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Marine ecogeology in semi-closed basin: case study on a threat of geogenic pollution of the southern Baltic Sea (Polish Exclusive Economic Zone)

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Modern migration of harmful geogenic substances into bottom sediments and bottom water has been demonstrated in the Polish Exclusive Economic Zone of the Baltic Sea. A geogenic substance is a matter (gas or liquid) whose formation, chemical composition and physical properties result from natural geological processes. The bedrock of the Baltic Sea contains rocks which are sources of geogenic pollutants migrating along fault zones and pinchouts of sedimentary formations. The pollutant source rocks include: oil- and gas-bearing reservoir rocks (Middle Cambrian, Rotliegend, Zechstein and Carboniferous); black shales (lower Paleozoic); effusive rocks (Rotliegend); salts (Zechstein), reservoir rocks for mineral and thermal waters (Paleozoic and Mesozoic). The main sources of geogenic contamination are oil and natural gas deposits as well as zones prospective for hydrocarbon accumulations because they produce increased concentrations of liquid and gaseous hydrocarbons in bottom sediments and bottom water. Hydrocarbons cause a lethal deficit of oxygen in bottom water. The migration activity of the fault zones and regional pinchouts is shown, for instance, by increased concentrations of vanadium and strontium in bottom sediments. Strontium comes from Zechstein salts while vanadium is from lower Paleozoic black shales and/or hydrocarbon-bearing sediments. The whole Polish Exclusive Economic Zone of the Baltic Sea is threatened by geogenic pollution. Areas at greatest risk of geogenic pollution have been defined in both the eastern part (East European Craton: western part of the Courland Block, Rozewie Block, Łeba Block, eastern part of the Żarnowiec Block) and the western part of the zone (European Paleozoic platform: western part of the Kołobrzeg Block, and Gryfice and Wolin blocks).

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INTRODUCTION

Environmental hazard to seawater caused by pollutants is perceived mainly as resulting from anthropogenic (mostly of industrial, agriculture and municipal origin) and biogenic contamination. It is often the case that the hazard posed by geogenic substances is underestimated. Geogenic substances are here understood as gaseous or liquid substances whose formation, chemical composition and physical properties result from natural geological processes. The paper deals with those geogenic substances which are derived from bedrock beneath the sea-floor (deep-seated geological structures).

The Baltic Sea as an intracontinental semi-closed sea basin is characterized by poor mixing of water with the world ocean and is thus particularly highly vulnerable to contamination by geogenic pollutants (*cf.* Jaworowski *et al.*, 2001). For this reason, the Polish Ministry of the Environment commissioned a research project to identify prospective zones for the occurrence of hydrocarbon deposits and to analyze the risk of seawater pollution by geogenic substances in the Polish sector of the Baltic Sea (Fig. 1).

The project was carried out in 2005–2008 by a special consortium including the Polish Geological Institute – National Research Institute, Warszawa (project leader); the "Petrobaltic" Oil and Gas Exploration and Exploitation Joint Stock Company, Gdańsk; "Kronos" Geological Services Company Ltd., Gdańsk; the Society of Research on Environmental Changes "Geosphere", Kraków and the Geosynoptics Society "Geos", Kraków.

The present paper is a study on marine ecogeology briefly demonstrating those research results of the project which indicate the threat of seawater pollution by geogenic substances de-

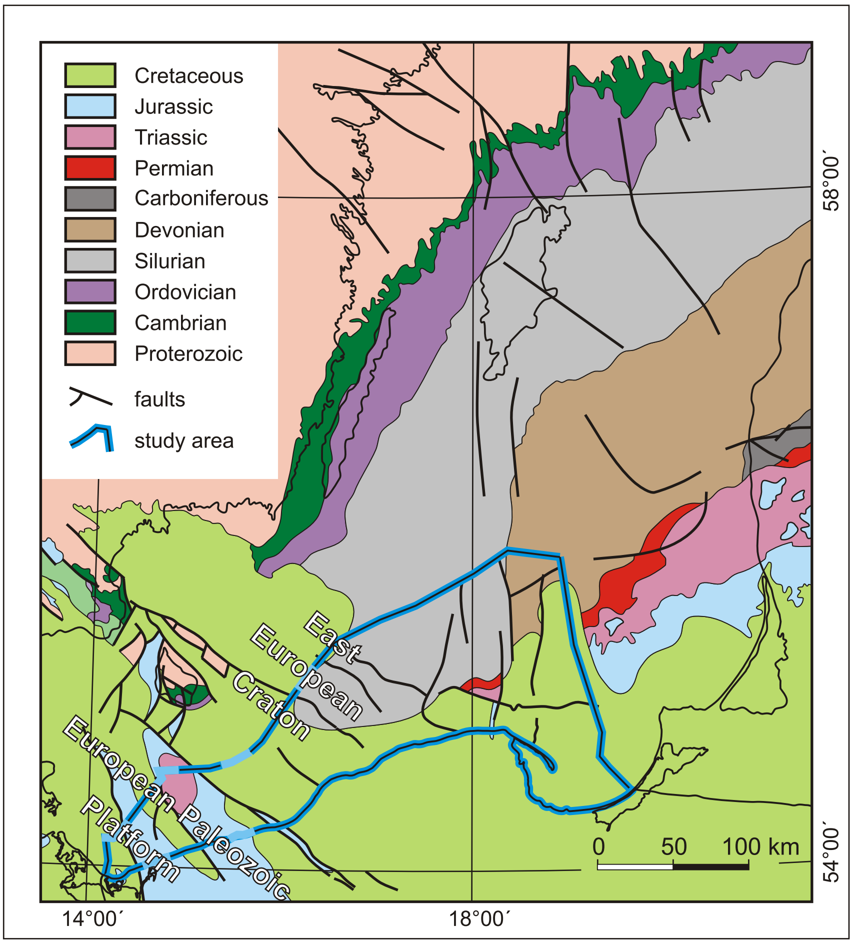

Fig. 1. Study area with geological map of the southern Baltic Sea without Cenozoic deposits (modified after Dadlez, 1995*b*)

rived from bedrock beneath the sea-floor (Jaworowski and Wagner, 2008). In addition, the authors employed all available data, both published and stored in archives, bearing on the risk of geogenic pollution of the southern Baltic Sea. Unfortunately not all geochemical and seismic data could be presented here. Some of these data, particularly those vital to the identification of prospective zones for the occurrence of hydrocarbon deposits (Anolik and Karczewska, 2008), remain as yet confidential.

GENERAL GEOLOGICAL SETTING

EAST EUROPEAN CRATON (FIGS. 1–3)

Eastern and central parts of the Polish Exclusive Economic Zone of the Baltic Sea are situated in the East European Craton (Precambrian platform) and comprise the southwestern portion of a large regional structural-tectonic unit called the Baltic Depression (Peribaltic Syneclise).

The geological structure of the sedimentary cover in the Baltic Depression is simple: the strata usually lie almost horizontally, dipping at small angles (a few degrees). The sub-Phanerozoic basement is composed of crystalline rocks represented by Paleoproterozoic granitoids and metamorphic rocks. The sedimentary cover begins with uppermost Ediacaran deposits. These are overlain by Cambrian, Ordovician and thick Silurian successions. The upper Paleozoic is represented by Devonian deposits encountered in the north-eastern part of the area. In its southern part, the Silurian is overlain by Permian and, further towards the north, by Mesozoic deposits.

The most important elements of the geological structure are fault zones, especially regional ones, marking the boundaries of individual tectonic units (Dadlez and Pokorski, 1995) referred to as tectonic blocks. The cratonic portion of the Polish sector of the Baltic Sea includes the following blocks: Gdańsk, Żarnowiec, Courland, Rozewie, Łeba, Smołdzino, Słupsk, Ustka and Darłowo (Figs. 2 and 3).

The faults are commonly normal, some are reverse faults. Most of them are dip-slip faults with steep or vertical fault planes. The faults locally pass into flexural bends. Displacements of the regional faults vary from tens to hundreds of metres. Sub-Permo-Mesozoic basement of the western part of the Darłowo Block is formed by a lower Paleozoic thrust-and-fold belt (Caledonides; Dadlez, 2000; Pokorski and Modliński, 2007; Fig. 3).

The present-day structural pattern of the Baltic Depression developed as a result of the superimposition of three main deformation phases: syn-Caledonian (after Silurian),

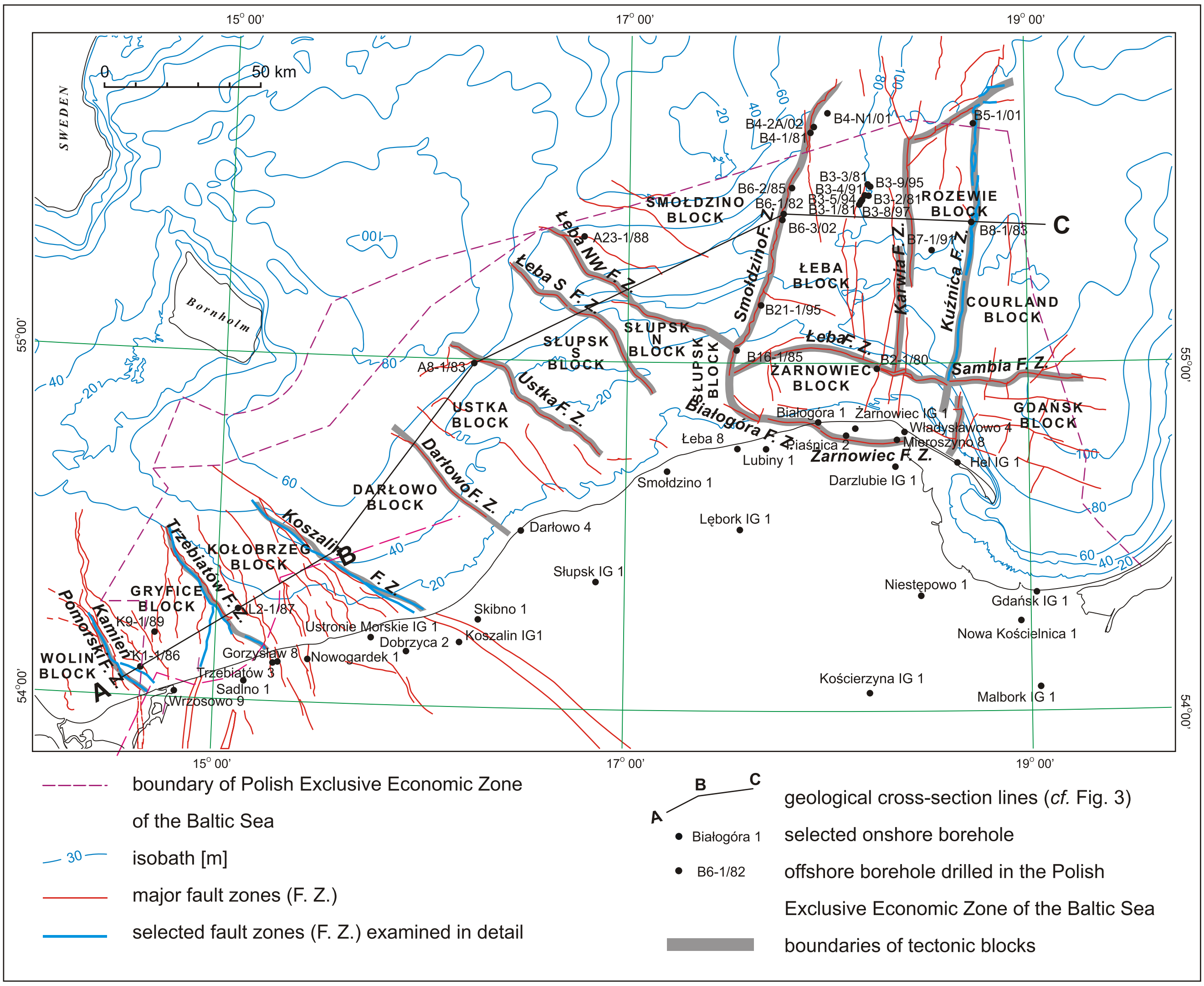

Fig. 2. Structural-tectonic sketch map of the Polish Exclusive Economic Zone of the Baltic Sea (partly after Anolik and Karczewska, 2008)

syn-Variscan (at the end of the Carboniferous and beginning of the Permian) and syn-Alpine (latemost Mesozoic or earliest Cenozoic). The major restructuring of the area occurred as a result of syn-Variscan deformation. Most of the faults developed or became reactivated probably at that time. Syn-Alpine deformation manifested itself mainly as the reactivation of some pre-existing faults, and is relatively weakly developed (Dadlez, 1990).

EUROPEAN PALEOZOIC PLATFORM (FIGS. 1–3)

The western part of the Polish Exclusive Economic Zone of the Baltic Sea is situated in the European Paleozoic Platform and is subdivided into the Kołobrzeg, Gryfice and Wolin tectonic blocks. These blocks are located west of the East European Craton. The craton boundary has been commonly assumed to run along the Koszalin Fault Zone (Dadlez, 2000).

The NW–SE-trending Koszalin Fault Zone is the eastern boundary of the Teisseyre-Tornquist Zone (TTZ), which is a fragment of a large global lineament extending from Dobrogea to Oslo (*cf.* Znosko, 1962, 1998). The Koszalin Fault Zone is rooted in the Moho and played an essential role in the tectonic evolution of Northern Poland and the southern Baltic Sea, affecting the palaeogeographic development of the sedimentary succession.

