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Assessing the Pollution Level in the Kuban River Basin by Multivariate Cluster Analysis

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Abstract: Considering features of hydrological conditions for hydro-chemical system, this paper analyses the performance of the hydro-ecological status of the Kuban river basin.. The results of the study on water chemical composition depending on the distance from the source are presented. By comparing the results with the reference values of water quality, increased aluminium, zinc, and copper content was established. Respective dendrograms of hydro-ecological studies obtained according to performed analysis for the Kuban River and its tributaries are presented. The relevance of the findings received is $p<0.0005$ and the correlation coefficient corresponds to 0.935...1. The results of multivariate cluster analysis showed that the Kuban basin has an increased content of particular heavy metals such as aluminium, copper, and zinc.

Key words: Hydro-ecological status, hydrological regime, mathematical model, multivariate cluster analysis, the Kuban river basin.

Introduction

The anthropogenic impact on the environment causes a significant decrease in the quality of surface water. The dynamics of natural water quality change as a result of anthropogenic transformation which has a spatial and temporal structure. The ecological status of the Kuban river basin plays a key role in the stable development of the economics and national economy as all economic sectors are concentrated within the Krasnodar Region (Olden et al., 2012). The dynamics of the chemical characteristics of the river system undergoes indeed significant changes over time (Kuchin et al., 2020; Praskievicz and Luo, 2019). The hydrological conditions of the Kuban River basin and, as a result, the Black Sea and the Sea of Azov are also subjected to changes (Evstigneev et al., 2020). The main task for the preservation of water resources in the Kuban River Basin is to develop mathematical models and algorithms for the differentiation of territories by types of anthropogenic influence. Landscape and geo-environmental research work of three large rivers in Northern Caucasus, namely Kuban, Terek, and Kuma, revealed that pollution of surface waters occurs largely within residential areas, as well as touristic and recreational centres (Kipkeeva et al., 2018). Agriculture, in particular, rice cultivation, also plays a significant role in reducing the water run-off of

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the Kuban river (Sun et al., 2016). Many researchers are implementing strategies to define the spatial and temporal dynamics of hydrochemical indices of water resources (Gholizadeh et al., 2016). Water samples taken from the Krasnodar Region rivers showed excessive content of heavy metals, oil products, and organic substances, including organometallic compounds and halogen derivatives. Some rivers in the Kuban basin, such as the Belaya River, the Laba River, the Fars River, etc., keep flooding throughout the year. In this regard, developing and implementing a comprehensive strategy for the water consumption management based on the hydro-ecological characteristics of the Kuban River basin at a regional scale is highly important for many large cities of Kuban. The effective principle for consolidating the hydro-chemical data sets is known to be a multivariate cluster analysis (Rotiroti et al., 2019). Multivariate statistical methods are often used to characterise and assess surface and freshwater quality, as well as to establish patterns of temporal and spatial changes in drainage basins characteristics caused induced by natural and anthropogenic factors (Hyvlud et al., 2019). Researchers often apply multivariate cluster principal components analysis to identify common spatial and temporal factors. Whereas the statistical method is used for spatial flotation characteristics of pollution in river waters (Kawanisi et al., 2017). The spatial and temporal variabilities were studied by using the method of pattern recognition, Collins histogram, pie chart, stiffness diagram, Sheller's semi-logarithmic chart, Piper diagram, hierarchical cluster analysis in Q-mode (HCA), K-means clustering (KMC), principal components analysis (PCA), and fuzzy k-means clustering (FKM) (De Jalón et al., 2019). Cluster analysis allows classifying objects on the principles of similarity to other objects contained in a cluster by a predefined selection criterion (Tabaghi et al., 2019a). Methods of multivariate cluster analysis are widely used not only to identify and group surface waters according to hydro-ecological and chemical indices but also to predict and assess groundwater scarcity and the spread of meteorological and hydrological droughts (Bhuiyan et al., 2006). Some authors propose to estimate the groundwater resources index by applying the cluster analysis (Bouguerne et al., 2017). The current research (the division of the Kuban River basin into hydro-chemical facies by pollution intensity, i.e., area groups with similar chemical characteristics) can be analysed. Spatial variability observed in the composition of these natural tracers can greatly contribute to an understanding of the heterogeneity and coherence of the aquifer, as well as physical and chemical processes that control the chemistry of water (Sabadash et al., 2018). Thus, a reliable classification scheme for dividing samples of the water chemical composition into homogeneous groups can serve as an important tool for the successful characterisation of hydrogeological systems (Sabadash et al., 2017).

