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ASSESSMENT OF CHANGES IN THE STATE OF WATER QUALITY BY THE DOKSUM–SIEVERS METHOD

The changes in the river water quality were estimated according to the Doksum–Sievers theory consisting in comparison of empirical cumulative distribution functions. The theory has been illustrated by the data obtained from the measurements of seven pollutants of the Vistula river water (cross-section Warsaw) and performed in the years 1965–1979. The changes occurring in successive years, referred to the appropriate class of water purity, were denoted by the terms: deterioration, improvement and no changes.

1. INTRODUCTION

It is often rather difficult to compare water quality[1] in rivers or in other natural water basins, observed in various periods or in various places. So, it is difficult to define such notions as improvement or deterioration. If a proper number of concentration measurements of a certain pollutant (or oxygen) have been made, then the simplest criterion would be that in which we compare the averages, e.g. for two periods. It is well known that such a relative estimate is limited and carries little information, though attractive as providing a sharp outline. The practical value, however, of this sharp answer is sometimes illusive. This gives a rise to find a method which would allow more careful evaluation of water quality changes. There exists such a method which, however, has not been used till now to our knowledge, in the branch we are interested in.

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[1]The term *quality* is used in this paper relatively; quality is understood in respect to an index.

It is the Doksum–Sievers theory [3] developed for comparing two empirical distribution functions. Due to the theory we can use such a language which seems more realistic.

Any change in the state of water quality with respect to a certain pollutant or other substance will be assessed in this paper in the following terms: improvement, no changes, and deterioration. This scale may be further widened: considerable improvement, improvement, no changes, deterioration, and considerable deterioration. These expressions will refer to each class of water quality. So, more exactly, they should be read: considerable improvement with respect to class I, etc. A class of water quality is determined by the highest admissible concentration of certain pollutants.

Table 1

Water quality indexes and respective periods investigated

Wskaźniki jakości wody w badanych okresach

Pollutant	Assessments for the years
ammonia nitrogen	1965–1979
iron	1965–1979
phenols	1972–1979
manganese	1965–1979
permanganate value	1971–1978
dissolved oxygen	1967–1979
chlorides	1975–1979

We apply the method to estimate changes in water quality that took place from year to year, in Warsaw's cross-section of the Vistula river. Table 1 contains the list of water quality indexes and respective periods under investigation. The references [4] and [5] contain some application of the theory. In the reference [4] one can find the computer program FUNO which calculates the limits of the confidence intervals of the random value $\Delta(x)$ (see section 4).

2. INTERPRETATION OF A MUTUAL POSITION OF TWO DISTRIBUTION FUNCTIONS DEFINED FOR A POLLUTANT CONCENTRATION

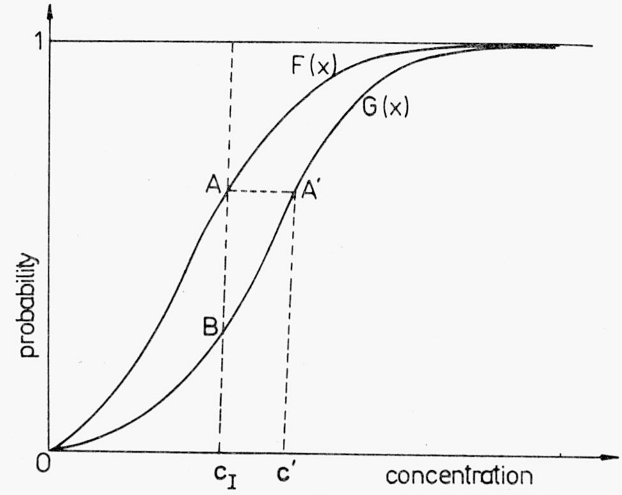
For any two periods being compared we have two random distribution functions. Their shapes and mutual position are the source of an approximate information about the water quality change. We assume that there exists a certain hypothetical continuous distribution function for every period under investigation.

Let $F(x)$ and $G(x)$ denote the theoretical distribution functions of a pollutant or oxygen concentration x in years N and $N+1$, respectively. Let c_{I} denote the concentration which determines first class water quality.

