Baltic Coastal Zone No. 6	
(27-35) 2003	Institute of Biology and Environmental Protection Pomeranian Pedagogical University Słupsk

REDOX STATUS OF THE WEST POMERANIAN RIVERS AND STREAMS SELECTED FOR SETTLEMENT WITH SALMON (*SALMO SALAR* L.) AND SEA TROUT FRY (*SALMO TRUTTA* MORPHA *TRUTTA* L.) - RESULTS OF RESEARCH IN WINTER

Gorzysław Poleszczuk[1], Józef Domagała[2]

[1]*Chemistry Department, Natural Science Faculty, University of Szczecin, Poland*
[2]*Zoology Department, Natural Science Faculty, University of Szczecin, Poland*

Abstract

The usefulness of the measures expressing redox status of water (redox potential Eh, indicators $pE = - \lg [e^-]$ and $rH = - \lg p_{H2}$) was examined for the evaluation of the quality of water in selected rivers and streams of West Pomerania (Otoczka, Mołstowa, Gardominka and Rekowa). The evaluation was done under conditions which may turn out to be difficult for the survival of the salmonide fry (salmon and sea trout), that is – in the winter, after the appearance of ice cover, when the oxygen saturation of waters declines (to 61–74%). It was found out that the changes in the redox indices values (Eh = 448–468 mV) signal worsening of environmental conditions, related not only to the decline in oxygen saturation, but also with the dissolution from sediments substances which may be harmful for the salmonide fry (dissolved organic matter, ammonium compounds, manganese and iron).

Key words: water chemistry, riverine and stream water, West Pomerania, redox indices, salmonide, reintroduction.

INTRODUCTION

In the period of living in the inland waters, the salmonide find the best conditions for reproduction and growth in cold, well oxygenated and extremely clean waters. It is assumed that temperature, dissolved oxygen concentration (or water saturation with oxygen, or the partial pressure of oxygen corresponding the given oxygen saturation), pH, concentration of dissolved organic matter and mineral substances (characterised by specific electrolytic conductivity), as well as the concentration of mineral nitrogen and phosphorus derivatives are the basic indicators of the quality of the aqueous habitat. They allow to evaluate the usability of these waters for salmonide settlement (Alabaster and Lloyd 1980).

In order to estimate if the indices characterising the redox status of natural waters, and especially the redox potential Eh (or the indices pE and rH) could be useful

for evaluating the quality of selected waters, a study was conducted to determine redox indicators of West Pomeranian streams and rivers intended for settlement with salmonide fry.

The "oxygen indicators" inform about the redox status, nevertheless it is well recognized that the value of redox potential of waters does not depend solely on the concentration of dissolved oxygen but also on the presence of other oxidixing and reducing agents (Sigg and Stumm 1989).

The research was scheduled for winter, the period difficult for the survival of ichthyofauna. In this period, water surface was covered with ice and oxygen conditions could seriously deteriorate, hence the indices of oxygen saturation of waters could reach lethal values.

MATERIAL AND METHODS

The following West Pomeranian streams and rivers which flow into the Baltic Sea were examined: Otoczka, Mołstowa, Gardominka and Rekowa. Water samples were collected at the measurement stations (Fig. 1) in December 2001.

It was decided to do the sampling after the mean daily temperature to dropped to –2 (on 07-09.12.2001 and on 13-14.12.2001), and the corresponding fall in water temperature resulted in partial freezing of the water surface and thus in the deterioration of the oxygen status of water. Water samples were taken to glass or plastic containers from spots free from ice, from underneath the surface layer - about 50 cm beneath the water surface. In the field temperature, pH, Eh and total alkalinity of the water were determined.

The samples were stabilized according to the Polish Standards and the remaining indicators of water quality were determined in land laboratory within 24 hours. The analysed indicators were: concentrations of ionic macroelements (calcium, magnesium, chlorides and sulphates), concentration of dissolved oxygen (in separate samples).

