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The approach to limology (barrier zones) in the Baltic Sea: a review

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Abstract Considering the processes of sedimentogenesis and ore formation, scientists have paid attention to various boundary zones in the ocean, where the processes of matter supply, transformation and re–deposition occurred more actively. These boundary zones strongly affect the quantities and composition of the material suspended in water as well as the bottom sediments. In order to define such areas (layers) the author has introduced the notion of "geochemical barrier zones". Often more than one barrier can be manifested within a small area of thin sea (ocean) water layer. The proposed research deals with creating and developing of a new scientific branch – lithologic–geochemical limology of the ocean. Limology, implied by the Latin word "limes" meaning "boundary", is defined as a science studying the system of boundary zones and divisions of various types in the environment. Some of the most important geochemical barrier zones in the Baltic Sea are studied in this report.[1]

Keywords *Limology • Sedimentology • Geochemistry • Geochemical barriers • Baltic Sea*

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INTRODUCTION

Natural objects, the scales of which range from colloid forms to oceanic environmental systems, are very variable, and this is an inherent feature of these objects. Processes of transformation of material occurring in the ocean are commonly transitive, and the distribution of physical, chemical and biological processes is neither random nor uniform throughout the whole length of the water strata: instead, they are focused in relatively narrow zones displaying active transport and transformation of material and energy, which are called boundary zones of the sea. These active zones indicates abrupt, jump like changes of natural processes, i.e., when the processes or activity on one side of such a boundary are substantially different from those on its other side.

This is why these active boundaries may be regarded as natural barriers (Fig. 1). In contrast to barriers, the remaining areas (those occurring between boundaries) of the ocean are thought to be relatively homogeneous, non–gradient, chemically inert, and biologically inactive areas. Such a picture of the ocean's structure, which is a subject of current, considerable interest, is based

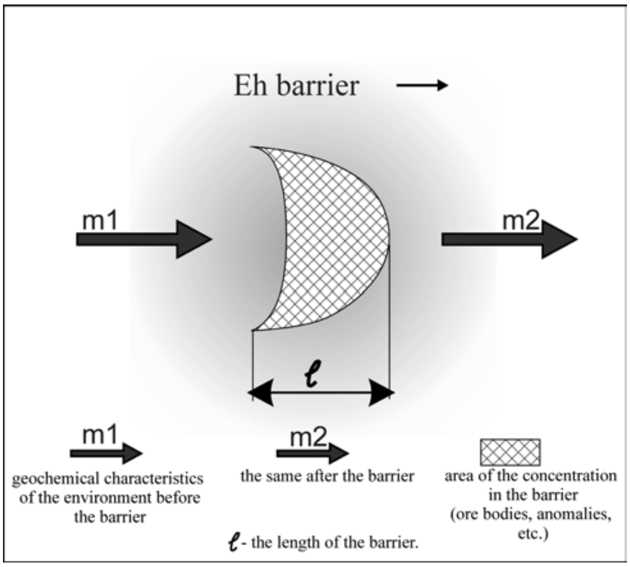

Fig. 1 Geochemical barrier (direction of the migration) (after Perelman 1989). These active zones are responsible for abrupt, jump–like changes of natural processes, i.e., when the processes on one side of such a boundary are substantially different from those on its other side.

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[1] The paper is based on reports have been read at the 10th Baltic Marine Geology Conference held in Saint–Petersburg, 24–27 August 2010, the 5th Conference *The Shores and the Sea Research* held in Palanga, Lithuania, 13–15 April 2011, and the 8th BSSC, held in Saint–Petersburg, 22–26 August, 2011.

on the existence of outer and inner active boundaries related to fronts, dispersions, and environmental and geological (sedimentary, hydrothermal, volcanic, etc.) systems.

The results of the first researches of the barrier zones in the Baltic Sea were published over twenty years ago (Emelyanov 1981, $1982_{1,2}$, 1984, 1991). The processes in the barrier zones of the Gdansk Basin were discussed in special chapter (Emelyanov 1986_1) and the role of the redox barrier "Eh" in the formation of manganese–carbonate mud and manganese–iron ores in the deeps of the Baltic Sea – in special publications (Emelyanov 2004, 2011). This article is written on the basis of two author books *"Barrier zones in the ocean"* (Emelyanov 1998, Russian version; Emelyanov 2005, English version).

The aim of the paper is to classify boundaries in the Baltic Sea, paying particular attention to the mechanisms that cause them and their dynamic functioning. Among a great many of natural boundaries/barriers – up until now we have succeeded in revealing only those barriers where the composition of substances and forms of their cross–boundary migration exhibit significant changes upon crossing these boundaries (barriers). All the natural barriers in the ocean and sea (Emelyanov 1998, 2005), as well as new methods for studying boundary effects, will make it possible to predict probable geological–geochemical and ecological consequences in the sea, mineral and biological resources, polluted and self–purifying zones, recreation areas, etc.

The report aims to focus of those barriers (or barrier zones), which are most important in the sedimentation in the Baltic Sea (*below in the classification they are shown by Italic).*

Classification of the geochemical barriers and the geochemical barrier zones in seas and oceans (Emelyanov 1998, 2005)

A. Geochemical barriers that exist depending on their position in space

I. *Hydromechanical*
- *I.1. Coastal zone or littoral (shore–sea; 1st mechanical barrier)*
- *I.2. Zone of sharp decrease in repetition of asymmetry phenomena of wave near–bottom currents (2nd mechanical or hydrodynamic barrier)*
- *I.3. Zone of strong currents of the main basin (the boundary of replacement of clastic sediments by clayey sediments) (3rd hydrodynamic barrier)*

II. Physicochemical and biogeochemical
- II.1. Alkaline–acidic barriers (strongly acidic, weakly acidic, neutral, weakly alkaline and alkaline)
- II.2. Oxidation–reduction barriers
  - *a. Redox Eh barrier in water and the* O_2*–*H_2S *layer in water*
  - b. Redox Eh barriers in sediments (usually +200 to +400 mV)

III. Salinity barriers
- *III.1. River–sea*
- III.2. Seawater–brines
- III.3. Springs of ground water–sea water
- *III.4. Halocline*

IV. Temperature and dynamic barriers
- IV.1. Thermocline (T), freezing point, Mendeleyev temperature (40°C), evaporation barrier, etc.
- IV.2. Dynamic (P) barriers—the changes of the state of matter with changing pressure

V. Light barriers

B. Geochemical barriers that exist independently of their position in space

VI. Authonomic barriers
- VI.1. Water–living matter
- VI.2. Water–suspended matter
- VI.3. Electrochemical barriers

C. Geochemical barrier zones

VII. Barrier zones
- VII.1. Ice–sea water
- *VII.2. River–sea*
- VII.3. Hydrofronts and divergences
- VII.4. Centres of submarine discharge
- VII.5. Hydrotherm–sea water
- *VII.6. Sea–atmosphere*
- *VII.7. Photic layer*
- *VII.8. Discontinuity (jump) layer (thermocline–halocline–pycnocline)*
- VII.9. Oxygen minimum layer
- VII.10. Critical levels of carbonates
  - a. Lysocline (for aragonite, calcite, etc.)
  - b. Calcium carbonate compensation depth
- VII.11. Water–bottom
- *VII.12. Upper active sediment layer*

D. Others barriers and barrier zones

THE SEDIMENTATION IN THE MAIN BARRIER ZONES

Hydromechanical barriers

They are found at the boundary between two layers of water column, each of which has its own hydrodynamic conditions. The essence of a barrier is as follows: under conditions of sharply decreased hydrodynamic activity of seawaters, certain heavy and large particles, which are responsible for the transportation of a certain group of chemical elements, cannot penetrate from one medium into another to be deposited there.