At the end of the Silurian, strong thrust-and-fold deformation of lower Paleozoic deposits occurred in the area situated west of the East European Craton. These deposits are observed in the Wolin, Gryfice and Kołobrzeg blocks and in the western part of the Darłowo Block (Pokorski and Modliński., 2007). The allochthonous lower Paleozoic, encountered by drilling in the western part of the Kołobrzeg Block, is represented largely by Ordovician (Caradoc) and, in other boreholes, also by Silurian deposits (Modliński, 1968; Podhalańska and Modliński, 2006). The Paleozoic platform subsequently developed upon the allochthonous lower Paleozoic rocks of the peneplanated Caledonides. Sedimentation of the platform succession started during the Eifelian, locally during the Emsian. Widespread Devonian, Carboniferous and Permian (mainly Zechstein evaporites) deposits are observed here. In other words, the Permo-Mesozoic succession, upper Rotliegend through Upper Cretaceous (Wagner, 1994; Dadlez, 1995*a*, *b*), is underlain in

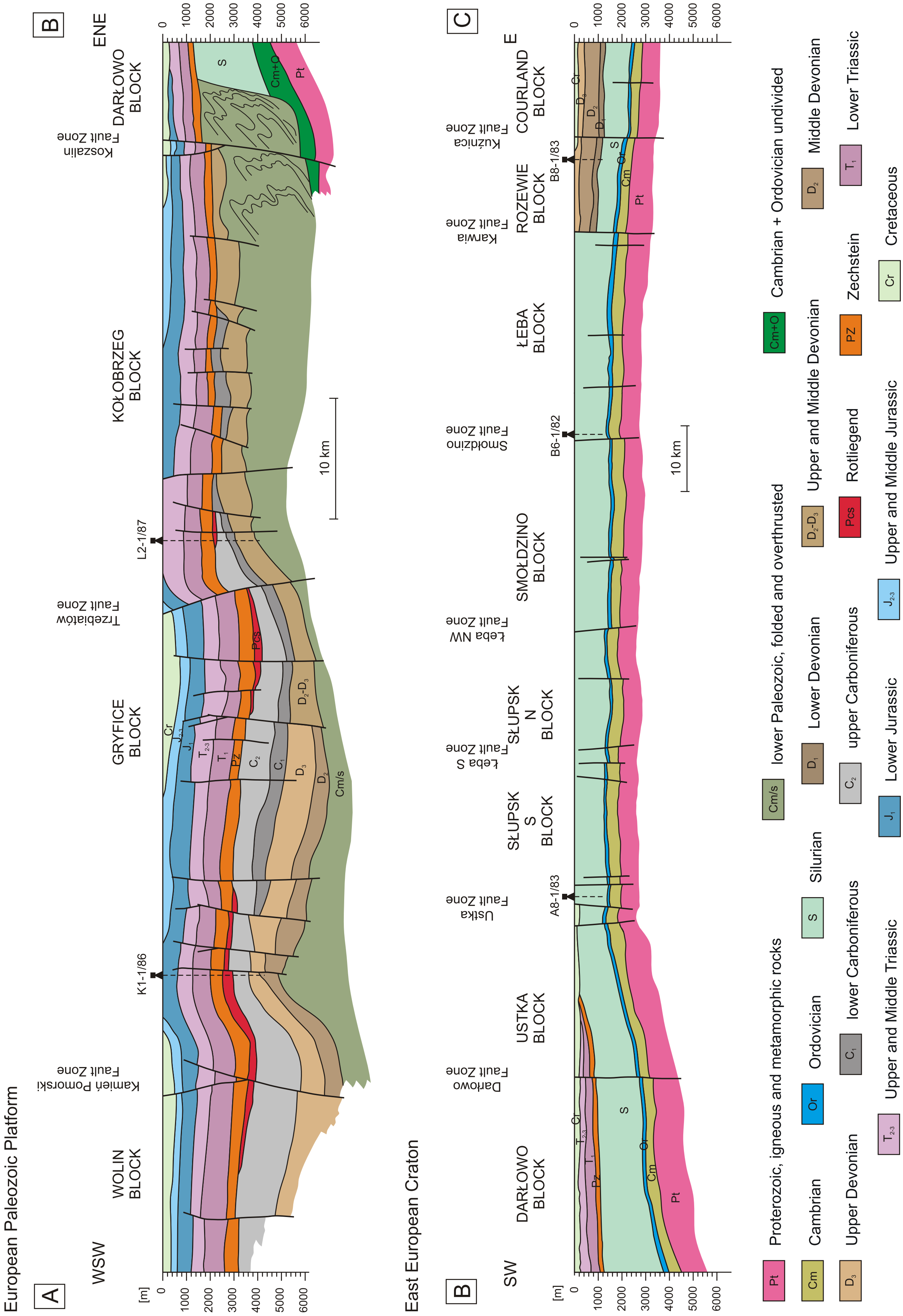

Fig. 3. Regional geological cross-sections: A–B and B–C

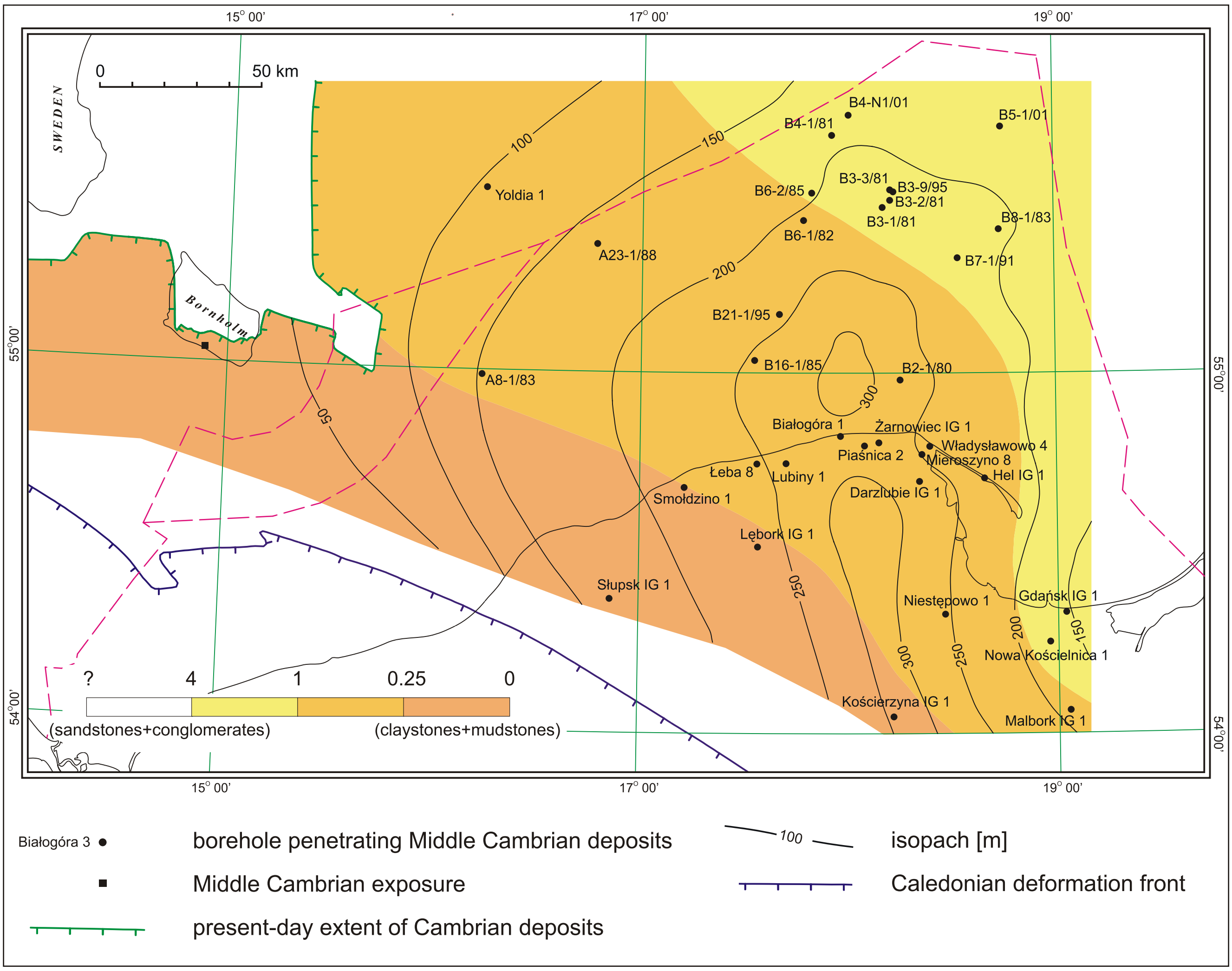

Fig. 4. Middle Cambrian thickness and lithofacies (slightly modified after Modliński and Podhalańska, 2010)

For other explanations see Figure 2

the Paleozoic platform area by different Devonian or Carboniferous formations (Matyja, 1993) resting upon folded lower Paleozoic deposits.

The Paleozoic platform in the Baltic region became dismembered into the Wolin, Gryfice and Kołobrzeg blocks as a result of syn-Variscan diastrophism. The major fault zones of Koszalin, Trzebiatów and Kamień Pomorski represent the boundaries of the blocks and are rooted in the crystalline basement.

During Mesozoic times, widespread thick Triassic, Jurassic and Cretaceous successions were deposited. The previously-mentioned fault zones became reactivated as a result of Cretaceous/Paleogene inversion (syn-Alpine deformation).

The sedimentary cover succession in the whole Polish sector of the Baltic Sea is overlain by Paleogene, Neogene and Quaternary deposits.

SOURCE ROCKS OF HARMFUL GEOGENIC SUBSTANCES

MIDDLE CAMBRIAN SANDSTONES

Middle Cambrian sandstones (Fig. 4) are the main hydrocarbon reservoir rocks in the cratonic area of the Baltic Sea (Górecki *et al*., 1992; Brangulis *et al*., 1993). In the eastern part of the Polish Exclusive Economic Zone, oil deposits (in the Rozewie and Łeba blocks; Fig. 2) and gas-condensate oil deposits (Łeba Block) were discovered. The total resources of the zone are 30 million tons of crude oil and 10 billion m^3 of natural gas (Strzetelski *et al*., 2004).

The main oil- and gas-bearing horizon is represented by the Dębki Formation (lower part of the *Paradoxides paradoxissimus* Zone). Petrographic investigations (Sikorska

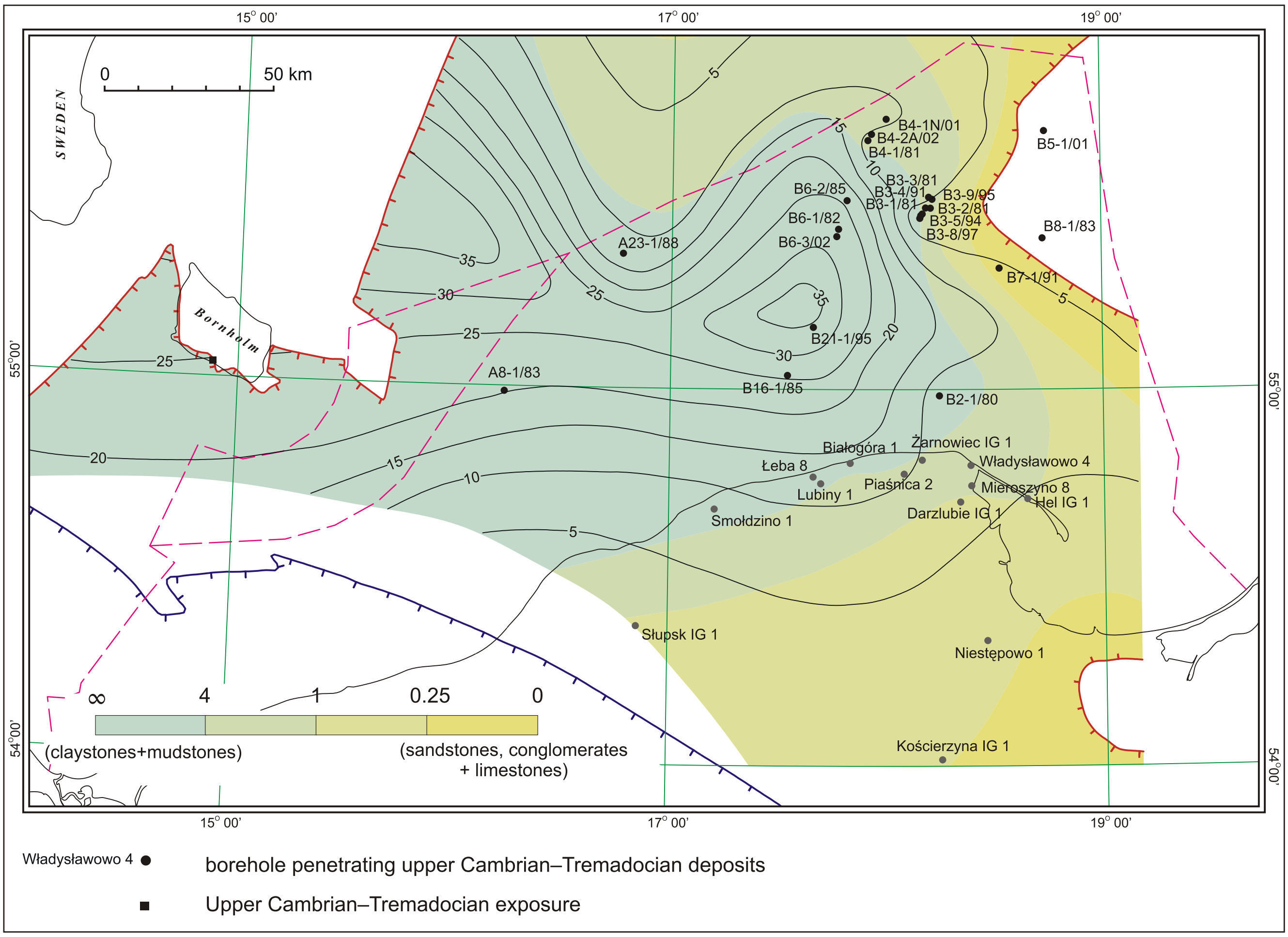

Fig. 5. Upper Cambrian–Tremadocian thickness and lithofacies (Piaśnica Formation *s.l.*) (slightly modified after Modliński and Podhalańska, 2010)

For other explanations see Figures 2 and 4

and Jaworowski, 2007) show that the sandstones making up the formation are characterized by very variable porosities ranging from nearly zero to over 20 vol.% (maximum of 24.5 vol.%). Apart from intergranular porosity, the sandstones also show fracture, mouldic (mostly after dissolved feldspars), microcrystalline (in glauconite, between clay mineral flakes) and sporadically intracrystalline porosity. Primary porosity was reduced mainly by cementation (27%) and compaction (10%). Silicification was the main process responsible for primary porosity reduction (Sikorska and Pacześna, 1997; Sikorska and Jaworowski, 2007). The permeability of the Middle Cambrian sandstones is variable and ranges from <1 mD to over 300 mD.

