A fluorescent tracer for hydrodynamic process studies

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Abstract The application of a fluorescent tracer to visualize the distribution of wastewaters in various water bodies was investigated. Tracer experiments were conducted on Seversky Doniets River, the lower Don River, the Taganrog Bay of the Azov Sea, and the Neva River Inlet of Finnish Bay. In addition, the applicability of the tracer to an investigation of pollutant transport in groundwater is presented.

INTRODUCTION

Identifying, quantifying, and verifying hydrologic processes in natural waters is extremely complicated. However, with the development of tracer techniques, most developed countries are taking an active interest in the application of tracers to determine hydrologic processes of aquatic systems. Tracers include naturally occurring substances or those experimentally applied to the system. It is most advantageous if the tracers used in experimental applications generally are conservative and easily detected in the aquatic system under investigation. Provided the tracer has a minimal interaction with other substances in the system, the movement of the tracer coincides with the spatial and temporal mobility of the water. Consequently, the distribution of the tracer in time reflects the parameters that describe the hydrodynamics of the system. If the tracer behaves ideally and can provide the necessary hydrodynamic information, there is less need to develop expensive hydraulic and hydrologic models nor to resolve the discrepancies between laboratory and field studies, despite the benefits of comparing all approaches.

When a tracer experiment is conducted under natural conditions, a physical model of the hydrodynamic process is represented by the process itself, as can be observed from the behaviour of the tracer. Under ideal conditions, the tracer reflects the water movement, and there is no need to process experimental results using criteria of similarity. The concept is simple. However, all tracers have some limitations primarily due to their interaction with the environment. For example, the isotopes of hydrogen and oxygen should be excellent tracers of water because they form the water molecule, but the amount of a given isotope is affected by phase changes of $\text{H}_2\text{O}$, which limits the broad spectrum of processes to which they can be applied.

Until now, no tracer is available that is inexpensive, inert to physical, chemical, and biological environmental factors, sanitary, environmentally safe, and detectable over a wide range in concentrations. The latter is particularly problematic because most tracers cannot be reliably detected accurately or precisely over the entire range of concentrations that occur in aqueous systems, particularly in the presence of pollutants. To adequately assess the problems in tracer detection for systems where
dilution is a major factor, unacceptably high concentrations or large volumes should be used. For example, 15 kg of sodium chloride is needed to trace stream water that is moving at a rate of 1 m$^3$s$^{-1}$ (Bykov & Vasiliev, 1977). For fluorescent tracers, such as Uranin, Rhodamine 6G, and Rhodamine B, less tracer is needed. But, even these tracers must be used at high enough concentrations so that a dilution by $10^6$ to $10^8$ can be detected. Furthermore, it is not uncommon for pollutants to be diluted by $10^{10}$ in natural systems.

For systems affected by high dilution rates, radioactive isotopes having short-lives, such as $^{131}$I, $^{82}$Br, or $^{198}$Au are good tracers (Paal, 1975; Eremeev & Ivanov, 1987). However, a high reagent costs, instrumentation costs, and rigorous safety requirements, which affects their application and sample processing, makes a wide application of these tracers not feasible.

Given the advantages of tracers and the limited number of inexpensive available tracers, a highly sensitive tracer for visualizing hydrodynamic processes was developed at the Hydrochemical Institute (Anon., 1987). Tracers of this type are environmentally and sanitary safe and may be used where high dilution rates ($10^{12}$) may occur. These tracers incorporate several indicators each with a different fluorescent colour which markedly expands the scope of their applicability.

These tracers have been used for several years at the Institute to investigate hydrodynamic processes in surface and ground waters. The purpose of this paper is to present results from several case studies of a variety of aqueous systems.

**TRACER EXPERIMENT ON THE SEVERSKY DONIETS RIVER**

The reach of the Seversky Doniets River between the cities Rubezhnoye, Severodonetsk, and Lisichansk (Ukraine) is characterized by a high density of industrial and municipal wastewater discharges. As a result, polluted waters are not completely mixed with river waters between discharge points. Also, pollutants in wastewaters of the various industrial enterprises in the region are similar. This similarity hampers the identification of the contribution from individual pollutant sources, which presents substantial difficulties to river pollution control. Consequently, the Rubezhansk Industrial Association, "Krasitel" ("Dye"), investigated pollutant contributions using the tracers to visualize the plume of wastewaters discharged by the association into the river. This investigation was undertaken to determine, within the control cross-sections, the location of discharge point having the highest pollutant concentration and to evaluate the mixing of the wastewater and river water.

