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THERMODYNAMIC CONTROL OF HEXAVALENT CHROMIUM AND BORON MOBILITY IN A RIVER SYSTEM: THE ILEK RIVER CASE STUDY

Annotation. Persistent contamination of river systems by inorganic pollutants is often sustained by secondary sources and subsurface transport processes rather than by active point discharges. This study investigates the thermodynamic and hydrogeological controls on the mobility of hexavalent chromium (Cr(VI)) and boron (B) in a technogenically disturbed river system, using the Ilek River (Kazakhstan) as a case study.

Field measurements show that both surface water and hydraulically connected groundwater are characterized by neutral to alkaline pH (7.2–9.0) and persistently oxidizing conditions (Eh +300 to +600 mV). Thermodynamic analysis in Eh–pH space demonstrates that these conditions fully coincide with the stability field of dissolved Cr(VI), rendering its natural reduction to Cr(III) thermodynamically unfavorable in the absence of external reducing agents. In contrast, boron is shown to be redox-insensitive, with its aqueous speciation controlled solely by acid–base equilibrium between H_3BO_3 and $B(OH)_4^-$, resulting in persistent dissolved behavior across the observed pH range.

Integration of thermodynamic calculations with hydrogeological data confirms that groundwater constitutes the dominant transport pathway for both contaminants from technogenic sludge repositories to the river, forming stable plume-type structures in permeable alluvial sediments. The absence of effective natural attenuation mechanisms explains the chronic nature of river contamination and the limited effectiveness of mitigation measures focused exclusively on surface waters.

Based on these findings, a thermodynamically justified management framework is proposed, emphasizing source stabilization, targeted Cr(VI) immobilization via reduction to Cr(III), and interception of groundwater flow. The results provide a transferable mechanistic basis for managing secondary contamination in other technogenically impacted river–groundwater systems.

Keywords: hexavalent chromium (Cr(VI)); boron; Eh–pH thermodynamics; groundwater–surface water interaction; secondary contamination; alluvial aquifer; river pollution; source–pathway–receptor concept; natural attenuation limits.

Introduction

Pollution of surface waters by persistent inorganic toxicants remains one of the major environmental challenges at the global scale, as these substances are characterized by high mobility, chemical stability, and the ability to persist in aquatic ecosystems over long time periods. Unlike organic contaminants, inorganic elements are not subject to biodegradation, and their behavior in natural water systems is governed by fundamental geochemical and

thermodynamic principles that control their speciation, mobility, and migration between different compartments of the hydrosphere [1,2].

Among such contaminants, hexavalent chromium (Cr(VI)) and boron (B) occupy a particularly important position. Cr(VI) is recognized as one of the most toxic and carcinogenic forms of chromium, characterized by high solubility and mobility under oxidizing conditions in aquatic environments [3,4]. Boron, despite its lower acute toxicity, is distinguished by high solubility, weak sorption behavior, and the ability to form persistent background contamination that exerts chronic effects on aquatic organisms and ecosystems [5–7].

Recent studies demonstrate that persistent river contamination is often sustained not by ongoing point-source discharges, but by secondary sources associated with technogenically disturbed areas and accumulated industrial wastes [8,9]. In such systems, technogenic waste repositories may function as long-term geochemical “reactors”, continuously releasing contaminants into groundwater and surface waters for decades after the cessation of active industrial operations [10]. Conceptually, this process is expressed as a stable linkage between the source (technogenic mass) → subsurface transport → discharge into the river**,** which ultimately controls the long-term contaminant load on the aquatic system. Figure 1 illustrates a conceptual scheme of secondary contamination of the Ilek River originating from chromium waste accumulation sites.

