CONTRIBUTION OF INDUSTRIAL ECONOMIC AGENTS ON WASTEWATER POLLUTION IN MEDIAŞ CITY

— research paper —

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Abstract: This paper presents the results of monitoring the degree of pollution of waters in Medias, in 2007. There have been assessed chemical and physical quality indicators, such as: pH, suspended solids, filterable residue dried at 105 °C, electrical conductivity, chemical oxygen demand (COD), biochemical oxygen demand (BOD), ammonium, nitrates, nitrites, phosphates/phosphorus, phenols, substances extractable in petroleum ether, heavy metals (lead, cadmium, nickel). There were values found exceeded the maximum permitted, set of norms, especially for BOD determinations. The BOD/COD ratio indicates a good capacity of biological self-purification of water. We are dealing also with a nitrogenous organic pollution of wastewater. In terms of acidity and heavy metal loading, the values obtained are kept within the limits prescribed by law.

Keywords: wastewater, chemical and physical indicators, monitoring, pollution, purge

1. INTRODUCTION

As defined, wastewaters are waters used for domestic or industrial needs and which, because of impurities added, had changed the original chemical composition and physical properties. The same category includes waters that are leaking in urban areas, industrial areas and agricultural fields, after falling rainfall (Duca et al., 1999).

Wastewaters come from the natural waters loading of such materials and substances which change the quality indicators, polluting them.

Water loads of pollutant materials and becomes wasted by use by man in the most diverse practical purposes and by contact of meteoric water (rain, snow) with products of human activity found in air and on ground (Ardelean and Maior, 2000).

In the first case, whereas the use of water takes the various forms (drinking water, water for industry, agriculture, fisheries, urban and recreational purposes), its pollution possibilities are very high.

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Large quantities of wastewater come from industrial units. Thus, to obtain one tonne of paper results about 100 - 200 m^3 of wastewater; for a tonne of rubber, 150 m^3; to process a tonne of fruits results about 10 - 20 m^3 wastewater. But also the wastewater that comes from domestic water consumption (sewage) is a large enough quantity. Thus, there was, for a non-industrialized district in Bucharest, a consumption rate of about 0.35 m^3/capita/day (Rojanschi, 1995).

In the second case, meteoric waters dissolve during rain, various toxic gases in the air (oxides of sulphur, nitrogen, ammonia) or load with dust containing metallic oxides, tars and other substances. Water from rain or snowmelt can become polluted during their flow on soil surface, as a result of contact with various products of human activity (pesticides, fertilizer, domestic or industrial waste, etc.).

„Indices of stress" the most significant appear to be pesticides used in agriculture and heavy metals. Electroplating industry wastewaters contain a real "hurricane" of mercury, cadmium, zinc, copper and chromium.

In industrial wastewaters meet relatively frequently, organic materials in suspension (cresol, methacrylic acid, tricresilphosphate, tributilphtalate etc.) that subject to part (~ 40 %) biological „mineralization", meaning decomposition to CO_2, water and simple inorganic substances. More than 60 substances whose concentration on active systems is normal, do not subject to biological decomposition (Duca et al., 1999).

In such circumstances, an acute problem is to support full biological value of natural waters or, in other words, reducing the content of foreign components to a concentration that provide the normal physiological and biological processes of aquatic organisms without adverse genetic consequences.

One of effective methods of protection for the aquatic environment elements against pollution is wastewater treatment before discharge into (Tobolcea and Ungureanu, 1993).

Under the influence of unsatisfactory treated wastewater, containing organic substances, begin to form in water receptor, large colonies of microorganisms (Oprean, 1995), which are driven by river water and then block from entering intakes, grates and filters at drinkable and industrial water plants.

Wastewater containing acids attack the metal parts of plants. High carbonates content of some industrial waters jeopardizes the operation of industrial water boilers of steam power stations (Negulescu, 1975).

Sometimes, the mutual action of industrial water in the water receptor can produce negative effects. Thus, waters from tanneries and from sulphite pulp

by contact with waters with high content of iron salts give a colour of ink and cause a high consumption of oxygen. In addition, waters containing free acids, when in contact with sulphurous waters, free hydrogen sulphide (Rojanschi et al.,, 2002).