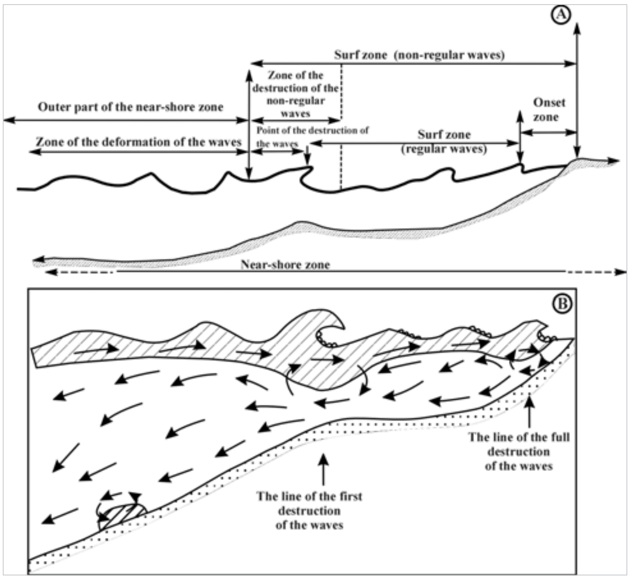

Fig. 2 Shore–sea GBZ. A. Division of the near–shore sedimentation area into characteristic parts (after Kos'yan, Pykhov 1991, p. 12). B. General scheme of the cross water circulation in the shore zone. Scheme is compiled on the basis of natural observations (after Leontyev 1989). Dashed parts—the transfer to the shore side.

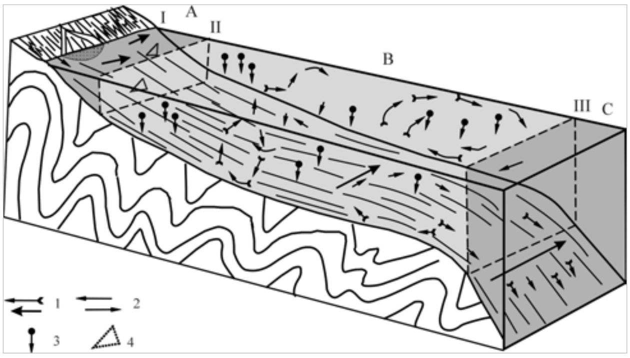

Fig. 3 Hydromechanical barriers. The block–scheme of the transfer of the sedimentary material in the water on the shelf in the non high–tide sea (after Aibulatov 1990). I. Coastal zone or littoral barrier; II. Zone of sharp decrease in repetition of asymmetry phenomena of wave near bottom currents; III. Zone of strong currents of the main basin: 1 – direction of the transfer; 2 – the transfer into the sea–side by the rip currents; 3 – evacuation into the sea–side; 4 –gravitational deposition. I, II, II – hydrodynamic barriers on the shelf during diametrical transfer of the sediments; A, B, C – upper, middle and lower dynamic part of the shelf: A – near shore deposition zone; B – rewashing and redeposition zone (or transit zone); C – deep-sea deposition zone.

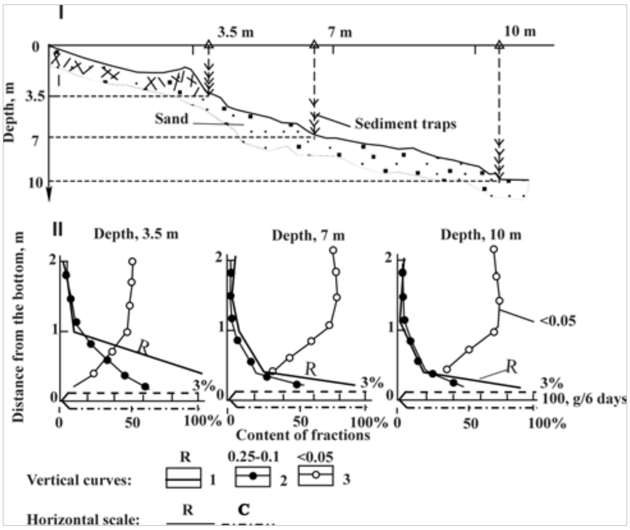

Fig. 4 Mechanical separation of sedimentary material (particulate suspended matter, further PSM) at the GBZ "shore–sea" near the northern part of the Sambian Peninsula (Svetlogorsk Bay), the Baltic Sea (after Aibulatov *et al.* 1984, p.64). I. Bottom relief at the submarine profile and three bottom stations (at depths 3.5; 7.0 and 10.0 m) with sediment traps (located at 20, 40, 100, 150 and 200 cm from the bottom). II. Concentration of the bulk suspended matter (in g per 6 days) (R), and fractions 0.25–0.1 and <0.05 mm in the bulk suspended matter (PSM) and content of the same fraction in the bulk PSM (in %). Horizontal scale: R – the bulk PSM and fractions in g/6 days, C – content the fractions in the PSM, %.

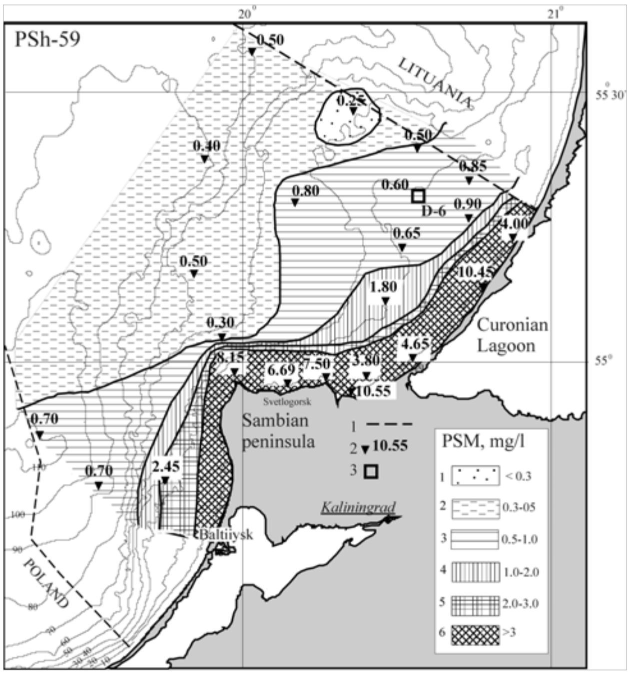

Fig. 5 The concentration of the particulate suspended matter (PSM) in March 2003, in the near–bottom water (1 m above the bottom), near Sambian Peninsula, the Baltic Sea. 1 – borders; 2 – station and concentration of PSM; 3 – location of oil platform D–6.

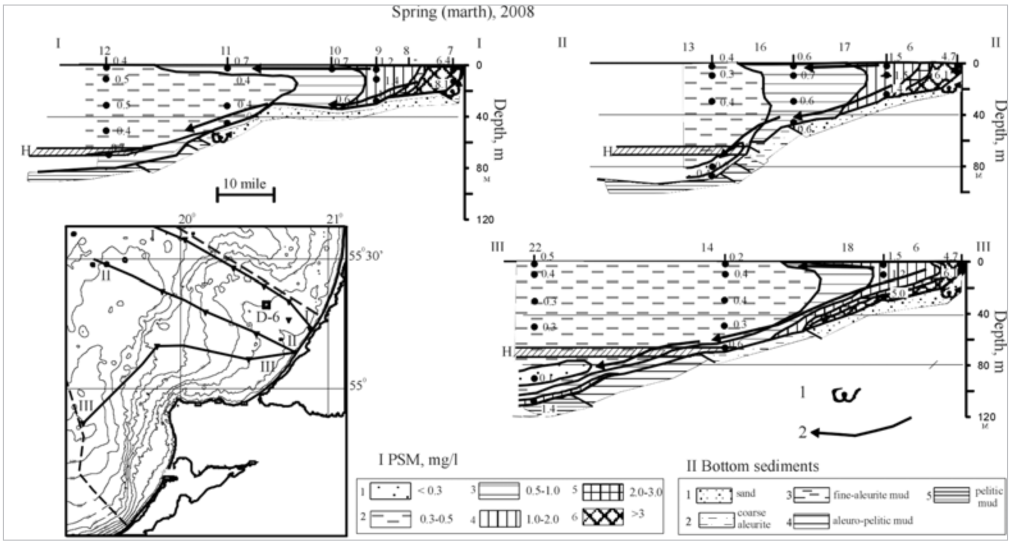

Fig. 6 The concentration of PSM in the three profiles near Sambian Peninsula.