The determination was done according to the procedures described in the Polish Standards (Water and waste water, Polish Standards), only the redox potential Eh was determined according to the procedures described in Standard Methods (1995).The values of the pE and rH indices defined as $pE = -\lg[e^-]$ and $rH = -\lg p_{H2}$ (analogous to the formula pH = lg a H+) were calculated from the formulae : $pE = Eh \cdot \frac{F}{2.3 \cdot R \cdot T}$ and rH = 2 (pH + pE) taken from the works of Pourbaix (1998), Sigg and Stumm (1989) and Hankus (1962). Salinity (approximate) was determined as the sum of the total concentration of chlorides, bicarbonates (as the total alkalinity), sulphates, calcium, magnesium and the sum of concentrations of sodium and potassium ions – calculated from the balance of ionic macroelements in natural waters (Polish Standards). Determining the concentration of the ionic macroelements made it possible to calculate the approximate values of the ionic force ($I = \frac{1}{2} \sum C_i \cdot Z_i^2$, where C_i – concentration, Z_i – charge, i – ionic macrocomponent of water).

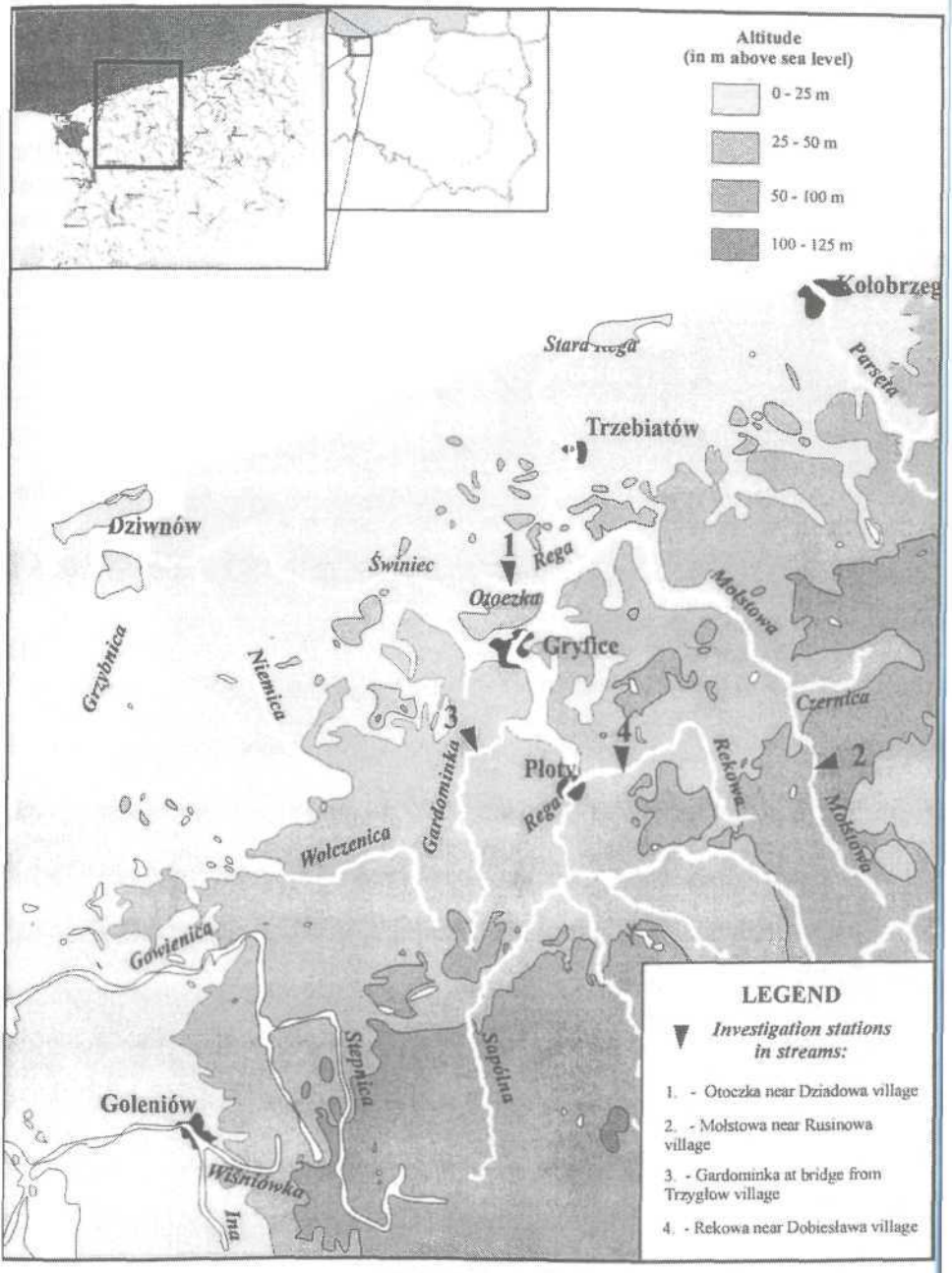

Fig.1. Rivers and streams in the Western Pomerania – location of measuring stations

Oxygen saturation was determined on the basis of the measured values of dissolved oxygen concentration, compared with the oxygen saturation of waters of identical ionic force and at the same temperature, taken from the tables by Poleszczuk (1998).The equilibrium partial pressures were calculated according to the formula:

$$p'_{O2} = p_{O2} \cdot \alpha_1 \cdot \alpha_2 \text{ (hPa)},$$

where: p_{O2} - pressure of O_2 in dry clean air at the atmospheric pressure of 1013 hPa, α_1 - a correction including the changes of barometric pressure and the presence of water vapour, α_2 - a correction of the oxygen pressure in a solution with the dissolved oxygen concentration different than the equilibrium concentration. Finally, after the substitution of values, this formula took the form:

$$p_{O2} = 0.209 \cdot \frac{P_b - \frac{W_{H2O}}{100} \cdot P_{H2O}}{1013{,}12} \cdot \frac{\%saturation}{100}$$