MATERIALS AND METHODS

In tests conducted on wastewater were followed parameters such as: pH, electrical conductivity, filterable residue dried at 105 °C, chemical oxygen demand (COD), biochemical oxygen demand (BOD), ammonium, nitrates, nitrites, phosphates/phosphorus, phenols, detergents, sulphurs, sulphates, substances extractable in petroleum ether, suspended solids, iron, heavy metals [8 - 25].

Sampling was done in accordance with the standard for sampling the wastewater (SR ISO 5667-10/1992 Water quality. Sampling. Part 10: Guidance on wastewater sampling) (*** SR ISO 5667-10, 1992), in plastic containers (polyethylene), sampled volume being of 2 litres of wastewater. The containers were filled to capacity, to limit sample contact with the gas phase and reduce agitation during transport. Thus, one avoids a series of transformations that can occur in the sample, such as: modifying the content of carbon dioxide, changes in pH, hydrogen carbonates do not turn into insoluble carbonates, iron (II) has fewer tendencies to corrode, downward trend of change colour etc.

There were collected average samples of water from industrial agents of Medias considered a significant impact on the wastewater treatment process.

The identification system was designed to ensure that the sample can not be confused physically or in the records, from the collection and for the entire duration of preservation in the laboratory, for analysis.

Sampling bottles and working glassware were marked with numbers that, once levy, corresponded to different samples. The identifying elements have been found still in the records of work stages.

Samples were received on the notes accompanying sampling. At the reception was envisaged sample integrity, that it is correctly identified, if the sample container is appropriate.

Handling samples was avoiding the possibility of their impurification or chemical contamination. Storage of samples was done in the refrigerator, when the program of the laboratory did not allow their immediate analysis.

Sampling and preservation of samples was done in the laboratory.

Indicator pH was immediately determined. The other indicators were analyzed follow within 24 hours of sampling. The preservation of the samples consisted, generally, in cold storage.
There was, additionally, a subsampling and a specific preservation for the following indicators:

- ammonium – water samples are fixed by acidification with H_2SO_4, 1+1 vol., to pH < 2, (checked with universal indicator paper);
- COD_{Mn} – if the sampling pending determination go more than 2 hours, the sample must be preserved by adding 2 ml of sulphuric acid 1+2, to every 100 ml of sample;
- COD_{Cr} – conservation by adding 10 ml of sulphuric acid, 4 mol/l, per litre of sample and kept at a temperature of 0 ... 5 °C;
- sulphides – conservation is done with 2 ml NaOH, de 4 % for each litre of sample to pH > 12, so samples are stable 2 days, if kept at 4 °C, in dark glass vessels, completely filled, no air bubbles remain in the plug (to prevent oxidation of sulphides);
- extractable substances – conservation with 5 ml of hydrochloric acid (d = 1,19), diluted 1+3, to 1 l of sample;
- suspended solids – if the analysis can not be done in max. 24 h, is added for conservation, 2 ml chloroform per litre of sample and shake well;
- heavy metals – conservation with 5 ml nitric acid, 65 % per litre of sample.

Analytical methods applied are standardized according to (*** SR ISO 10523, 1997) (***SR EN 27888, 1997) (***STAS 9887, 1974) (***SR ISO 6060, 1996) (***SR 7587, 1996) (***SR ISO 7150-1, 2001) (***SR ISO 5815, 1991) (***SR ISO 6332, 1996) (***SR 7510, 1997) (***STAS 9187, 1984) (***SR ISO 9297, 2001) (***STAS 8601, 1970) (***STAS 6953, 1981) (***SR ISO 7890-3, 2000) (***SR ISO 6777, 1996) (***SR ISO 6439, 2001) (***SR EN 1189, 2000) (***SR EN ISO 11885, 2004) (Table 1).

