

Original Research

**LONG-TERM PERSISTENCE OF FLUORIDE CONTAMINATION IN
ALLUVIAL GROUNDWATER: A CASE STUDY OF THE CARINA WELLFIELD
IN KLADOVO (SERBIA)**

DOI: 10.5937/EcoTER26201P

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Abstract

The paper analyzes the long-term persistence of fluoride contamination in the alluvial aquifer of the Carina wellfield in Kladovo, resulting from an accidental release in 1997. The research is based on the analysis of results from thirty years of monitoring of groundwater regime and quality under conditions of abstraction for public water supply purposes. The results show that after the initial contamination event, fluoride concentrations decreased and, after a certain period, stabilized at levels close to the legally permitted maximum values, indicating the establishment of a quasi-stationary state in the aquifer and long-term persistence of pollution. The long-term presence of fluoride in the aquifer represents a significant sanitary and public health issue, especially when groundwater constitutes the only resource for the water supply of the local population. The results of long-term monitoring and comprehensive investigations indicate that the persistence of fluoride contamination in such systems is the result of the interaction between natural and anthropogenic processes, where the management of the abstraction regime plays an important role in controlling groundwater quality.

Keywords: fluoride, groundwater, pollution, long-term monitoring, wellfield.

INTRODUCTION

Fluorine is one of the most reactive chemical elements and occurs in nature in the form of its compounds. Some of them may occur in groundwater originating from natural sources, but it can also be of anthropogenic origin, particularly in areas of intensive industrial activity. For instance, high fluoride (ion of fluorine) concentrations in groundwater represent a significant sanitary and public health issue, especially when contamination enters aquifers used for public water supply. Long-term exposure to concentrations exceeding 1.5 mg/L is considered harmful to human health according to the guidelines of the World Health Organization (2011), while the legislation of the Republic of Serbia prescribes an even stricter maximum allowable concentration of 1.2 mg/L. In heterogeneous and anisotropic alluvial aquifers of high permeability with weak protective cover layers, intensive infiltration, transport, and

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retention processes of contaminants within the porous medium often result in their long-term persistence.

The Carina wellfield in Kladovo depicts a representative example of such a system. The issue of fluoride contamination was first recognized in the mid-1990s, when detailed hydrochemical and geochemical investigations were conducted to determine the origin of contamination, the mechanisms of fluoride migration, and the risk posed to groundwater intended for public water supply. It was established that hydrofluoric acid (HF) and sulfuric acid (H_2SO_4) were used in the production of crystal glass, resulting in the generation of large quantities of waste products rich in fluorides and sulfates. Incomplete neutralization of the waste and its long-term disposal within the wider sanitary protection zone of the wellfield enabled the gradual infiltration of fluorides through a single-layer porous medium and their migration into the aquifer (Figure 1).

The long-term presence of fluoride, occurring at spatially variable concentrations, indicates complex mechanisms governing its distribution and retention. The aim of this paper is to identify the dominant transport and retention processes and to analyze the persistence of fluoride contamination based on the results of long-term monitoring of groundwater balance and quality regime parameters.

