FSBSI «Marine Hydrophysical Institute of RAS»

CARBONATE SYSTEM TRANSFORMATION IN THE SEVASTOPOL BAY (THE BLACK SEA)

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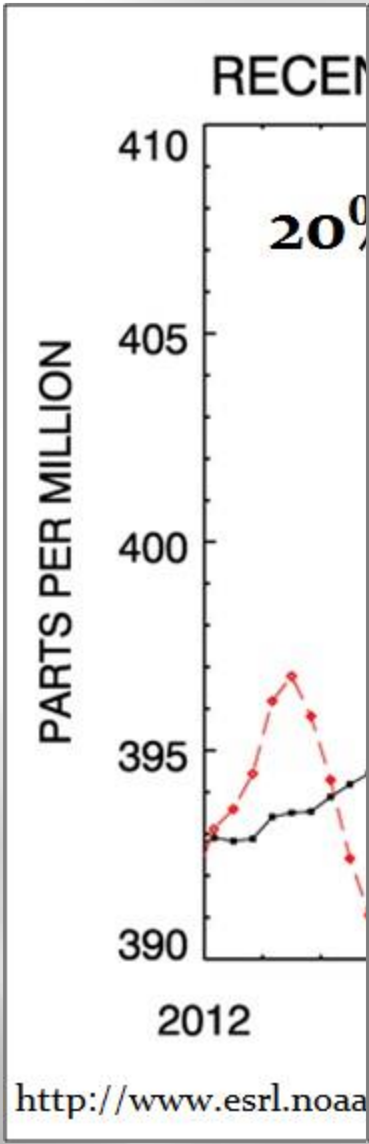
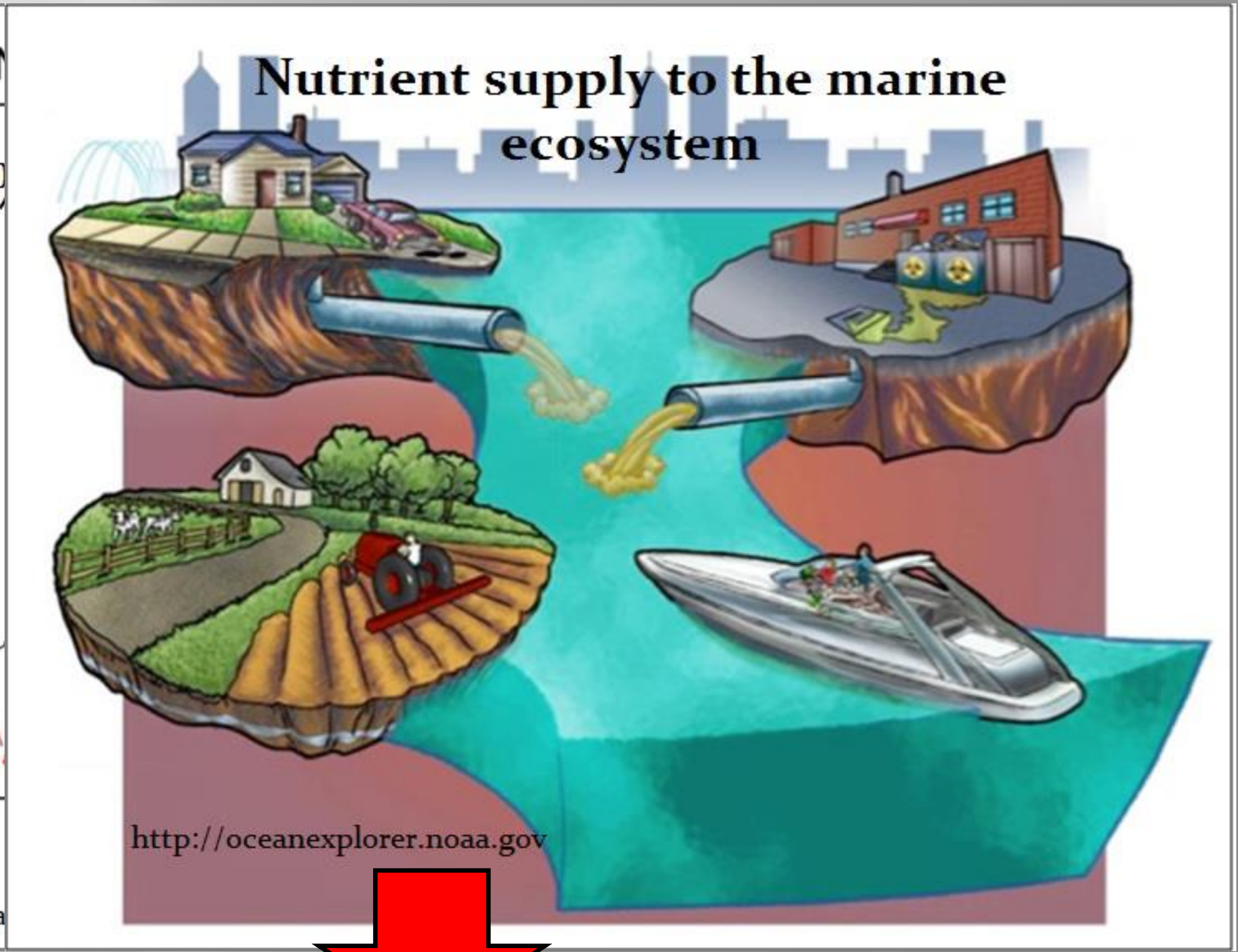
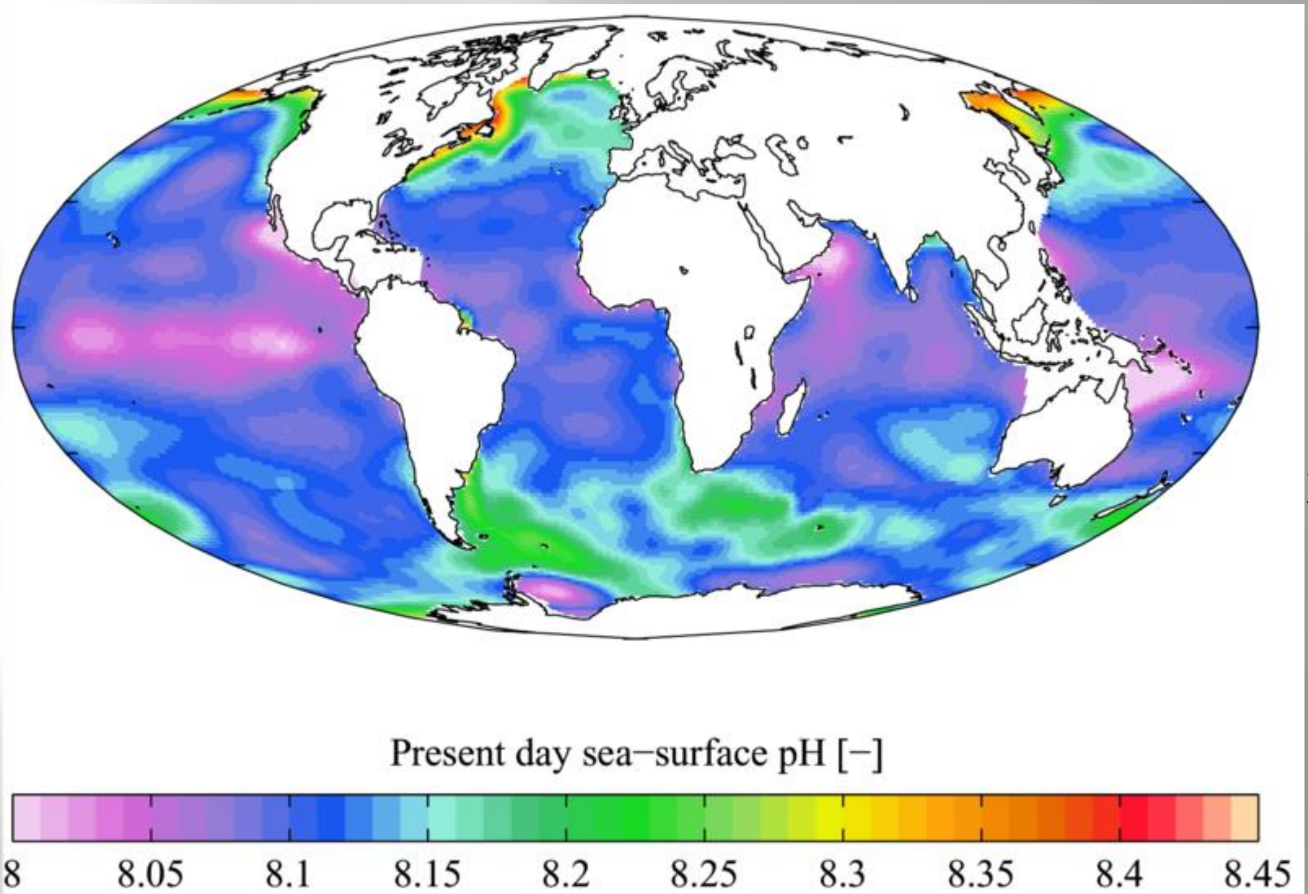