The inequality

$$F(c_{\mathrm{I}}) > G(c_{\mathrm{I}}) \tag{1}$$

means that the frequency of concentration exceeding c_{I} in the year $N+1$ was higher than that in the year N (figure). Hence, we can state that the water quality in the year $N+1$ was lower as compared with that in the year N. If the difference $F(c_{\mathrm{I}}) - G(c_{\mathrm{I}})$ is big, the deterioration in water quality will be



Theoretical distribution functions of a pollutant or oxygen concentration
Teoretyczne funkcje rozkładu dla polutanta i stężenia tlenu

estimated as considerable. Consequently, we can state that no change in water quality took place from the viewpoint of class I, if the difference is negligible.

When the roles of the distribution functions $F(x)$ and $G(x)$ are reversed the assessment of the water quality state is opposite.

Consider now two classes of water quality. Let class II be less exacting. The most interesting case is that in which the intersection point of the distribution functions is located to the right from the admissible concentration limit of class I, and to the left from that of class II. If for a pollutant

$$F(c_{\mathrm{I}}) > G(c_{\mathrm{I}}),$$
$$F(c_{\mathrm{II}}) < G(c_{\mathrm{II}}),$$

then within class I a deterioration of water quality state took place, whereas within class II an improvement occurred. If the inequalities were opposite then our corollary would be opposite. When no intersecting point of $F(x)$ and $G(x)$ occurs in the interval $(c_{\mathrm{I}}, c_{\mathrm{II}})$, then the changes with respect to both classes have the same direction.

3. GENERAL IDEAS OF THE DOKSUM-SIEVERS THEORY AND INTERPRETATION OF THE CONFIDENCE INTERVALS OF THE DISTRIBUTION FUNCTIONS SHIFT

If $F(x)$ and $G(x)$ are increasing functions, then for every x there exists a well defined horizontal shift of $G(x)$ with respect to $F(x)$ and that of $F(x)$ with respect to $G(x)$. The aim of the Doksum-Sievers theory is to estimate the width of the confidence zones of the shift having two empirical distribution functions. In previous section the "shift" in vertical direction has been discussed. It is easy to translate horizontal shifts, to the left and to the right, into the vertical ones, up and down. However, serious problems arise when trying to translate the value of horizontal shift estimated by the Doksum–Sievers method to that of "vertical" shift at a given point for a real case. For such a case the question should be answered: is horizontal shift sufficiently large to consider the vertical one (i.e. difference between frequencies) to be significant enough to represent the considerable deterioration (improvement) of water quality or just deterioration (improvement)? There are no recognized mathematical methods to answer this question. The authors, however, believe that a practicing engineer having some experience will be able to give quite a reasonable answer to such a question, based on the confidence interval limits for horizontal shifts.

Let us denote the horizontal shift between theoretical distribution functions $F(x)$ and $G(x)$ by $\delta(x)$, and the empirical distribution functions by $F_m(x)$ and $G_n(x)$, respectively; m and n are the numbers of samples. We define the random variable

$$\Delta(x) = G_n^{-1}\big(F_m(x)\big) - x. \tag{2}$$

The width of the confidence interval of the random variable $\Delta(x)$ for a certain confidence level is determined by the lower limit $\underline{\Delta}_s(x)$ and upper limit $\bar{\Delta}_s(x)$ in a statistics S, or, respectively, by $\underline{\Delta}_w(x)$ and $\bar{\Delta}_w(x)$ in a statistics W which will be defined in section 4. Widths of these confidence intervals are

$$\bar{\Delta}_s(x) - \underline{\Delta}_s(x)$$

or

$$\bar{\Delta}_w(x) - \underline{\Delta}_w(x),$$

respectively.

The confidence zone is formed by determining the limits of confidence intervals of the random variable $\Delta(x)$ for each x.