Fractures and microstylolitic seams played an important role as hydrocarbon migration avenues (Strzetelski, 1977, 1979). The hydrocarbon accumulations are associated mostly with structural traps (near-fault anticlines). Preliminary estimates indicate that prognostic resources of natural gas in the Baltic Sea region are 100 billion m^3, whereas prognostic resources of crude oil are a few hundred million tons (Górecki and Szamałek, 2004).

The Middle Cambrian sandstones are thickest in a meridional zone (Fig. 4) extending from the northern part of the Łeba Block (just below 200 m) towards the southern end of the Żarnowiec Block (over 300 m). Over the remaining area, the thickness of the Middle Cambrian deposits decreases to approximately 200–150 m in the east (Courland Block) and to below 150 m in the southeastern part of the Gdańsk Block. In the western area (western part of the Ustka Block), the thickness decreases to 100 m. In the Darłowo Block, it is locally below 50 m.

The oil- and gas-bearing Middle Cambrian sandstones (Dębki Formation) are one of the most dangerous sources of harmful geogenic substances.

LOWER PALEOZOIC BLACK SHALES

A few intervals of black shales containing considerable amounts of radioactive substances, concentrations of heavy metals and increased proportions of organic matter are observed in the eastern part of the Polish sector of the Baltic Sea (Figs. 2 and 3).

The oldest interval is represented by the Upper Cambrian–Tremadocian Piaśnica Formation *s.l.* This is the main lower Paleozoic succession of black shales, being also the main source rock for oil (Burchardt *et al.*, 1998). The horizon is composed of black bituminous claystones, locally with limestone lenses and nodules. They contain a U-V-Mo geochemical association, typical of black claystone deposits (Morawski, 1973), and are conspicuous by high concentrations of heavy metals (Zn, Pb, Ni, Co and Cu). U, V and Mo concentrations are high in the Polish sector of the Baltic Sea. Uranium concentrations vary from a few g/t to 400 g/t. Molybdenum concentrations exceed 690 g/t. Onshore observations show that we can expect a westward increase in uranium concentration. The so-called "alum shales" of Sweden, which are an equivalent of this interval, contain much higher concentrations of uranium with an average of 100 g/t. In the Billingen mining area, the average concentration is 300 g/t, with a maximum of 3000 g/t in carbonaceous lenses (Morawski, 1973).

The Piaśnica Formation *s.l.* (Fig. 5) occurs in an area extending from the Bornholm region to the Rozewie Block in the east. This formation attains its maximum thickness (up to 35 m) in two depocentres. One of these is situated in the southwestern part of the Łeba Block, whereas the other is located north-east of Bornholm. The formation is absent both in the eastern part of the Rozewie Block and in the Courland Block.

Another black shale interval is associated with the Słuchowo Formation (Modliński and Szymański, 1997) assigned basically to the lower Arenigian, although towards the west it probably is also upper Arenigian and Llanvirnian in age (in the northern part of the Ustka Block). These are black and dark grey bituminous claystones interlaminated with grey-green claystone containing abundant glauconite. The basal layer of this succession is represented by a conglomerate containing redeposited fragments of Upper Cambrian and Tremadocian black claystones with uranium concentrations of up to 120 g/t (Morawski, 1973). On wireline logs, the formation is conspicuous by high gamma ray values.

The Słuchowo Formation occurs in the southern Baltic Sea in an area extending from the Ustka Block as far east as the northern part of the Courland Block. The maximum thickness of the deposits is about 60 m (north of the Ustka Block). The formation gradually thins from the west towards the east and it wedges out in the eastern part of the Rozewie Block.

In the Upper Ordovician succession, black shales are represented by the Sasino Formation (Modliński and Szymański, 1997) included in the uppermost Llanvirnian–Caradocian. This formation consists of black, dark grey and green bituminous (especially in the upper part of the section) claystones. There is no detailed data on the contents of radioactive substances and heavy metals. On wireline logs, the rocks are characterized by high gamma ray values.

The Sasino Formation is observed in the bedrock of the whole southern Baltic Sea in the East European Craton area. It attains a thickness of up to approximately 60 m along a zone running evenly with a parallel of latitude from the northern part of the Ustka Block to the southwestern part of the Łeba Block. Both to the north and to the south of the zone, the thickness decreases to about 20–30 m.

The thick Silurian succession is represented by the lower Llandovery Jantar Member (composing the lowermost part of the Pasłęk Formation *sensu* Modliński *et al.*, 2006). These are black bituminous, non-calcareous claystones with abundant pyrite, containing laminae and interbeds of calcareous claystones and scarce thin interbeds and nodules of marly limestones. On wireline logs, the rocks are manifested by anomalously high gamma ray values. The thickness of the Jantar Member is relatively uniform (Fig. 6) commonly ranging from 5 to 10 m.

In the western part of the Polish Exclusive Economic Zone of the Baltic Sea, i.e. on the Paleozoic platform, lower Paleozoic deposits have been encountered in several onshore and three offshore boreholes. They are represented by small fragments of thick Ordovician and Silurian claystone-mudstone successions, where identification of individual black shale horizons is difficult. There is no information about the concentrations of heavy metals and radioactive substances in these deposits. Organic matter investigations in onshore boreholes (Grotek, 1999) indicate that only few Caradoc and Wenlock shale horizons show weak features of source rocks for oil generation.

UPPER PALEOZOIC OIL- AND GAS-BEARING ROCKS

Upper Paleozoic source rocks for the generation of liquid and gaseous hydrocarbons occur on the Paleozoic platform (Figs. 1–3) and are represented by Devonian/Carboniferous transition and lower part of upper Carboniferous deposits.

In the Devonian succession, source rocks occur within the Sąpolno Formation (Famennian) (Matyja, 1993) where the Devonian/Carboniferous chronostratigraphic boundary runs. The lower, Devonian part of the Sąpolno Formation is dominated by two lithofacies types: (1) dark grey marly limestones, rich in organic remains including brachiopods, echinoderms, chlorophyta algae, agglutinated foraminifers, benthonic ostracods and stromatoporoids; (2) dark grey marls containing cephalopods, entomozoids, conodonts, trilobites, bivalves, gastropods, brachiopods and solitary corals.

The upper (lower Carboniferous) part of the Sąpolno Formation is dominated by black finely laminated claystones containing rare fragments of organisms indicating sedimentary continuity from the Devonian to the Carboniferous. About 300 m of strata are included in the Tournaisian. The lower Carboniferous part of the formation represents a relatively deep-water carbonate ramp system (Lipiec and Matyja, 1998). Source rocks of the Sąpolno Formation, which could generate liquid and gaseous hydrocarbons, occur both onshore and offshore in the Kołobrzeg Block. These rocks may be responsible for anomalous shows of hydrocarbons along the Koszalin and Trzebiatów fault zones.

The occurrence area of the upper Carboniferous is much smaller than that of the lower Carboniferous. The upper Carboniferous deposits of the Gryfice Block and the northern part of the Wolin Block continue towards the north-west to Rügen. They are represented largely by clastics, mostly sandstones with mudstone and claystone interbeds. Their thickness varies from 100 m in the east, onshore in the Kołobrzeg Block, to over 1000 m in the western part of the Polish Exclusive Economic Zone of the Baltic Sea. They unconformably overlie Devonian and lower Carboniferous rocks.

Source rocks of the Wolin Formation (Westphalian A-B) contain abundant plant detritus and several cm-thick hard coal interlayers. The Westphalian source rocks are responsible for

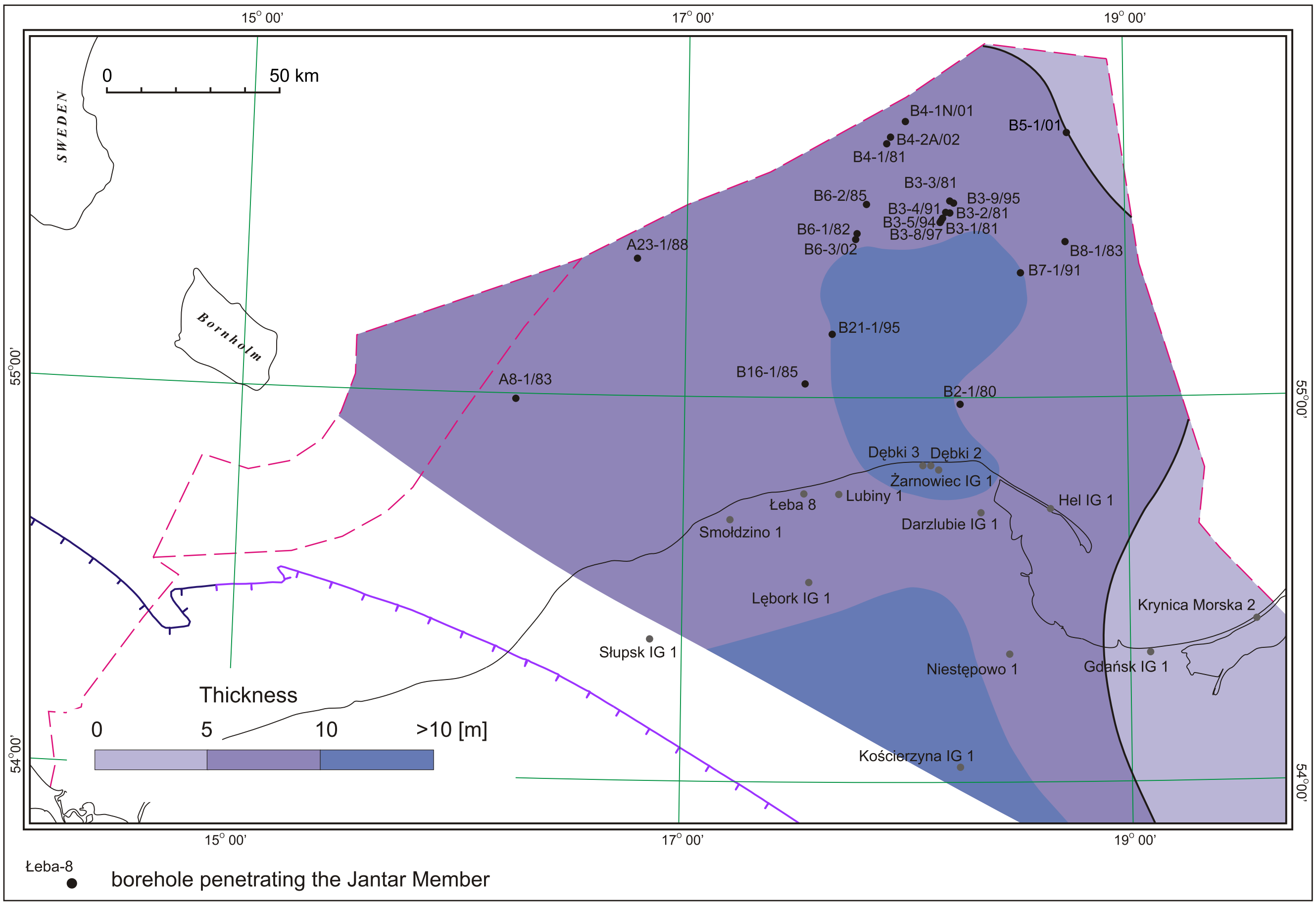

Fig. 6. Thickness of the Jantar Member (Llandovery)

For other explanations see Figures 2 and 4

the occurrences of gaseous hydrocarbons along the Kamień Pomorski and Trzebiatów fault zones.

Hydrocarbon accumulations observed onshore in the Gryfice and Kołobrzeg blocks (Wrzosowo and Gorzysław fields) show that the upper Paleozoic source rocks (Kotarba *et al.*, 2005) and the fault zones mentioned above are responsible for occurrence of geogenic methane-containing gases in bottom water and bottom sediments of the Baltic Sea.