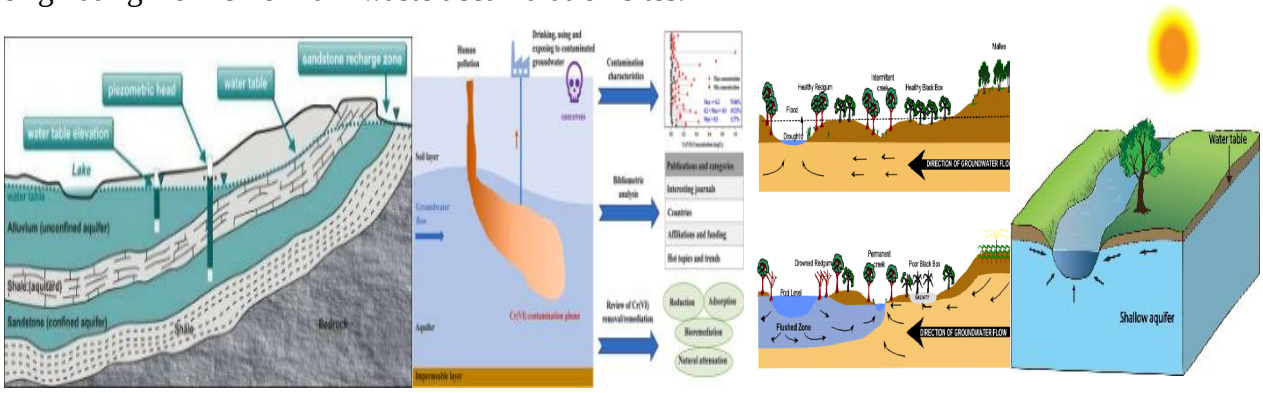

Figure 1 – Conceptual model of secondary contamination of the Ilek River (compiled by the author)

A key aspect that remains insufficiently considered in the analysis of such systems is the thermodynamic control of contaminant migration**.** For Cr(VI), stability and mobility are directly governed by Eh and pH conditions under which dissolved chromium oxyanions are thermodynamically favored, while the transformation to the less mobile Cr(III) species is strongly constrained in the absence of external reducing interventions [10,11].

Similarly, boron remains predominantly in dissolved form across a wide range of hydrochemical conditions and is not subject to redox transformations , variations in pH primarily control the distribution between boric acid (H_3BO_3) and the borate ion ($B(OH)_4^-$) [5,6]. These patterns are collectively summarized within the thermodynamic framework of Eh–pH control governing the coupled migration of chromium and boron.

A conceptual Eh–pH diagram illustrating the thermodynamic controls on the coupled mobility of Cr(VI) and boron in the Ilek River system is presented in Figure 2.

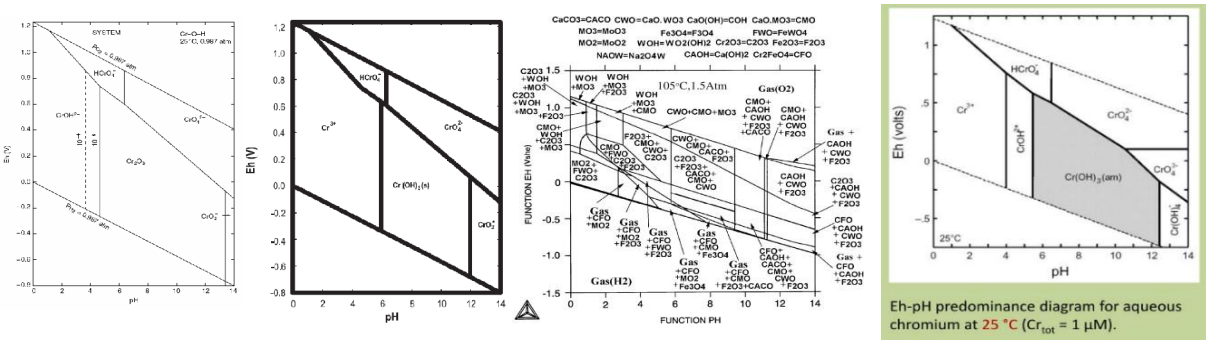

Figure 2 – Conceptual Eh–pH diagram controlling the coupled mobility of Cr(VI) and boron in the Ilek River system (constructed by the author)

Despite the availability of extensive monitoring data, most studies addressing river contamination by Cr(VI) and boron remain largely limited to the description of concentration levels and risk assessment. Such approaches are insufficient to explain the persistence of contamination and to support the development of effective long-term management strategies [7,12]. As a result, management measures often focus on surface manifestations of pollution, while secondary fluxes mediated by groundwater and thermodynamic constraints on natural attenuation remain inadequately formalized.

In this context, the Ilek River represents a representative example of a technogenically disturbed river system, where contamination by Cr(VI) and boron is of secondary origin and is sustained by groundwater discharge [13,14]. However, the thermodynamic drivers of contamination persistence and the role of technogenic sludge repositories as long-term contaminant sources have not yet been sufficiently integrated into a unified mechanistic framework suitable for supporting management and remediation decisions [15,16].

The objective of the present study is to provide a thermodynamic justification for the stability and mobility of Cr(VI) and boron in a technogenically impacted river system, using the Ilek River as a case study, and to subsequently evaluate the implications of these findings for the management and remediation of contaminated sites.