pronounced carbon cycle transformation in coastal areas.



https://en.wikipedia.org/wiki/File:WOA05_GLODAP_pd_pH_AYool.png

Acidification and CO_2 increase in the water column and appearance of oxygen minimum zones are reported for worldwide.

This makes ecological assessment of aquatic systems, including key cycles of elements, an important social and scientific task.

Main line

to present information on dynamics of the inorganic part of the carbon cycle and its transformation in the Sevastopol Bay from 1998 – 2015:

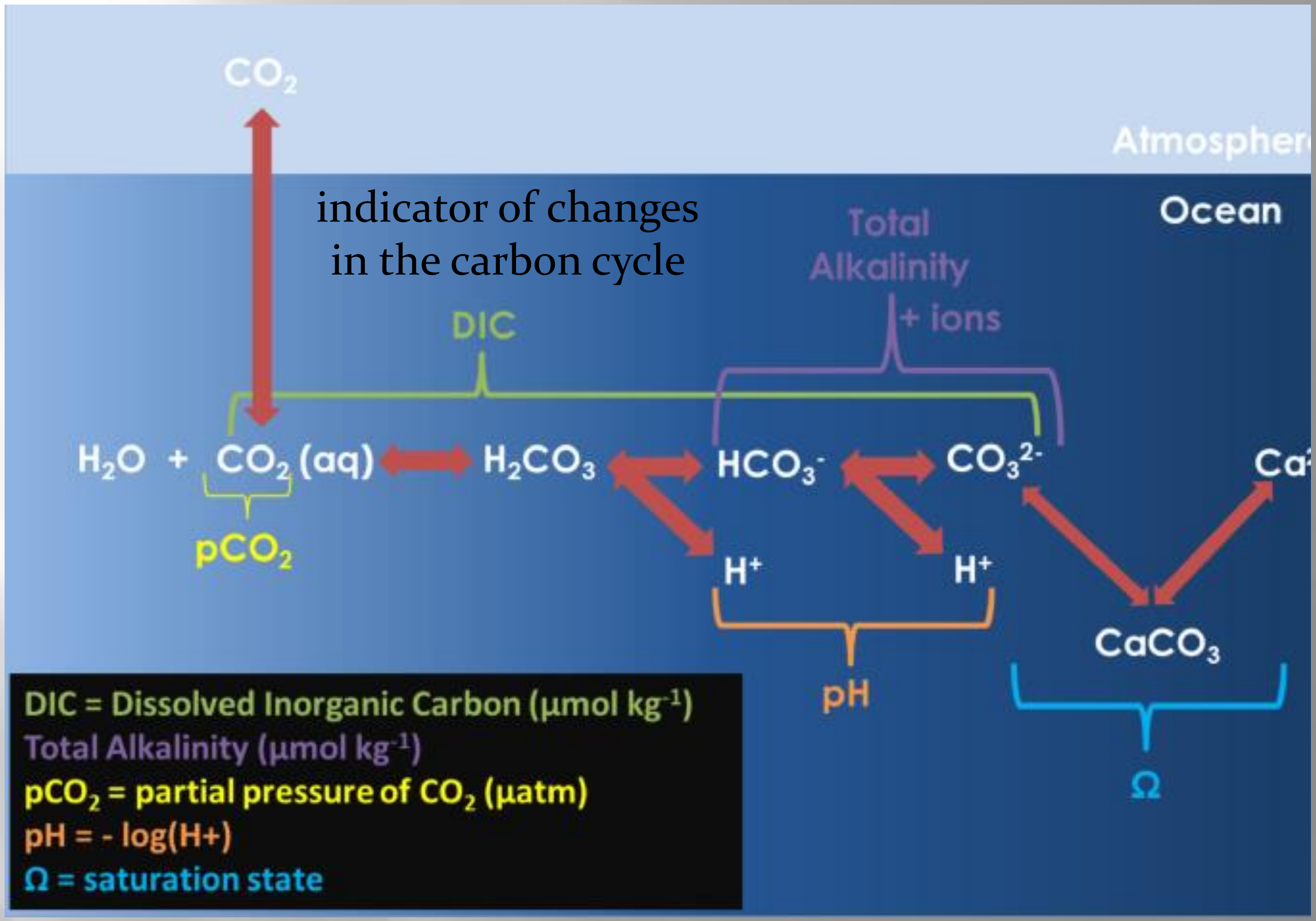
- long-term observations of the carbonate system's components;
- analysis of seasonal changes in the carbonate system's components;
- factors and processes influenced variations in the carbonate system's components;
- Sea-atmosphere CO_2 Fluxes (directions, changes)

Sevastopol Bay - semi-enclosed estuarine type bay.

The bay is under heavy anthropogenic pressure

It results in negative consequences for the bay's ecosystem

The Carbon cycle in marine systems



https://wattsupwiththat.com/2015/02/17/claim-versus-pr-hype-doesnt-hold-up-satellite-images-reveal-ocean-acidification-from-space/

Main processes result in variability of components of the carbon cycle

(1) photosynthesis:

