleagues for observed decreasing DO in JES

”...the reduction or cessation of the supply of the new bottom water, the increase of falling organic materials, …” (Gamo et al., 1986)

We assume that the increasing of falling organic materials is main reason of acidification of interior of the JES for two reasons:

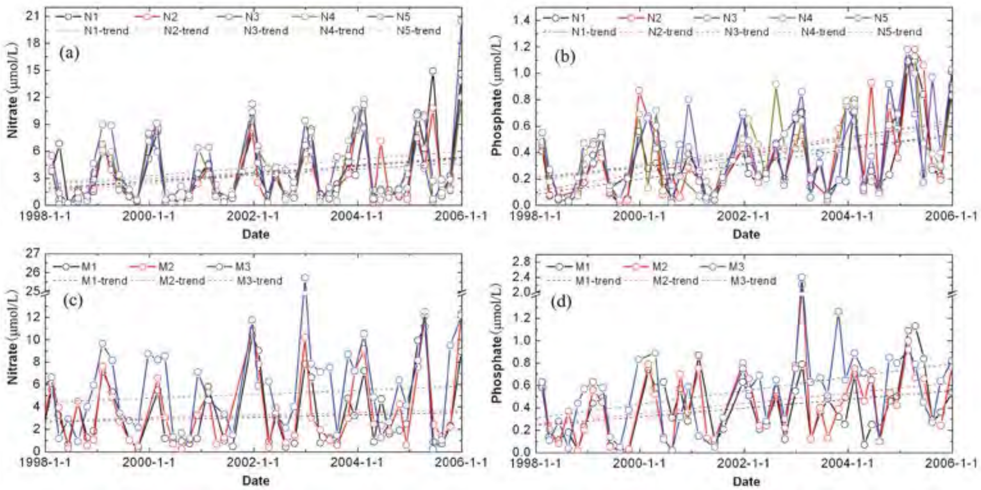
i) Increasing of Atmospheric Nitrogen Deposition.



Time series of N* (mM) (red line), N (nitrate, mM) (blue line), and P (phosphorus, mM) (black line) (A) in the region southwest of Cheju Island (box 5), (B) off the east coast of Korea (box 15), (C) off the west coast of Korea (box 6), and (D) in the region east of Oki Island (box 26). The color gradations indicate the confidence interval (P = 0.05) from the mean of the measurements collected over a 2-month interval. The dotted lines in (A) to (D) correspond to N* = 0 mM.

T.-W. Kim, K. Lee, R.G. Najjar, H.-D. Jeong, H. Jin Jeong “Increasing N Abundance in the Northwestern Pacific Ocean Due to Atmospheric Nitrogen Deposition” // SCIENCE, 2011, V. 334, pp. 505-508.

ii) Increasing of Export of organic matter and nutrients from the East-China Sea to the Japan/East Sea because eutrophication of the ECS is going.



Temporal variations of nitrate and phosphate concentrations at the serial stations in the southeastern YS during 1998–2005. The upper and lower rows are the sections N1–N5 and M1–M3, respectively, as shown in Fig. 1a. The dash line is the linear regression versus time (year) for each serial station. (He et al., Biogeosciences, 2013. V. 10. P.4721-4739.)

The seas off China have been hit by their largest ever growth of algae, ocean officials said, with vast waves of green growth washing onto the shores of the Yellow Sea Picture: AFP / GETTY IMAGES

Thank you for attention!