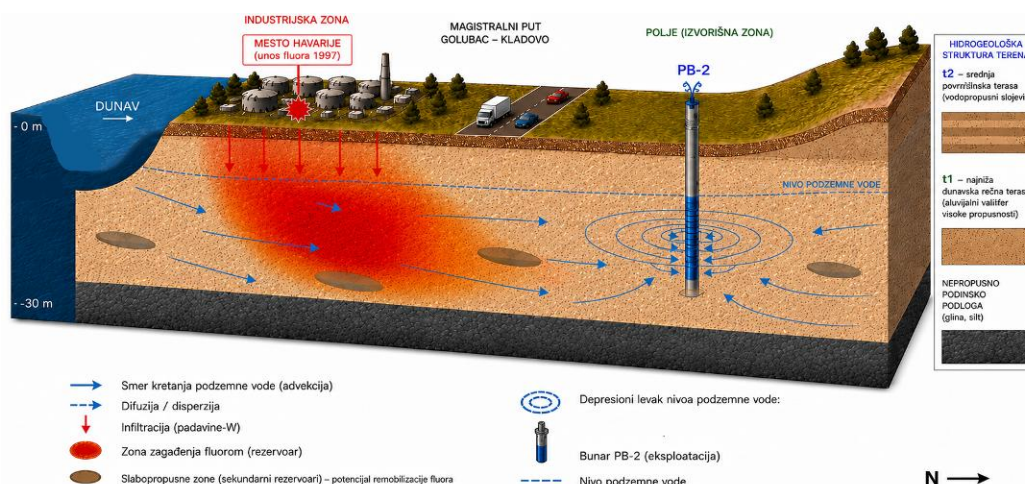


Figure 1 Conceptual model of fluoride transport in aquifer

MATERIALS AND METHODS

Methodological approach

The methodological approach applied in this study is based on the integration of two key aspects derived from the results of long-term monitoring:

1. analysis of the groundwater hydrodynamic regime (quantitative approach) and
2. analysis of geochemical processes (qualitative approach).

The first part of the methodological approach involves determining the groundwater regime and water balance, which represents the primary prerequisite for further defining contaminant migration. It is based on the results of continuous long-term monitoring of all influencing regime factors (groundwater and surface water levels, vertical water balance

parameters, groundwater abstraction at the wells of the Carina wellfield, as well as the operation of the groundwater protection system).

The second part of the methodological approach refers to the identification of geochemical processes and governing principles that determine the chemical behavior of fluorine in a porous medium. Particular importance is given to the analysis of the conditions under which fluorine remains dissolved in groundwater or precipitates into the solid phase, since these processes directly control its mobility, migration, and long-term persistence within the aquifer. One of the most important factors affecting dissolved fluoride concentrations is the relationship between calcium and fluoride in groundwater. Under conditions of elevated calcium content, fluoride ions become bound through the formation of sparingly soluble mineral phases, thereby reducing fluoride concentrations in solution and limiting its migration through aquifer layers:



In contrast, in environments with lower calcium content, fluoride remains more mobile and is more easily transported through the aquifer.

Adsorption and desorption processes within fine-grained sediments also play a significant role. Silty and clayey interlayers present within the alluvial aquifer, due to their high content of clay minerals and iron oxides, represent important adsorption surfaces where fluoride can be temporarily retained. Such layers function as secondary contamination reservoirs because changes in hydrochemical conditions may lead to the gradual release of adsorbed fluoride back into the groundwater. This process contributes to the long-term persistence of contamination even after the cessation of active fluoride input into the system.

An important factor in assessing fluoride behavior is the acidity of the environment. Variations in pH values directly affect fluoride mobility, adsorption intensity, and the potential for the formation of complex compounds. The prolonged presence of acidic components may alter the geochemical equilibrium within the aquifer, increase fluoride mobility, and intensify its migration through groundwater.

Long-term monitoring of the groundwater regime

Long-term monitoring represents the basis for understanding the “slow” hydrogeological and geochemical processes that develop over several decades. During the thirty-year period from 1995 to 2025, systematic regime observations [1] were carried out in the zone of the Carina wellfield in Kladovo as illustrated in Table 1.

Table 1 Monitoring data Gantt chart

		95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
		Water Quantity Monitoring																														
Hydrological parameters																																
Climatic parameters																																
Groundwater levels																																
Water source exploitation																																
		Water Quality Monitoring																														
Groundwater Quality	Standard																															
	Detailed																															
River Quality																																

Contamination of the Carina wellfield with fluorides

Research results have shown that fluoride contamination of the Carina wellfield is directly related to the operation of a crystal glass factory, most likely of the K_2O – PbO – SiO_2 type, in which hydrofluoric and sulfuric acids were used during chemical processing. Under such conditions, fluorine occurs in highly soluble and extremely mobile forms, capable of rapid infiltration through porous sediments and migration through groundwater. In the glass processing industry, fluorine is most applied in the form of hydrofluoric acid or gaseous hydrogen fluoride, where it causes etching of the glass and reacts with SiO_2 , forming gaseous silicon fluorides (H_2SiF_6). The solutions used in this process contain various agents such as K_2O , CaO , PbO , or a mixture of $HF + H_2SO_4 + H_2O$, while after completion of the technological process, neutralization and proper waste storage are required. In the basins of the former glass factory in Kladovo, both soluble waste phases ($KHSO_4$, KHF_2) and insoluble phases ($PbSO_4$, K_2SiF_6) were detected, indicating the presence of fluoride compounds of varying solubility and mobility within industrial waste. Based on this knowledge, in the period 1995–1997, detailed investigations were carried out in the wider zone of the Carina wellfield by the Faculty of Mining and Geology. These studies included hydrochemical analyses of groundwater (from production and dug wells, piezometers, and even deeper artesian wells), geochemical analyses of soils and sediments, and assessment of fluoride migration through soil and aquifer layers. It was determined that the sources of contamination were the old and new crystal glass factories “Kristal,” where the technological process involved the dissolution of silicon dioxide and the formation of soluble fluoride compounds.