where: p_b, d W_{H2O} and p_{H2O} are, respectively, barometric pressure (hPa), relative humidity (%) and air saturation pressure with water vapour at a given temperature.

The general pressure, air temperature and humidity were determined in the field, at the measurement station, with portable measuring instruments: a barometer, a thermometer and a hygrometer.

The redox status of the analysed waters was determined on the basis of rH values according to the criteria described in Hermanowicz et al. (1976).

RESULTS

The results of measurements of the selected West Pomeranian streams and waters, and from the ensuing calculations are presented in Table 1 and in Fig. 2, in which the results of the Eh measurements are presented in the function of pH of the investigated waters.

In this graph, the relationship Eh = f(pH) in well oxygen saturated inland waters is also presented, after Garrels (1960).

The redox potential in the analysed streams varied from ca. 450 mV (Mołstowa near Rusin) to ca. 470 mV (Gardominka).The measurement were done at the *in situ* temperature of 2-4 °C. The pH values of the stream watersfell between 8.50-8.90 and oxygen concentration - 8.2 to 9.6 $mgO_2\ dm^{-3}$, while salinity from ca.0.40 to 0.65‰, and the ionic force from 16 to 22 $mmols\ dm^{-3}$.Oxygen saturation of waters reached from 60 to 75 %, and the equilibrium partial pressures of O_2 – from ca.130 to ca.155 hPa.

Table1

Redox potential Eh and pE and rH indices of the Western Pomeranian stream waters with other selected physico-chemical parameters

No.	Water quality indices		Stream, date, station number			
			Otoczka 12.12.2001	Mołstowa k.Rusinowa 12.12.2001	Gardominka 17.12.2001	Rekowa 17.12.2001
			No. 1	No. 2	No. 3	No. 4
1.	Eh	(mV)	459	448	468	462
2.	Temperature	(°C)	3,00	4,00	2,00	2,50
3.	pE	(pE units)	8,67	8,43	8,87	8,75
4.	rH	(rH units)	33,32	33,54	34,34	33,94
5.	pH	(pH units)	7,99	8,34	8,30	8,22
6.	$O_{2\ dissolved}$	($mgO_2\ dm^{-3}$)	8,2	9,6	9,6	9,1
7.	Ionic strengh	($mmol\ dm^{-3}$)	21,50	17,25	16,13	16,59
8.	Salinity	(‰)	0,644	0,463	0,389	0,401
9.	O_2 saturation	(%)	61,4	73,8	70,0	67,0
10.	Partial pressure O_2	(hPa)	129,70	155,03	146,92	140,84