LOWER PERMIAN VOLCANIC ROCKS

In the western onshore and adjacent Baltic Sea area (Figs. 2 and 3), the lower Rotliegend succession (Odra Subgroup) is composed mainly of effusive rocks (Volcanigenic Formation) with subordinate pyroclastic and clastic rocks (Świniec Formation) at the base (Pokorski, 1990).

The Volcanigenic Formation consists of effusive traps with intervening beds of pyroclastic rocks. Petrographic and geochemical investigations of the traps enabled identification of two volcanic cycles (Ryka, 1978): (1) an older cycle – andesites, dacites, rhyodacites (ignimbrites); (2) a younger cycle – dacites (perlites), latites, rhyolites.

The Wolin Block is characterized by a uniformly thick effusive rock cover of approximately 300 m or even more, in both onshore and offshore areas of the block. The greatest thickness variations of the effusive rocks are observed in the western part of the Gryfice Block along the Kamień Pomorski Fault Zone. The maximum thickness of the effusive rock cover, ranging from 504 to over 600 m, was demonstrated onshore in the southern part of the block. In the coastal area and off the coast, there are two palaeoelevations devoid of effusive rocks. Offshore in the western part of the Gryfice Block, the effusive rocks are 260 m thick, whereas in its eastern part the thickness is smaller, oscillating around 100 m. Both offshore and onshore in the Kołobrzeg Block, there are a number of small isolated effusive rock covers, 65 m to nearly 240 m in thickness.

The effusive rocks may be the source of occurrences and concentrations of harmful geogenic substances, including: gaseous CO_2 and CO; increased contents of: solid sulphur, H_2S, SO_3 and H_2SO_4; increased contents of: mercury, arsenic compounds and thermal waters.

ZECHSTEIN EVAPORITES

Zechstein deposits in the East European Craton cover the southern part of the Polish Exclusive Economic Zone of the Baltic Sea. On the Paleozoic platform they occur all over the zone (Wagner, 1990, 1994). In the cratonic area, they were recognised in only one borehole drilled in the northern part of the Żarnowiec Block and in numerous seismic profiles, which

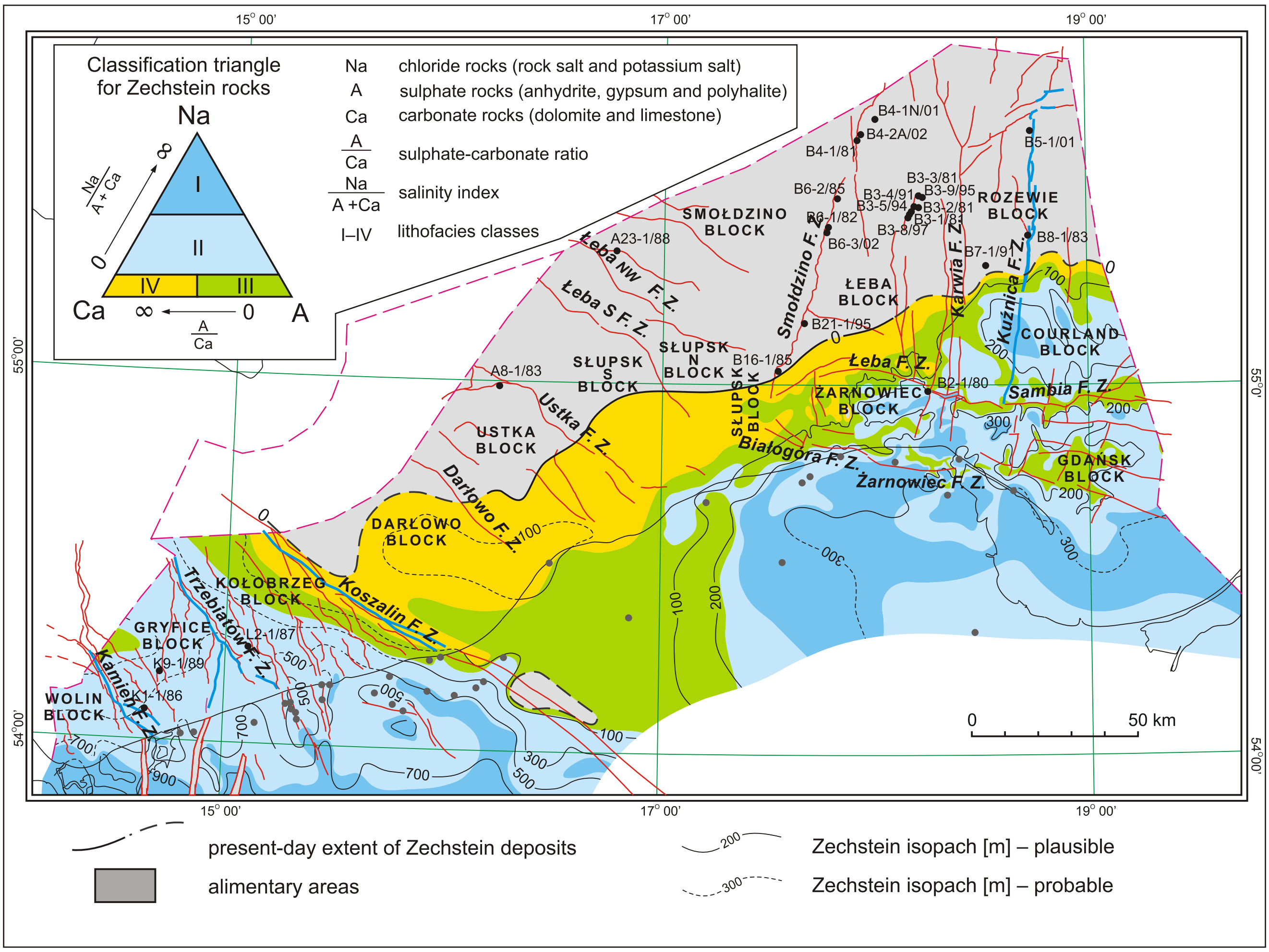

Fig. 7. Zechstein thickness and lithofacies

For other explanations see Figure 2

were the basis for the construction of the map of the main lithofacies and of Zechstein thickness (Fig. 7). Reflection seismic data show that Zechstein deposits of the Żarnowiec and Gdańsk blocks, in the southern part of the Courland Block and in a small portion of the Łeba Block, are represented by saline lithofacies, attaining thicknesses of 300 m. The PZ1 cyclothem reflects a complicated mosaic of saline basins separated by anhydrite ridges, in which the Oldest Halite attains a thickness of up to 250 m (Fig. 7). The upper cyclothems contain no rock salt. In the southern parts of the Słupsk, Ustka and Darłowo blocks, the Zechstein deposits are thin (<100 m) and composed of anhydrite-carbonate and carbonate lithofacies. At the limit of the extent of the Zechstein deposits, the carbonates subcrop at the sub-Cenozoic and sub-Upper Cretaceous surface.

In the Paleozoic platform, excluding the eastern part of the Kołobrzeg Block and northwestern portion of the Gryfice Block, the Zechstein is represented by saline lithofacies. Its thickness ranges from 100 to over 600 m (Wagner, 1990). Partly pierced salt stocks occur in the southern area of the Wolin Block.

In this area, the Zechstein basin formed a vast embayment extending parallel to the Teisseyre-Tornquist Zone (TTZ) northwards almost to the geographical parallel of Bornholm. The Zechstein deposits are penetrated by one borehole drilled in the western part of the Kołobrzeg Block, two boreholes drilled in the Gryfice Block and by one borehole drilled off the German Baltic Sea coast. The network of reflection seismic profiles is dense, but no thickness and facies maps have been constructed for this area. The seismic data were used only to determine the main lithofacies types and their extents (Wagner, 1990). Rock salt occurs in all the four cyclothems (PZ1 to PZ4), but the extent of the youngest salts is limited to the southern part of the research area.

The Zechstein deposits contain highly mineralised brines. The latter migrate into the Baltic Sea waters in areas of sub-Cenozoic subcrops of those deposits and along fault zones. This is an especially important process in the East European Craton, i.e. in the eastern part of the Polish sector of the Baltic Sea, where a wide belt of such outcrops is observed (Fig. 7).

In the Paleozoic platform area, the Zechstein's Main Dolomite (Ca2) is a source of methane containing toxic hydrogen sulphide, heavy hydrocarbons and oil.

RESERVOIR ROCKS FOR MINERAL AND THERMAL WATERS

In the Polish Exclusive Economic Zone of the Baltic Sea, bedrock sedimentary formations contain mineral and thermal waters under considerable reservoir pressure. Ascent of confined groundwater into seawater occurs in some areas, causing alteration of its hydrochemical and physical properties. As a consequence, there is a high risk of geogenic contamination of seawater. The information given below originates from boreholes partly drilled onshore along the southern Baltic Sea coast (*cf.* Bojarski, 1996).

Cambrian and Devonian aquifers occur in the eastern part of the Polish sector of the Baltic Sea, i.e. in the East European Craton (Figs. 2 and 3).

Water mineralisation in the Middle Cambrian deposits increases from <150 g/dm^3 at a depth of 1000–2000 m to >200 g/dm^3 at 4500 m. The brines are enriched in iodine and bromine. In the Gdańsk Block, bromine content is up to 1650 mg/dm^3. Reservoir pressure gradient values vary from 1.03 to 1.13 hPa × 10^3/10 m, occasionally attaining 1.23 hPa × 10^3/10 m. The highest discharge (3.94 m^3/h) was observed in the Rozewie Block, immediately to the south of a zone of pinchout of Cretaceous deposits. In the other regions, the discharge is below 2 m^3/h.

In the Rozewie and Courland blocks, the topmost Middle Devonian strata contain weakly mineralised water, as shown by data from onshore areas (Kondratas and Wajtekunas, 1990). At the base of the Devonian succession, water mineralisation is probably of several g/dm^3, whereas under the Cretaceous overburden it can exceed 20 g/dm^3. Groundwaters from the top of the Devonian succession are of SO_4-HCO_3-Ca-Mg or SO_4-Ca-Mg types, whereas groundwaters from its basal part represents a Cl-Na-Ca type with the bromine content exceeding 100 mg/dm^3. Groundwater discharge from sandstones is >20 m^3/h; from dolomites it is below 1 m^3/h.

Devonian, Carboniferous and Rotliegend aquifers occur in the western part of the Polish sector of the Baltic Sea, i.e. in the Paleozoic platform (Figs. 2 and 3).

Devonian deposits of the area exhibit very poor reservoir properties. They are commonly conspicuous by a total lack of inflow, or show inflows below 0.6 m^3/h. The only horizons characterized by a higher discharge (e.g. 27 m^3/h from a depth of 2560–2604 m, onshore to the south of the Kołobrzeg Block) are terrigenous-cavernous Middle Devonian deposits. Highly altered Cl-Ca-Na type brines with mineralisation of 195–265 g/dm^3 are predominant. Values of the hydrochemical index are as follows: rNa:rCl = 0.39÷0.56, Cl:Br <100 and $rSO_4 \cdot 100/rCl$ <0.01. The iodine content is 30–51 mg/dm^3. The bromine content attains 1850 mg/dm^3. The reservoir pressure gradient decreases northwards from 1.20–1.04 × 10^3 hPa/10 m onshore to 1.00 × 10^3 hPa/10 m offshore.

The mineralisation of brines coming from the Carboniferous deposits is 220–260 g/dm^3 in onshore areas, and it decreases to approximately 150 g/dm^3 in offshore areas. Locally, there are brines of mineralisation >300 g/dm^3, containing 92–98% mval of NaCl. These are genetically associated with a leaching of Zechstein rock salts injected into vertical fault fractures. These are Cl-Ca-Na type brines showing a high level of alteration of their chemical composition expressed by the ratios rNa:rCl = 0.450.65 and Cl:Br = 100. The iodine content is up to 40 mg/dm^3; the bromine content is up to 2500 mg/dm^3. The maximum brine discharge is 5 m^3/h. Reservoir pressure gradients commonly exceed 1 × 10^3 hPa/10 m. The anomalously high brine discharge of 65 m^3/h was observed onshore immediately to the south of the Kołobrzeg Block due to strong rock fracturing. There are also zones of anomalously increased reservoir pressure, where the gradients reach values of 1.35 × 10^3 hPa/10 m.

The mineralisation of brines from the Rotliegend can be estimated with reference to data from onshore areas, where it exceeds 220 g/dm^3. Saturated brines of mineralisation exceeding 300 g/dm^3 are locally observed. These brines represent a Cl-Ca-Na type. The values of rNa:rCl and Cl:Br are 0.52–9.70 and <100, respectively. Maximum bromine and iodine contents are 1822 mg/dm^3 and 18 mg/dm^3, respectively. Brine discharge is commonly 0.1–1.4 m^3/h. Reservoir pressure gradient values do not exceed 1.10 × 10^3 hPa/10 m and decrease northwards. Brines of a similar type probably occur also in offshore areas, however, their mineralisation is lower.

Numerous aquifers have been found in the Zechstein, Triassic, Jurassic and Cretaceous deposits of all the tectonic blocks in the Polish sector of the Baltic Sea.