Temporal dynamics of fluoride concentration

Long-term monitoring analysis indicates three characteristic phases in the evolution of contamination. The first phase is the “accidental peak” phase (1995–1998), during which maximum fluoride concentrations were recorded immediately after the incident (in the nearest well PB-2, average values exceeded 4.0 mg/L, significantly above the maximum allowable concentration [2] (MAC 1.2 mg/L)). This was followed by an “intensive attenuation” phase, during which, due to natural aquifer flushing and the cessation of the contamination source, fluoride concentrations decreased (in PB-2 to an average of about 2.0 mg/L). Over the last 15 years, a phase of establishment of a “quasi-stationary” state has occurred, in which the decreasing trend has completely stopped. Concentrations have stabilized in the range of 1.0–1.2 mg/L (around the MAC), indicating that the system has reached a dynamic equilibrium. Figure 4 presents the temporal dynamics of fluoride concentration over the monitoring period 1995–2025 (note: complete data series were not available for PB-2 in 2005 and for PB-1 in 2008).

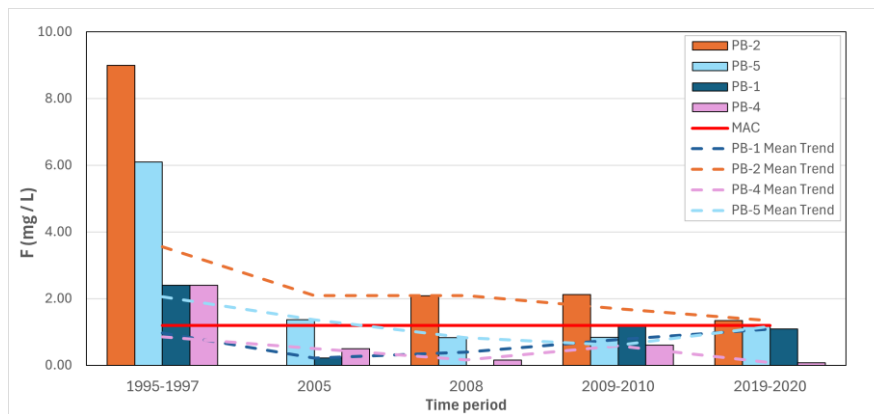


Figure 4 Temporal dynamics of fluoride concentration during monitoring period 1995–2025

Spatial migration dynamics of the contamination as a function of groundwater regime

Results of the three-decade monitoring indicate pronounced spatial heterogeneity in fluoride distribution within the aquifer of the Carina wellfield in Kladovo. In addition to geochemical processes, the degree of contamination is primarily influenced by the established groundwater regime, whose parameters were continuously monitored throughout the entire study period (Figure 3). Data analysis shows that contaminant migration within the aquifer is strictly controlled by the dominant hydraulic gradient, which is governed both by natural conditions (influence of the Danube River) and anthropogenic factors (operation of production wells and the peripheral protection system of the settlement).

Figure 5 presents the spatial distribution of average fluoride concentrations for the period 1995–1997 (contamination phase).