The tracer experiment to evaluate mixing was conducted at the discharge 40 and 1 m$^3$s$^{-1}$, for the river and wastewater, respectively. During a 20-min period, 200 l of a 0.135 g·l$^{-1}$ river water and dye solution was mixed with the wastewater, so that the dye and wastewater would mix completely prior to discharging the wastewater to the river.

The river was sampled at two downstream cross sections, each containing five vertical sampling locations having two or three sampling points. The sample collection was timed to coincide with a travel time approximated from the average flow velocity and the distance between the discharge point and the cross sections.

Tracer concentrations for the sampling of each cross-sections are shown in Fig. 1. The highest pollution occurred at the first cross section, 500 m downstream of the
wastewater discharge point, and consisted of two fields, their centres located 11 and 32 m from the left bank. The highest concentrations in each field was 33700 and 44600 particles l\(^{-1}\), respectively. The mixing in the cross section was calculated by the Rodziller-Frolov formula:

\[
P = \frac{S^*}{S_{\text{max}}} \times 100\%
\]  

(1)

where: \(P\) is the degree of mixing; \(S^*\) is the average tracer concentration, in particles \(l^{-1}\), in the cross section; and \(S_{\text{max}}\) is maximum tracer concentration, in particles \(l^{-1}\), in the cross section (34\%). In cross section 2, 2000 m downstream of the wastewater discharge point, the degree of mixing increased to 36\%, and the maximum tracer concentration decreased to 12 600 particles \(l^{-1}\). The centre of the highest pollution zone was located 12 m from the left bank. Tracer travel time from the wastewater discharge point to cross section 1 was 0.40 m s\(^{-1}\) and between cross sections 1 and 2, the tracer travel time was 0.42 m s\(^{-1}\).

The lateral dispersion coefficient, \(D_y\), was calculated by the following formula (Paal & Suurask, 1975):
\[ \Delta y = \frac{v \Delta \sigma_y^2}{2 \Delta x} \]

where: \( v \) is the river discharge predicted from the tracer experiment; \( \Delta \sigma_y \) is the change in tracer concentration as the tracer dispersed across the river; and \( \Delta x \) is the distance, in m, downstream of the wastewater outflow.

Coefficient \( D_y \), which describes the mixing process in the river (Filkin, 1986), was used to calculate the distance \( (L) \) to the cross section where 85% mixing of wastewaters and river waters occurs (Filkin, 1986):

\[ L_{85} = \frac{0.25 (B^*)^2 v}{D_y} \]

where \( B^* \) is the average river width in the study reach. For this study, \( B^* \) was 72 m; \( D_y \) was 0.035 m² s⁻¹; and \( L_{85} \) was 14 800 m. The distance between the wastewater outflow at "Krasitel" and the nearest downstream wastewater discharge, which was from a chemical plant, is 2150 m.

It is apparent from this investigation that if a monitoring station was placed at a point where the river was completely mixed, it would be impossible to determine the industry responsible for the pollution. The investigation provided a means of determining the zone of the highest pollution in cross section 2; the zone was located between 5 and 35 m from the left bank (Fig. 1). Mixing in the zone was 52% which indicates that the tracer concentration was relatively homogeneous in the zone. Investigations carried out during various hydrologic events and at different river flows suggest that the central part of the zone is relatively stable under all flow regimes. These investigations provided sufficient information to site a sampling station, which was located 25 m from the left bank, that would provide an estimate of the water pollution of the Seversky Doniets River caused by wastewaters from "Krasitel". Similar investigations were conducted for other industrial plants discharging their wastewaters into rivers including the Seversky Doniets, Tom, and Belaya.

**DON RIVER TRANSPORT THROUGH TAGANROG BAY TO THE AZOV SEA DURING SPRING FLOOD**

The Russian economy currently controls and uses almost all of the water (60% probability of occurrence) of the Azov Sea basin. Irreversible usage of river water is about 30% of the average annual flow. The average annual river flow of the Azov Sea basin was 28.1 km³ in 1988, whereas wastewater discharges into the Don River were 9.4 km³ with 1.4 km³ of them untreated (Barshipotets & Ivanov, 1991). At the Lower Don River, pollution by organic compounds is the one of the worst and is growing (Bessonov et al., 1988; Volovic & Hrustalev, 1989). Fisheries resources have decreased considerably, and the economic losses due to fishing alone were about 68 million roubles a year in 1985.