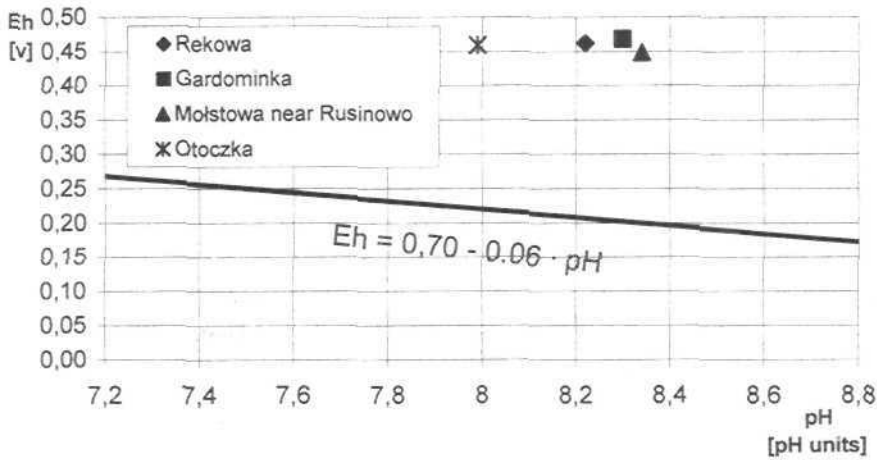

Fig. 2. Eh and pH Western Pomeranian stream water measuring data with correlation Eh = f(pH) for good oxygenation of surface freshwater, after Garrels (1960)

DISCUSSION

The redox status of the studied waters was always oxidizing (rH > 25), and in the case of the streams Otoczka, Mołstowa, Gradominka and Rekowa, it has been particularly oxidizing (rH > 33).The Eh values and other redox indices (pE and rH) in these waters were clearly higher than the Eh values of well oxygen saturated inland surface waters (Garrels 1960), though such values are encountered in case of natural water reservoirs with muddy bottom (Perfiliew 1972) in the situation of a limited access of oxygen from the atmosphere, e.g. when the water surface is frozen, or under a fast development of phytoplankton (Poleszczuk 1997), or with the abundant floating flora (Obolewski 2001). The analysed waters were not well saturated with oxygen, which was the result of a thin layer of ice covering the water surface. The low saturation with oxygen of the waters shows that the measured redox potential was influenced not only by the dissolved oxygen concentration (and indirectly by dissolved organic matter) but also by other oxidizing and reducing agents making up redox pairs, most probably nitrogen and manganese derivatives (Kölling 1986).The decrease in oxygen saturation is usually accompanied by the appearance of large amounts of dissolved organic matter and phosphorus, as well as manganese and iron (Perfiliew 1982).These substances, even in low concentration, disqualify the waters from salmonide settling (Decree 1991).The examination of the chemical composition of these waters (Domagała et al., in press) proved that there occurred unfavourable changes in the chemistry of the investigated streams and waters. These waters were disqualified according to the Decree (1991) due to the large content of dissolved organic matter (measured as COD-Cr) and the excessive concentrations of phosphorus and iron. Simultaneously, this disqualification made these waters unacceptable for salmonide settlement.

CONCLUSIONS

1. The waters in the West Pomeranian rivers and streams Otoczka, Mołstowa, Gardominka and Rekowa investigated in December 2001 showed an oxidizing status, as measured according to the Eh redox potential and the pE and rH redox indices.
2. The high redox status of the examined waters, which indicated a comparatively low oxygen saturation, was typical of the streams and reservoirs with muddy bottoms, large amount of organic matter and rich in mineral manganese and iron compounds.
3. The redox potential of the waters examined in December was influenced not only by the content of dissolved oxygen in water, but also by of other oxidising and reducing agents making up redox pairs.
4. As the changes of Eh values depend on the changes of the chemical composition of natural waters, the results of the research of the redox potential Eh of streams and rivers can be useful for characterising and evaluating the quality of the natural environment chosen to be settled with salmonide.

Acnokledgement
Authors of this publication express their gratitude to Aneta Sikorska M.Sc. and Radosław Urbański M.Sc. for their technical assistance in preparation this paper to press.