Materials and Methods

Study of the chemical composition of the Kuban river waters was released from June 2017 to July 2019.

Samples were taken from 21 monitoring sites in the Kuban River Basin. Seven rivers were surveyed, namely, the Urup River, Bolshoi Zelenchuk River, the Teberda River, the Psysh River, the Bolshaya Laba River, Psekups River, and the Kuban River itself. Samples were selected within 3 years. Each of the rivers was analysed at three different sites. The results were obtained by averaging three parallel samples.

Each section was monitored in the direction from upstream to downstream.

Methods of Hydro-chemical Investigations

All water samples were taken in July. Sampling was performed according to ISO 5667-17: 2008 (ru) and GOST R 51592-2000. Determination of concentrations of chemical impurities in water was carried out by atomic absorption spectrometry following GOST R 51309-99. The pH level and the content of chlorides and nitrates were estimated by the ionometric technique using ion-selective electrodes. The surface-active substances, nitrites, total iron, and chromium were determined with the help of photometry or spectrophotometry. The X-ray fluorescent method was used as an alternative for the measurement of dry matter content.

Methods of Statistical Calculations

For statistical interpretation of hydro-ecological investigation results and water quality characteristics of the target areas in the Kuban River basin, which were averaged data based on the monitoring site and the name of the hydro-ecological indicator was used. The analysis was carried out after standardizing the initial data. The data analysis matrix for the monitoring site consisted of seven variables (river name)×18(water quality index). For the analysis, straight and inverted matrices were used.

Cluster analysis utilising STATISTICA7.0 software was used to identify spatial and temporal differences in the chemical composition of river water. For this purpose, all data were rationed, i.e., the ratio of deviations from mean value to standard deviation was established. Objects were clustered according to Ward's method.

The relevance of the obtained results was estimated by the correlation analysis in the STATISTICA7.0 software. The Kaiser-Meyer-Olkin test (KMO) and Bartlett's tests were performed to determine the validity of multivariate cluster analysis. The KMO test is a scale that indicates the proportion of variance in applied variables. Thus, the value closer to 1 shows high reliability, and value less than 0.5 means that the analysis is invalid. Bartlett's test shows a significant relationship when each variable indicates an existing correlation with the other variables. At that, a value closer to 0 indicates the highest relevance.

Results

The investigation results of the hydro-ecological status in the Kuban river basin for the classification of natural waters into hydro-chemical facies representing natural water types are given in Table 1. The data arranged in columns represent sampling locations, and that in rows show chemical indices of water quality. The entire database presented in the table consists of 3402 averages based on experimental results (Figure 1).

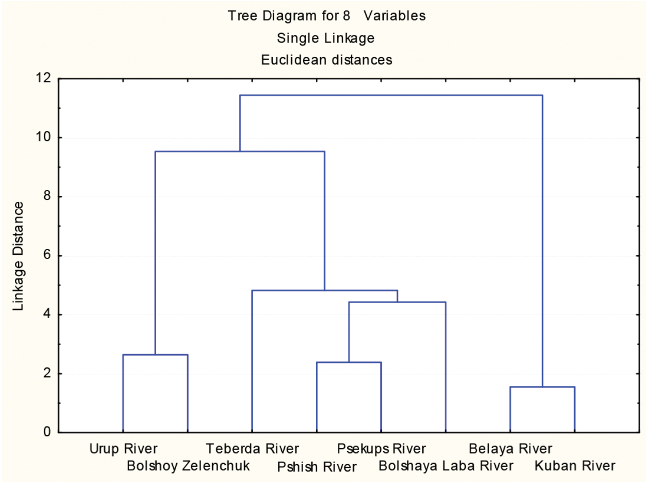

Figure 1: Results of multivariate cluster analysis of hydro-ecological situation in the Kuban river basin.

The obtained results of the hydro-ecological analysis were processed using an iterative K-means algorithm resulting in two cluster formation. Results of estimating the chemical content in each of the rivers are shown in Figures 2, 3, and Tables 2, 3.