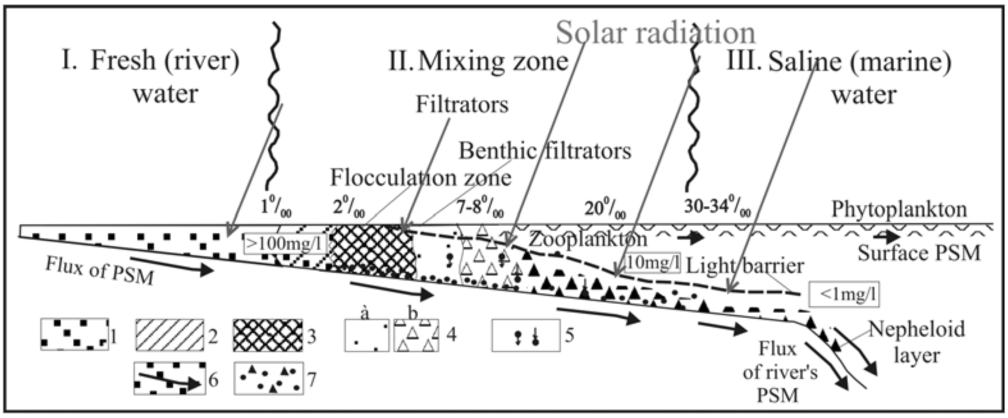

Fig. 7 River–sea barrier zone (salinity barrier and main sedimentological processes) (after Lisitzin (1998) with some changes and additional symbols of author). I – fresh (river) water; II – mixing zone; III – marine (saline) water. 1 – river's particulate suspended matter (PSM); 2 – muddy cork (the most high concentration of PSM); 3 – muddy PSM and product of flocculation; 4 – phyto– and zooplankton (a – phytoplankton; b – zooplankton) as bottom filtrators; 5 – pellets; 6 – flux of PSM; 7 – flux of the PSM and pellets to the deep.

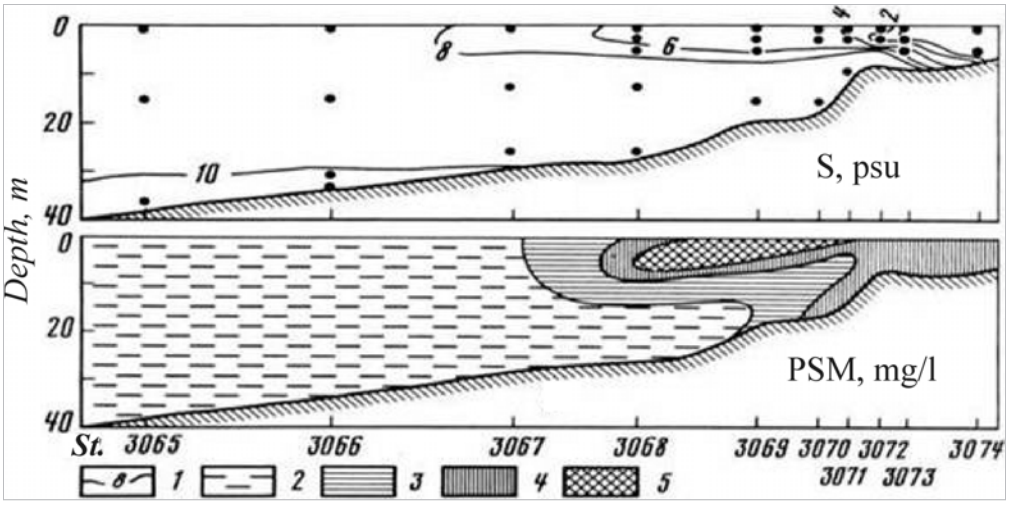

Fig. 8 Salinity (S, psu) and particulate suspended matter (PSM) in mg/l (Lukashin *et al.* 1986). 1 – isohalines (psu); 2–5 – concentration of PSM, in mg/l: 2 – <0.5; 3 – 0.5–1; 4 – 1–3; 5 – >3.

The coastal zone is commonly divided into the main elements as follows (Figs 2, 3 A, B, C). The zone of destruction of non–regular waves is part of a profile where non–regular waves are destroyed. Non–regular waves collapse at one point to form a line of alongshore degradation. The surf zone is the area between the shoreline (over–splashing of waves) and the outermost limit of the breakers. The outer area of the coastal zone is that part located seaward of the surf zone. This zone near the water's edge is dominated by return (translational) movements of water after the final collapse of waves. The upper limit of this zone over–splash zone is the line of maximum over–splash, and the lower line is the place of collision between an occurring wave and water outflow (Kos'yan, Pykhov 1991, p. 13).

The coastal–sea barrier zone (BZ) is responsible for the enrichment of sediments in terrigenous SiO_2 and, under more favourable conditions, in Fe, Ti, Zr, Sn, Au, Pt, and other elements to amounts that make them attractive for industry. The enrichment process occurs predominantly at zone of breaking waves, i.e., within the band where processes of natural mineralogical and geochemical sorting are the most intense and where heavy minerals