Literature Review

Chromium (VI) behavior in aquatic and groundwater systems

Hexavalent chromium (Cr(VI)) is widely recognized as one of the most problematic inorganic contaminants in aquatic environments due to its high toxicity, carcinogenicity, and mobility under oxic conditions. Numerous studies have demonstrated that, unlike trivalent chromium (Cr(III)), which tends to form sparingly soluble hydroxides and is readily immobilized in sediments, Cr(VI) predominantly exists as soluble oxyanions (CrO_4^{2-}, $HCrO_4^-$), enabling its efficient transport in both surface and groundwater systems [10,11,15,16].

The stability and speciation of chromium in natural waters are strongly controlled by redox potential (Eh) and pH. Classical thermodynamic studies and Pourbaix diagrams indicate that Cr(VI) is thermodynamically favored under oxidizing and neutral to alkaline conditions, whereas Cr(III) becomes stable only under reducing environments [27,34]. Field-based investigations in contaminated aquifers and rivers confirm that where Eh values remain positive and oxygen is readily available, natural reduction of Cr(VI) is strongly limited, even over long time scales [18,19].

Several studies emphasize that persistent Cr(VI) contamination is often associated with secondary or legacy sources rather than active industrial discharges. Alluvial aquifers impacted by chromite ore processing residues, tailings, or sludge deposits have been shown to generate long-lived Cr(VI) plumes, sustained by groundwater flow and characterized by limited attenuation [8,18,20]. These findings highlight that Cr(VI) persistence is frequently governed by thermodynamic constraints rather than by the absence of reactive surfaces or microbial activity alone.

Boron mobility and speciation in natural waters

Boron behaves fundamentally differently from redox-sensitive metals such as chromium. In natural waters, boron does not participate in oxidation–reduction reactions and exists predominantly in dissolved form, controlled by acid–base equilibria between boric acid (H_3BO_3) and the borate ion ($B(OH)_4^-$) [5,6]. The dissociation constant of boric acid ($pK_a \approx 9.2$

at 25 °C) implies that over the pH range typical for most rivers and aquifers, boron remains highly soluble and weakly reactive with mineral phases.

Experimental and field studies consistently demonstrate low sorption capacity of boron onto common sedimentary minerals, especially under neutral to alkaline conditions, resulting in conservative transport behavior similar to that of major ions [6,7]. As a consequence, boron contamination frequently manifests as diffuse, long-lasting background pollution rather than localized accumulation zones. This property makes boron a useful tracer of groundwater flow paths but simultaneously complicates remediation efforts, as changes in redox conditions do not lead to its immobilization.

In technogenically impacted systems, elevated boron concentrations are commonly associated with industrial residues, coal combustion products, and metallurgical wastes, from which boron is readily leached into groundwater [5,20]. Long-term monitoring data confirm that boron concentrations often remain stable over time, reflecting continuous input from secondary sources rather than episodic contamination events.

Groundwater–surface water interaction and secondary contamination

The role of groundwater as a dominant pathway for contaminant transport to rivers has been increasingly emphasized in recent hydrological and geochemical studies. Groundwater discharge can sustain elevated concentrations of dissolved contaminants in surface waters even in the absence of direct surface inputs, a phenomenon widely referred to as secondary or legacy contamination [8,21].

In alluvial river systems with high-permeability sediments, groundwater–surface water exchange facilitates efficient transfer of contaminants from technogenic deposits to the river channel. Studies conducted in Europe, North America, and Asia demonstrate that such systems often exhibit persistent contamination plumes, where contaminant fluxes are controlled primarily by hydraulic gradients and aquifer properties rather than by surface water processes [22,33].

This conceptual framework is particularly relevant for contaminants that remain thermodynamically stable in dissolved form, such as Cr(VI) under oxidizing conditions and boron across a wide pH range. In these cases, the absence of effective geochemical barriers results in sustained contaminant delivery to rivers, limiting the effectiveness of remediation strategies focused solely on surface water treatment [21-24].

Limitations of concentration-based approaches and need for thermodynamic interpretation

Although extensive literature exists on the occurrence and environmental risks of Cr(VI) and boron, most studies rely primarily on concentration measurements and statistical correlations. While such approaches are essential for regulatory assessment, they provide limited insight into the fundamental reasons for contaminant persistence and the failure of natural attenuation processes [7,12,16].

Recent reviews highlight the need to integrate thermodynamic principles into the interpretation of field data, particularly through the use of Eh–pH frameworks and stability field analysis. Without such integration, remediation strategies may target symptoms rather than causes, leading to short-lived or ineffective outcomes. Despite this recognition, few studies have combined groundwater flow analysis with thermodynamic constraints to develop unified conceptual models applicable to management decision-making [20].