Table 4 shows the element content of the 2nd hazard category. The content of toxic elements in the basin of the Kuban River mainly did not exceed the maximum permissible concentration (Figure 4, Table 5).

Table 1: Hydro-ecological status in the Kuban river basin

No.	*Kuban River*	*Bolshaya Laba River*	*Psekups River*	*Belaya River*	*Pshish River*	*Urup River*	*Bolshoy Zelenchuk*	*Teberda River*
pH	7.6	7.96	7.81	7.3	7.94	6.5	6.5	7
Soluble oxygen, mgO_2/dm^3	4.9	4.1	4.2	4.4	4.6	4.8	4	4.03
BOD5, mgO_2/dm^3	4	3.9	4	4	5	2	2	2
COD(Mn), mgO_2/dm^3	5.1	4.1	4	5.1	4.2	2	2.5	2
Ammonia, mg/dm^3	0.43	0.39	0.39	0.44	0.28	0.3	0.4	0.3
Nitrite nitrogen, mg/dm^3	0.15	0.18	0.23	0.14	0.21	0.1	0.08	0.1
Nitrate nitrogen, mg/dm^3	35.2	24.2	27.9	34.2	27.4	25	20	22
Chlorides, mg/dm^3	32.2	44.7	42.4	31.2	40.4	40	30	31
Surfactants, mg/dm^3	0.31	0.35	0.42	0.3	0.26	0.005	0.002	0.005
Total iron, mg/dm^3	0.092	0.088	0.095	0.091	0.073	0.03	0.03	0.09
Copper, mg/dm^3	0.1	0.097	0.135	0.1	0.068	0.031	0.014	0.011
Zinc, mg/dm^3	0.96	1.14	0.93	0.96	1	0.01	1.3	0.08
Lead, mg/dm^3	0.00014	0.00014	0.00014	0.0001	0.00014	0.0003	0.0001	0.0007
Cadmium, $\mu g/dm^3$	0.005	0.005	0.005	0.004	0.005	0.0009	0	0
Manganese, mg/dm^3	0.077	0.061	0.029	0.074	0.0094	0.005	0.005	0.007
Chromium, $\mu g/dm^3$	0.9	0.9	0.4	0.67	0.06	0.008	0.004	0.003
Nickel, $\mu g/dm^3$	0.4	0.9	0.4	0.48	0.6	0.002	0.004	0.002
Arsenic, $\mu g/dm^3$	0.001	0.0001	0.005	0.0013	0.0002	0.0003	0.0025	0.0001

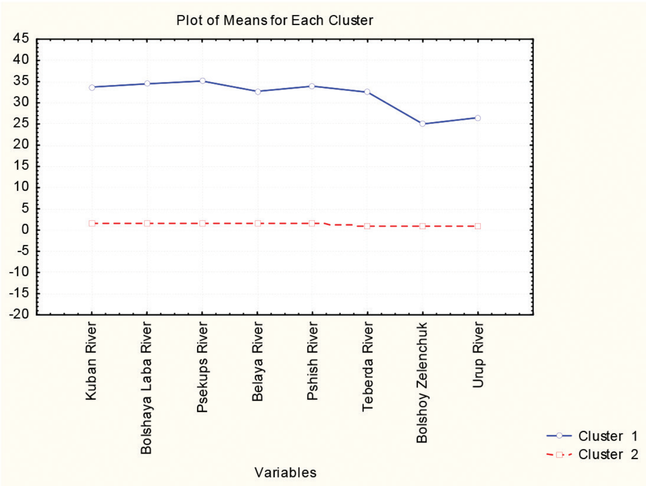

Figure 2: Results of *k*-means clustering for the hydro-ecological status of individual rivers in the Kuban river basin.