Our interpretation (see section 2) of the position of the distribution functions $F(x)$ and $G(x)$ with respect to each other is based on the difference in frequencies of certain concentrations. When applying the Doksum–Sievers theory the direct assessment of the value $\delta(x)$ is obtained, being measured in terms of concentration. So we should translate the horizontal shifts into the "vertical" ones. If $F(x) > G(x)$, then $x' = G^{-1}(F(x)) - x > x$, as it happens in figure where $c' = x'$, $c_{\mathrm{I}} = x$. The lenght of the segment AA' represents the limit value $\delta(x)$ of the random variable $\varDelta(x)$ (when m and n approach infinity), and the points A and A' of this segment represent the limits of random positions of those random points A_m and A'_n which are determined by the empirical distribution functions $F_m(x)$ and $G_n(x)$. The intervals $(\underline{\varDelta}_s(x),\ \bar{\varDelta}_s(x))$ or $(\underline{\varDelta}_w(x),\ \bar{\varDelta}_w(x))$ correspond to the segments A_m, A'_n derived in our previous considerations.

Applying simplified symbols we can distinguish the following cases:

a) $\underline{\varDelta} > 0$ and $\bar{\varDelta} > 0$,

b) $\underline{\varDelta} < 0$ and $\bar{\varDelta} > 0$,

c) $\underline{\varDelta} < 0$ and $\bar{\varDelta} < 0$.

Let us denote:

$$m[\varDelta(x) = \frac{1}{2}[\bar{\varDelta}(x)] - \underline{\varDelta}(x)]$$

which may be also written shortly as $m_\varDelta$. We have:

in the case a) $m_\varDelta > 0$,

in the case b) $m_\varDelta > 0$, $m_\varDelta < 0$ or $m_\varDelta = 0$,

in the case c) $m_\varDelta < 0$.

The direction of the horizontal shift of the distribution function $G(x)$ with respect to $F(x)$ agrees with the sign of $m_\varDelta$ (if $m[\varDelta(x_0)] = 0$, the distribution functions intersect at x_0). If the number of measurements m and n is sufficiently large ($m, n > 40$), then our assumption is justified.

Let $A = (x, F(x))$, $A' = (x', G(x'))$, $B = (x, G(x))$, (figure).

Then:

A' lies to the right from A, and

B lies below A or

A' lies to the left from A, and

B lies above A.

Hence, we can apply the interpretation formulated in section 2 to the assessment of water quality based on comparison of the frequencies of concentrations exceeding a certain standard. The interpretation, if expressed in terms of shifts, is as follows:

1. If $m[\varDelta(x_0)] > 0$, then a deterioration took place in the following period represented by distribution function $G_n(x)$, in comparison with the preceding period, represented by function $F_m(x)$, with respect to a water quality class determined by maximum admissible concentration x_0.

2. If $m[\Delta(x_0)] < 0$, then in statement 1 the word "deterioration" is replaced with "improvement".

3. If $m[\Delta(x_0)] = 0$, then we can state that water quality remained unchanged.

The inequalities 1 and 2 and equality 3 require some comments. Let us start with the latter. Only in very few cases it may happen that $m_\Delta = 0$. Hence, this condition may be approximated if m is close to zero. To decide that $m[\Delta(x_0)]$ is sufficiently close to zero one should take into account two factors:

a) the kind of the substance examined,

b) the difference $|x_0 - \bar{x}|$ where $\bar{x}$ is mean value of measurements.

If x_0 differs considerably from $\bar{x}$, then the distribution function at x_0 is more flattened than at the mean value, and hence, even for small differences in frequencies the horizontal shift between the distribution functions is big. This is reflected by the diagram of the confidence zone $(\underline{\Delta}(x), \bar{\Delta}(x))$. If great and small values of the variable x were identically probable, then the confidence zone would be the narrowest at the mean value of measurements and would widen with the increasing distance from the mean. We have to deal, however, with such a variable x which has only nonnegative values and large values rarely occur. Therefore, the hypothetical continuous function of concentration distribution is strongly flattend for high concentrations and more acute for the low ones. For that reason, all the diagrams show that for low concentrations the width of confidence zone is small and for high concentrations big. Then, in each case considering both the intensity of the influence of substance S on biocenosis and the value of the concentration x_0, we must answer the question whether $m[\Delta(x_0)]$ should be considered practically equal to zero or not.