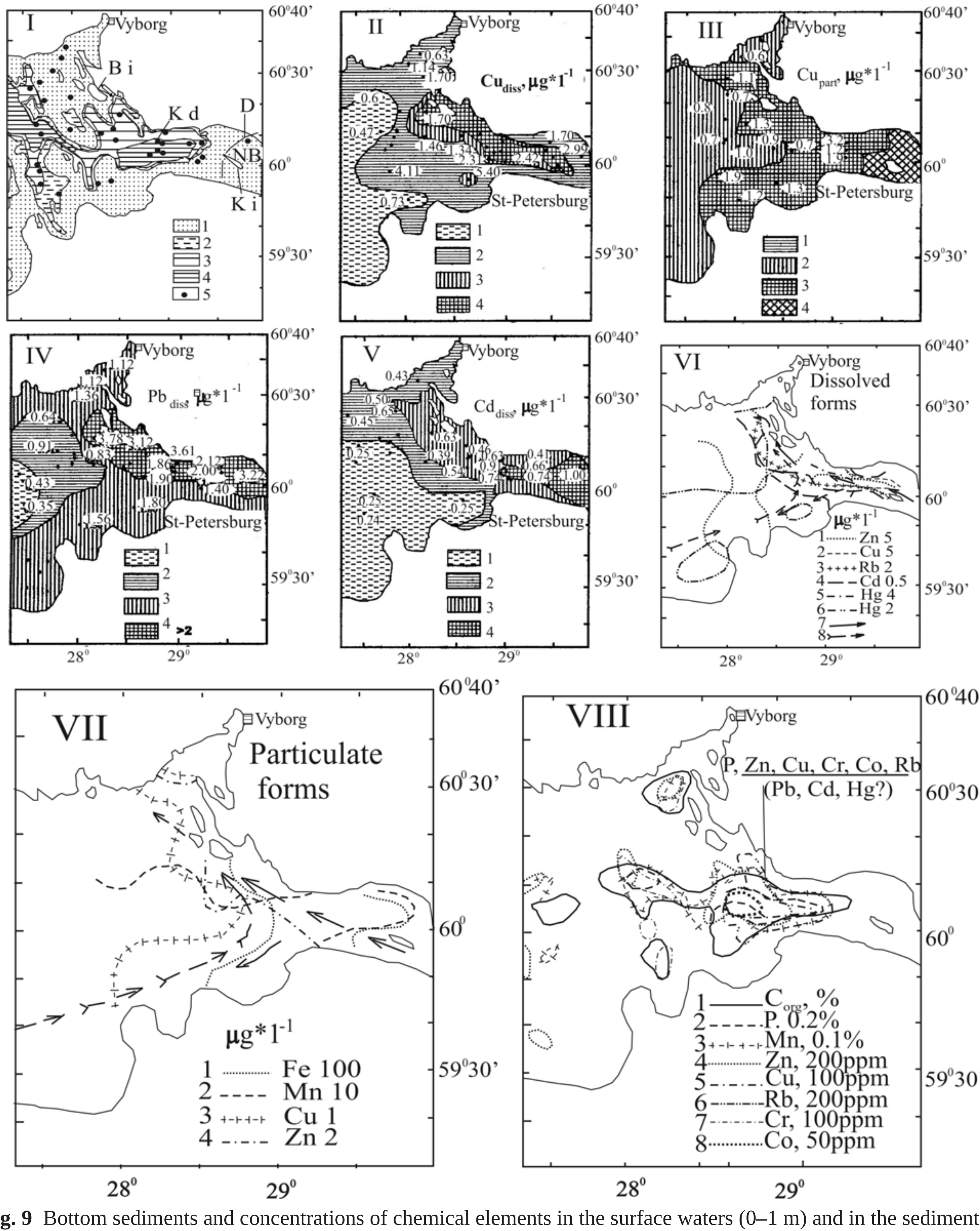

Fig. 9 Bottom sediments and concentrations of chemical elements in the surface waters (0–1 m) and in the sediments of the eastern part of the Gulf of Finland near the mouth of the Neva river (after Emelyanov 1995; Emelyanov, Kravtsov 1997). I. Surficial (0–5 cm) terrigenous bottom sediments: 1 – sand, mainly fine, gravel, stones; 2 – coarse aleurite (silt) and fine silty mud; 3 – aleuro-pelitic mud; 4 – pelitic mud; 5 – geological stations. D – dam; NB – Neva Bay; Ki – Kotlin island; Kd – Kotlin deep (40–45 m); Bi – Berezovyje islands. II. Concentrations of dissolved forms of Cu in the surface waters of the eastern part of the Gulf of Finland, in µg*l^{-1}: 1 – <1, 2 – 1–5, 3 – 5–5.5, 4 – >5.5. III. Concentrations of particulate form of Cu in the surface waters of the eastern part of the Gulf of Finland, in µg*l^{-1}: 1 – 0.01–0.1, 2 – 0.1–1.0, 3 – 1.0–3.0, 4 – >3.0. IV. Concentrations of dissolved forms of Pb in the surface waters of the eastern part of the Gulf of Finland, in µg*l^{-1}: 1 – <0.5, 2 – 0.5–1, 3 – 1–2, 4 – >2. V. Concentrations of dissolved forms of Cd in the surface waters of the eastern part of the Gulf of Finland, in µg*l^{-1}: 1 – <0.3, 2 – 0.3–0.5, 3 – 0.5–0.7, 4 – >0.7. VI. The isolines of the equal concentrations of dissolved forms of elements in the surface waters, in µg*l^{-1}; 7 – the flux of the polluted waters; 8 – general currents of the sea water. VII. The isolines of the equal concentrations of particulate forms of elements in the surface waters, in µg*l^{-1}. VIII. The isolines of the equal hightened contents of chemical elements in surficial bottom sediments (0–5 cm), C_{org} – Mn – in %, Zn – Co in 10^{-4}%.

precipitate (fall down) from the water on the bottom and form the placers. This band (zone) may be called as the second hydromechanical (geochemical) barrier zone. The total supply of abrasional and bottom erosional material to the Baltic Sea is about 5.4 million m^3 per year (Boldyrev *et al.* 1976, p. 147). And all this volume of the clastic material has to be sorted in the barrier zone "shore–sea" (Figs 4, 5, 6).

The active mechanical separation of clastic material is finishing at 3rd mechanical barrier (or zone within the influence of strong currents). This barrier is observed on the bottom as the "debris (sand–silt) sediments–pelitic (clayey) mud" interface and represents the last stage of sedimentogenesis, which is of the greatest importance for seas and oceans: coarse sediment (sand –sized and clay–sized particles) is progressively sorted from fine sediment containing the smallest non–clayey substance.

River–sea GBZ

Three zones are commonly recognized in the river–sea system: I – freshwater (river) zone; II – zone of water with low salt content; III – saline (marine) water zone (Fig. 7). In the freshwater zone, there are high concentrations of water suspension, high current. The most important features related to river–sea GBZs are salinity fronts. In estuaries, there are extraordinarily sharp lateral and transverse gradients of velocities and density. These gradients are related to frontal systems and play an important role in the dynamics of estuarine circulation.

River–sea GBZs are characterized by abrupt variations not only in salinity, but also in such features as pH, alkalinity (Alk), the amount of nutrients, and the hydrodynamic situation. In addition, current velocities and the concentration of suspension are sharply diminished there (Fig. 8). The phenomenon of a "biological contour" (or "filter") is present (and very distinct) at the river–sea boundary. Also, the river–sea GBZ is a place where other GBZ, such as land–sea, air–water, water–bottom, water–living substance, and acidic–alkaline (the value of pH may increase from 7 to 8), intersect, each of which grows stronger or weaker due to the influence of other barriers. The concentrations and forms of migration almost of the all chemical elements are changing here (Fig. 9; Lukashin *et al.* 1986; Emelyanov, Kravtsov 1997; Galkus, Jokšas 1997). Owing to such circumstances, the river–sea GBZ plays one of the most important roles. This GBZ is very important in sediment type distribution on the bottom (Fig. 10).

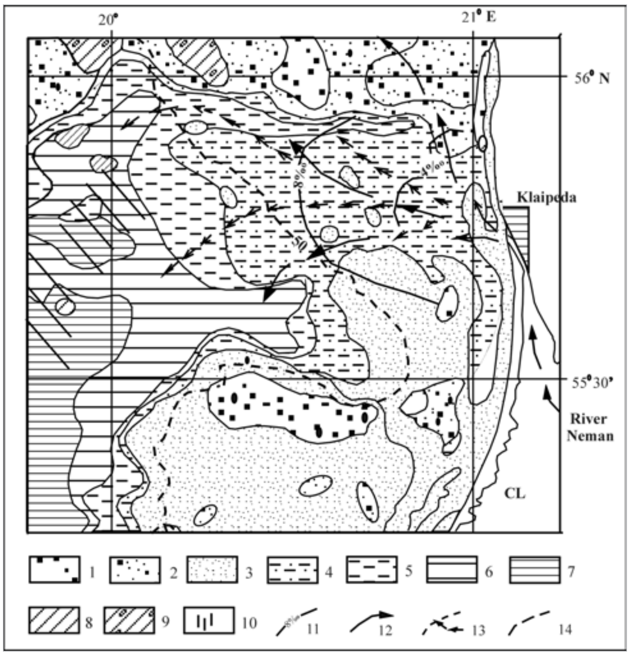

Fig. 10 Sediments and sedimentation at the Klaipėda strait (at the outflow of the Neman river water), the Baltic Sea (after Emelyanov 2005). 1–10 – terrigeneous bottom sediment: 1 – sand, gravel, boulders; 2 – sand, mainly coarse, with gravel; 3 – sand; 4 – coarse aleurite (silt); 5 – fine–aleuritic (silty) mud; 6 – aleuro–pelitic mud; 7 – pelitic (clayey or illitic) mud ; 8 – homogeneous clay, lacustrine (Hl_1); 9 – till with the boulders and pebble; 10 – sapropel like mud (3–5% C_{org}); 11 – isohalines of 4 and 8 psu; 12 – the main paths of the water; 13 – the distribution (the slow slump) of the near–bottom turbidite waters with the fine (pelitic) material; 14 – isobath, 50 m; CL – Curonian Lagoon (the trap for the Neman river load).