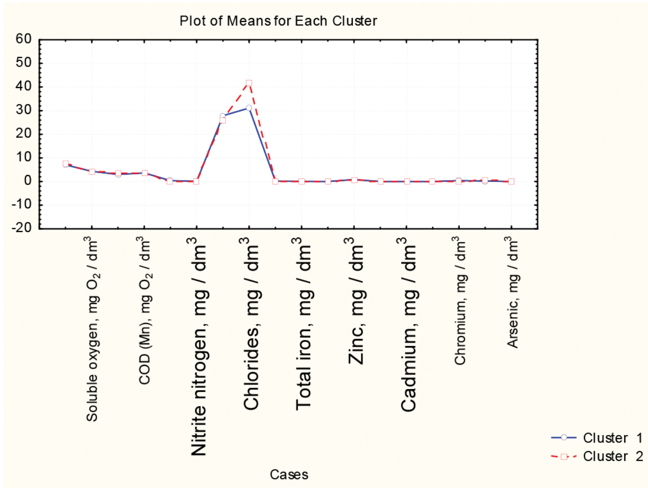

Figure 3: Results of *k*-means clustering for the hydro-ecological indices in the Kuban river basin.

Table 2: Statistical assessment of multidimensional clustering for the hydro-ecological status of selected rivers in the Kuban River basin

Name	*Analysis of variance*					
	Between SS	*df*	*Within SS*	*df*	*F*	*signif.p*
Kuban River	1835.943	1	91.3584	16	321.5369	0.005
Bolshaya Laba River	1928.884	1	289.0485	16	106.7715	0.004
Psekups River	2020.134	1	184.1516	16	175.5193	0.001
Belaya River	1730.141	1	84.9065	16	326.0324	0.001
Pshish River	1864.039	1	175.9843	16	169.4732	0.001
Urup River	1765.453	1	170.3044	16	165.8632	0.003
Bolshoy Zelenchuk	1019.516	1	102.6301	16	158.9424	0.001
Teberda River	1158.104	1	98.5894	16	187.9478	0.001

Discussion

Figure 1 depicts the results of the multivariate cluster analysis of hydro-chemical indicators in the Kuban river basin. It should be noted that the task of this research was to show not only a mathematically structured model of environmental management in the Kuban River basin but also numerical ranges of changes in concentrations. On the dendrogram, two cascade systems can be distinguished that simulate the ecological situation of the hydrological system:

(1) Cascade system corresponding to the mountainous area of the basin, including rivers Urup, Bolshoy Zelenchuk, Teberda, Pshish, Bolshaya Laba, and Psekups;
(2) A system including the Kuban River near the Krasnodar Reservoir and the Belaya River.

The multivariate cluster analysis method was used to determine the main ions as indicators of anthropogenic impact on the Kuban River basin.

Performed studies have shown an excessing MPCs in some water quality indicators. High content of organic substances, in particular, oil products, was detected. Obtained results are consistent with those received by other authors while investigating the hydro-chemical composition of surface waters (Belyuchenko, 2016). In the mentioned studies, a higher content of phenols was revealed, while in this research, the content of phenols and other organic substances was not considered as an independent indicator but included in BOD5 and COD. Some authors attribute the increased concentrations of heavy metals and chlorine in the plain part of the river basin to the outcome of agricultural activities and the influence of industrial enterprises (Qdais et al., 2018).

Table 3: Statistical assessment of multidimensional clustering in relation to hydro-ecological indicators of the Kuban river basin

Name	*Analysis of variance*					
	Between SS	*df*	*Within SS*	*df*	*F*	*signif.p*
pH	0.4095	1	2.15	6	1.14	0.326
Soluble oxygen, mg O_2/dm^3	0.017	1	0.8562	6	0.12	0.740
BOD5*, mg O_2/dm^3	1.0513	1	8.71	6	0.72	0.427
COD (Mn), mg O_2/dm^3	0.02	1	11.57	6	0.01	0.922
Ammonia, mg/dm^3	0.0055	1	0.02	6	1.47	0.271
Nitrite nitrogen, mg/dm^3	0.0078	1	0.01	6	3.58	0.107
Nitrate nitrogen, mg/dm^3	5.9512	1	199.94	6	0.18	0.687
Chlorides, mg/dm^3	232.2	1	16.39	6	85.01	0.0001
Surfactants, mg/dm^3	0.0218	1	0.1897	6	0.69	0.437
Total iron, mg/dm^3	0.0000	1	0.0053	6	0.04	0.847
Copper, mg/dm^3	0.0014	1	0.013	6	0.62	0.459
Zinc, mg/dm^3	0.0060	1	1.61	6	0.02255	0.885
Lead, mg/dm^3	0.0000	1	0.0000	6	0.27586	0.618
Cadmium, µg/dm^3	0.0000	1	0.00	6	1.07045	0.341
Manganese, mg/dm^3	0.0004	1	0.01	6	0.37946	0.5621
Chromium, µg/dm^3	0.0055	1	1.1430	6	0.02866	0.871
Nickel, µg/dm^3	0.1290	1	0.6198	6	1.24915	0.306
Arsenic, µg/dm^3	0.0000	1	0.0000	6	0.01815	0.897

*BOD – biochemical oxygen demand; COD – chemical oxygen demand.