The Zechstein aquifer is characterized by a huge variability of reservoir properties and mineralisation of brines, as well as by the presence of toxic hydrogen sulphide. The mineralisation of onshore brines varies from 320 to 390 g/dm^3, whereas the mineralisation of offshore brines is merely 170 g/dm^3. In the Łeba Block, brine mineralisation values are below 50 g/dm^3. These are Cl-Ca-Na type brines. In the western part of the Kołobrzeg Block, the reservoir pressure gradient is 1.09 × 10^3 hPa/10 m; in onshore areas it commonly ranges between 1.75 and 2.12 × 10^3 hPa/10 m. The Zechstein aquifer is characterized by a small brine discharge. Some 90% of observations have shown no inflow or only percolation of brine (0.02–0.7 m^3/h). Much higher brine discharges were recorded only along fault zones.

In the Triassic succession, the best quality reservoir rocks are Buntsandstein sandstones. Groundwater mineralisation in these rocks from the eastern part of the Polish sector of the Baltic Sea is below 50 g/dm^3; slightly higher values are only observed in a small area in the southern part of the Żarnowiec Block. In the western portion of the sector, groundwater mineralisation is over 200 g/dm^3, as shown by data obtained from the land area. Upper Triassic brines show mineralisation of 75–150 g/dm^3. The values decrease northwards and are variable with brine discharges ranging from percolation to 50 m^3/h. Reservoir pressure gradient values are commonly around 1.05 × 10^{3}hPa/10 m, sporadically reaching 1.10 × 10^3 hPa/10 m. Onshore in the Gdańsk Block, there is an artesian spring from the Buntsandstein aquifer, yielding inflow of pressurised thermal water of temperature 22–24°C. Thermal waters of similar temperatures were also observed onshore on the extension of the Ustka Block.

Onshore data show that mineralisation of the Lower Jurassic groundwater varies within a wide range from freshwater (0.4 g/dm^3) to concentrated brines (170 g/dm^3) that show a low level of alteration of their chemical composition expressed by the ratio rNa:rCl>0.85. These are commonly Cl-Na type waters. Brine discharge is very high in onshore boreholes, reaching about 50 m^3/h. Reservoir pressure conditions are very favourable for groundwater inflow. Reservoir pressure gradient values vary from 1.02 to 1.06 × 10^3 hPa/10 m. Lower Jurassic deposits from a depth of 600–1300 m yield thermal water with mineralisation of several to >50 g/dm^3 and discharge of 50 m^3/h. Thermal water inflows were observed e.g., in onshore areas immediately to the south of the Gryfice and Wolin blocks, where the water temperatures were 23 and 27^{o}C, respectively.

Onshore on the extension of the Wolin Block, Lower Cretaceous deposits contain Cl-Na type brines with mineralisation of 35–45 g/dm^3. The brines show increased concentrations of iodine, bromides and boron. Brine discharge is 1.8–6.0 m^3/h. Onshore in the Kołobrzeg region, there are Cl-Na brines with mineralisation of 4–14 g/dm^3. Groundwater of the Upper Cretaceous aquifer is weakly mineralised with the content of total dissolved solids below 5 g/dm^3. Higher mineralisation values of 10–20 g/dm^3 may be expected only in the southern part of the Wolin Block.

MIGRATION AVENUES OF HARMFUL GEOGENIC SUBSTANCES

FAULT ZONES

Fault zones and associated fracture systems are the main migration pathways of geogenic substances originating from deeply seated geological structures. In the Polish Exclusive Economic Zone of the Baltic Sea, seismic investigations revealed a number of deeply rooted fault zones (Figs. 1–3). In the East European Craton, i.e. in the eastern part of the research area, the faults penetrate a very thick cover of Silurian clay- and mud-shales, and locally Zechstein evaporites, which are the rocks sealing older formations and preventing any solutions from direct migrating through the lower Paleozoic strata. In the Paleozoic platform, i.e. in the western part of the research area, the fault zones cut lower and upper Paleozoic, Mesozoic and Cenozoic formations. They were rejuvenated at the end of Mesozoic times, during the Cretaceous tectonic inversion. As in the cratonic area, fault zones in the Paleozoic platform are migration avenues for geogenic substances.

Interpretation of the geogenic activity is based on the intensity of the outflow and seepage of geogenic substances. These depend on a number of different factors such as the type of sea bottom sediments, bottom water agitation and seismic activity. The variability of these factors greatly affects the concentrations of analytically identifiable geogenic substances (Tkachenko and Mazurek, 2008*a*, *b*). On shoals with a depth of 20–30 metres below sea surface, samples were taken only during calm sea conditions (Beaufort number 1). At greater depths sampling was possible during a light or gentle breeze (Beaufort numbers 2 and 3). Of fundamental importance was seismic activity. Even during very distant earthquakes the amount of migrating geogenic substances increased several-fold.

Four major fault zones were selected for thorough investigations carried out to check the possibility of vertical migration of geogenic substances. These were the Kuźnica Fault Zone in the cratonic area, and the Koszalin, Trzebiatów and Kamień Pomorski fault zones on the Paleozoic platform (Figs. 2 and 3). Each fault zone was examined by producing three geochemical profiles running parallel to the fault strike: along the fault axis and on both its sides. The average distance between the profiles was 500 m. Those situated in the fault axes were sampled more densely (twice as many samples) with a 500 m sample interval. Along the fault sides, the sample interval was 1000 m. The total number of samples collected was 1054, including 50 samples taken for examination of isotopic composition of gas. Several thousand analyses were made on these samples (Tkachenko and Mazurek, 2008*a*).

Characteristics of geogenic activities in the fault zones studied are given in Tables 1–4 set separately for each zone. The tables present concentrations of liquid and gaseous hydrocarbons in bottom sediments and bottom waters characterized by their minimal and maximum values, median values and arithmetic means. The indices obtained are a reliable measure of pollution because of the large number of samples analysed.

KUŹNICA FAULT ZONE

The Kuźnica Fault Zone is situated on the East European Craton in the eastern part of the Polish Exclusive Economic Zone of the Baltic Sea. This is a N–S-trending, 100 km long deeply rooted tectonic fracture zone. It separates two tectonic blocks of Courland in the east and Łeba in the west (Figs. 2 and 3). Together with the more westerly Karwia and Smołdzino faults of similar direction and origin, the zone played a very important role in the tectonic evolution of the region.

The Kuźnica Fault Zone was selected for studies of geogenic phenomena because, as previously demonstrated, the zone showed geogenic activity (Jaworowski *et al.*, 2001). Two oil fields (B5 and B8) occur in Cambrian deposits on the western upthrown side of the fault. Thus, by examining almost the whole fault zone, we could determine its present geogenic activity. For that purpose, 400 samples were collected from bottom sediments and bottom water along three profile lines to determine the concentrations of hydrocarbons and gases (Fig. 8).

The sea depth in the fault region varies within the interval of 80–90 m, increasing to 105 m only in the northern part of the area. The considerable depths prevented the hydrocarbon accumulations from being washed away by wave activity during fair-weather conditions (Beaufort number up to 3). The sea bottom sediments are represented mainly by Holocene tills, clays and clayey muds with subordinate fine-grained sands. The character of the bottom sediments favoured sorption of liquid hydrocarbons within the deposit.

Comparison of the median values and arithmetic means (Table 1) shows that the concentrations of liquid hydrocarbons in bottom waters are many times greater along the fault axis (profile C). This relationship should be treated as robust and independent of any other factors because the differences between the concentration values are very large. The arithmetic means for liquid hydrocarbons in sediments reveal a slightly different pattern. The concentrations in the fault axis (profile C) and on the downthrown side (profile E) are similar and only slightly greater in the latter area. The concentrations of methane in bottom waters are highest along profile E while along profile W methane is always accompanied by heavy hydrocarbons.

The Kuźnica Fault is the best-explored geogenic pollution zone (Wagner, 2008). The greatest intensity of geogenic phe-

Table 1

Geochemical characteristics of geogenic activity in the Kuźnica Fault Zone

	Geochemical profiles		
	W (Łeba Block)	C (fault axis)	E (Courland Block)
Liquid hydrocarbons in bottom water [mg/l]	0.74 to 51.00 (101) **2.25** (6.43)	1.12 to 195.00 (202) **6.75** (23.06)	1.12 to 27.00 (101) **3.00** (4.39)
Liquid hydrocarbons in sediments [wt.%]	0.0055 to 0.5277 (98) **0.0518** (0.0966)	0.0093 to 0.8308 (190) **0.0543** (0.1128)	0.0106 to 0.5493 (96) **0.1012** (0.1650)
Methane concentration in water [$\times10^{-4}$ vol.%]	5.6 to 96 500 (100) **30.80** (2 455.25)	4.50 to 328 100 .00 (200) **31.10** (4 827. 61)	6.7 to 627 500.00 (101) **42.25** (8 974.38)
Methane concentration in sediments [$\times10^{-4}$ vol.%]	17.45 to 141.31 (29) **57.90** (64.12)	3.64 to 149.03 (86) **38.61** (56.02)	8.96 to 145.17 (93) **30.64** (36.78)

Range of geochemical parameters is given as numerator, median value in denominator (**bold**); in parentheses – number of analyses (numerator) and arithmetic mean (denominator)

nomena is observed in the northern and central parts of this tectonic zone (Fig. 8). Strong and very strong anomalies of liquid hydrocarbon concentrations in bottom waters, ranging from 50 to 200 mg/l, and in bottom sediments, reaching up to 0.9 wt.%, are of outflow nature. They are related to the Middle Cambrian oil fields B5 and B8, being hazardous to the natural environment. The outflow substances spread out onto the sea-floor along the tectonic zone despite the large thicknesses (1000–1700 m) of Silurian clay-shales, which are rocks of good sealing properties.

The absence of hydrocarbon concentration anomalies in the southern part of the Kuźnica Fault may be due to a seismic silence during sampling and, as is more probable, due also to the occurrence of sealing Zechstein rock salt layers in this region. Gaseous anomalies are observed only in this area. Gases, being more mobile, can easier migrate through rock salt.

The isotopic composition of the gases in most of the samples shows that methane formed mainly as a result of thermogenic processes of alteration of fossil organic matter (Kotarba *et al.*, 2008).

KOSZALIN FAULT ZONE

The NW–SE-trending Koszalin Fault Zone (Figs. 2 and 3) constitutes the northern part of the Teisseyre-Tornquist Zone (see chapter: European Paleozoic Platform). The sea depth in the southeastern part of the Koszalin Fault is small, oscillating around 10 m, and gradually increases to approximately 50 m in the northwestern area. This is a shallow-marine zone prone to storm effects. Bottom sediments in the area consist exclusively of sand and gravel. These are extremely unfavourable conditions for liquid hydrocarbon accumulations because of the lack of sorption ability of the deposits. Thus, no analyses have been made in this region. The weather was good during sampling along profiles C and W (sea condition: wavelets), and it by no means affected the hydrocarbon concentration in the bottom waters. Profile E was analysed in less favourable conditions, close to stormy. Geodynamic activity along profile C was very weak and it increased during work on profiles W and E.

The Koszalin Fault Zone was examined by three parallel geochemical profiles spaced 500 m apart (Fig. 9A). In total, 249 samples were collected. Comparison of the median values (excluding profile W) and arithmetic means (Table 2) shows that the concentrations of methane and liquid hydrocarbons in the bottom waters are slightly greater in the fault axis (profile C), although the values are comparable. These data suggest that the Koszalin Fault Zone and both its sides can be considered as very weakly active as regards the migration and seepage of liquid and gaseous hydrocarbons.

The geochemical anomalies of the Koszalin Fault Zone are characterized by low concentrations of liquid and gaseous hydrocarbons in bottom waters. They are absent in the central part of the fault zone. The research results show that the Koszalin Fault Zone is a very insignificant source of geogenic pollution.

TRZEBIATÓW FAULT ZONE

The Trzebiatów Fault Zone is one of the most important tectonic elements of the Paleozoic platform, separating the Kołobrzeg Block from the Gryfice Block (Figs. 2 and 3). The Trzebiatów Fault Zone is a set of several faults trending approximately NW–SE. The major fault of the zone is deeply rooted in the crystalline basement. The fundamental restructuring of the area took place in latest Cretaceous and earliest Paleogene times.

The sea depth in the fault region is small: from about 10 m in the southeastern area to approximately 30 m in the northwest. Thus, the fault is situated in a shallow-marine zone of the sea, prone to storm effects. The bottom sediments are composed exclusively of sand and gravel. These are extremely unfavourable conditions for liquid hydrocarbon accumulations in sediments due to lack of sorption ability. Thus, no hydrocarbon analyses have been made in this region.

The weather was good during sampling along all the profiles (sea condition: wavelets), and it by no means affected the hydrocarbon concentrations in bottom waters. Geodynamic activity was increased.