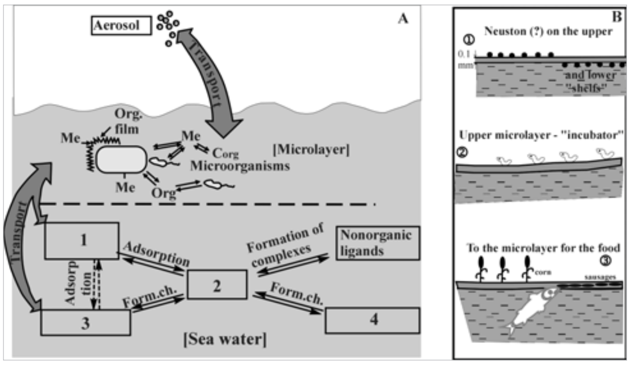

Fig. 11 A. Scheme of alternative changes of microelements at atmosphere–water boundary (at upper ocean millimetre) (after Lion, Leckie 1981). It has been proposed that there is competition between microelements and between microelement and main cations for a place in adsorption and in possible formation of ligands. 1 – nonorganic suspended particulate matter; 2 – dissolved microelements; 3 – surface–active organic ligands; 4 – surface–nonnative organic ligands. Symbols: Form. ch. – formation of ligands; org. – organic, Me – metals, C_{org} – organic carbon; white square with rounded corners types a suspended particle. B. The upper microlayer (after Emelyanov, 19863) as the incubator for the neuston and "food".

The ocean–atmosphere boundary

It separates two different phases, air and liquid. The surface film of water (or surface microlayer, SML) has surprising physical, chemical and biochemical properties (Horne 1972). One of such properties is surface tension, which is much higher than that for other liquids. The thickness of the SML is a few tenths of a millimetre. The ocean–atmosphere interface is

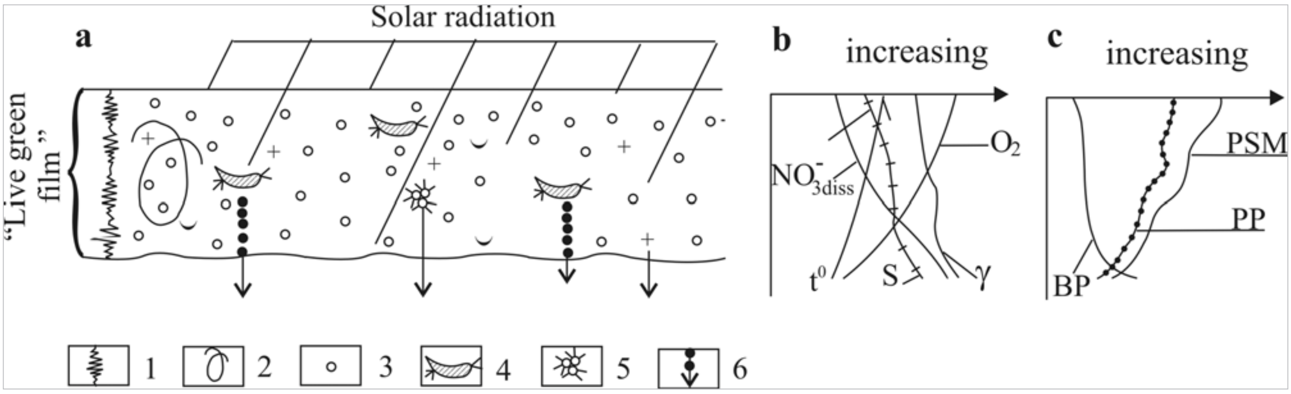

Fig. 12 Principal scheme of the biogeochemical processes in the GBZs photic layer (after Emelyanov, 1998). a – scheme of biochemical processes; b – distribution of temperature (t), oxygen (O2), salinity (S), density (γ) and dissolved nitrate (NO3diss) in the layer; c – distribution of primary production (PP), particulate suspended matter (PSM) and bacterioplankton (BP) in the photic layer. 1— microturbulence; 2— intensive water mixing; 3—phytoplankton; 4—zooplankton; 5—shells of zooplankton; 6— fecal pellets.

characterized by sharp changes in its physical and chemical parameters, including the thermal structure (Hunarzhua *et al.* 1977), disordering of water structure and other phenomena. "In the SML, the orientation of water molecules is such that negatively charged oxygen atoms move outward relative to the aqueous phase" (Horne 1972, p. 246). Owing to these and some other properties, there is a tendency for the surface area of water to reach the minimum for the given volume and under the given external conditions.

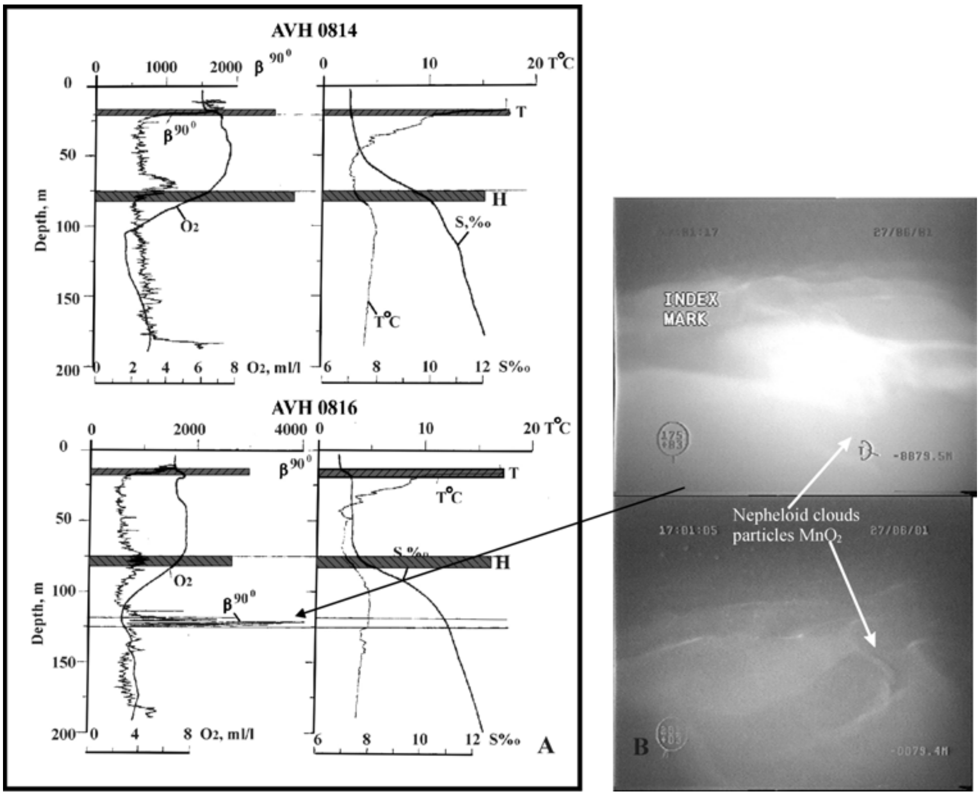

Fig. 13 Vertical profiles of temperature (TºC), salinity (S ‰), oxygen (O_2) and indicator of light dispersion β^{90° on two stations of Gotland Basin, the Baltic Sea (Summer, 1994) (A). T – thermocline; H – halocline. Nepheloid clouds (mainly fresh particles of MnO_2) in the redox–barrier (B) (after V. Paka, by written permission).