$$6CO_2 + 6H_2O \rightarrow 6H^+ + 6HCO_3^- \rightarrow C_6H_{12}O_6 + 6O_2$$

$\Rightarrow$ $\downarrow$DIC, $\uparrow$pH, $\downarrow CO_2$

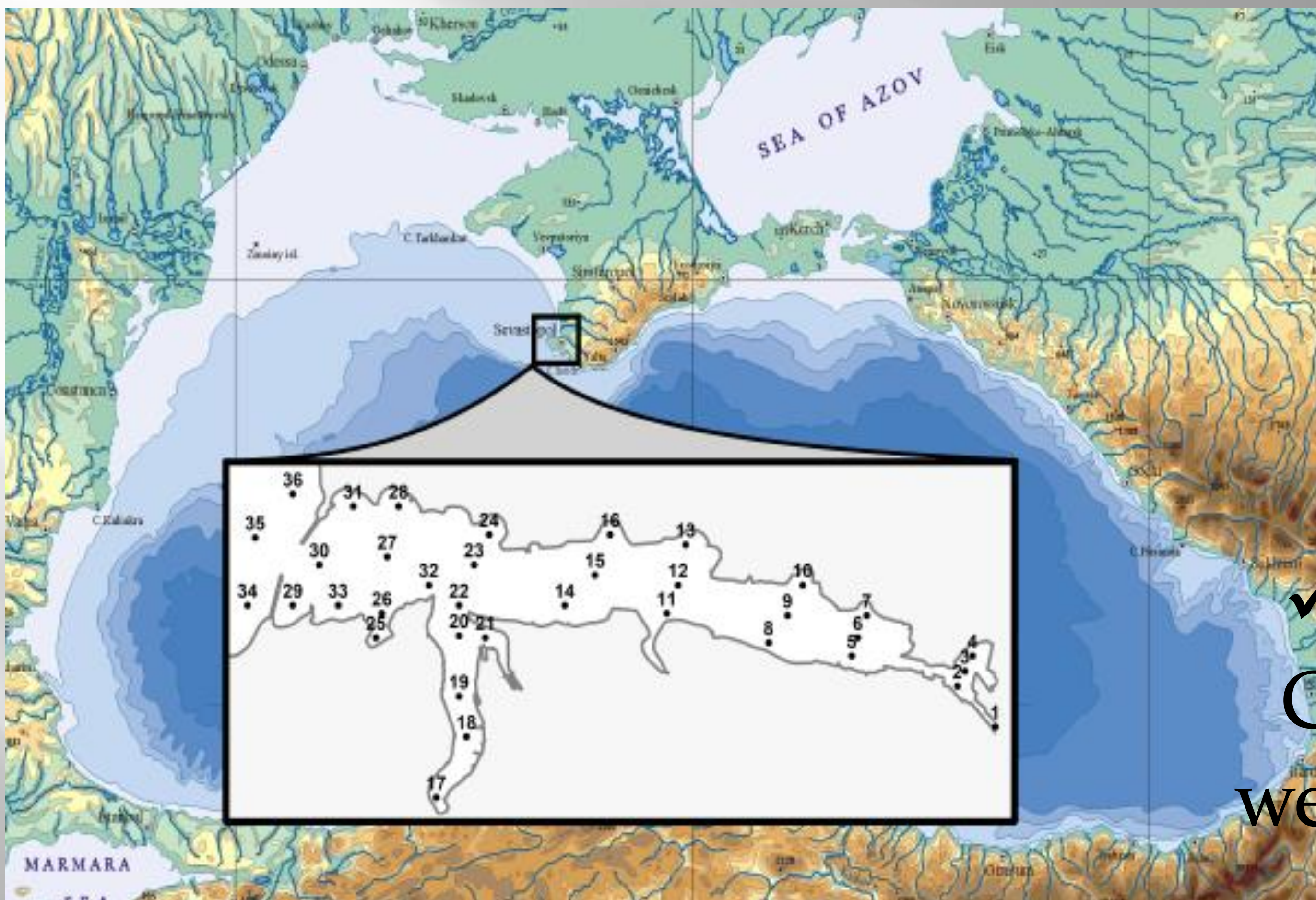
(2) biogeochemical organic carbon oxidation:

$$C_6H_{12}O_6 + 6O_2 \leftrightarrow 6CO_2 + 6H_2O \leftrightarrow 6H^+ + 6HCO_3^-$$