Table 1. Analytical methods used

Nr. crt.	**Determination**	**Standard**	**Nr. crt.**	**Determination**	**Standard**
1.	pH	SR ISO 10523/1997	10.	Filterable residue dried at 105 °C	STAS 9187/1984
2.	Electrical conductivity	SR EN 27888/1997	11.	Chlorides	SR ISO 9297/2001
3.	COD_{Mn}	STAS 9887/1974	12.	Sulphates	STAS 8601/1970

4.	COD_{Cr}	SR ISO 6060/1996	13.	Suspended solids	STAS 6953/1981
5.	Solvent extractable substances	SR 7587/1996	14.	Nitrates	SR ISO 7890-3/2000
6.	Ammonium	SR ISO 7150-1/2001	15.	Nitrites	SR ISO 6777/1996
7.	BOD	SR ISO 5815/1991	16.	Phenols	SR ISO 6439/2001
8.	Iron	SR ISO 6332/1996	17.	Phosphor	SR EN 1189/2000
9.	Sulphides	SR 7510/1997	18.	Metals	SR EN ISO 11885/2004

In accordance with the norm setting load limits of pollutants in industrial and municipal waters at their discharge into the natural receivers and sewers networks/treatment stations (***H.G. 188/2002) (*** H.G. 188 / M.O. 187, 20 March 2002) modified and completed by H.G. 352/2005), amounts of pollutants will not exceed the limits specified in Table 2.

Table 2. Quality indicators of wastewater

Nr. crt.	Water category	Quality indicators	Permitted values
1.	Treated faeces - household waters, treated industrial wastewater and rainwater Technological waters that do not require treatment	pH	6.5 – 8.5
		Suspended solids	60 mg/l
		BOD	25 mg/l
		COD	125 mg/l
		Fixed residue	2000 mg/l
		Ammonium (NH_4^+)	3 mg/l
		Nitrites (NO_2^-)	2 mg/l
		Detergents	0.5 mg/l
		Extractable substances	20 mg/l
		Total phosphor	1 mg/l
		Phenol	0.3 mg/l
		Total ionic iron	5.0 mg/l
		Total chrome (Cr^{3+} + Cr^{6+})	1.0 mg/l
		Hexavalent chrome (Cr^{6+})	0.1 mg/l
		Cadmium (Cd^{2+})	0.2 mg/l

		Nickel (Ni^{2+})	0.5 mg/l
		Lead (Pb^{2+})	0.2 mg/l
		Manganese	1.0 mg/l
		Zinc	0.5 mg/l
2.	Rain water	Petroleum products	non-iridescent

Pollution depends on the amount of industrial activities, which are closely related to economic situation. It also depends on the modernization of production technologies.
The main economic agents which, by their discharges of wastewater, load with pollutants the influent of Medias treatment station are presented in Table 3.

Table 3. Monitorized economic agents – dynamics of their work

Nr. crt.	Economic agent	Domain of activity	Wastewater discharge
1.	Armax Gaz	Machining, pneumatic fitting, burners' assembly, metal coatings, plating, painting.	Târnava Mare River
2.	Automecanica	Design, manufacture and sale of equipment-automobiles-special vehicles, spare parts.	Târnava Mare River
3.	B.A.T.	Motor transport of goods and people, repair and periodic inspection of vehicles endowment.	Ighiş Rill
4.	Emailul	Production and marketing of enamelled vessels.	Târnava Mare River
5.	Felam	Production and marketing of fasteners and strip wire.	Târnava Mare River
6.	Geromed	Production of drawn glass, safety glazing materials and duplex windows, mirrors.	Sewage of Mediaş
7.	Medimpact	Dyeing and finishing leathers, making leather: footwear, riding.	Târnava Mare River
8.	Relee	Production of apparatus for distribution and power control.	Moşna Rill
9.	Vitrometan	Production and marketing of glassware (common household), glassware (crystal) and glassware for lighting fixtures.	Târnava Mare River

In order to reduce the sewage flow and the degree of pollution, given the composition of the environment – water, policy and strategy of industrial

agents should aim, first, improving production process and the pre-treatment process (Tobolcea and Ungureanu, 1993).

RESULTS AND DISCUSSIONS

a) Monitoring economic agents of Mediaş, 2007

In Table 4 are presented values of indicators followed by monitoring, in 2007, the economic agents of Medias, given the load of sewage with polluting substances, coming from their specific activity. Above the maximum permissible values are listed in bold and red characters.