At the ocean–atmosphere boundary, there is an active exchange of elements between air and water. The upper film is responsible for accumulation of great amounts of pleiston[2] (Cheng, 1975) and bacterioplankton (Sorokin, 1977), which play an important role in the chemical exchange between the atmosphere and hydrosphere. The amount of neuston[3], which also includes saprophytic bacteria, is several orders of magnitude greater than those in any other horizons of the ocean (Zaitsev 1979). Neuston is food for organisms belonging to the next level of the food chain – protozoa and invertebrates. The latter are food for larvae, young fish and larger invertebrates, whereas larvae and young fish are food for fish and physalia. So, the upper film (SML) of water is the actual "nursery" of the ocean (Zaitsev 1979). The upper film is a place where many chemical elements are involved in the food chain (Fig. 11). At this barrier, aeolian material, which initially entered the ocean in "dry" form, experiences desorption (to a lesser degree,

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[2] The group of the alive organisms, living ***in*** the upper sea millimetre.

[3] The group of the alive and vegetal organisms ***on*** the upper sea millimetre.

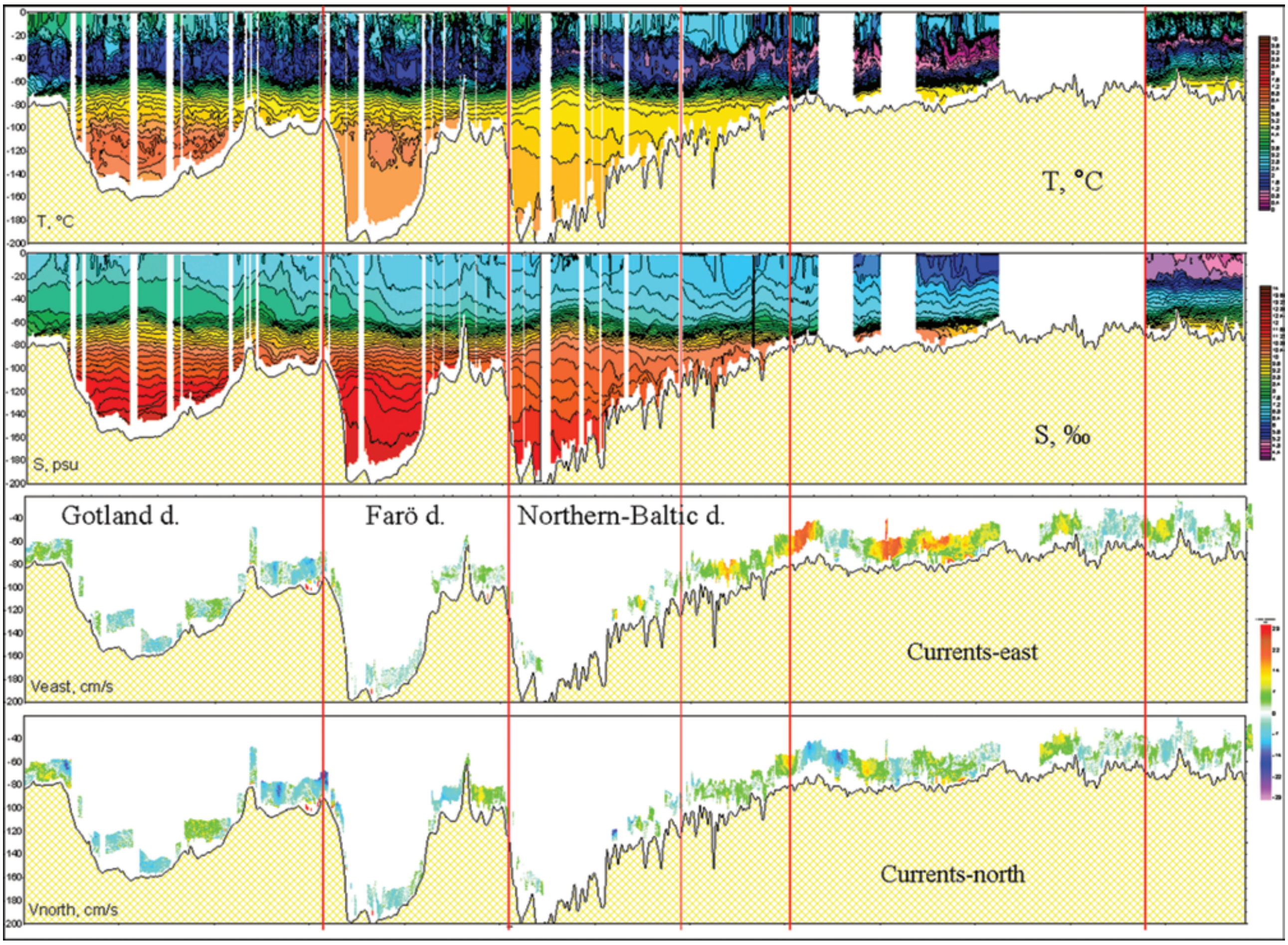

Fig. 14 Temperature (T), salinity (S) and current velocity profiles along the gas pipeline Nord Stream in the Northern Baltic Sea (after V. Paka, by written permission). Currents-east – current in the near–bottom water to the east; currents-north – the same to the north, in cm/s.

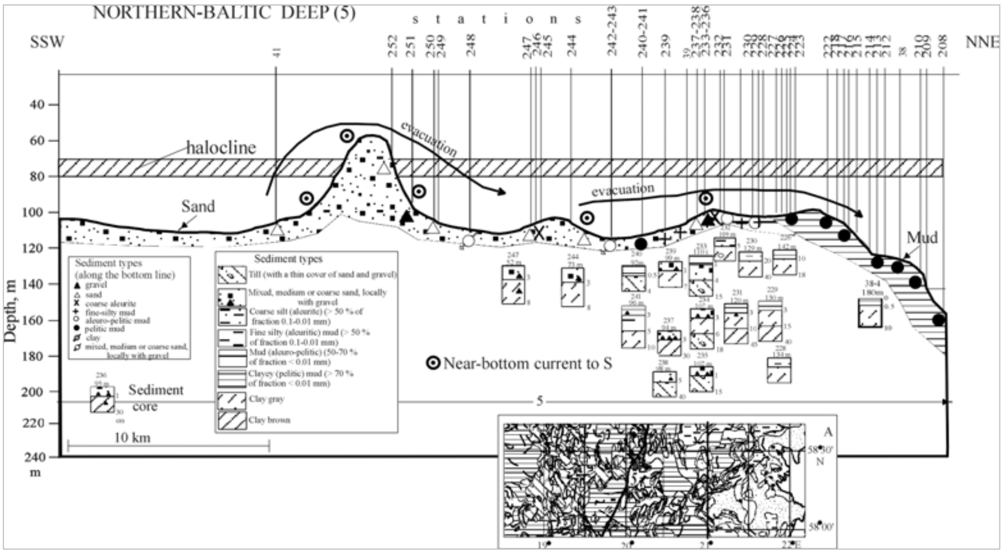

Fig. 15 Sedimentological profile along the gas pipeline Nord Stream in the Northern Baltic Deep (for the profile location see the inset A). Near–bottom currents to the South are shown. A – sediment map; 5 – the position of the profile; Gi – Gotland island. Compiled by E. Emelyanov.

this material adsorbs microelements from water). As a result of intensive biogeochemical processes, water suspension in the upper film (10–100 µm) is enriched in Fe, Cu, Ni, Pb, and other elements to values from 6 to 50 times (periodically, as much as up to 1000 times) greater than those present in deep–sea suspensions (McIntyre 1974).

Photic zone

Photosynthesis is the process in which carbohydrates (saccharine, starch) are manufactured from abiotic material and water in the presence of chlorophyll, which uses light energy and releases oxygen. The deficiency in light is an inhibitory barrier for organisms with photosynthesizing functions. In the photic layer, there are some specific features: intensive horizontal and vertical mixing of waters, normal contents of oxygen (3–8 ml/l), and decreased contents of phosphates and nitrites (Fig.