$\Rightarrow$ $\uparrow$DIC, $\downarrow$pH, $\uparrow CO_2$

(3) physical process of CO_2 transport

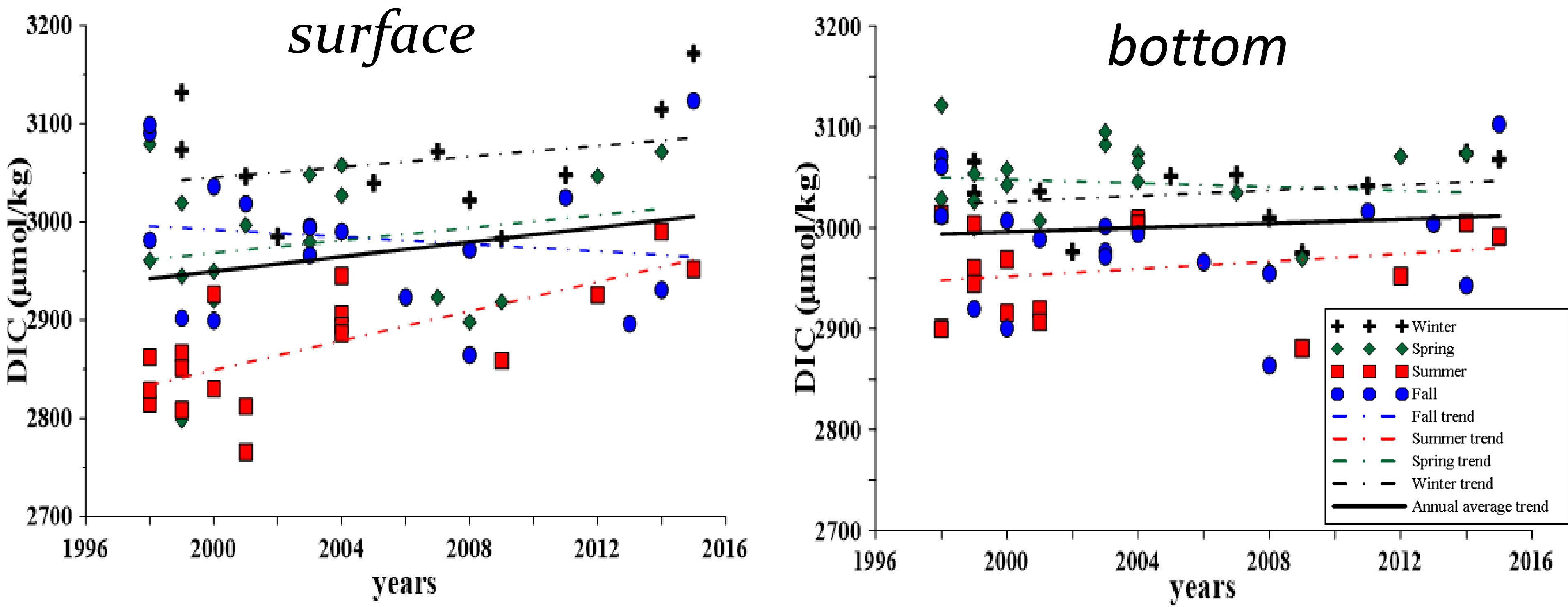
Sampling in the Bay of Sevastopol



Determined parameters:

- ✓pH, alk. – analytically;
- ✓CO_2, HCO_3^-, CO_3^{2-}, pCO_2 – were calculated

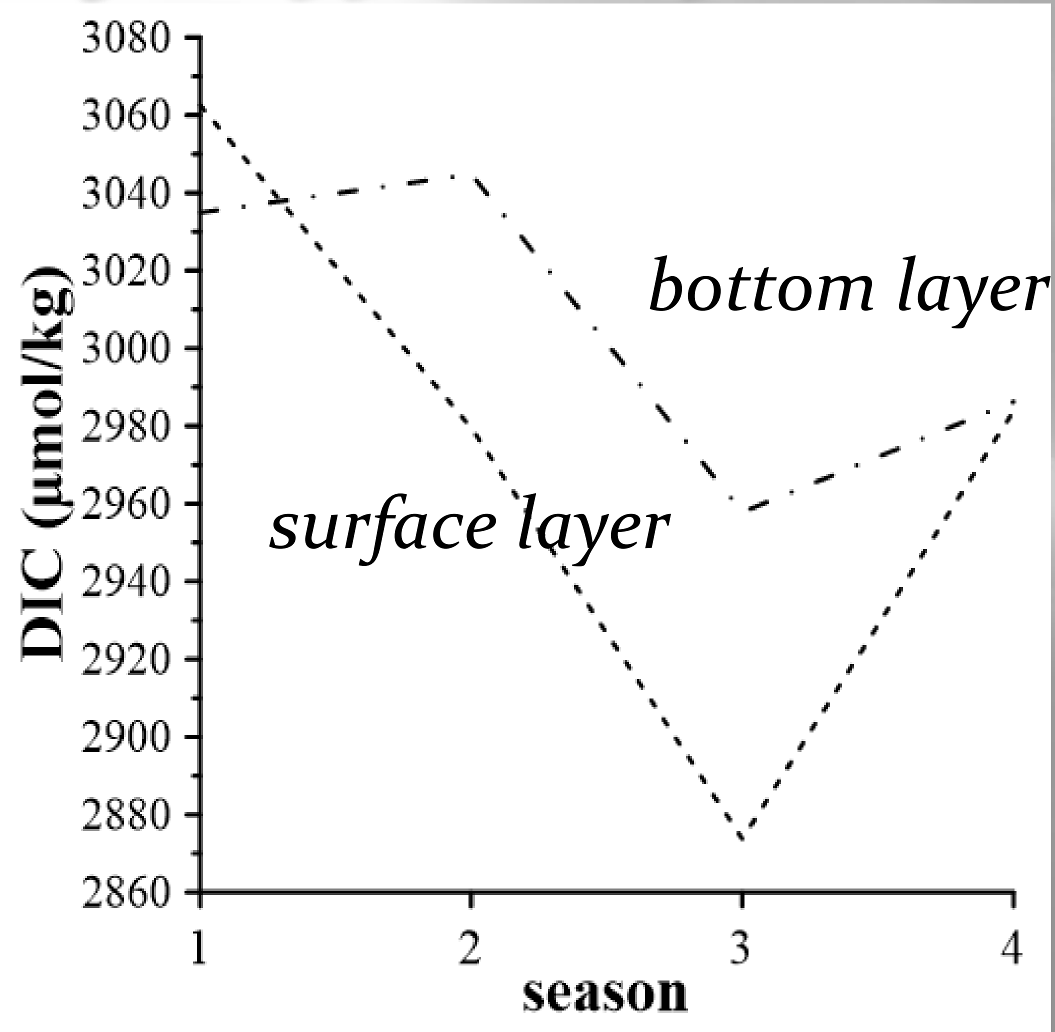
Variations in the DIC in 1998 – 2015



DIC changes are insignificant and reveal up to 2% increase from 1998 – 2015.

This is evidence for the bay’s carbonate system recovers.

Seasonal DIC variability averaged for 1998 – 2015



1 – Winter, 2 – Spring, 3 – Summer, 4 – Fall

Winter: DIC surface is maximum (ventilation, ↑CO_2 solubility).