The above comments refer also to inequalities 1 and 2. In each case we must decide separately whether $m[\Delta(x_0)]$, if positive, should be considered, either so great that a considerable deterioration occurred or only practically greater than zero so that simply a deterioration took place. Obviously similar reasoning is applied to the case when $m_\Delta < 0$.

4. ON THE CONFIDENCE INTERVALS OF $\Delta(x)$

Two tests have been applied in this paper to the search of confidence intervals (and hence of the confidence zones) of the random variable $\Delta(x)$. One of them is based on the Kolmogorov–Smirnov statistics (eq. (4)), and the other on the so-called W-statistics (eq. (9)). Each of them is obtained from the following equation:

$$\Phi_\varphi(F_m, G_n) = \sqrt{M} \sup_x |F_m(x) - G_n(x)| / \varphi\big(H_N(x)\big) \tag{3}$$

where $M = mn/(m+n)$.

When $\varphi(H_N(x)) = 1$, then we have the Kolmogorov–Smirnov statistitcs called also the S-statistics. When

$$\varphi(H_N(x)) = (1 - H_N(x))^{1/2}(H_N(x))^{1/2}$$

where $H_N(x) = \lambda F_m(x) + (1-\lambda)G_n(x)$, $\lambda = m/(m+n)$, $x \in \{x: a \leqslant F_m \leqslant b\}$, $0 \leqslant a \leqslant b \leqslant 1$ we have the so-called W-statistics. The former is denoted by Φ_S and the latter by Φ_W.

At a significance level a we will verify the hypothesis H_0 stating that both the distribution functions are equal, H_0: $F = G$.

Based on the S-statistics we obtain

$$\Phi_S(F_m, G_n) = \sqrt{M} \sup_x |F_m(x) - G_n(x)|. \tag{4}$$

We assume that for the significance level a the following inequality is valid

$$\sqrt{M} \sup_x |F_m(x) - G_n(x)| \leqslant K \tag{5}$$

where K is the statistics critical value read from the Kolmogorov–Smirnov tables. On solving inequality (5) we get

$$\underline{h}(F_m(x)) \leqslant G_n(x) \leqslant \overline{h}(F_m(x)) \tag{6}$$

where $\underline{h}(x) = x - K/\sqrt{M}$, $\overline{h}(x) = x + K/\sqrt{M}$.

After determining confidence intervals for $G_n(x)$, the confidence intervals for $\Delta(x)$ have to be determined. Let us denote:

$$G_{\Delta,n}(x) = G_n(x + \Delta(x)).$$

Because of discontinuity and monotonity of the empirical distribution functions it is necessary to decide what values the function $G_n^{-1}(x)$ will take at all the points. Let

$$G_n^{-1}(u) = \inf\{x: G_n(x) \geqslant u\}$$

and

$$G_n^{-\mathrm{I}}(u) = \sup\{x: G_n(x) \leqslant u\}$$

be left and right-hand reciprocals of G_n and let K be chosen so that

$$P_{F=G}(\Phi_S(F_m, G_n) \leqslant K) = 1 - a. \tag{7}$$

Hence, it follows that the confidence interval for $\Delta(x)$ is given by

$$\left(G_n^{-1}\left(\underline{h}\left(F_m(x)\right)\right)-x,\ G_n^{-1}\left(\overline{h}\left(F_m(x)\right)\right)-x\right). \tag{8}$$

This interval is called the S-interval and is denoted by $\left(\underline{\Delta}_S(x),\ \Delta_S(x)\right)$. For the W-statistics we have

$$\Phi_W(F_m, G_n) \quad \sqrt{M}\ \sup |F_m(x)-G_n(x)|/H_N(x)\left(1-H_N(x)\right)^{1/2}, \tag{9}$$
$$\{x\colon a \leqslant F_m(x) \leqslant b\}.$$

Table 2

The Vistula river water quality in the Warsaw cross-section with respect to ammonia nitrogen, iron and manganese

Jakość wody w Wiśle (przekrój Warszawa) w odniesieniu do zawartości azotu amonowego, żelaza i manganu