Research gap and conceptual contribution of the present study

Based on the reviewed literature, it is evident that while the individual behaviors of Cr(VI) and boron are well documented, their coupled persistence in technogenically disturbed

river–groundwater systems has not been sufficiently addressed from a thermodynamic perspective. In particular, there is a lack of integrative studies that link secondary sources, groundwater transport, and Eh–pH-controlled stability into a single mechanistic framework.

The present study addresses this gap by applying a thermodynamic interpretation to the coupled migration of Cr(VI) and boron in the river Ilek system. By combining hydrochemical observations with Eh–pH analysis, this work provides a mechanistic explanation for the long-term stability of contamination and offers a scientifically grounded basis for the development of effective management and remediation strategies [23-24].

Materials and Methods

Study system and technogenic background

The Ilek River is considered a technogenically disturbed river system, whose functioning is governed by the interaction between surface water and groundwater within an alluvial valley. The alluvial deposits are composed predominantly of sand and gravel with high hydraulic permeability, creating favorable conditions for intensive infiltration recharge of groundwater and its subsequent discharge into the river channel [25-26].

Within the river basin, technogenic sludge repositories formed as a result of chromium production are present. These facilities contain substantial amounts of trivalent chromium compounds, residual quantities of Cr(VI), and associated elements, including boron. Under alkaline conditions and in the presence of oxygen, these technogenic deposits function as long-term secondary sources of contamination, supplying dissolved forms of Cr(VI) and boron to groundwater over extended periods [4,10,11].

Sampling design and field measurements

Sampling of surface water and groundwater was conducted within the river channel of the Ilek River and the adjacent alluvial aquifer in order to assess hydrochemical conditions and the migration forms of Cr(VI) and boron. Surface water samples were collected directly from the river channel, whereas groundwater samples were obtained from monitoring points hydraulically connected to the zones influenced by technogenic sludge repositories [27-28].

Sampling was performed under quasi-steady hydrological conditions, which minimized the influence of short-term flood events or accidental disturbances and allowed the focus to be placed on persistent mechanisms of secondary contamination. All samples were collected in pre-cleaned, chemically inert containers, immediately cooled, and transported to the laboratory for subsequent analysis.

Field parameters, including pH and redox potential (Eh), were measured *in situ* using calibrated portable instruments. Measured Eh values were converted to the standard hydrogen electrode (SHE) by accounting for the type of reference electrode used [29].

Groundwater–surface water interaction

Groundwater is considered the primary vector for contaminant transport from technogenic sources to the river system. Migration of dissolved Cr(VI) and boron occurs within the alluvial aquifer, forming zones of persistently elevated concentrations analogous to “chromium plumes” described in other technogenically impacted alluvial systems [26-28].

Groundwater discharge into the river channel sustains chronic contamination even in the absence of active surface discharges, fundamentally distinguishing this type of pollution from short-term contamination episodes associated with accidental or episodic industrial releases.

Analytical methods

The concentrations of hexavalent chromium (Cr(VI)) were determined using a selective colorimetric method based on diphenylcarbazide, which is widely applied for the analysis of

Cr(VI) in natural waters. Total chromium concentrations were measured after preliminary sample mineralization, followed by instrumental analysis. Boron concentrations were quantified using instrumental analytical techniques providing low detection limits and high analytical reproducibility [30-32].

All analytical procedures were performed in accordance with internationally accepted methodological protocols for the determination of trace elements in aquatic environments. The method detection limits were substantially lower than the concentration ranges observed in the studied system, thereby minimizing the risk of analytical artifacts during data interpretation [32-33].

Quality assurance and quality control (QA/QC)

Quality control of the analytical data was ensured through the systematic use of method blanks, duplicate samples, and certified reference materials. Measurement precision was evaluated using a series of parallel determinations, with deviations not exceeding the acceptable limits established for trace-level analysis [33].

Instrument calibration was performed using standard solutions prepared from certified reference materials. All data that did not meet the predefined quality assurance criteria were excluded from subsequent analysis.

Hydrochemical framework

The hydrochemical conditions of both river water and groundwater are characterized by neutral to slightly alkaline pH values and an oxidizing environment, which represent key controlling factors governing the speciation, stability, and mobility of chromium (Cr) and boron (B).

To systematize these conditions and clarify their role in contaminant migration, a generalized set of hydrochemical parameters was applied (Table 1), reflecting the thermodynamically controlled stability fields of Cr(VI) and dissolved boron species under the prevailing pH–Eh conditions [34-35].