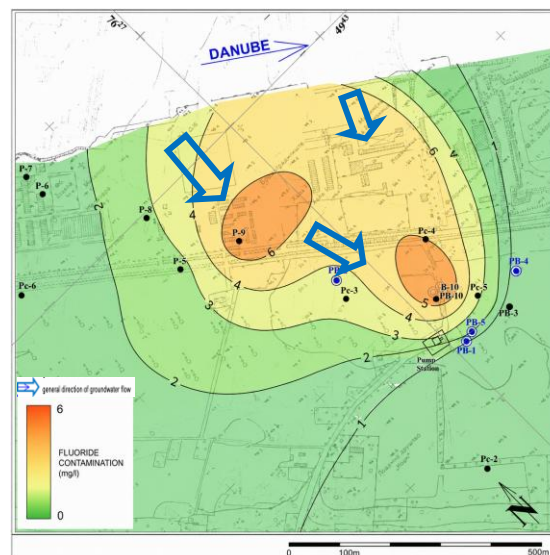


Figure 5 Fluoride contamination of the Carina groundwater wellfield – spatial distribution

Within the wellfield, distinct zones can be identified: zones of minimal impact (“clean zones”), which include water facilities located upstream or in close proximity to the Danube River, as well as wells positioned laterally relative to the main contaminant flow path (PB-4),

where fluoride concentrations remain stable and close to natural background levels ($< 0.5\text{--}1.0\text{ mg/L}$). In contrast, a zone of maximum impact is also identified, encompassing the immediate vicinity of well PB-2 (formerly PB-10) and the associated piezometer network. The contaminated wells are located along the direct hydraulic flow path from the primary source (the glass factory) and consistently record the highest fluoride concentrations throughout the entire monitoring period (values per period shown at Figure 4). The established groundwater regime, together with intensive abstraction at the wellfield, has created a stable pathway of the contamination front directed toward the most productive part of the wellfield.

Correlation of changes in fluoride concentration with other relevant parameters

For the purpose of interpreting the basic hydrochemical composition of groundwater at the Carina wellfield, the Schoeller diagram was used. This representation indicates that at location the source groundwater is primarily of the bicarbonate-calcium type (Figure 6).

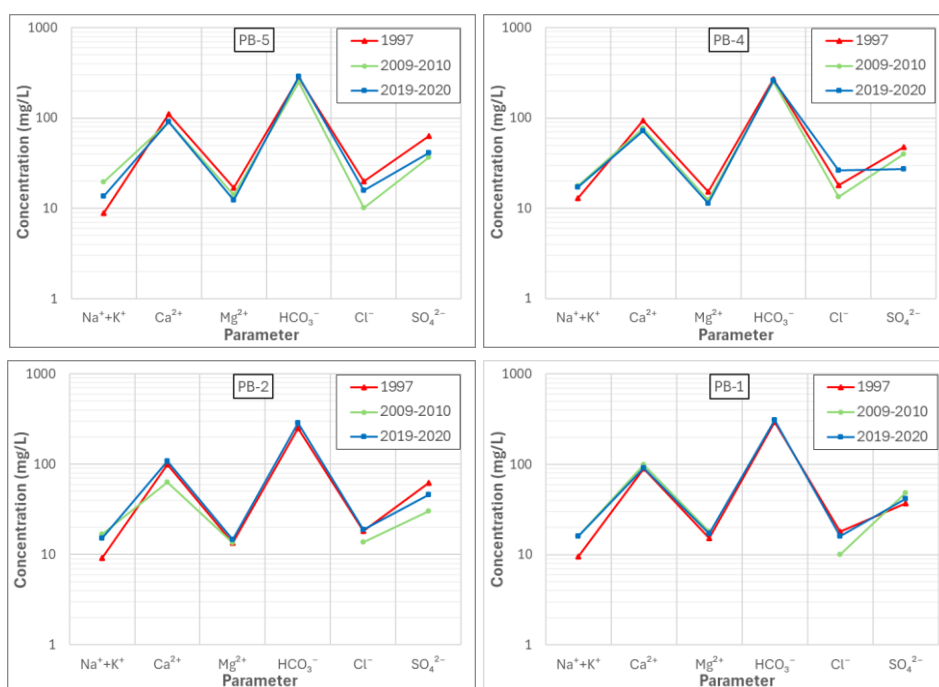


Figure 6 Schoeller diagram of the basic hydrochemical composition of groundwater

Statistical data processing and correlation analysis of the investigated parameters enabled the identification of the key correlation factors controlling the distribution and persistence of fluoride in the aquifer. It should be noted that the presented data include all monitoring locations, which are spatially unevenly distributed with respect to the contamination trend, resulting in the nonlinearity of the observed functions.

- Coupled migration of F^- and SO_4^{2-} ions:

A pronounced positive correlation was identified, indicating the synchronous migration of these ions and representing a direct indicator of the anthropogenic origin of contamination, i.e., that fluoride originates from the same technological process in which sulfuric acid was used (Figure 7A).