12). Processes that are the most intensive in the GBZ photic layer are also characteristic of self–contained GBZ, such as water–living matter and water–suspended matter. The intensity of the photosynthetic processes is different for various places throughout the Baltic Sea. The intensity is highest in the biological contours[4] (river–sea, coastal–sea, etc.), which boundaries are falling into category I according to the classification established for the marine environmental system (see Part IV in Emelyanov 1998, 2005).

In addition to active production of organic matter, the following processes occur within the photic layer: extraction of such elements as C, Si, P, N, Fe, Cu, Ni, Zn, Mn, Al, and Ti from seawater; migration of these elements by means of suspended biogenic material; use of the "living green film" by zooplankton; passing of elements into soft or hard parts of the zooplankton shell and formation of faecal pellets; rapid settling of chemical elements such as Cu, Mg, Si, Ca, C_{org}, Fe, and others onto the bottom with faecal pel-

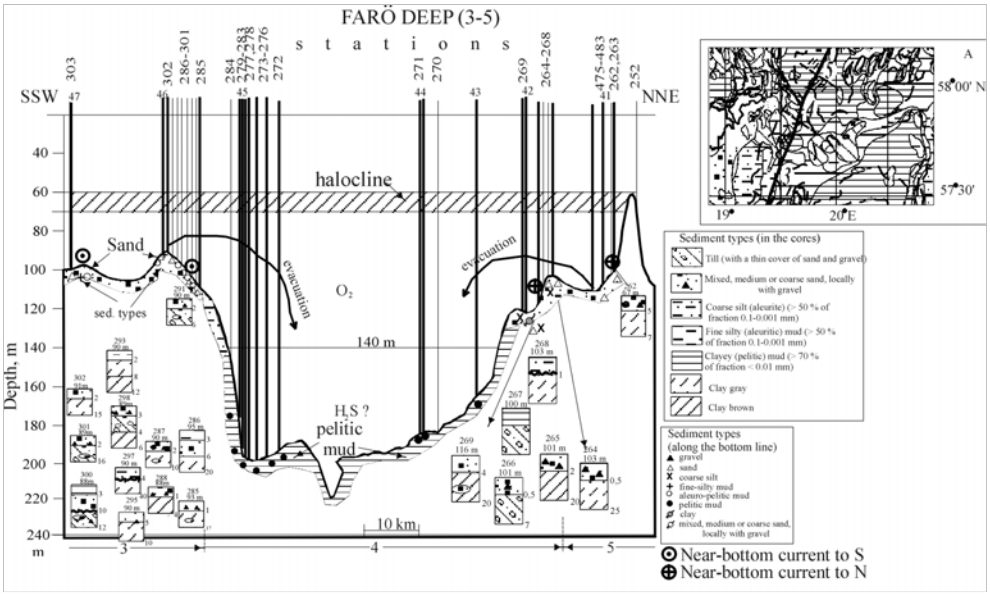

Fig. 16 Sedimentological profile along the gas pipeline Nord Stream in the Farö Deep (for the location see points 3–5 on the sediment map A). Near–bottom currents to the South and to the North are shown. O_2 – oxygen in the water; H_2S – hydrogen sulphide in the water. Compiled by E. Emelyanov.

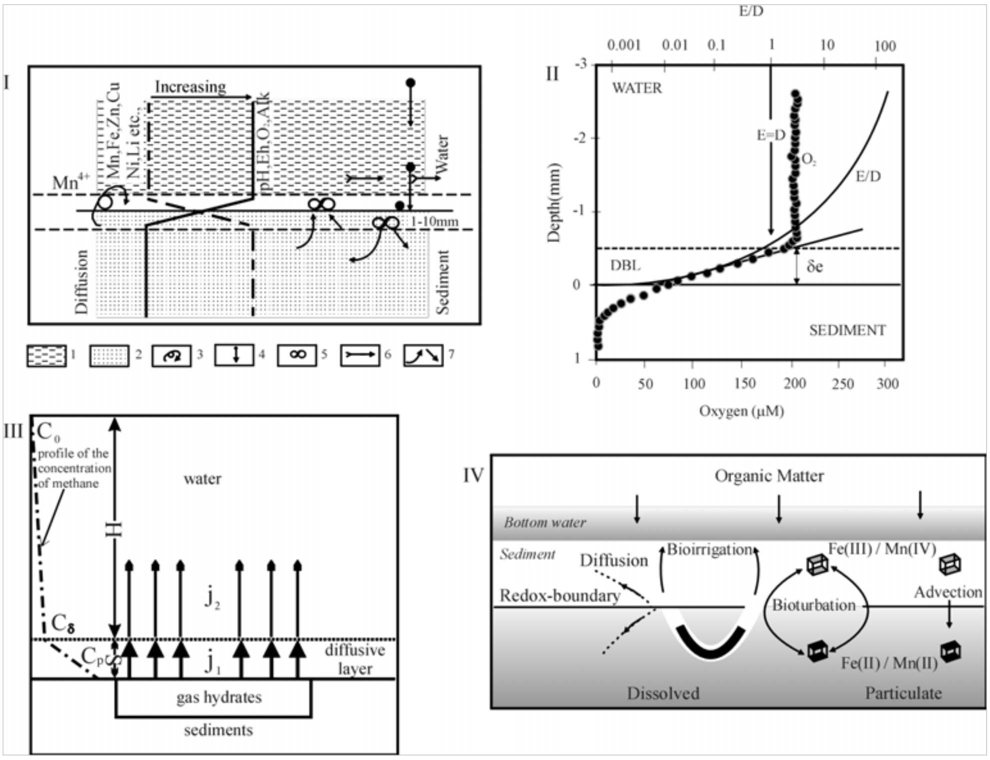

Fig. 17 Main processes in the water–bottom GBZ. I. Main parameters: 1 – water; 2 – bottom; 3 – diffusion of Mn^{2+} and other elements; 4 – deposition of fecal pellets from the photic layer; 5 – FMNs (ferromanganese nodules); 6 – near–bottom currents; 7 – the main directions of the flux of the chemical elements during the formation of the nodules and their back current. II. Oxygen microgradient (n) at the sediment–water interface compared to the ratio, E/D (logarithmic scale), between the vertical eddy diffusion coefficient, E, and the molecular diffusion coefficient, D. Oxygen concentration was constant in overflowing seawater. It decreased linearly within the diffusive boundary layer (DBL) and penetrated only 0.7 mm into the sediment. DBL had a thickness of 0.45 mm. Its effective thickness δ_e is defined by the intersection between the linear DBL gradient and the constant bulk water concentration. Diffusive boundary layer occurs where E becomes smaller than D, i.e., where E/D = I (arrow). Data from Aarhus Bay, Denmark, at 15 m water depth during fall 1990 (after Jorgensen 2000). III. Model of the exchange through the water–sediments interface (after Egorov 2001). j_1 – flux of molecular diffusion; j_2 – flux of convective diffusion; H – characteristic scale of decreasing concentration; Cp – dissolution of methane; Cs – concentration on the upper border of the layer; Co – concentration of methane. IV. Modes of transport in the sediment: molecular diffusion, bioirrigation, bioturbation and advection (after Haese 2000, p.243).

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[4] Biological contour – the most enriched in biogenic material near-shore zone.