Table 1 – Hydrochemical conditions controlling Cr(VI) and boron mobility in the river–groundwater system

Parameter	Typical range	Dominant form	Implication for mobility
pH	7.2–8.8	CrO_4^{2-} / $HCrO_4^-$	High Cr(VI) solubility
Eh (mV)	+300 to +600	Oxidizing conditions	Stabilization of Cr(VI)
Chromium speciation	Cr(VI)	Aqueous oxyanions	High mobility
Boron speciation	H_3BO_3 / $B(OH)_4^-$	Dissolved forms	Persistent background
Redox sensitivity	Cr: high , B: negligible	—	Limited natural attenuation

Note – compiled by the author based on [34–37]

Thermodynamic and statistical analysis

The interpretation of Cr(VI) and boron behavior was carried out using a thermodynamic approach based on the analysis of element stability fields in Eh–pH space. For chromium, Pourbaix diagrams and thermodynamic parameters reported in classical studies of aqueous geochemistry [32,35], as well as modern interpretations of natural aquatic systems, were employed.

For boron, the analysis was restricted to the acid–base equilibrium between H_3BO_3 and $B(OH)_4^-$, while the influence of redox conditions was considered negligible due to the redox-insensitive nature of boron in natural waters [5–6].

Statistical data treatment included descriptive analysis and comparison of the observed ranges of hydrochemical parameters with the thermodynamic stability domains of the corresponding elemental species. This integrated approach enabled the observed

concentration patterns to be interpreted within the framework of fundamental geochemical constraints governing the system.

Results

Hydrochemical conditions of the river–groundwater system

The results of field measurements indicate that both surface water and groundwater within the investigated system are characterized by stable neutral to alkaline pH values and an oxidizing redox regime. In surface waters, pH values ranged from 7.2 to 8.8, whereas in groundwater hydraulically connected to technogenic sludge storage facilities, the pH range was slightly higher, varying between 7.4 and 9.0.

The redox potential (Eh), normalized to the standard hydrogen electrode, ranged from +300 to +600 mV, corresponding to persistently oxidizing conditions (Table 1).

The observed pH–Eh ranges fully overlap with the thermodynamic stability field of dissolved hexavalent chromium species and are consistent with conditions typically reported for alluvial aquifers characterized by active gas exchange and unrestricted oxygen availability [34,39-40]. These hydrochemical conditions establish a geochemical framework within which further transformations of Cr and B are thermodynamically constrained, thereby limiting their possible speciation and mobility pathways.

Chromium speciation and thermodynamic stability

The analysis of chromium speciation indicates that dissolved hexavalent chromium (Cr(VI)) is the dominant form in the investigated waters. This finding is consistent with both the analytical results and the thermodynamic stability calculations of chromium species in Eh–pH space (Fig. 2).

The key reaction governing the potential transformation of Cr(VI) into the less mobile trivalent form, Cr(III), can be expressed as:

$$CrO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Cr(OH)_3(s) + 5OH^- \qquad (1)$$

Under standard conditions, the equilibrium potential of reaction (R1) is significantly lower than the measured Eh values. Substitution of representative field conditions (pH ≈ 8 and corresponding hydroxide ion activities) into the Nernst equation demonstrates that, at Eh > +300 mV, equilibrium (R1) is strongly shifted toward the stability of dissolved Cr(VI) oxyanions. Consequently, the reduction of Cr(VI) to Cr(III) under the natural conditions of the system is thermodynamically unfavorable in the absence of an external reducing agent [10,35].

Thus, the observed predominance of Cr(VI) in the aqueous phase does not represent an anomaly or a result of random variability, but rather reflects the expected and thermodynamically controlled state of the system under the prevailing hydrochemical conditions.

Behavior of boron in the river–groundwater system

In contrast to chromium, boron is insensitive to redox conditions and remains in the dissolved phase across the entire range of measured Eh values. Its behavior is primarily controlled by acid–base equilibrium, expressed as:

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \qquad (2)$$

The dissociation constant of this reaction (pKa ≈ 9.2) indicates that at pH < 8 the neutral species boric acid (H_3BO_3) predominates, whereas at higher pH values the proportion of the borate ion ($B(OH)_4^-$) increases [5,6]. Both species exhibit high aqueous solubility and weak interactions with the mineral phase, which explains the absence of pronounced boron accumulation zones in solid sediments.

As a result, boron forms a persistent background contamination, spatially associated with groundwater discharge zones, but without exhibiting the sharp concentration gradients typical of elements strongly affected by sorption or precipitation processes [7,35].

Coupled Cr–B transport and groundwater control

Integration of the hydrochemical dataset with the results of the thermodynamic analysis confirms that groundwater represents the dominant transport pathway for Cr(VI) and boron from technogenic sludge storage facilities to the river channel (Fig. 1). The high permeability of alluvial deposits facilitates efficient migration of dissolved contaminant species with minimal alteration of their chemical speciation along the flow path.