Spring: DIC bottom is maximum; DIC surface – high values due to seasonal flood of r. Chernaya (riched with Corg, CO2 and PSM)

Summer: DIC is minimal (photosynthesis, ↓ CO_2 solubility, strong vertical stratification).

Fall: ↑ DIC , DIC bottom=DIC surface (vertical ventilation, Corg oxidation in the bottom)

Variations in other components of the carbonate system

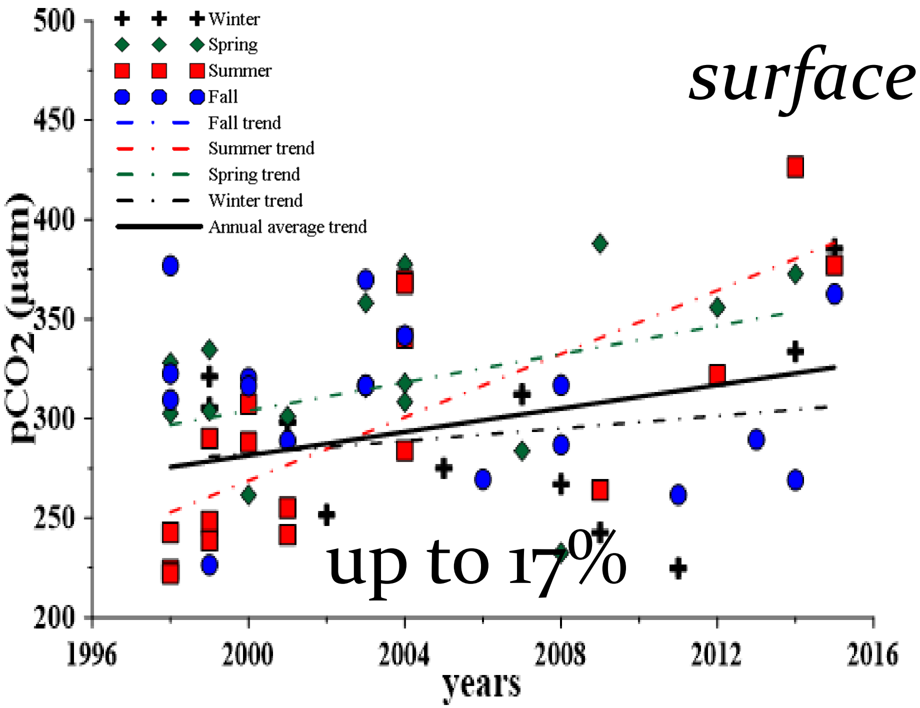
Species	Surface Layer	Bottom Layer
HCO_3^-,	up to 4%	up to 1%
CO_2	up to 20%	down to 2%
CO_3^{2-}	down to 17%	up to 2%
pH	down to 1%	down to 0,1%