REFERENCES

Alabaster, J.S., Lloyd, R. 1980. Water Quality Criteria for Freshwater Fish, Ed. FAO UN –Butter Worths, London – Boston, 237 pp.

Domagała, J., Poleszczuk, G. 2002. Podstawowe hydrochemiczne wskaźniki jakości wód strumieni i rzek Pomorza Zachodniego zasiedlanych narybkiem łososia (*Salmo salar*) i troci (*Salmo trutta* morpha *trutta*) w okresie zimowym – wyniki wstępnych badań.[General hydrochemical indicators of water quality of the West Pomeranian rivers and streams chosen for the settlement with salmonide fry - salmon (*Salmo salar* L.) and sea trout (*Salmo trutta* morpha *trutta* L.); results of winter measurements], Acta Ichtyol. Piscat. (in press)

Garrels, R.M. 1960. Mineral equilibria at low temperature and pressure, Harper and brothers publ, New York, 306 pp.

Hankus, A. 1962. Potencjały utleniająco-redukujące w wodach naturalnych [The redox potentials in natural waters]. Zesz. Nauk. Polit. Krakowskiej, 8: 4-26 (in Polish)

Hermanowicz i inni. 1976. Fizyczno–chemiczne badanie wody i ścieków [Physico-chemical investigation of water and wastewater]. Wyd. Arkady, Warszawa, 841pp, (in Polish).

Kolling, M. 1986. Vergleich verschiedener Methoden zur Bestimmung des Redoxpotentials naturlicher Wasser, Meyniana, 38: 1-19.

Obolewski, K. 2001. Badania chemizmu wód powierzchniowych starorzecza Słupi(37,96 km rzeki) w okresie marzec – grudzień 1999) [Investigation of the chemistry of surface waters of the old river-bed of Słupia (37.96 km of the river) in the period from March to December)] Słupskie Prace Naukowe, Limnologia, (in Polish).

Perfiliew, B.W. Mikrozonalnoje strojenije iłowych oziernych otłozenij i metody jego issljedowanija., Izd. Nauka, Leningrad, 215pp. (in Russian)

Poleszczuk, G. 1997. Charakterystyka chemiczna toni wodnej Zalewu Szczecińskiego [Chemical characteristic of the waters of the Szczecin Lagoon.]. Rozpr. Ar w Szczecinie, 179: 1–102 (in Polish)

Poleszczuk, G. 1998. Środowisko abiotyczne toni wodnej Zalewu Szczecińskiego [Abiotic environment of the waters of the Szczecin Lagoon.]. Rozpr. Stud. Uniw. Szczecińskiego, 292:1-207 (in Polish)

Pourbaix, M. 1978. Wykłady z korozji elektrochemicznej [Lectures on electrochemical corrosion]. PWN, Warszawa, p.112-113 (in Polish)

Sigg, L., Stumm, W. 1989. Aquatische Chemie, Verlag Fachvereine Zurich, Zurich, p. 260-262.

Standard Methods for the Examination of Water and Wastewater, 1995, Ed. Am.

Publ.Health Ass., Washington, p. 2-73–2-77.
Rozporządzenie Ministra Ochrony Środowiska, z dnia 5 listopada 1991, w sprawie klasyfikacji wód oraz warunków, jakim powinny odpowiadać ścieki wprowadzane do wód lub do ziemi [The Decree of the Polish Ministry of Environmental Protection, from the 5 November 1991, on the classification of waters and the requirements of the wastewater to be discharged into the surface waters or into the ground]. Dz.U.1991, nr 116, poz. 503.