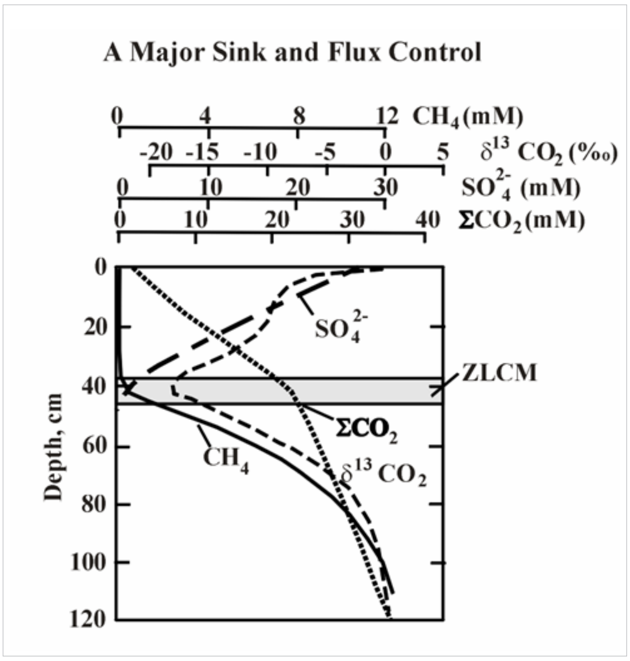

Fig. 18 Schematic diagram showing depth distribution of the methane, sulphate, total carbon dioxide, and the carbon isotope ratio of carbon dioxide in interstitial waters of marine sediments. All the distributions show breaks or slope changes in the stippled area, which represents the zone of anaerobic methane oxidation (after Reeburgh 1982).

lets (pelitic transport). When elements are removed from solution, they participate in biogenic migration.

Solar energy accumulating in the photic zone via photosynthetic processes leaves the photic zone and moves downwards as the energy of organic material. The photic layer is a global factory which works to transform solar energy. This energy is accumulated both in living and nonliving matter and is used consequently not only for transformation of this material in the photic layer or throughout the whole length of the water strata of the World Ocean, but also for transformations in the sequence of bottom sediments, at all stages of their development, up to katagenesis (Emelyanov 1998, 2005).

Halocline (pycnocline)

Barriers such as thermocline (temperature), halocline (salinity), and pycnocline (density) are especially distinct in the transition layer GBZ. The halocline is the most important barrier in the Baltic Sea. It is found in this sea at depths 60–80 m (Figs 13, 14). The general distribution of the main physical, chemical and biogeochemical characteristics are shown in Emelyanov (1998, p. 39, and 2005, p. 39), and the major processes and their role in terms of geological processes are described there. The most important role of the halocline (pycnocline) in the Baltic Sea is the rewashing resuspension and redistribution of the sediments at the halocline (pycnocline) level and just beneath it (Figs 15, 16; Emelyanov $1986_{1,2}$).

Redox barrier Eh

The redox boundary Eh is found in the water column at the O_2–H_2S boundary between oxygenated and reducing waters in the water strata. This barrier is the most important in the processes of iron–manganese ore formation in the Baltic Sea deeps. This process was described earlier by Emelyanov ($1986_{1,2}$, 1995, 1998, 2004, 2005, 2011) and Huckriede and Meishner (1996). In addition to published data it should be noted that Dr. V. Paka (pers. comm., 2002) discovered very dense clouds of particulate suspended matter (smallest manganese oxide particles) in the O_2–H_2S layer in the Gotland Deep. As written by the author in previous publications there are about one million ton of manganese removed from the surface of the sea floor to the stagnant waters as well as in the O_2–H_2S interface in the Baltic Sea deeps.

The water–bottom barrier zone

It is found at various depths and in different tectonic and facial environments (Fig. 17). It is evident that this barrier zone encompasses the near–bottom water layer, which has a thickness ranging from 1 to 100 cm (depending on facial conditions), and the uppermost centimetre of the sediment column (or the millimetre film which covers solid rocks) (see Fig. 15). The water–bottom GBZ can exist in a variety of physicochemical conditions: the seabed may either experience erosion by strong bottom currents or provide the main substrate for particle-by-particle deposition of sediments; the near–bottom waters can be saturated with oxygen, contain free H_2S, etc. According to V. Vernadsky (1965), the water–bottom boundary is another (second) living film. Various animals, ranging from micro–organisms (micro–benthos) to large molluscs, echinoderm, fish, etc., accumulate within this boundary. Organisms such as filter–feeders, mud–eaters and burrowing animals play an important role in geochemical processes. These organisms disturb the sediments as they forage for food, with the result that the water–bottom GBZ extends down (into sediments) to a depth of about 10–20 cm or more below the sediment surface. The water–bottom GBZ is dominated by processes including the disintegration of the main mass of faecal pellets, decomposition of the remains of bios that settled on the bottom or were buried there, and also the regeneration of biogenic elements. This boundary is the end point for the transfer of matter and energy from the photic layer down to the bottom sediments through various food chains. The water–bottom GBZ is an intersection of other GBs (or their activities are evident in a particular place), but the most important among these barriers are hydrodynamic, reduction–oxidation (or redox) (Eh), and acidic–alkaline (pH). These and many other GBs tend to form strong gradients of particular properties of water, suspended matter, and sediment, leading to a variety of biochemical interactions (see Fig. 16).

Upper active sediment layer (UASL)

The bottom boundary of UASL in the sediments is "the zone of low concentration of methane" (ZLCM) (Fig. 18). The ZLCM is a specific geochemical barrier, where concentrations of sulphates ion (SO^{2-}_4), CH_4, ΣCO_2, $\delta^{13}CO_2$ and some other components of interstitial water on one side of this barrier are different from those on the other side (Reeburgh 1982). The thickness of UASL in the Baltic Sea deeps is up to 5–6 m (all the Litorina mud is UASL).

The regeneration of sedimentary material does not terminate at the water–bottom boundary, but can continue in the upper layer of the sediment sequence, i.e., after burial of sedimentary material and submersion to a certain depth below the seabed. This layer is cold "upper active sediment layer" (UASL). This behaviour is clearly seen in the quantitative and qualitative regeneration of biogenic elements, first of all, organic matter, which originates in the photic layer and sinks to the seabed to be buried in the bottom sediments (Emelyanov 1995, 1998, 2005).

Two main types of diagenesis can be distinguished: anaerobic and aerobic (Emelyanov *et al.* 1986). The former is typically found in the peripheral areas of the ocean, and in the deeps of Baltic Sea, i.e., in areas with high concentrations of organic matter (OM) in the bottom sediments.

A major source of biogenic components (Si, NH_4, P) in porous waters is OM. Ammonium nitrate (NH_4) accumulates in the porous waters as a result of decomposition of the remains of biota that have settled on the bottom or were buried there. In seawater, the content of NH_4 is about 0.01 mg/l, in porous water it is 0.1–20 mg/l (Gursky 2003). Alkaline reserve (Alk) is an indicator of the type of water and the rate with which mineralization of OM occurs (Gursky 2003). Maximum amounts of biogenic components (NH_4, P, and Si) and Alk are found in porous waters in coastal areas of the seas.

This is in evidence that the UASL is dominated by the following processes: intensive diffusive exchange by elements between interstitial water and seawater (across the water–bottom interface), active regeneration of sediments by bottom organisms (mud–eaters), sulphate–reducing reactions (the initial stage of diagenesis), initiation of the development of chemogenic–diagenetic minerals (which, depending on Eh, pH and Alk, are hydroxides, sulphates, sulphides, carbonates), the active diffusion of methane from the sediments to the bottom water.

CONCLUSION

The reader together with the author has traced the migration of a particle and covered hundreds of miles – from the borders of catchments basin to deeps of the Baltic Sea where the particle settles down on the sea floor and became of bottom sediment. Other particles started their journey to the deeps from the sea–surface. Falling down the particle encountered many obstacles / barriers on its way. At these barriers the particle has been transformed: it passed through the stomach of living organism, dissolved partially losing some atoms and molecules acquiring others. It, however, invariably was moving towards its destination – the floor where it joined other particles and became part of what we call bottom sediment.

Geochemical barrier zones play an important role in determining various physical systems and characteristics of the seas and oceans, e.g. hydrodynamics, salinity, temperature and light, sources of sedimentary material on the land and in the sea, supply of sedimentary material and their distribution. Among the topics discussed are the processes of inflow, transformation and precipitation of the sedimentary layer of areas such as the Baltic and other seas.

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