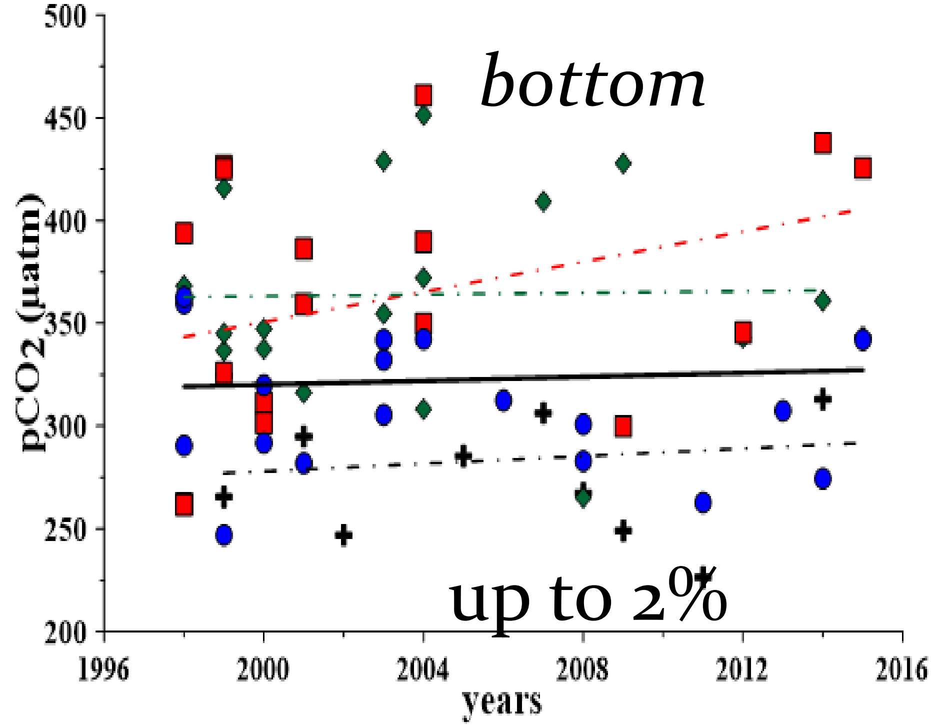
const

Additional flux of C_{org} from sewage and coast

Analytically negligible
or ?
Source of carbonates

Variation in pCO2



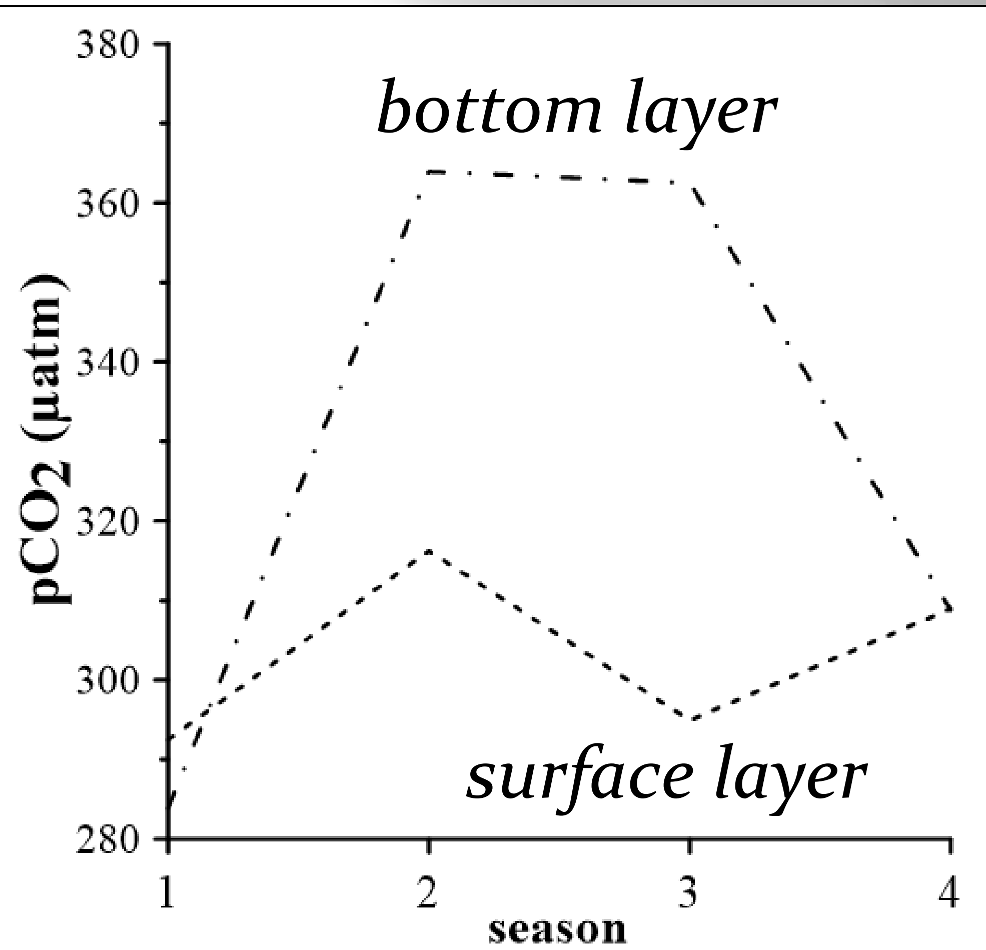


pCO2 bottom > pCO2 surface

Surface: a persistent upward trend in winter (by 9%), spring (by 19%) and especially in summer (up to 46%), due to ↑Corg oxidation rate

Bottom: uprising trend is traced for summer (by 17%). In winter and spring, this upward trends are ~6 and 1% respectively. In fall, a 6% decrease of the pCO_2 is observed.

Seasonal variations of pCO_2



1 – Winter, 2 – Spring, 3 – Summer, 4 – Fall

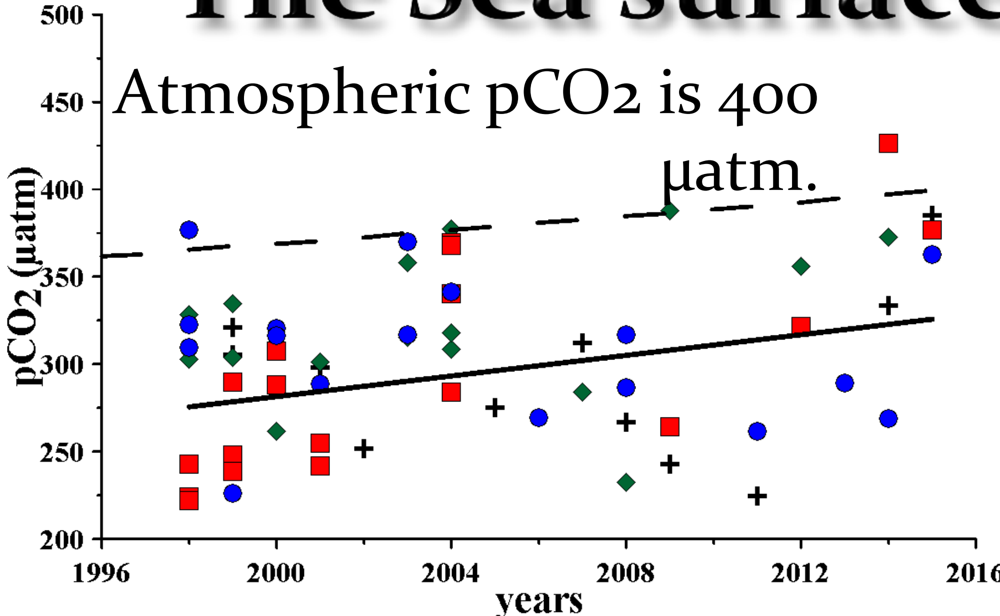
Winter: pCO_2 minimum (vertical mixing, ↓Corg oxidation, ↑gas solubility and absorption of CO_2 from the atmosphere).