The Trzebiatów Fault Zone was examined by three parallel geochemical profiles running 500 m apart (Fig. 9B). In total, 181 samples were taken. Comparison of the median values and arithmetic means (Table 3) indicates that the highest concentrations of liquid hydrocarbons in bottom waters occur along pro-

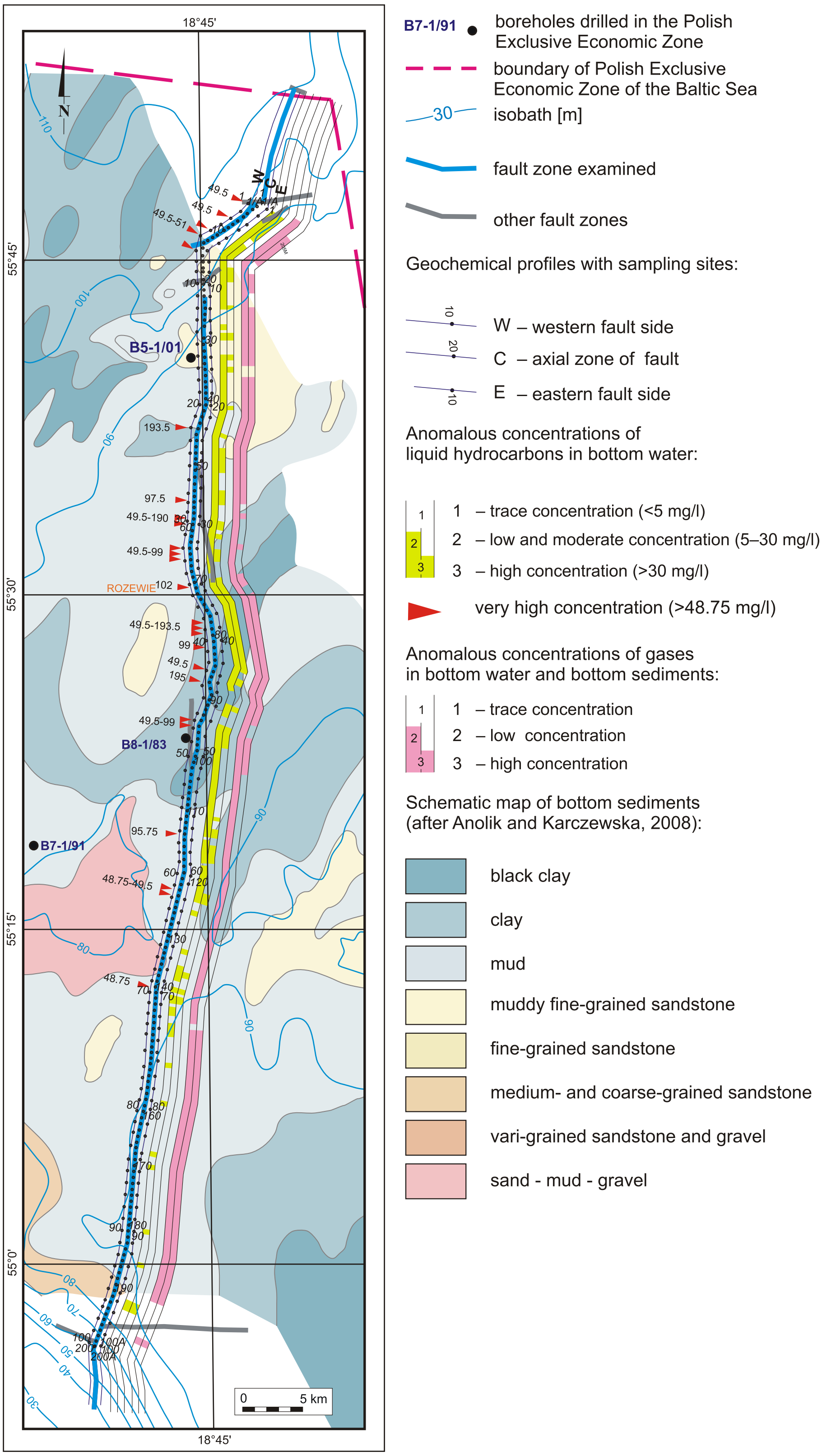

Fig. 8. Geogenic activity in the Kuźnica Fault Zone

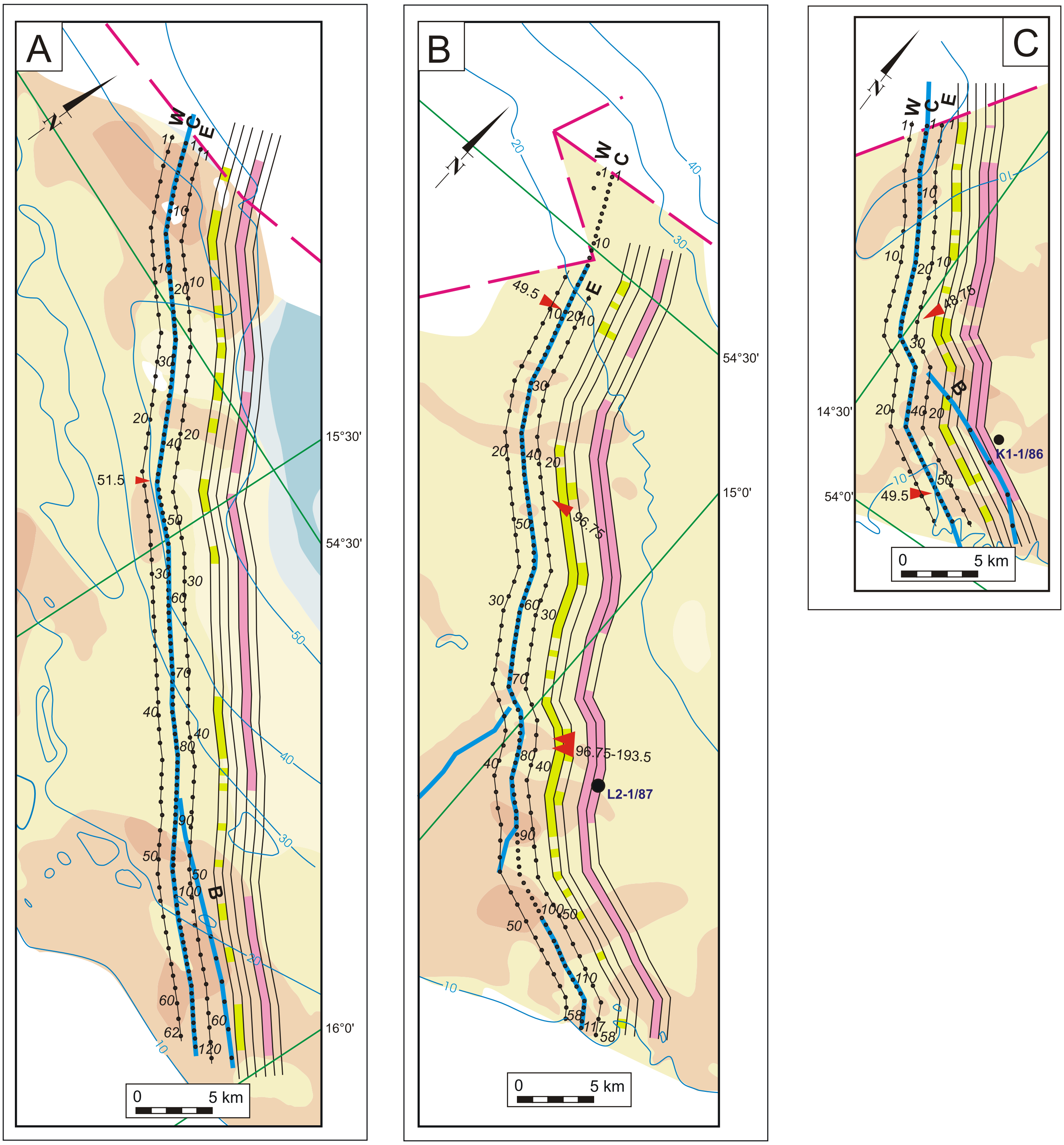

Fig. 9. Geogenic activity

A – Koszalin, **B** –Trzebiatów, **C** – Kamień Pomorski fault zones; for explanations see Figure 8

file E. The methane concentration in bottom waters is slightly higher in profile C. This situation, i.e. a higher geogenic activity along profile E, can be explained by the incorrect location of the fault axis zone in the map of bottom sediments (Fig. 9B). This led to the location of profile E, instead of profile C, in the fault axis (Tkachenko and Mazurek, 2008*c*).

The Trzebiatów Fault Zone is very active in the processes of migration and seepage of liquid and gaseous hydrocarbons (Fig. 9B). In terms of liquid hydrocarbon seepage into bottom waters, the most active is the central part of profile E, crossing the axial fault zone. The concentrations of liquid hydrocarbons, which are a serious hazard to the environment here, reach values of 96–193 mg/l. Profiles W and C are characterized by more poorly marked anomalies, but a few analyses revealed relatively high values of 30–50 mg/l. High methane concentrations in water (2.0–2.5 $\times$ 10^{-4} mg/l) are observed in the southern part of the fault zone.

Table 2

Geochemical characteristics of geogenic activity in the Koszalin Fault Zone

	Geochemical profiles			
	W (Kołobrzeg Block)	C (fault axis)	E (Darłowo Block)	B (Darłowo Block)
Liquid hydrocarbons in bottom water [mg/l]	1.50 to 21.00 (62) **3.75** (4.20)	1.50 to 51.00 (120) **2.25** (4.88)	1.50 to 25.50 (62) **2.25** (4.79)	2.25 to 4.50 (6) **1.5** (2.50)
Methane concentration in water [$\times 10^{-4}$ vol.%]	3.84 to 8.86 (62) **5.28** (5.75)	4.20 to 11.58 (131) **5.54** (6.19)	0.00 to 11.13 (62) **5.31** (5.90)	7.52 to 8.48 (6) **8.15** (8.11)
Methane concentration in sediments [$\times 10^{-4}$ vol.%]	–	14.57 to 5 674.81 (4) **144.12** (1 550.03)	341 to 592.73 (2) **467.22** (467.22)	–

Explanations as in Table 1

Vertical migration of gaseous and, especially, liquid hydrocarbons occurs despite the occurrence of the sealing Zechstein rock salt horizons. The isotopic composition of the gases suggests that methane was formed in most of the samples as a result of thermogenic processes of alteration of fossil organic matter (Kotarba *et al.*, 2008).

KAMIEŃ POMORSKI FAULT ZONE

The Kamień Pomorski Fault Zone (Figs. 2 and 3) is one of the most important tectonic elements of the Paleozoic platform, separating the Gryfice Block from the Wolin Block. The Kamień Pomorski Fault Zone is a set of several faults trending approximately NW–SE. In the German sector of the Baltic Sea, it passes into the Adler Fault Zone, so it is also referred to as the Kamień–Adler Fault. The major fault of the zone is deeply rooted in the crystalline basement. The main stage of tectonic restructuring of the area occurred at the late Carboniferous/Permian transition and during the latest Cretaceous–earliest Paleogene.

The sea depth in the fault region is small: from about 8 to 14 m. In general, the fault is situated in a very shallow-marine zone, prone to storm effects. The bottom sediments are composed exclusively of sand and gravel. These are extremely unfavourable conditions for liquid hydrocarbon accumulations in sediments because of their lack of sorption ability. Thus, no hydrocarbon analyses have been made in this region.

The weather was good during sampling along all the profiles (sea condition: wavelets), and it by no means affected the hydrocarbon concentration in bottom waters. Geodynamic activity was increased during sampling along profile C and in the northern part of profile E (sampling sites 1–18), which increased the values of geochemical indices.

The Kamień Pomorski Fault Zone was examined by three parallel geochemical profiles running 500 m apart (Fig. 9C). Profile C is located in the fault axis, profile W crosses the Wolin Block, whereas profile E is situated in the Gryfice Block. In addition to these profiles, an eastern branch of the Kamień Pomorski Fault was analysed in its southeastern part (profile B). In total, 117 samples were collected. Due to the variable inclination of the fault, profile C, intended for examination of the axial fault zone, runs across the zone in its northeastern part comprising points 1–19, whereas in the remaining area (points 20–58) it zigzags across the axial zone into the Wolin and Gryfice blocks (Fig. 9C).

Comparison of the median values and arithmetic means (Table 4) suggests that the highest concentrations of liquid hydrocarbons in bottom waters occur along geochemical profile E. Methane concentrations in the bottom waters are comparable in all the profiles. Methane concentrations in the sediments are slightly higher in profile E.

Any comparisons of the median values and arithmetic means along individual profiles in order to show the highest activity of the axial fault zone make no sense in the case of the

Table 3

Geochemical characteristics of geogenic activity in the Trzebiatów Fault Zone

	Geochemical profiles		
	W (Gryfice Block)	C (fault axis)	E (Kołobrzeg Block)
Liquid hydrocarbons in bottom water [mg/l]	2.25 to 51.00 (45) **4.50** (5.93)	1.50 to 49.5 (117) **3.75** (5.63)	2.25 to 193.5 (30) **6.00** (19.33)
Methane concentration in water [$\times 10^{-4}$ vol.%]	0.00 to 10.51 (64) **7.30** (7.01)	4.70 to 60.10 (117) **8.10** (8.94)	4.52 to 20.00 (61) **7.30** (7.71)
Methane concentration in sediments [$\times 10^{-4}$ vol.%]	7.07 to 7.69 (2) **7.38** (7.38)	0.00 to 10.51 (117) **7.76** (8.24)	–

Explanations as in Table 1

Table 4

Geochemical characteristics of geogenic activity in the Kamień Pomorski Fault Zone

	Geochemical profiles			
	W (Wolin Block)	C (fault axis)	E (Gryfice Block)	B (Gryfice Block)
Liquid hydrocarbons in bottom water [mg/l]	9.00 to 24.75 (28) **9.00** (6.75)	1.50 to 49.5 (56) **3.00** (5.00)	1.50 to 75.00 (28) **3.00** (7.63)	3.00 to 6.00 (5) **4.50** (4.50)
Methane concentration in water [$\times 10^{-4}$ vol.%]	7.50 to 12.10 (27) **10.05** (9.88)	6.30 to 16.70 (57) **9.55** (9.66)	7.70 to 10.4 (27) **8.40** (9.33)	8.30 to 9.40 (5) **8.90** (8.96)
Methane concentration in sediments [$\times 10^{-4}$ vol.%]	4.71 to 9.14 (27) **7.71** (7.29)	0.00 to 10.40 (55) **8.51** (7.00)	3.74 to 10.34 (27) **7.67** (7.59)	0.00 to 8.58 (5) **5.25** (8.48)

Explanations as in Table 1

Kamień and Trzebiatów fault zones. This results from the fact that the sampling locally missed the axial zone due to the variable inclination of the fault zone. Nevertheless, it permits comparing the intensity of geogenic phenomena in individual fault zones.