The most complicated environmental situation in the Lower Don and the Taganrog Bay occurs in spring, when high runoff causes the washoff of large volumes of pollutants. Also, industrial wastes, stored during other times of the year, are discharged into the rivers during the spring. The largest volumes of pollutants enter
the Don River from its major tributary, the Seversky Donets River. One industry, the Rubezhansk Industrial Association, "Krasitel," has three wastewater storages, totalling $3 \times 10^6$ m$^3$, on the Seversky Donets River that are partially emptied into the river during the spring high-water period.

In the spring of 1989, industrial wastewaters were discharged from the storages into Seversky Donets River when the river discharge was high, in the range of 170 to 180 m$^3$ s$^{-1}$. Meanwhile, the discharge of the Don River was relatively small ranging from 400 to 500 m$^3$ s$^{-1}$. Consequently during this period, the highly polluted Seversky Donets River was not diluted much by the Don River. This period was used to model the effect of the polluted Don River on Azov Sea through the Taganrog Bay. The spring runoff period is also extremely important for fisheries reproduction in Azov Sea (Shishkin, 1988).

Although extremely high pollutant concentrations were observed in wastewaters (for example, at the "Krasitel" wastewater outflow, the Seversky Donets River contained $3 \times 10^6$ MACs of aniline, 100 thousand MACs of nitrophenol, 10 thousand MACs of chlorobenzene, and 800 MACs of trichlorobenzene), chemical evaluation of sources in Taganrog Bay proved to be difficult. Therefore, fluorescent tracers were used to study transport in the Don River estuary and the Taganrog Bay. The investigation was conducted in cooperation with Azov Scientific Research Institute of Fishery.

The tracer was added to the Don River at 45th Street in the city of Rostov. The tracer was injected uniformly across the channel, which improved mixing. Sampling sites coincided with those of an existing monitoring network established by the Azov Scientific Research Institute of Fishery. The tracer was injected at 26 April 1989 at 19 h. Water sampling was conducted along channels in of the Don estuary and in the eastern part of the Taganrog Bay on 27-28 April 1989.

The observations were evaluated for a non-stationary input, and the results indicated that the most of the pollution travels along the main branch of the Don. The highest tracer concentration occurred at the 0 km station at 20 hours, on 27 April 1989 (Fig. 2) and was 300 particles l$^{-1}$. The travel time from the injection point to the station was 25 h. In the Kalancha channel, samples were collected at the Rogozhino village and the highest tracer concentration was on 27 April 1989 at 13 h and was 120 particles l$^{-1}$.

These results indicate that pollutants entering the Don River are transported predominantly along the main channel and left channels in the estuary. The tracer concentrations in the Kalancha and Mertvy Donets channels were from 2 to 3 and from 5 to 6 times less than those in the main channel, respectively. Consequently, wastewater discharges from the right bank in the city of Rostov, which includes the highly polluted Temernik River, are transported primarily through the right estuary channels.

The tracer concentrations in the eastern part of the Taganrog Bay on 28 April 1989 are shown in Fig. 2. Most of the polluted water is in the navigable canal zone. The highest tracer concentrations (200 to 250 particles l$^{-1}$) occurred along the navigable canal, and the tracer reached the Ochakovskaya sand bar area on 28 April 1989 at 15 h. The pollutant transport was significantly faster than calculated, ranging from 22 to 23 cm s$^{-1}$ (Ereameev & Ivanov, 1987).

The last sampling throughout the Taganrog Bay was conducted on 11-13 May 1989. The corresponding tracer concentrations in the area are shown on Fig. 3. The
Fig. 2 Tracer distribution in the eastern part of the Taganrog Bay at 0.5 m below the surface on 28 April 1989: 1 — tracer injection site; 2 — the Mertvy Donets channel at the Kalinin site; 3 — the Bolshaya Kalancha channel at the Rogozhino site; and 4 — main channel at the 0 km site.
dots on the figure designate sampling stations, and the numerator is the tracer concentrations, in particles l$^{-1}$, in the surface layer (0.5 m below the surface) and the denominator is that near the bottom for locations where depth exceeded 6 m.

Between the first and the second sampling, strong eastern and western winds were observed in the Bay area. The winds promoted intensive mixing of water masses in the Bay. Regardless, a zone of high tracer concentration was maintained as evidenced by the last sampling. The persistence of high levels of pollution in the Bay suggests that the movement of polluted flood waters from the Bay to the Azov Sea was extremely complicated during the investigation. Practically speaking, the pollution does not move out of the Bay rapidly enough to provide a clean water for ecosystem functions during this particularly vulnerable time of the year.