Years	Ammonia nitrogen W-statistics				Iron S-statistics				Manganese S-statistics			
	I class 1.0 mg/dm^3	II class 3.0 mg/dm^3	III class 6.0 mg/dm^3	Upper limit of concentrations	I class 1.0 mg/dm^3	II class 1.5 mg/dm^3	III class 2.0 mg/dm^3	Upper limit of concentrations	I class 0.1 mg/dm^3	II class 0.3 mg/dm^3	III class 0.8 mg/dm^3	Upper limit of concentrations
1965/66	+	+		3.0	—	—	—	44.2	—	—	+	1.16
1966/67	—	+		2.82	+	+	+	30.0	—	—	+	1.13
1967/68	—	+		2.8	—	—	—	15.0	+	—	0	1.16
1968/69	—	—		4.04	+	—	—	15.0	—	—	—	1.4
1969/70	+	—		4.84	—	—	—	24.0	+	—	—	1.66
1970/71	—	—		4.86	+	+	—	24.2	—	+	—	1.66
1971/72	—	—		4.42	—	—	—	13.5	0	—	—	6.0
1972/73	—	—		4.84	+	—	—	14.0	0	—	—	6.0
1973/74	+	+		4.86	—	—	—	14.0	+	+	—	1.51
1974/75	—	+		4.24	+	—	—	11.2	0	—	+	0.8
1975/76	—	+		3.3	—	—	—	8.5	—	—	+	0.7
1976/77	—	0		3.3	—	—	—	8.5	—	—	+	0.8
1977/78	—	+		3.3	—	—	—	12.0	+	—	—	2.9
1978/79	—	+		3.26	—	—	—	12.0	—	—	—	2.9

— deterioration,
+ improvement,
0 lack of any changes.

Table 3

The Vistula river water quality in the Warsaw cross-section with respect to permanganate value and phenols

Jakość wody w Wiśle (przekrój Warszawa) w odniesieniu do utlenialności i zawartości fenoli

	Permanganate value S-statistics					Phenols S-statistics			
Years	I class 10 mg/dm^3	II class 20 mg/dm^3	III class 30 mg/dm^3	Upper limit of concentrations	Years	I class 0.005 mg/dm^3	II class 0.02 mg/dm^3	III class 0.05 mg/dm^3	Upper limit of concentrations
1971/72	−	+		20.7	1972/73	−	+		0.03
1972/73	−	+		20.5	1973/74	+	+		0.03
1973/74	0			16.1	1974/75	−			0.017
1974/75	+			16.1	1975/76	−	+		0.03
1975/76	−	0		27.4	1976/77	−	+		0.0145
1976/77	+	0		27.4	1977/78	+			0.3
1977/78	+	+		22.6	1978/79	+			0.014

− deterioration.
\+ improvement.
0 lack of any changes.
Upper limit of concentrations refers to both of the years.

Applying the same procedure as for the S-statistics we get the confidence interval for $\Delta(x)$ of the form (8) but not for all values of x, only for those which belong to the set $\{x\colon a \leqslant F_m(x) \leqslant b\}$.

The confidence interval

$$\Big((G_n^{-1}\big(h^-\big(F_m(x)\big)\big)-x,\ G_n^{-1}\big(h^+\big(F_m(x)\big)\big)-x\Big),$$

where

$$h^{\pm}(u) = \frac{u+\frac{1}{2}c(1-\lambda)(1-2\lambda u)\pm\frac{1}{2}\sqrt{c^2(1-\lambda)^2+4uc(1-u)}}{1+c(1-\lambda)^2}, \qquad c = K^2/M,$$

$u = F_m(x)$, is called the W-interval and is denoted by $\big(\underline{\Delta}_W(x),\ \bar{\Delta}_W(x)\big)$.

For $a = 0$, $b = 1$ the values of K were tabulated by Canner [1], and for $a > 0$ and $b < 1$ they are given by Borovkov and Sycheva [2].