From this point of view, the Kamień Pomorski Fault Zone is a very important area, especially for the gas phase emission. Worth noting is the special role of butylene in the composition of the hydrocarbon gas phase. The butylene contents are greater than the contents of other gaseous hydrocarbons, including methane, by an order of magnitude. Together, they form huge concentrations that demonstrate their petroleum origin (Tkachenko and Mazurek, 2008*c*).

The Kamień Pomorski Fault Zone is characterized by high concentrations of methane, butylene and heavy hydrocarbons in bottom waters, severely polluting the natural environment. During sampling in 2006, decaying dead mollusc remains were found – probably victims of the specific composition of the gas phase, that depleted oxygen from the water in the process of oxygenation (Tkachenko and Mazurek, 2008*c*).

The concentrations of liquid hydrocarbons are generally small with isolated large seepage spots where the concentration values range from 48.75 to 75 mg/l. The isotopic composition of the gases suggests that methane was formed in most of the samples as a result of thermogenic processes of alteration of fossil organic matter.

PINCHOUT ZONES OF SEDIMENTARY COMPLEXES

In addition to faults, regional pinchout zones of sedimentary units are important migration avenues of harmful geogenic substances (Jaworowski *et al*., 2001). A special role in transmitting geogenic liquids and gases is played by erosional pinchout zones related to post-Cretaceous erosion. Much significant information on pinchout zones is given by the geological map of the sub-Quaternary surface accompanied with geological-seismic cross-sections published by Kramarska *et al.* (1999). The map and cross-sections are based on boreholes and high-resolution seismic reflection data which allowed insight into the geological structure down to several hundreds metres depth. They were taken into account while drawing the extents of some sedimentary formations shown in Figure 10.

In the cratonic area of the Polish sector of the Baltic Sea (Gdańsk, Courland, Rozewie, Łeba, Żarnowiec, Smołdzino, Słupsk, Ustka and Darłowo blocks; Figs. 2 and 3), the pinchout zones resulted from erosional truncation of gentle, broad elevations of the Permo-Mesozoic sedimentary succession later covered by Cenozoic deposits.

The thick Silurian succession, mostly of clay- and mud-shales, prevents geogenic substances from migrating along pinchout zones of the lower Paleozoic deposits. Lower Paleozoic geogenic substances most probably first migrated along the faults cutting the lower Paleozoic formations, and subsequently through fault zones and pinchouts in younger deposits i.e. along pinchouts within the Permo-Mesozoic cover (Jaworowski *et al*., 2001). In the Courland and Rozewie blocks, there is a regional zone of pinchout of Cretaceous deposits overlying the Devonian succession. The erosional boundary between occurrence areas of the Cretaceous and Devonian deposits subcrops at the sub-Quaternary surface in this region. Three regional, NE–SW and E–W- trending pinchout zones are observed in the southern part of the Łeba Block. These are expressed by erosional boundaries between the occurrence areas of the following deposits (when moving in a S to N direction): Cretaceous and Triassic, Triassic and Zechstein, and Zechstein and Silurian. Further westwards, within the Słupsk Block, there are similar zones associated with erosional boundaries of the northern extents of Cretaceous, Triassic and Zechstein deposits, occurring on the extension of the previously mentioned pinchout zones.

Towards the west, within the Ustka Block, the Cretaceous deposits overlap Triassic and Zechstein, thus directly overlying the Silurian succession. It means that the sub-Cretaceous pinchouts of Triassic and Zechstein deposits and the pinchout zone of Cretaceous rocks occur upon the Silurian basement in this area. The pinchout zones from the southwestern part of the Łeba Block and the Słupsk and Ustka blocks are overlain by both Quaternary and Tertiary deposits over almost the whole areas, reducing their migration potential. The zones so sealed stretch between the meridians of Karwia and Jamno, about 30–40 km off the coast. On the Paleozoic platform of the Polish sector of the Baltic Sea, i.e. on the Kołobrzeg, Gryfice and Wolin blocks, lower and upper Paleozoic formations occur beneath the Permo-Mesozoic cover. Partly explored Devonian and Carboniferous deposits of this area form a number of

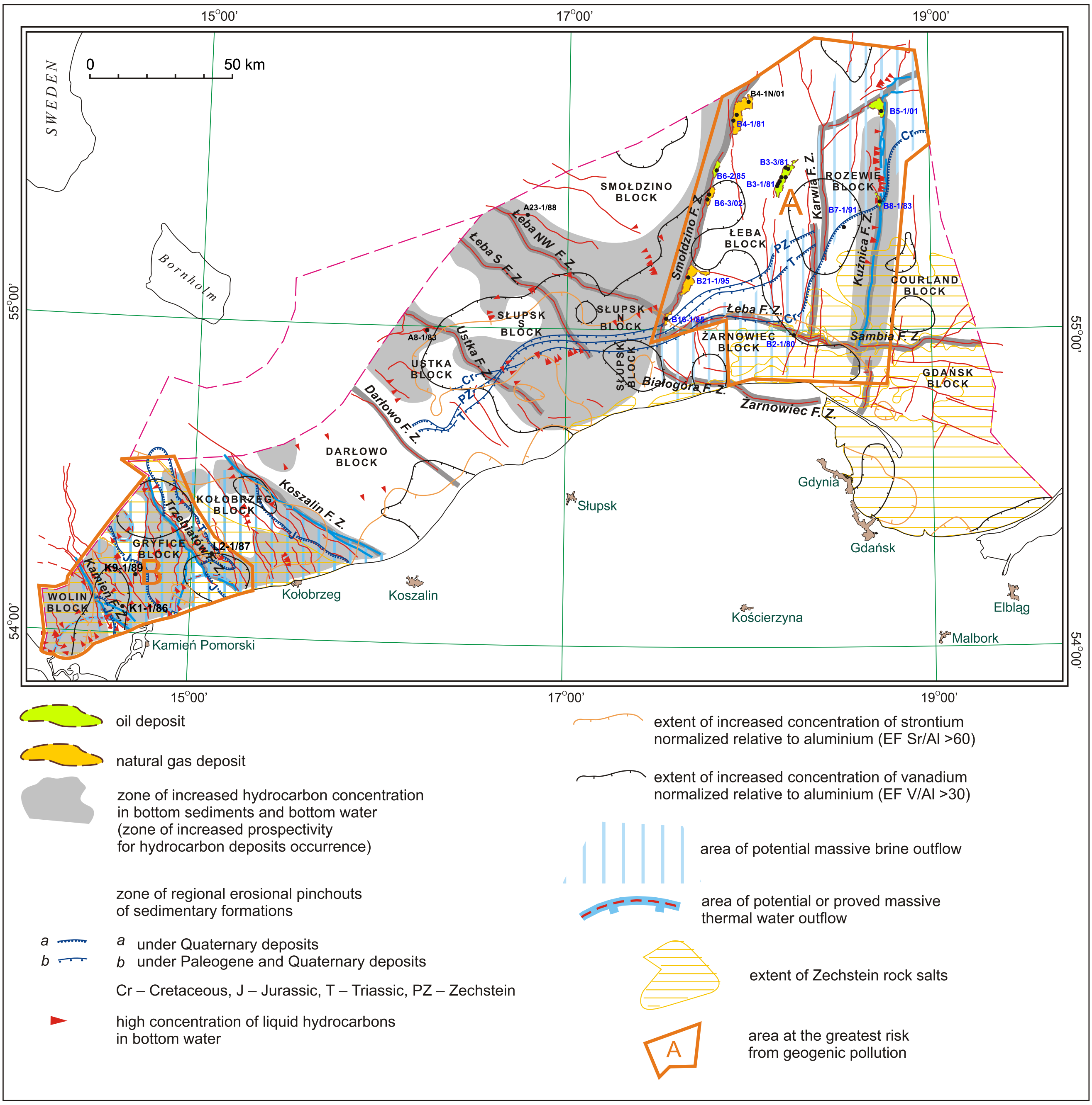

Fig. 10. Areas at the greatest risk from geogenic pollution

Hydrocarbon deposits and zones of increased prospectivity for hydrocarbon deposits after Anolik and Karczewska (2008); for other explanations see Figure 2

sub-Permian antithetic blocks represented by half-horsts and half-grabens with strata dipping towards the NE (Dadlez and Pokorski, 1995). Seismic data show signs of angular disconformities and pinchout zones within these deposits. However, the pinchout zones are sealed by a thick Permo-Mesozoic cover and they play no role in migration of geogenic substances. The only regional pinchout zones capable of transmitting the geogenic substances in the Paleozoic platform are linked with Mesozoic deposits. These are erosional pinchouts formed as a result of truncation of relatively steep and narrow folds. In consequence, pinchout zones with erosional discontinuities at the top are mainly observed along the anticlinal flanks in this area. In the Kołobrzeg Block, regional zones of this type are represented by erosional boundaries between the occurrence areas of Triassic, Jurassic and Cretaceous deposits, subcropping at the sub-Quaternary surface. In the Gryfice Block, there are analogous boundaries between the occurrence areas of different Jurassic and Cretaceous stages.

Credible evidence for migration of geogenic substances along pinchout zones, at least in the cratonic part of the study area, was provided by increased contents of strontium and vanadium in bottom sediments. These are derived from deep-seated sedimentary formations. Strontium comes from Zechstein salts while vanadium is from lower Paleozoic black shales and/or hydrocarbon-bearing strata. In this paper, "increased" values of the metals denote those concentrations normalised relative to aluminium (i.e. Sr/Al and V/Al) represented by an Enrichment Factor (EF): for strontium of >60, and for vanadium of >30. Data on strontium and vanadium distribution in bottom sediments (Fig. 10) are given in papers by Szczepańska and Uścinowicz (1994) and Uścinowicz *et al.* (2004). These papers contain results of investigations based on samples taken at 368 points arranged in a regular 10 × 10 km grid covering the whole Polish Exclusive Economic Zone. Bottom sediments were sampled with the use of a Niemisto core-sampler (muds) and Van-Veen grab-sampler (sands). The metal content was determined using atomic spectrometry (ASA) and atomic emission spectrometry with plasma excitation (ICP) methods, after microwave dilution in HNO_3 1 + 1.

In the cratonic area, increased Sr/Al values are observed on the Słupsk and Żarnowiec blocks. These are certainly associated with a zone of regional erosional pinchouts of Permo-Mesozoic deposits (Fig. 10). They were the pathways for migrating Sr-rich Zechstein brines and thermal waters. Increased Sr/Al values were also recorded on the Gryfice and Kołobrzeg blocks of the Paleozoic platform, as a result of migration along a dense fault network. However, it must be borne in mind that there are also pinchout zones of Triassic, Jurassic and Cretaceous deposits in this area (Fig. 10). In addition to faults, they could be the migration pathways for brines and thermal waters predominantly from the Zechstein deposits.

High V/Al values are observed mainly in the cratonic sector of the Polish economic zone of the Baltic Sea along the Smołdzino Fault, and in the middle part of the Karwia Fault (Fig. 10). An especially strong anomaly is recorded in the last-mentioned area. It probably reflects a local near-fault inflow of geogenic substances and, notably, is related to a zone of erosional pinchout of Cretaceous deposits. Migration of geogenic substances along regional pinchouts of Permo-Mesozoic deposits is also shown by the presence of an extensive zone of increased V/Al values on the Słupsk and Żarnowiec blocks. It stretches transverse to the regional fault zones and almost parallel to the pinchout zones (Fig. 10). It suggests that the zones took an active part in transmitting geogenic substances. Vanadium, tending to concentrate in crude oil, is one of the most characteristic elements occurring in black shales of Scandinavia (*cf.* Morawski, 1973). Their facies equivalents are Cambrian–Tremadocian black mud and clay shales of the Piaśnica Formation *s.l.* (Fig. 5). The zones of regional pinchouts of Permo-Mesozoic sedimentary formations run evenly with a parallel of latitude across the Courland, Rozewie, Łeba, Słupsk and Ustka blocks (Figs. 2 and 10). In addition to other substances, they transmit also geogenic liquids and gases originating from lower Paleozoic black shales.

On the Paleozoic platform, high V/Al values are observed along the Kamień Pomorski and Trzebiatów faults, at sites where they merge with the pinchout zones. They are related here to migration of bitumens that are often accompanied by vanadium.

Increased Sr and Va values were also observed in some regions immediately to the north of the Polish coast (Fig. 10). They are associated with local erosional pinchouts of Mesozoic and Tertiary deposits at sites of deep furrows in the sub-Quaternary surface (*cf.* Kramarska *et al.*, 1999).

AREAS OF THE GREATEST RISK OF GEOGENIC POLLUTION

The results of these investigations have fully confirmed the earlier assumptions (Jaworowski *et al*., 2001) as regards the threat posed to the Polish Exclusive Economic Zone of the Baltic Sea by geogenic pollutants. It has been shown that geogenic substances derived from deep-seated geological structures currently migrate into bottom waters and sediments. The whole Polish sector of the Baltic Sea is threatened by geogenic pollutants. Two areas (A and B) at the greatest risk from geogenic pollution have been defined after analysing all the demonstrated and potential hazards to the environment.