**WASTEWATER POLLUTION OF THE NEVA RIVER INLET**

Wastewater pollution of the Neva River Inlet by wastewater facilities in St Petersburg was evaluated. The Neva River Inlet has been modified considerably through the construction of a dam to protect St Petersburg from floods driven upstream from the Baltic Sea. The dam has modified the hydrodynamics markedly which in turn is expected to have a major impact on the aquatic ecosystem. A comprehensive study and forecasts of pollution of the Neva River Inlet are feasible only with a real time evaluation of the wastewater distribution from these major pollution sources, because stagnant areas are feared to form at numerous sites in the dammed area. The principle wastewater discharges occur at the North and South-West Aeration Stations (Municipal wastewater treatment facilities) and their locations are far from optimal with respect to the altered hydrodynamics of the Inlet. Wastewater discharges from these plants are
anticipated to occur in zones having low velocity currents that will be ineffective in removing the pollution from the Neva River Inlet.

To investigate the actual wastewater transit from the North and South-West Aeration Stations, a joint expedition of the Hydrochemical Institute and the State Hydrological Institute (SHI) was conducted in July 1990. The special study focused on wastewaters plume visualization from the above sources using two different colour (red and green) tracers. The tracers were injected at the wastewater outflows and the resulting plume was tracked in space and time.

The red tracer was injected in the Inlet from the SHI expedition vessel "Preeboy" at the North wastewater treatment outflow. The green tracer was similarly injected at the South-West wastewater treatment outflow. The tracer was prepared aboard the vessel using water from the Inlet at a concentration of $1.6 \text{ g} \cdot \text{l}^{-1}$ and 200 l of tracer solution was injected through a hose 0.5 m below the surface. The entire volume of tracer was ejected in 15 min and it formed a cloud that was stretched by the long-shore current.

The tracer cloud was studied by dip sampling with a bathometer at pre-determined sites. Locations of the sites were designated on a 1:25 000 scale map aboard the base "Fiord" vessel. The "Preeboy" vessel was guided to a sampling site by radio signal from the anchored base vessel, using on-board radar. At each site, a 1-l sample was collected 0.5 m below the surface and if depth exceeded 3 m, a 1-l sample was collected from the bottom. To monitor tracer cloud movement and locate the centre of highest concentration, a 100-ml aliquot of each sample was filtered and the tracer content on the filter was semi-quantitatively determined on board the "Fiord". An on-board analysis of these data provided a basis for refining the timing and location of future sample collections. The tracer concentrations were determined more accurately and precisely on the remaining sample in the laboratory after the experiment.

The tracer was injected at the North wastewater outflow on 3 July 1990 at 14 h. The tracer concentration in the cloud formed at the injection site was 930 000 particles l$^{-1}$. A southwest wind moving at 5-10 m s$^{-1}$ was observed over the Neva River Inlet. The tracer cloud spread rapidly and moved along the bank. On 4 July from 0 to 1 h, the cloud was surveyed along four transects. At that time, the cloud centre had a concentration of 19 700 particles l$^{-1}$ and was 4120 m from the tracer injection point. The tracer moved at an average speed of 11 cm s$^{-1}$ and spread 3050 m laterally (Fig. 4).

After the early morning sampling on 4 July, the tracer did not disperse as rapidly and the wind changed direction to the east having an average speed from 2 to 5 m s$^{-1}$. Water near the bank was sampled from a motor boat at 1 m below the surface to verify independent predictions of the tracer mobility. The results from this sampling proved the forecasts to be wrong, i.e. no tracer was detected in samples taken along the bank.

The next survey was conducted on the 4 July from 10:44 to 13:18. The cloud had spread laterally to 6520 m and it contained two centres with high concentrations (5220 and 4660 particles l$^{-1}$). Between the two surveys, the cloud had moved 4850 m to the dam, which equates to a speed of 12 cm s$^{-1}$.

The tracer began to move through the dam on 4 July at 19-20 h. The highest concentrations passed through the dam on 5 July from 9:40-17:10. The tracer was detected first at the bridge and hydraulic structure No. 4 (M and B$_4$ in Fig. 4). These
Fig. 4 Spatial-temporal evolution of tracer single injection in the Neva River, 3 July 1990: 1 — water sampling vertical locations; 2 — isolines of tracer concentrations, in $10^3$ particles l$^{-1}$; 3 — dam hydraulic structures; 4 — bridge; 5 — the city of Kronshtadt; 6 — Leningrad Sea Canal; and 7 — the Lisy Nos cape.

results indicate that compared to the transport in the open inlet, the tracer movement decreased near the dam to 7-8 cm s$^{-1}$. Although it might seem easy to conclude that the change in velocity was caused by the dam, it's important to note that the same phenomenon was observed before the dam had been constructed (Azernikova & Monosov, 1979). The velocity decrease is attributed to rock fill in the Inlet between the Lisy Nos cape and the island of Kotlin, which was put there during the reign of Peter the Great. Water depths in this area are generally range from 1.2 to 1.8 m and ship traffic is confined to a narrow 7 m deep channel. The tracer travelled from the injection point to the dam in two days at an average velocity of 9-10 m s$^{-1}$, which corresponds to the average velocity of the Neva River Inlet before the dam had been constructed (Azernikova & Monosov, 1979).