POLISH STANDARDS:

PN-73/C-04537.02. Water and wastewater. Determining the dissolved orthophosphates by the colorimetric molybdenum method with tin chloride as the reducing agent.
PN-77/C-04537.09. Water and wastewater. Tests for the content of phosphorus compounds. Determining total phosphates by the colorimetric method or the colorimetric-extraction method.
PN-74/C-04540.03. Water and wastewater. Tests for pH, acidity, alkalinity. Determining the mineral or total acidity and alkalinity by the titrimetric method with indicators.
PN-78/C-04541 Water and wastewater. Tests for dry residue, residue after ignition, losses during ignition, dissolved substances, dissolved mineral substances and dissolved volatile substances.
PN-72/C-04545.02. Water and wastewater. Tests for the content of dissolved oxygen. Determining the dissolved oxygen by the Winkler method.
PN-81/C-04551.01. Water and wastewater. Tests for the content of calcium.
PN-71/C-04554.02. Water and wastewater. Tests for hardness. Determining the total hardness over 0.357 mval/dm3 by the EDTA method.
PN-75/C-04562.01. Water and wastewater. Tests for the content of magnesium.
PN-74/C-04566.09. Water and wastewater. Tests for the content of sulphur and its compounds. Determining sulphates by the gravimetric method.
PN-76/C-04576.01. Water and wastewater. Tests for the content of nitrogen compounds. Determining ammonium nitrogen by the indophenol colorimetric method.
PN-73/C-04576.06. Water and wastewater. Tests for the content of nitrogen compounds. Determining the nitrite nitrogen by the colorimetric method with sulphanil acid and 1-naphthylamine.
PN-87/C-04576.07. Water and wastewater. Tests for the content of nitrogen compounds. Determining the nitrate nitrogen after reduction in the cadmium column.
PN-85/C-04578.02. Water and wastewater. Tests for the oxygen demand and the content of organic carbon. Determining the chemical oxygen demand (COD) by the permanganate method.
PN-90/C-04578/03. Water and wastewater. Tests for the oxygen demand and the content of organic carbon. Determining the chemical oxygen demand (COD) by the dichromate method..

PN-77/C-04584. Water and wastewater. Temperature measurements
PN-73/C-04586.05. Water and wastewater. Tests for the content of iron
PN-75/C-04590.01. Water and wastewater. Tests for the content of manganese. Determining manganese by the permanganate colorimetric method.
PN-88/C-04632.03. Water and wastewater. General recommendations for sampling for physical, chemical and biological investigations. The procedure sampling.
PN-86/C-04632.04. Water and wastewater. General recommendations for sampling for physical, chemical and biological investigations. Sample stabilisation and storage.
PN-88/C-04638.02. Water and wastewater. Ionic balance of water. The procedure of calculating the ionic balance of water.
PN-75/C-04617.02. Water and wastewater. Tests for the content of chlorides. Determining the chloride in water and wastewater by argentometric titration
PN-74/C-04620/01. Water and wastewater. Sampling. Vessels, instruments and equipment.
PN-81/C-06501.Chemical analysis. Preparing the solutions of indicators.
PN-81/C-06504.Chemical analysis. Preparing buffer solutions.

STATUS REDOX WÓD STRUMIENI I RZEK POMORZA ZACHODNIEGO TYPOWANYCH DO ZASIEDLENIA NARYBKIEM ŁOSOSIA (*SALMO SALAR* L.) I TROCI (*SALMO TRUTTA MORPHA* L.) – WYNIKI BADAŃ W OKRESIE ZIMOWYM

Streszczenie

W grudniu 2001 roku badano potencjał redox i określano wartości wskaźników redox $pE = - \lg [e^-]$ i $rH = - \lg p_{H2}$) wód wybranych rzek i strumieni Pomorza Zachodniego (Otoczka, Mołstowa, Gardominka i Rekowa). Oprócz Eh oznaczano także pH, stężenie tlenu rozpuszczonego i stężenia składników makrojonowych wód, tak, by móc obliczyć siłę jonową i zasolenie badanych wód oraz stopień ich natlenienia, a także równowagową prężność O_2 w wodach. Badania prowadzono w warunkach, które mogły okazać się przeżyciowo trudnymi dla narybku ryb łososiowatych (łosoś, troć) po wystąpieniu zimowych mrozów i zalodzenia, kiedy to pogarsza się natlenienie wód.

Stwierdzono, że spadek natlenienia badanych wód łączył się zawsze ze wzrostem wartości Eh, sygnalizującym przechodzenie z osadów do toni wodnej szeregu substancji (rozpuszczalna materia organiczna, mineralne związki azotu, mangan i żelazo), których obecność w wodach zasiedlonych narybkiem ryb łososiowatych jest wysoce niepożądana.