- Thermodynamic control of fluoride saturation (correlation between F^- and Ca^{2+} concentrations):

A moderate inverse correlation was observed, indicating that fluoride concentrations in the aquifer are controlled by equilibrium with the mineral fluorite (CaF_2). Under conditions of elevated calcium content, fluorite precipitation occurs to a certain extent, thereby naturally limiting fluoride mobility. In contrast, a decrease in calcium concentration in groundwater induces an increase in fluoride concentrations. However, the moderate strength of the correlation suggests that additional natural factors also influence aquifer contamination (Figure 7B).

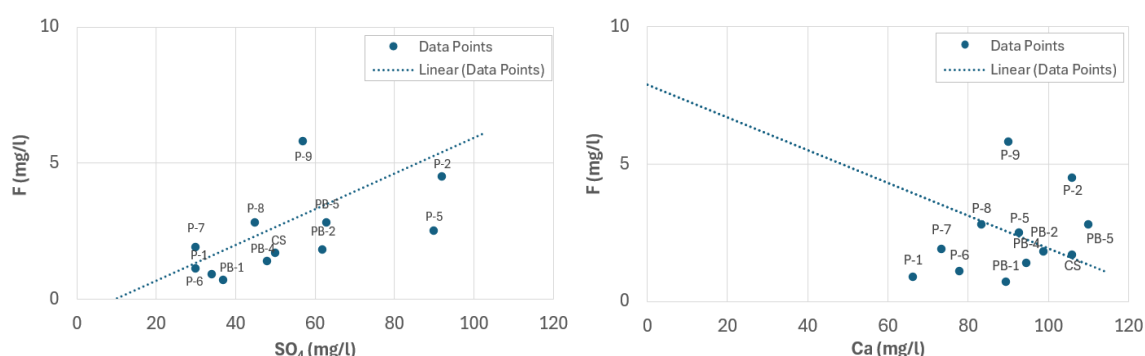


Figure 7 Correlation of fluoride concentrations with sulfate concentrations (7A) and calcium ion concentrations (7B) during the 1995–2025 period

- Cation exchange processes:

A negative correlation between sodium (Na^+) and calcium (Ca^{2+}) suggests ion-exchange processes occurring on clay and fine-grained mineral surfaces. Adsorption of Ca^{2+} accompanied by the release of Na^+ further decreases solution saturation with respect to fluoride-bearing minerals, thereby facilitating additional fluoride mobilization into groundwater.

- Desorption mechanisms under alkaline conditions (F^- and HCO_3^-):

The positive correlation indicates that alkaline conditions promote fluoride desorption from the surfaces of iron and aluminum oxides, contributing to its persistence in the aquifer even after the flushing of the primary contamination source.

- Heavy metal mobility and aquifer neutralization capacity:

Despite the confirmed presence of Pb in the waste material, Pb concentrations in groundwater remained below the detection limit throughout three decades of monitoring. This is attributed to the formation of sparingly soluble lead sulfate ($PbSO_4$) within the initial contamination zone, which prevented further migration of this metal toward the pumping wells. Contamination by sulfur, silicon, and other harmful substances was not detected within the wider source area due to their generally limited migration capacity. In addition, analyses showed no significant relationship between pH and fluoride concentrations, indicating that the initially acidic wastewater was largely neutralized along its flow path toward the groundwater abstraction zone.

CONCLUSION

Thirty years of quantitative and qualitative monitoring at the Carina wellfield provided valuable insight into the long-term dynamics of fluoride contamination in an alluvial aquifer, as well as the key factors controlling its persistence. A major contribution of this study is the identification of anthropogenic influences on contamination fate. Intensive groundwater abstraction modifies hydraulic gradients and potentially remobilizes contaminated water from silty and clayey sediments, thereby sustaining contamination long after the primary pollution source was removed. As a result, continuous exploitation reduces the natural flushing capacity of the aquifer and maintains the system in a quasi-stationary state. Hence, groundwater exploitation cannot be seen only as a remediation mechanism, but also as a possible driver of contaminant transport. Therefore, sustainable management of such resources requires integrated (long-term) monitoring and optimized abstraction strategies to effectively control long-term environmental risk.

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