Spring: pCO_2 surface < pCO_2 bottom. pCO_2 is maximum in the surface due to influx of CO2 with r. Chernaya waters.

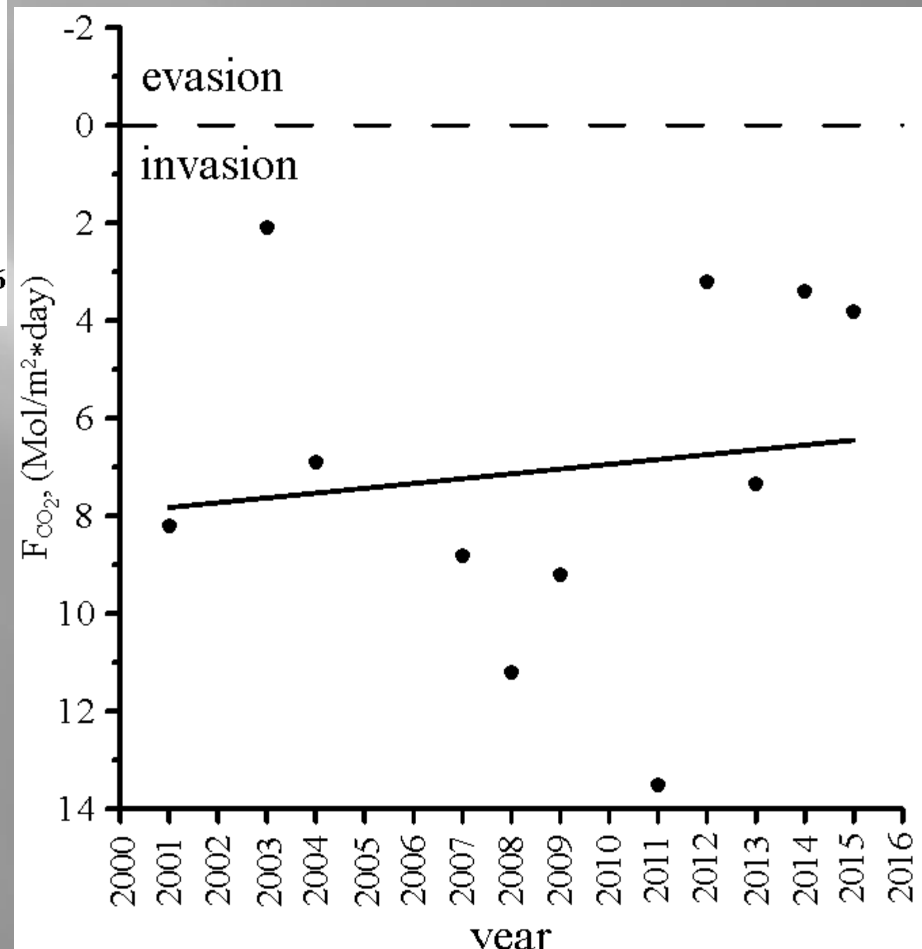
Summer: pCO_2surface ↓ (eutrophycation). pCO_2 bottom is equal spring value (Corg oxidation). Maximal difference between layers (strong vertical stratification)

Fall: pCO_2 surface = pCO_2 bottom (↑ solubility of CO_2 in cooling waters at surface; vertical mixing).

The Sea surface Flux of pCO_2



Bay's waters mainly absorb CO2 from the atmosphere (that is unusual for the coastal ocean



Invasion (waters absorb CO_2 from the atmosphere) is typical, but this ability to consume CO_2 from the atmosphere has decreased by 20% from 2001 to 2015.

Summary

- DIC changes are analytically insignificant. Increase of pCO_2, CO_2 and HCO_3^- in the surface indicates anthropogenic pressure.
- In warm seasons the main processes are Corg respiration in bottom and photosynthesis in the surface layers.
- In cold seasons, water dynamics and mixing promote system's recovery.
- Seasonal oscillations are far more pronounced, and reveal extremes for appearance of oxygen minimum zones.
- The surface waters still absorb CO_2 from the atmosphere, but this ability has decreased by 20% from 2001 to 2015.

Ecosystem Sevastopol Bay remain reversible, and the carbonate system can be restored.

THANKS FOR YOUR ATTENTION

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The total alkalinity was determined by direct titration by hydrochloric acid with a potentiometric end-point detection, pH was determined with a potentiometric pH-meter with NBS buffer solutions [1]. The standard deviation of measurement of 10 parallel samples did not exceed 0.02 pH units. Whereas CO_2, HCO_3^-, CO_3^{2-} concentrations and pCO_2 values were calculated as suggested in [7]. The dissociation constants of carbonic acid, recommended by the Department of Marine Sciences of UNESCO, were used [7]. Boron was assumed a conservative part of salinity; therefore, the boron content was calculated from the salinity [4]. The effect of dissociation of water, phosphoric acid, sulfuric acid, hydrofluoric acid and other acids were not taken into account.