Table 4. Monitoring economic agents of Mediaş, 2007

Economic Agent / Analyzed indicator	Armax Gaz	Automecanica	B.A.T.	Emailul	Felam	Geromed	Medimpact	Relee	Vitrometan
pH [pH units]	7.71	7.07	7.67	**8.76**	7.33	3.0	7.89	7.69	8.55
Suspended solids [mg/l]	79.0	16.0	3.0	19.0	146.0	**928.0**	55.0	7.0	3.0
Filterable residue dried at 105 °C [mg/l]	464.0	484.0	832.0	1468.0	560.0	1271.0	700.0	612.0	480.0
Electrical conductivity [µS/cm]	684.0	673.0	1142.0	1931.0	952.0		795.0	939.0	803.0
COD_{Cr} [mg/l O_2]	82.5	**128.0**		20.7	92.1	62.0	112.0	20.0	39.6
BOD_5 [mg/l O_2]	37.0	**53.0**	**32.0**		36.0			8.0	
Ammonium [mg/l]	33.65	2.84		0.45			37.5		
Nitrates [mg/l]				0.88			2.22		
Substances extractable in petroleum ether [mg/l]	absent	4.4	absent		18.8	absent	absent	absent	absent
Zinc [mg/l]	0.215			0.007	0.087			**1.162**	0.031
Copper [mg/l]					0.008			0.021	0.0105
Manganese [mg/l]				0.017	0.093			0.046	
Lead [mg/l]				0.0025					
Cadmium [mg/l]				0.0023		0.00025			
Iron [mg/l]	0.408			0.174	0.097	0.020		0.015	0.037
Chromium [mg/l]				0.0004/ 0.0004			absent		
Nickel [mg/l]				0.00062					

In general, it was found values exceeding the maximum permissible under current norms, according to the specific profile of activity of each unit, but

most often occur to determine exceedances of biochemical oxygen demand in five days (BOD_5), which correlated with values found for organic matter content (COD_{Cr}) indicates an intense microbiological activity in the wastewater.
These increases in water parameters due to uncontrolled discharge of wastewater from economic agents, and water from industrial and wastewater treatment plant of Medias.
Exceeding the maximum permissible limits for polluters, generally leads to increasing operating costs and to hinder the technological process of sewage treatment, with the risk of exceeding the limits listed in legal rules, for the discharge of treated water into the receiver.

b) Monitoring the wastewater from treatment plant discharges from Medias

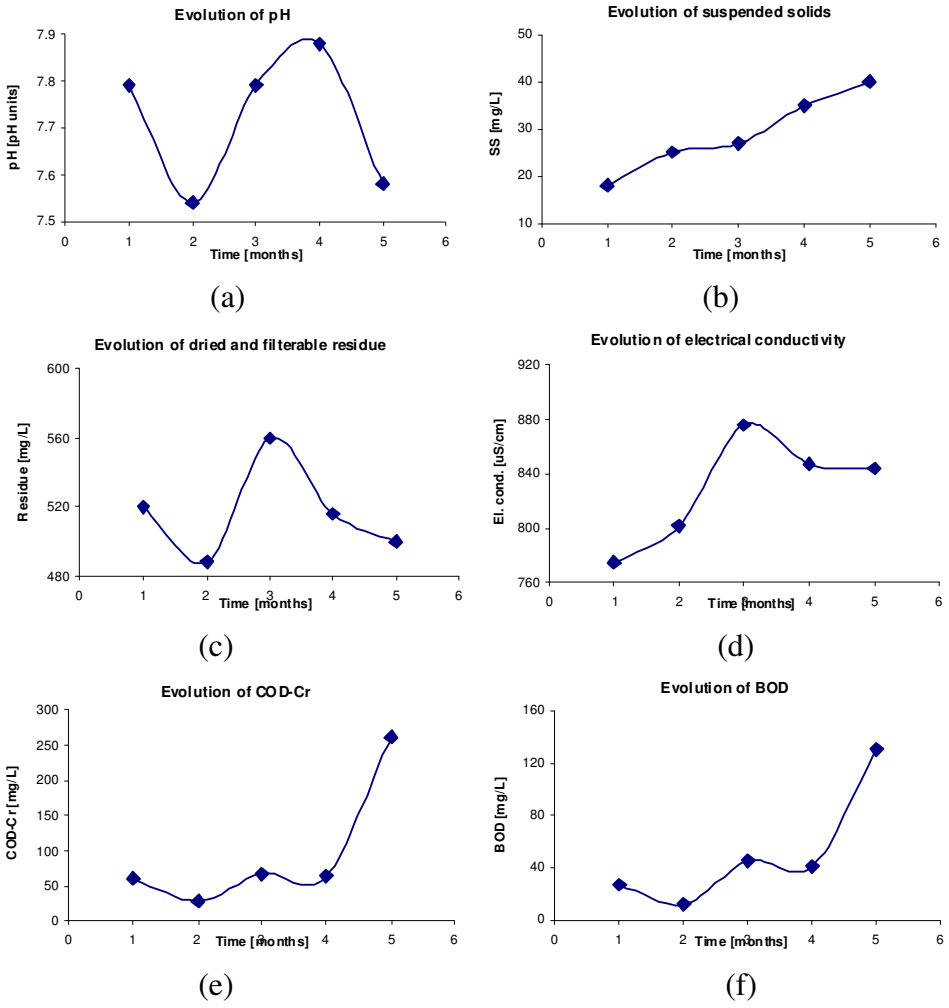
Following the visits paid to the economic agents of Medias, it was found that, in general, they have already pre-treatment stations in operation, equipped with everything necessary, but their technology is obsolete and poorly controlled.
We believe that a permanent consultation between the local wastewater operator, that is Water - Sewage Company, and the pollutants is necessary, in order to find new ways to develop a partnership with respect to compliance with wastewater's legal norms.
To determine the level of pollution of Medias, the physical and chemical indicators were monthly Monitorized, in 2007, for the water from Târnava Mare River, crossing the city of Medias. The obtained data are presented in Table 5.