Table 4: Concentrations of heavy metals in surface waters of the Kuban river basin

No.	*Distance from the source (km)*	*Ag, µg/L*	*Al, mg/l*	*As, µg/L*	*Cd, µg/L*	*Mo, µg/L*	*Pb, µg/L*
1	7.52	0.11	0.094	0.11	0.043	0.38	0.46
2	20.7	0.14	0.199	0.43	0.16	0.12	0.52
3	31.1	0.12	0.102	1.01	0.051	0.08	0.17
4	38.3	0.2	0.139	0.65	0.046	0.19	0.33
5	54.5	0.12	0.1	0.83	0.039	0.31	0.41
6	89.0	0.16	0.19	0.82	0.052	0.22	0.56
7	149.7	0.08	0.112	0.79	0.049	0.16	0.31

High surfactant concentrations indicate that the main sources of pollution in the Kuban River basin are attributed to municipal wastewater. Up to 95 percent of the total wastewater from the Kuban basin is reported to be generated from housing and utilities. Even though some authors consider the level of pollution of the Kuban River as exceeding the MAC by several tens of times, the results only partially correspond to them. By processing experimental data by multivariate cluster analysis, a dendrogram was constructed (Figure 1), which enables estimating the Kuban River basin as a cluster of moderately polluted waters in the western part and a cluster of low polluted waters in the mountainous part representing the territory of Karachay-Cherkessia and Adygea. Water quality in rivers is determined by the interaction of pollutant loads from inflows, hydrological

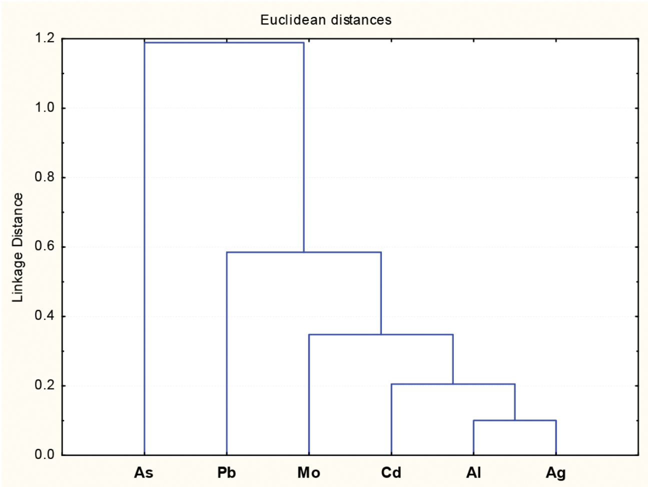

Figure 4: Results of multivariate cluster analysis of microelement composition in the Kuban river basin.

characteristics, sediments, and metabolism in water, as well as seasonal and adjusted seasonal factors. Through cluster analysis, the specifics of river drainage basins are often determined (Gholizadeh et al., 2016). In this study, spatial characteristics of water quality distribution have been analysed using the position and varying characteristics of water quality as a function of the season. In this research, establishing time characteristics was a secondary task as the aquifer system is most intensively exploited in the period June-July. The results of the *k*-means clustering for the hydro-ecological status of individual rivers in the Kuban river basin allowed identifying two clusters of natural water pollution with respect to its concentrations. These are:

1. pH, Soluble oxygen, BOD5, COD (Mn), Ammonia, Nitrite nitrogen, Nitrate nitrogen, Chlorides, and Surfactants.
2. Total iron, Copper, Zinc, Chromium, Nickel, Lead, Cadmium, Manganese, and Arsenic.