Within the groundwater flow system, a zone of persistently elevated dissolved chromium concentrations develops, analogous to the chromium plume reported for other technogenically impacted alluvial environments [26,28]. In contrast, boron exhibits a more uniform spatial distribution, reflecting its high intrinsic mobility and the absence of thermodynamic or geochemical barriers to migration under the prevailing hydrochemical conditions.

Absence of effective natural attenuation

The obtained results unequivocally indicate the absence of effective natural attenuation mechanisms within the studied system. For Cr(VI), reduction to the less mobile Cr(III) form is strongly inhibited by the persistently oxidizing redox conditions, whereas for boron, no processes of precipitation or irreversible fixation within the solid phase are operative.

Consequently, under the prevailing hydrochemical regime, the system remains in a thermodynamically stable state that favors the long-term persistence and migration of both contaminants. As long as these conditions are maintained, neither chromium nor boron is subject to significant natural removal, allowing their continued transport within the river–groundwater system [34].

Discussion

Why Cr(VI) remains thermodynamically stable in the river–groundwater system

The hydrochemical results (Section 3.1) demonstrate that both surface water and groundwater are characterized by persistently neutral to alkaline pH values and oxidizing conditions (pH 7.2–9.0 , Eh +300 to +600 mV). These conditions fully correspond to the thermodynamic stability field of dissolved hexavalent chromium species. This relationship is clearly illustrated by the position of the river-water “window” relative to the Cr(VI)/Cr(III) stability boundary on the Eh–pH diagram.

In other words, the thermodynamic control of chromium speciation is expressed by the Eh–pH boundary of the Cr(VI)/Cr(III) redox couple, which lies well below the typical Eh–pH range observed for the river–groundwater system (Fig. 3). Under such conditions, the reduction of Cr(VI) to Cr(III) is thermodynamically unfavorable, ensuring the long-term persistence of mobile Cr(VI) species in both surface and subsurface waters.

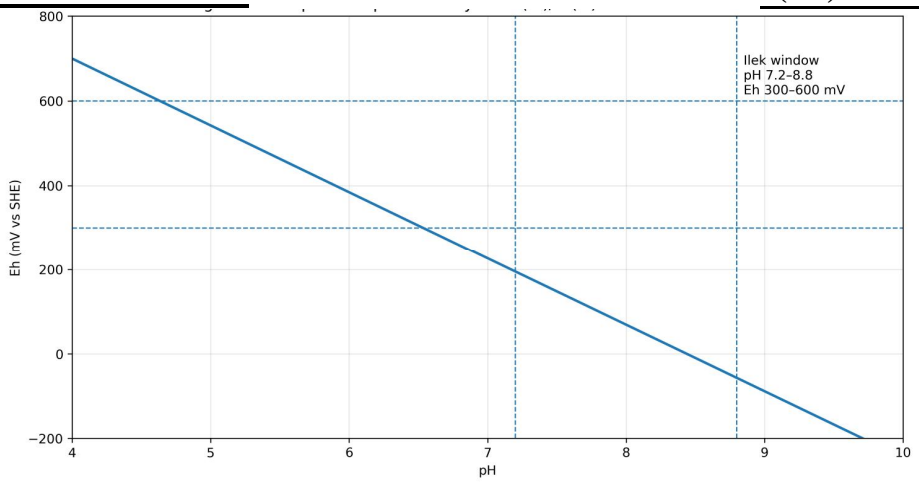

Figure 3 – Conceptual Eh–pH boundary for the Cr(VI)/Cr(III) redox couple in comparison with the river-water domain (constructed by the author)

The equilibrium line for the Cr(VI)/Cr(III) redox couple was calculated using the Nernst equation for the reaction

$$CrO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O \qquad (3)$$

assuming equal activities of dissolved species at the equilibrium boundary. The typical pH–Eh range of river water (pH 7.2–8.8 , Eh +300 to +600 mV) lies well above this boundary, indicating the thermodynamic stability of dissolved Cr(VI) under oxidizing, neutral to alkaline conditions [10,11].

From a thermodynamic perspective**,** this implies the following. At elevated Eh values, the system energetically favors chromium species at their highest oxidation state. Under such conditions, the reduction of Cr(VI) to Cr(III) can occur only in response to a substantial decrease in redox potential or in the presence of a strong reducing agent**.**

Calculations based on the Nernst equation for the Cr(VI) reduction reaction (Section 3.2) demonstrate that at Eh > +300 mV, equilibrium is strongly shifted toward dissolved Cr(VI) oxyanions (CrO_4^{2-} and $HCrO_4^-$)**,** whereas the stability field of Cr(III) is confined to significantly lower Eh values (Fig. 3). Consequently, under the natural conditions of the investigated system, Cr(VI) reduction is thermodynamically unfavorable and cannot be regarded as an effective mechanism of natural attenuation [10–11].