The tracer injection at the South-West Aeration Station outflow was conducted on 9 July 1990 at 12:35. Unfortunately, weather conditions deteriorated rapidly and prevented sample collection of the tracer movement to the region of planned
construction of the dam’s southern part (the dam has not been constructed to the south of the Kotlin island). However, samples were collected on 10 July 1990 at 9:35-11:20 and these data indicate that the main movement of the tracer toward the Leningrad Sea Canal began to the west at a rate of 22 cm s\(^{-1}\). Under a strong south wind, the tracer spread and covered the area to the north of the Sea Canal. Meanwhile, part of tracer cloud moved slowly along the south bank of the Neva River Inlet.

**TRACER INVESTIGATIONS OF GROUND WATER POLLUTION**

As the aforementioned studies suggest, tracer techniques have proved extremely useful for investigating surface water hydrodynamics, but they also can contribute to understanding hydrogeological problems as well. The tracers were primarily developed for application in studies of water migration in fractured rocks, porous collectors, and in investigations of surface and ground water interactions through alluvial deposits in river valleys. The first experimental application of the fluorescent tracers was conducted in the Central Donbass, where the situation has become so complicated that safety of mining operation in several industrial regions was threatened by uncontrolled input of pollutants from the surface.

Investigations were conducted in the Donbass region near the city of Gorlovka (Ukraine). The region is marked by a narrow belt of linear folds stretched from northwest to southeast, covering the western part of a monocline. Rocks on the sides of the monocline dip sharply (47°-79°). The crest part of the anticline is divided by a system of tectonic fractures which occur along the entire length. Additional single small-amplitude fractures complicate the structure. The region is composed of Carboniferous deposits overlain by a 0.2-10.0 m layer of Quaternary deposits. Lithologically, the Quaternary deposits are represented by loams and the Carboniferous deposits by fractured sandstones, siltstones, and argillites interlayered with limestone and coal. Ground-water is recharged by atmospheric precipitation and surface-water infiltration in the areas where fractured Carboniferous rocks are exposed at the surface or where they are covered by a thin layer water permeable loams.

The Gorlovka Industrial Complex (GIC) includes several plants that generate environmentally hazardous materials (a coke factory, an industrial association "Styrol", a chemical plant, storages of raw materials and chemical products disposed in open landfills). These plants and related activities are potential sources of pollutants to ground waters which are used for mining operations. The objective of this investigation was to determine, by means of field tracing experiments, the migration rates and distributions of pollutant from their sources to the main aquifers and mines, and to estimate the travel time (minimum, maximum and average) for pollutants to reach the mines. For this investigation, sampling was conducted at 0.3 to 13 km from the tracer injection sites.

Results of the experiments have demonstrated that it is possible for pollutants to migrate rapidly to the mines. The time for first arrival and maximum concentrations to reach the mines were estimated. Fractures, the mining operation itself including the physical alteration of the landscape, i.e., abandoned and operating mines and pits, and significant water pumping from mines, have a significant effect on pollutant migration. Migration routes of pollutants from each of the environmentally hazardous sources
were evaluated. The sources were ranked by their potential for polluting ground water with toxic organic substances. Individual mines that have the highest threat of pollution from surface sources were identified. This investigation revealed the following advantages of the new type of tracers:

1. Although large amounts of impurities, including fluorescent ones, existed in the mine waters, the new tracers were reliably identified.

2. This type of investigation was comparatively complex and costly and the cost was primarily associated with the sampling; the price of sampling exceeded that of the analysis by an order of magnitude. For this type of study, the use of several tracers may prove extremely cost effective.

3. The simplicity of sample processing and ability to store the samples for long periods decreased analytical costs and increased the analytical efficiency by processing many samples (over 1000) at one time.

Consequently, experimental investigations conducted in the Central Donbass also demonstrated the successful use of these fluorescent tracers for a ground-water investigation involving fracture flow and mining.

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