Table 5. Monthly monitoring (2007) of physical and chemical indicators for the water from Târnava Mare River

Month (2007) / Analyzed indicator	January	February	March	April	Mai
pH [pH units]	7.79	7.54	7.79	7.88	7.58
Suspended solids [mg/l]	18.0	25.0	27.0	35.0	40.0
Filterable residue dried at 105 °C [mg/l]	520.0	488.0	560.0	516.0	500.0
Electrical conductivity[µS/cm]	774.0	801.0	876.0	847.0	844.0
COD_{Cr} [mg/l O_2]	59.9	28.2	67.4	63.4	262.0
BOD_5 [mg/l O_2]	27.0	11.8	45.2	40.5	130.0
Ammonium [mg/l]	13.45	16.2	33.3	34.9	33.7
Nitrites [mg/l]	0.045	0.041	0.231	0.3	0.06

Nitrates [mg/l]	2.96	13.3	0.33	0.86	0.68
Phosphates/phosphor [mg/l]	4.24 1.38	5.14 1.67	10.3 3.35	10.0 3.26	9.04 2.94
Phenols [mg/l]	0.001	0.004	0.010	0.006	0.009
Substances extractable in petroleum ether [mg/l]	absent	absent	absent	absent	absent
Lead [mg/l]	0.0105	0.014		0.0044	0.003
Cadmium [mg/l]	0.00017	0.002		absent	0.0004
Nickel [mg/l]	0.005	0.0053	0.0059	0.0018	0.0035

The evolution of key quality indicators registered at the wastewater treatment plant of Medias, in 2007 is shown in Figure 1.