As to the toxic elements presented in Table 4, the aluminium content in natural waters of the upper reaches in the Kuban River basin ranged from 0.094 mg/dm^3 to 0.2 mg/dm^3. Cluster analysis showed that all elements can be conditionally divided into two clusters. Arsenic acts as a separate cluster due to its highest content in natural waters compared to other trace elements. However, it should be taken into account that for good visibility of the dendrogram, the concentration of aluminum is given in mg/dm^3 rather than µg/L as in other elements. The concentration of arsenic in the basin of the Kuban River is reported to not exceed MAC. Other elements were in trace amounts, despite the presence of tailing ponds of mining and processing enterprises in the Kuban river basin. Natural waters in the Central Caucasus are characterised by increased molybdenum content (Simmonds et al., 2017). However, the results of the current study showed that molybdenum concentrations in the upper waters of the Kuban River did not exceed 0.38 µg/dm^3.

In contrast to chromium and zinc, the manganese concentration was higher in only one sample of the Bolshaya Laba River. The content of nickel in Kuban waters did not exceed MAC. Higher concentrations were observed in the waters of the Bolshaya Laba, the Pshish, the Psekups, and the Kuban rivers. In June 2018, elevated concentrations of molybdenum, nickel, aluminium, and zinc were found in the upper reaches of the Urup and the Teberda rivers. Other researches pointed out the repeated excesses of lead concentrations as well, although this relates to the presence of lead-zirconium deposits in the Caucasus. A comparison of the pollution levels in the northern part of the Kuban River with the Urup and the Teberda rivers, which represent the eastern part of the basin, showed that in the Kuban river, molybdenum and manganese concentration is 32% less, but nickel and lead content is twice as high. This

Table 5: Concentrations of heavy metals in surface waters of the Kuban river basin

	Kuban River	*Bolshaya Laba River*	*Psekups River*	*Belaya River*	*Pshish River*	*Urup River*	*Bolshoy Zelenchuk*	*Teberda River*
Kuban River	1	0.935	0.964	1	0.967	0.955	0.964	0.971
Bolshaya Laba River	0.935	1	0.996	0.934	0.994	0.996	0.993	0.989
Psekups River	0.964	0.996	1	0.963	0.999	0.998	0.998	0.997
Belaya River	1	0.934	0.963	1	0.967	0.954	0.963	0.971
Pshish River	0.967	0.994	0.999	0.967	1	0.996	0.998	0.997
Urup River	0.955	0.996	0.998	0.954	0.996	1	0.998	0.997
Bolshoy Zelenchuk	0.964	0.993	0.998	0.963	0.998	0.998	1	0.999
Teberda River	0.971	0.989	0.997	0.971	0.997	0.997	0.999	1

is reflected in the *k*-means clustering results presented in Figures 2-3 and Table 3. Regarding the Caucasus rivers studied by other authors, there is an increased molybdenum content reported for the Terskol and Garabashi Rivers (Qdais et al., 2018). Research has shown that in the waters of the Pshysh River, Bolshaya Laba River, Psekups River, and Kuban River there is a slight increase in the content of cadmium and other heavy metals, which can be a consequence of anthropogenic impact. The data in Table 3 show a fairly high relevance of the findings (p~0.5) but noteworthy is that the content of heavy metals in the Earth's crust can vary quite strongly resulting in a fluctuation of their level in natural waters. Very low relevance was observed for arsenic as its concentration varied within quite a wide range from 0.0001 to 0.005. Table 5 presents the data on the correlation analysis of the conducted studies. The values of the correlation coefficient tend to 1, which indicates a high reliability of calculations.

Conclusions

The analysis of the hydro-ecological situation in the Kuban river basin showed the highest level of pollution in its western part. The presence of cadmium, molybdenum, aluminium, and other element compounds in the Kuban River and the Belaya River is associated with anthropogenic sources. The application of multivariate cluster analysis allowed distinguishing clusters of territorial and elemental type. The dendrograms of hydro-ecological studies based on multivariate cluster analysis for the Kuban River and its tributaries were presented, namely, for the Bolshaya Laba River, Psekups River, Belaya River, Pshish River, Urup River, Bolshoi Zelenchuk River, and Teberda River. The method of multivariate cluster analysis was applied for grouping territorial regions that are homogeneous in chemical composition and pollution level of natural waters. The relevance of the obtained data is $p<0.0005$, and the correlation coefficient is close to 1. Obtained results contribute to setting priorities for the strategy development on water quality improvement needed to implement the basic principle of water resources management.

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