Thus, the persistent presence of Cr(VI) in the aqueous phase is not the result of episodic or random contamination inputs, but rather reflects a fundamentally constrained thermodynamic state of the system**,** as confirmed by the calculated Eh–pH stability boundary (Fig. 3). Specifically, waters within the river–groundwater system occupy a pH range of **7.2–9.0** and an Eh interval of +300 to +600 mV (vs. SHE) (Table 1).

Under these conditions, Cr(VI) remains the thermodynamically favored dissolved species, as described by the Nernst equation applied to the Cr(VI)/Cr(III) redox couple**,** which forms the theoretical basis of Pourbaix diagrams [36,42]. To define the stability boundary, the chromate reduction half-reaction expressed in acidic form is used:

$$CrO_4^{2-} + 8H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O \qquad (4)$$

For this redox couple, the standard electrode potential (E^0) at 25 °C is reported in classical thermodynamic references and is routinely applied in the construction of Eh–pH (Pourbaix) diagrams. The corresponding Nernst equation can be written as:

$$E = E^0 - \frac{0.0591}{3} \log \left(\frac{a_{Cr^{3+}}}{a_{CrO_4^{2-}}\, a_{H^+}^8} \right) \qquad (5)$$

To obtain an analytically transparent stability boundary, the standard simplifying assumption commonly used in illustrative thermodynamic analyses is adopted, namely equal activities of the dissolved chromium species at the equilibrium boundary**:**

$$a_{Cr^{3+}} \approx a_{CrO_4^{2-}}$$

Under this assumption, $\log\left(a_{Cr^{3+}}/a_{CrO_4^{2-}}\right) = 0$,

and equation (1) simplifies to:

$$E \approx E^0 - \frac{0.0591}{3}(8\,pH) = E^0 - 0.1576\,pH \qquad (6)$$

Thus, with increasing pH, the Cr(VI)/Cr(III) stability boundary shifts sharply toward lower Eh values**,** becoming relatively low under neutral to alkaline conditions**.** This behavior is clearly illustrated in Fig. 3, where at pH ≈ 8 the calculated equilibrium Eh lies well below +300 mV**,** whereas the measured Eh values of the system consistently fall within the range of +300 to +600 mV**.**

Accordingly, the river–groundwater system resides entirely within the thermodynamic stability field of Cr(VI**)**, and in the absence of external reduction or immobilization processes, the natural reduction of Cr(VI) cannot be considered a viable or sustainable mechanism of self-attenuation**.**

In simpler terms, the river water and alluvial groundwater are too oxidizing to promote the spontaneous conversion of Cr(VI) to Cr(III) , as a result**,** Cr(VI) persists in solution and remains mobile within the system.

Thermodynamic evidence for boron behavior: speciation control and redox irrelevance

The results indicate that boron behaves as a stable dissolved constituent under the measured Eh and pH conditions. This behavior arises because boron in natural waters is not redox-sensitive , instead, its aqueous speciation is controlled solely by acid–base equilibria rather than by oxidation–reduction processes [5,6].

$$H_3BO_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \qquad (7)$$

At 25 °C, this equilibrium is characterized by a dissociation constant pK**a** ≈ 9.2, a value widely applied in hydrochemical calculations of boron speciation [5,34]. The fraction of the borate ion can be expressed as:

$$\alpha_{B(OH)_4^-} = \frac{1}{1 + 10^{(pK_a - pH)}} \qquad (8)$$

Within the pH range of 7.2–8.8, characteristic of the investigated river–groundwater system, boric acid (H_3BO_3) is the dominant aqueous species, while the contribution of $B(OH)_4^-$ increases only as pH approaches ≈**9** (Fig. 4). This distinction is critical because both species remain entirely dissolved**,** and therefore even substantial variations in Eh do not create a thermodynamic precipitation or immobilization barrier for boron**.**

As a result, boron manifests as a chronic background contaminant spatially associated with groundwater transport pathways, rather than with localized fixation or accumulation in solid phases [5,6]. Unlike chromium, boron cannot be attenuated through redox manipulation and can be effectively controlled only by managing hydrological pathways (e.g., infiltration and groundwater flow) or by applying specialized removal technologies.

The calculated distribution of dissolved boron species within the river-water pH range is shown in Fig. 4**,** confirming the conservative transport behavior of boron under the prevailing hydrochemical conditions.