AREA A (FIGS. 2 AND 10)

Situated in the eastern part of the Polish Exclusive Economic Zone of the Baltic Sea, in the East European Craton, this covers the Courland Block (western part), Rozewie Block, Łeba Block (including the Smołdzino Fault Zone) and Żarnowiec Block (eastern part).

COURLAND BLOCK

The western portion of the block is part of a larger area of the highest prospectivity for hydrocarbon accumulation. The area extends meridionally along both the flanks of the Kuźnica Fault Zone separating the Courland and Rozewie blocks. In the northern part of the highest pollution risk area on the Courland Block, there is a regional pinchout zone marked by the extent of the Cretaceous deposits overlying Devonian rocks. The zone subcrops at the sub-Quaternary surface. The forefield of the pinchout zone belongs to the area of potential massive brine inflows. The bedrock of the block contains sedimentary formations which can be the source of harmful geogenic substances. These are the lower Paleozoic black shales, Middle Cambrian and Devonian deposits, as well as Zechstein salts and Lower Triassic and Upper Jurassic deposits occurring in the southern part.

ROZEWIE BLOCK

In the eastern part of the block, there is a part of the area of the highest prospectivity for hydrocarbon accumulation. This area extends meridionally along both the flanks of the Kuźnica Fault Zone. In the Rozewie Block, there is the western part of the most prospective area. High concentrations of liquid hydrocarbons in bottom waters, directly linked with the Kuźnica Fault Zone, were discovered in the northern segment of the area.

The greatest intensity of migration of geogenic substances along the Kuźnica Fault is observed in both its northern and middle part. Strong and very strong anomalies of the concentrations of liquid hydrocarbons in bottom water, recorded in the northern and middle section of the fault, are hazardous to the environment. They are associated with oil fields B5 and B8 discovered in the eastern part of the Rozewie Block. Middle Cambrian hydrocarbons migrate up to the sea-floor along the Kuźnica Fault despite the large thickness (1000–1700 m) of the Silurian clay shale seal. The lack of anomalous concentrations of liquid hydrocarbons in bottom waters in the southern part of the fault is probably related to the presence of sealing Zechstein salts, which are absent in the middle and northern parts of the zone. Gas anomalies only are observed in this area.

In the central area of the block, there is a NE–SW-trending zone of regional pinchouts, defined by the extent of Cretaceous deposits overlying the Devonian. It appears at the sub-Quaternary surface. At the site where the pinchout zone merges with the Karwia Fault Zone (marking the western boundary of the block), increased V/Al values are observed. These are indicative of the activity of both the pinchout zones and the sub-Quaternary fault zones transmitting hydrocarbons and geogenic substances originating from the lower Paleozoic black shales.

The area of increased V/Al values "straddles" the Karwia Fault Zone. Further towards the west is a region where regional pinchouts observed in the Łeba Block merge with the Karwia Fault Zone. Part of the Rozewie Block, situated north of the above-mentioned pinchouts of Cretaceous deposits, is an area of high potential brine inflow. The bedrock of the block is composed of sedimentary formations supposed to be the sources of geogenic substances: lower Paleozoic black shales, Middle Cambrian and Devonian deposits, and – in the south –Triassic deposits and Zechstein salts.

ŁEBA BLOCK

In the Łeba Block, crude oil and natural gas fields have been discovered along the eastern flank of the Smołdzino Fault Zone. High concentrations of liquid hydrocarbons in bottom waters are recorded in the northeastern part of the block. They are associated with meridionally trending faults observed at the sub-Quaternary surface. NE–SW-trending regional pinchout zones, defined by the boundaries between the occurrence areas of Cretaceous and Triassic, Triassic and Zechstein and Zechstein and Silurian deposits occur in the southern part of the block. The western portion of the pinchouts zone is covered by Paleogene deposits, whereas the eastern portion subcrops at the sub-Quaternary surface. In the southern part of the Łeba Block, increased V/Al values are observed especially at sites where the regional pinchout zones merge with the Karwia Fault. These are related to the activity of both the pinchout zones and the fault zone, indicating migration of hydrocarbons and geogenic substances originating from the lower Paleozoic black shales. To the south of the pinchouts zone and in the northeastern part of the Łeba Block, there is an area of potential massive brine outflows. The bedrock of the block is composed of sedimentary formations supposed to be the sources of geogenic substances: lower Paleozoic black shales, Middle Cambrian deposits, and – in the south –Triassic and Zechstein deposits without salt-bearing facies.

ŻARNOWIEC BLOCK

In the northeastern portion of the block, at the crossing of the Kuźnica and Łeba–Sambia fault zones, there is the southern end of a zone of the greatest prospectivity for hydrocarbon accumulation known from the border zone between the Courland and Rozewie blocks. Near the Łeba Fault Zone, representing the northern boundary of the block, there is a regional pinchout zone marked by the boundary between the occurrence areas of Cretaceous and Triassic deposits. The zone is entirely covered by Paleogene deposits. Increased Sr/Al and V/Al values, indicating migration of brines, hydrocarbons and geogenic substances originating from lower Paleozoic black shales, are observed over the whole Żarnowiec Block. The migration is related to a network of fault zones that reach the sub-Quaternary surface. The Żarnowiec Block lies in an area of strong potential brine outflows, although the Zechstein salts occur only in its eastern portion. That is why this part of the Żarnowiec Block is included in the area of the highest geogenic pollution risk. Other sedimentary formations composing the bedrock of the Żarnowiec Block, being potential sources of harmful geogenic substances, are represented by the lower Paleozoic black shales, Middle Cambrian and Lower Triassic deposits, and – in the southeastern end – by Upper Jurassic deposits.

AREA B (FIGS. 2 AND 10)

This area is situated in the western part of the Polish Exclusive Economic Zone of the Baltic Sea, within the European Paleozoic platform. Area B covers the western portion of the Kołobrzeg Block and the Gryfice and Wolin blocks.

KOŁOBRZEG BLOCK

Extensive areas of increased prospectivity for hydrocarbon accumulation occur along the Trzebiatów and Koszalin fault zones marking the block boundaries.

The Trzebiatów Fault Zone, representing the boundary between the Kołobrzeg and Gryfice blocks, is very active in respect of migration and outflow of liquid and gaseous hydrocarbons. The concentrations of liquid hydrocarbons in bottom waters are so high that they pose a serious hazard to the natural environment. The methane concentration in water reaches significant levels along the southern part of the fault. Migration of gaseous and especially liquid hydrocarbons occurs despite the occurrence of sealing Zechstein salts. That is why the Trzebiatów Fault Zone and the whole western part of the Kołobrzeg Block represent the areas of the highest geogenic pollution risk. A sub-Quaternary regional pinchout zone is marked here by an erosional boundary between the occurrence areas of Triassic and Jurassic deposits.

Almost the whole area of the block is conspicuous by increased Sr/Al values. An increased V/Al ratio is observed in the western and northeastern regions of the block. These values prove the presence of brine and hydrocarbon inflows in the area of a dense network of fault zones reaching up to the sub-Quaternary surface. Worth noting are the occurrences of increased V/Al values at sites where the regional pinchout zones merge with the fault zones. A similar situation is observed in area A. Almost the whole Kołobrzeg Block is included in the area of strong potential brine outflows. Geogenic substances can originate from the Devonian, Carboniferous, Zechstein Main Dolomite and salt deposits constituting the bedrock of the entire block, and additionally from the Lower Triassic, Lower and

Upper Jurassic and Lower Cretaceous deposits. Local Rotliegend effusive rocks can also generate harmful geogenic substances (e.g., heavy metals).

GRYFICE BLOCK

Almost the whole area of the block is covered by two zones of increased prospectivity for hydrocarbon accumulation. Chaotically distributed sites of high concentrations of liquid hydrocarbons in bottom waters indicate the presence of a dense network of fault zones reaching up to the sub-Quaternary surface.

The Kamień Pomorski Fault Zone, marking the boundary between the Gryfice and Wolin blocks, is characterized by high concentrations of both gaseous (methane, butylene) and heavy hydrocarbons in bottom waters, causing serious environmental pollution. As noted above, during sampling in the zone, decaying dead mollusc remains were found. Increased Sr/Al values are observed throughout the whole area of the Gryfice Block. Increased V/Al values are recorded in its southwestern and eastern parts (the last ones continue into the western part of the Kołobrzeg Block). A distinct regional pinchout zone, marked by the erosional extent of Jurassic and of Cretaceous deposits, runs NW–SE approximately along the axial part of the block. A small pinchout zone at the boundary of Cretaceous and Jurassic occurrence areas was mapped in the southeastern end of the Gryfice Block. The pinchout zones discussed above subcrop at the sub-Quaternary surface. The whole Gryfice Block is included in the area of potential massive brine outflows, and its southeastern part is at risk of thermal water outflows. The latter were observed in the northern segment of the block close to the boundary of the Polish sector of the Baltic Sea.

Devonian, Carboniferous and Zechstein Main Dolomite and salt deposits, occurring throughout the whole area, as well as Lower Triassic, Lower and Upper Jurassic and Lower Cretaceous deposits form the bedrock of the Gryfice Block. They can be sources of harmful geogenic substances. Rotliegend effusive rocks occur in the bedrock over large areas and can also generate harmful geogenic substances.

WOLIN BLOCK

Almost the whole block is a zone of increased prospectivity for hydrocarbon accumulation, being the second in the prospectivity rank for the Polish Exclusive Economic Zone of the Baltic Sea. In the southeastern part of the block at the sub-Quaternary surface, there is part of a regional pinchout zone determined by the erosional boundary between the occurrence areas of Jurassic and Cretaceous deposits. Increased Sr/Al values are recorded over most of the Wolin Block. Its southeastern region (extension of a similar area from the western part of the Gryfice Block) is characterized by increased V/Al values. This suggests migration of brines and hydrocarbons through a dense network of faults reaching up to the sub-Quaternary surface. A narrow area extending along the Kamień Pomorski Fault Zone can yield massive brine outflows, whereas the southern part of the block is an area of potential thermal water outflows. Devonian, Carboniferous and Zechstein Main Dolomite and salt deposits, occurring throughout the whole area, as well as Lower Triassic, Upper Jurassic and Lower Cretaceous deposits composing the bedrock of the block, are supposed to be the pollutant source rocks. Rotliegend effusive rocks occur in the bedrock over large areas and can also generate geogenic substances harmful to the environment.

CONCLUSIONS

1. Bottom waters and bottom sediments of the Polish Exclusive Economic Zone of the Baltic Sea are polluted by modern migration of geogenic substances derived from bedrock beneath the sea-floor (deep-seated geological structures).

2. Pollutant source rocks, occurring in the bedrock of the Polish sector of the Baltic Sea, include: (a) oil- and gas-bearing reservoir rocks (Middle Cambrian, Rotliegend, Zechstein, Carboniferous); (b) black shales (Upper Cambrian, Lower and Middle Ordovician, Lower Silurian); (c) effusive rocks (Rotliegend); (d) salts (Zechstein), (e) reservoir rocks for mineral and thermal waters (Cambrian, Devonian, Carboniferous, Rotliegend, Zechstein, Triassic, Jurassic and Cretaceous).

3. Fault zones and zones of regional erosional pinchouts of sedimentary formations are migration avenues for harmful geogenic substances (the strongest emissions are observed in axial zones of the faults). Large thicknesses of sealing rocks (Silurian clay-shales: 1000–2500 m, Zechstein salts: 100–300 m) need not comprise obstacles on the hydrocarbon migration pathway along the fault zones.

4. The main sources of pollution are oil and natural gas deposits, as well as zones prospective for hydrocarbon deposits because they are manifested by increased concentrations of liquid and gaseous hydrocarbons in bottom waters and bottom sediments.

5. Hydrocarbons that migrate through the fault zones are represented mainly by oils and methane. Proven seepages of liquid hydrocarbons, ranging from 50 to 210 mg/l, are a serious source of pollution of the Baltic Sea waters. Values of 200 mg/l may be considered as indicative of surface outflows. Considerable methane concentrations of up to $2.0–3.0 \times 10^{-4}$ mg/l are accompanied by large contents of heavy hydrocarbons. They cause a lethal deficit of oxygen in bottom waters. The amount of migrating hydrocarbons depends on the level of seismic activity in the Baltic region. Under strong seismic activity, the amount can be greater than that measured during the present research.

6. Methane has accumulated mainly as a result of thermogenic processes of alteration of fossil organic matter.

7. Migration activity in the fault zones and regional pinchouts is shown, for instance, by areas of increased strontium and vanadium concentrations in bottom sediments. Strontium comes from Zechstein salts while vanadium is from lower Paleozoic black shales and/or hydrocarbon-bearing reservoir rocks.

8. The whole Polish Exclusive Economic Zone of the Baltic Sea (Figs. 1 and 2) is threatened by geogenic pollutants. Two areas of the greatest risk of geogenic pollution have been identified: (i) area A (Fig. 10) is situated on the East European Craton and covers the western part of the Courland Block, Rozewie and Łeba blocks (including the Smołdzino Fault

Zone) and the eastern part of the Żarnowiec Block; and (ii) area B (Fig. 10) is situated in the European Paleozoic platform and covers the western part of the Kołobrzeg Block, and Gryfice and Wolin blocks.

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