Table 4

The Vistula river water quality in the Warsaw cross-section with respect to dissolved oxygen and chlorides

Jakość wody w Wiśle (przekrój Warszawa) w odniesieniu do zawartości rozpuszczonego tlenu i chlorków

Years	Dissolved oxygen S-statistics: I class 6.0 mg/dm^3 O_2	II class 5.0 mg/dm^3 O_2	III class 4.0 mg/dm^3 O_2	Upper and lower limits of concentrations
1968/69	+			18.7 5.1
1969/70	–	0	+	17.5 1.0
1970/71	+	+	+	17.5 1.0
1971/72				14.0 10.0
1972/73	+			15.0 5.6
1973/74	+			19.0 6.4
1974/75				19.0 6.4
1975/76				15.2 6.5
1976/77	+			15.4 5.0
1977/78	+			15.5 5.0
1978/79				14.2 6.5

Years	Chlorides S-statistics: I class 250 mg/dm^3	II class 300 mg/dm^3	III class 400 mg/dm^3	Upper limit of concentrations
1975/76				180.0
1976/77				180.0
1977/78				163.0

– deterioration.
\+ improvement.
0 lack of any changes.
Both the limits refer to both the years.
In the second item in fact a comparison is given of the state in the year 1970 with that in the year 1968.

5. APPLICATION OF THE DOKSUM-SIEVERS METHOD TO THE VISTULA RIVER CROSS-SECTION NEAR WARSAW

The Doksum-Sievers method was applied to assess the course of changes in the Vistula river water quality in the cross–section of Warsaw with respect to several pollution indexes. The period examined were the years 1965–1979 (tab. 1).

We used three-rank assessment: improvement, no changes, deterioration. It can be seen from the tables that even such a poor ranking offers quite a rich information.

In tables 2–4 deterioration is denoted by –, improvement is denoted by + and the lack of any changes is denoted by 0.

If the concentration between the upper limit of concentrations in class K, K=I, II, III, and the upper limit concentrations in class $K+1$ was not noted, then the proper cell in the table is empty. If the maximum noted concentration $c_{\max}$ is much lower than c_K, then the proper cell is also left empty. If $c_{\max}$ differs from c_K to a small degree only an assessment is made.

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OCENA ZMIAN STANU CZYSTOŚCI WÓD METODĄ DOKSUMA–SIEVERSA

Do oceny zmian czystości wód rzecznych zastosowano teorię Doksuma–Sieversa, polegającą na porównaniu dystrybunt empirycznych. Teorię zilustrowano danymi z pomiarów stężenia siedmiu substancji zanieczyszczających wodę Wisły (przekrój Warszawa) wykonanymi w latach 1965–1979. Do oceny zmian zachodzących w kolejnych latach zastosowano terminy: pogorszenie, polepszenie i brak zmian, odnoszące się do odpowiedniej klasy czystości wód.

BESPRECHUNG DER ÄNDERUNGEN DES GEWÄSSERSAUBERKEITSZUSTANDES MIT HILFE DER DOKSUM-SIEVERS METHODE

Zur Besprechung des Flusswasserqualitätszustandes wurde die Theorie von Doksum-Sievers angewendet, die auf dem Vergleich der empirischen Verteilungsfunktionen beruht. Die Theorie wurde mit Daten aus der Messung der Konzentration von sieben Verunreinigungsstoffen des Flusses Wisła (Profil Warszawa), die in den Jahren 1965-1979 durchgeführt wurden, illustriert. Zur Besprechung der Änderungen, die in den folgenden Jahren auftraten, wurden folgende Termine verwendet: Verschlechterung, Verbesserung sowie Unveränderung, die dem entsprechenden Reinheitsqualität des Gewässers entsprach.

ОЦЕНКА ИЗМЕНЕНИЯ СТЕПЕНИ ЧИСТОТЫ ВОД МЕТОДОМ ДОКСУМА-СИВЕРСА

Для оценки изменения чистоты речных вод была применена теория Доксума-Сиверса, состоящая в статистическом сравнении эмпирических функций распределения. Теория проиллюстрирована данными, которые получили, измеряя концентрацию семи веществ, загрязняющих воду Вислы (сечение Варшава). Измерения проводились в годы 1965-1979. Для оценки изменений, происходящих в очередные годы (из года в год), применены термины; ухудшение, улучшение и отсутствие изменений, которые отнесены к соответствующим классам чистоты вод.