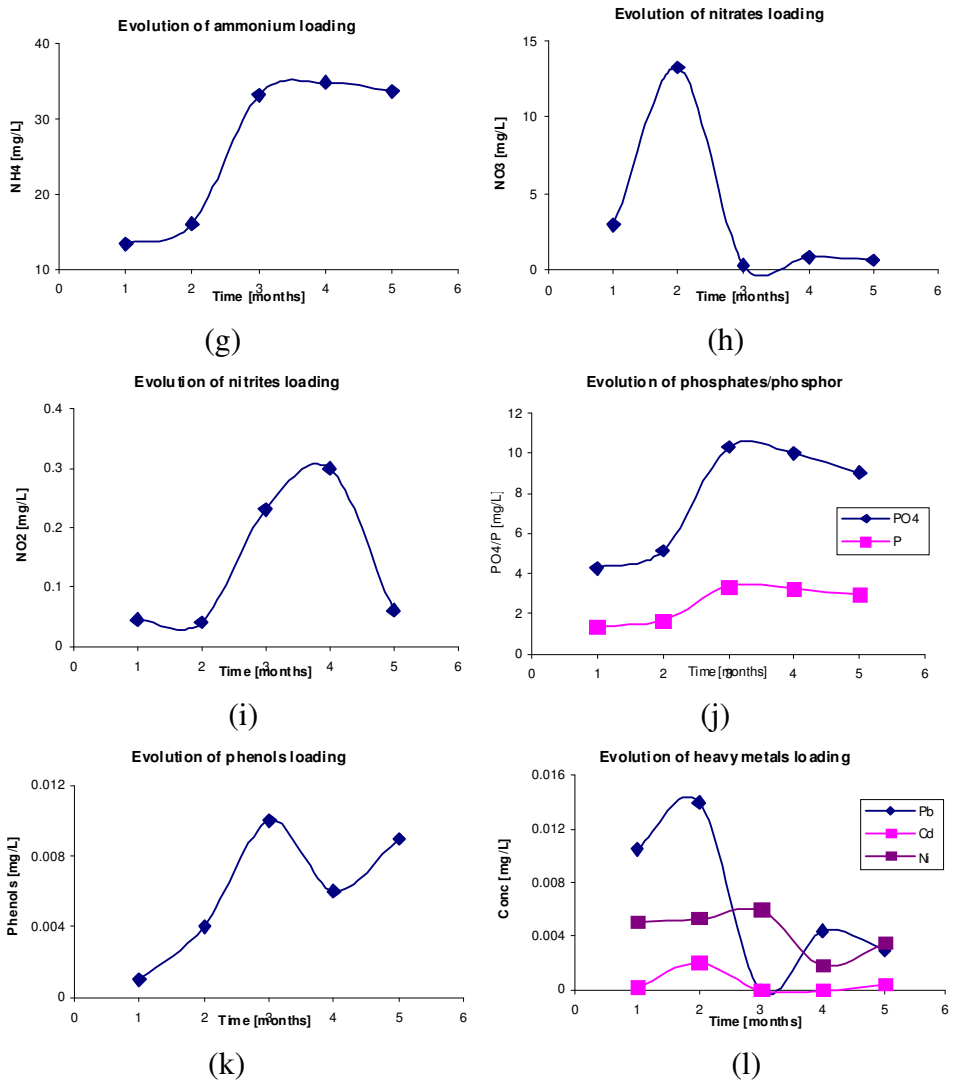


Figure 1. Evolution of key quality indicators registered at the treatment plant of Medias, in 2007:
(a) – pH; (b) – SS; (c) – filterable and dried residue;
(d) – electrical conductivity; (e) – COD_{Cr};
(f) – BOD; (g) - ammonium; (h) – nitrates; (i) – nitrites;
(j) – phosphates/phosphor; (k) – phenols; (l) – heavy metals.

CONCLUSIONS

The monitoring of economic agents could achieve a characterization of the biodegradability of effluents, aiming COD and BOD indicators, and the relationship between them. The results obtained are due to the combination of chemical and biochemical processes, which are not of strict and clear character, but provide an indication on whose basis wastewater quality can be assessed.

The ratio BOD/COD gives information about biological self-purification capacity: if more than 0.6 self-purification will be easy, if between 0.2-0.4 self-purification will occur only in favorable thermal regime, and the ratio under 0.2 biological self-purification can not be produced.

Examining the value of the ratio of indicators (BOD/COD) during the monitoring period, an average of 0.53 is obtained, thus falling within the optimum range shown in the previous paragraph.

According to the charting of progress outlined above, the following conclusions are to be drawn:

✓ pH is kept within the limits standardized (6,5 - 8,5), which means that treatment and self-purification processes are not disturbed by its value.

✓ heavy metals are toxic to microorganisms involved in biological treatment of water and sludge fermentation. Of the metals monitored, lead has the highest quantitative values, but is kept below the admitted limit.

existence of ammonium ions is the result of bacterial decomposition of organic matter containing proteins, respectively aminoacids. The values found for nitrogen as ammonia exceed those permitted by the norm, which highlights the degree of nitrogenous organic pollution of wastewater.

✓ chemical and biochemical oxidability (COD and BOD) are global indicators for organic substances.

✓ suspensions usually carry many pollutants fixed on them, thus getting beyond dosages, if filtered water is analysed. In addition, suspensions were highly variable levels in rivers, for which the results' degree of accuracy for the standard tests is lower in their case, if not used a collection front instead of a single collection point, in case of rivers.

A real solution to stop the training of particulate matter in river water is applying, in industrial enterprises, the closed water circulation systems.

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