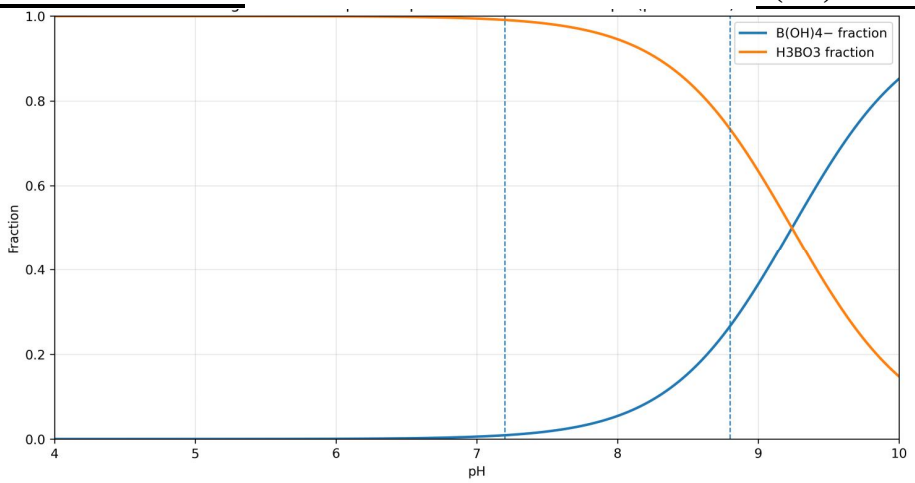

Figure 4 – Aqueous speciation of boron as a function of pH (constructed by the author)

The relative fractions of H_3BO_3 and $B(OH)_4^-$ were calculated using pKa ≈ 9.2 and standard acid–base speciation relationships [5]. Within the pH range typical of river water (7.2–8.8)**,** boron remains predominantly in the dissolved phase, confirming its conservative transport behavior in the aquatic system [6].

From a practical perspective, this indicates that boron functions as a conservative tracer of groundwater transport**:** its spatial distribution reflects hydraulic connectivity and flow paths**,** rather than the presence of localized geochemical barriers. Consequently, boron forms a smoothed, chronic background of contamination coincident with groundwater discharge zones, in agreement with the calculated distribution of dissolved boron species (Fig. 4) and the field observations [11].

Why the groundwater pathway becomes dominant (as implied by thermodynamics)

Thermodynamic calculations indicate that, under the measured Eh–pH conditions, the system does not develop natural geochemical barriers capable of significantly retarding the migration of Cr(VI) and boron. As a consequence, hydraulic controls become dominant. Groundwater flow within highly permeable alluvial sediments efficiently transports dissolved contaminant species from the source areas toward the river, forming a persistent plume-type structure (Fig. 1). This behavior represents a typical scenario for technogenically impacted alluvial systems and is consistent with observations reported in previous studies [25-26,28].

Direct implications for management: which measures are effective and why

Given that thermodynamic analysis demonstrates that

Cr(VI) is stable under the observed Eh–pH conditions (Fig. 3 , Eq. 2), and boron remains dissolved throughout the entire hydrochemical window of the system (Fig. 4 , Eq. 3),any effective management strategy must necessarily focus on controlling flow pathways and locally modifying chromium thermodynamics.

Accordingly, the following measures are required:

1. For Cr(VI): the deliberate creation of localized reducing zones to promote the reduction of Cr(VI) to Cr(III), followed by its immobilization within the solid phase [10,35].

2. For boron: regulation of inputs and migration through control of infiltration and interception of groundwater flow, and/or the application of specialized sorptive or treatment technologies, as redox manipulation is ineffective for boron attenuation [5,6].

3. For the system as a whole: the primary management target is the integrated pathway “sludge storage facility → groundwater transport → river discharge” (Fig. 1). This framework is fully consistent with the widely accepted source–pathway–receptor

approach and with integrated water resources management principles within the total environment concept.

Management implications

The results of the thermodynamic and hydrogeological analyses clearly demonstrate that the persistent contamination of the river system by Cr(VI) and boron arises from a reproducible and systematic mechanism involving technogenic sludge storage facilities as the source, groundwater as the dominant transport pathway, and the river as the ultimate receptor. Under these conditions, effective pollution management requires targeted intervention in this mechanism itself, rather than localized or reactive responses to its individual manifestations.

Fundamental management logic

The key management conclusion is that reductions in Cr(VI) and boron concentrations in river water can only be achieved by disrupting the "source–groundwater pathway–river" linkage. Because thermodynamic calculations demonstrate the stability of Cr(VI) under the characteristic pH and Eh conditions of the system, and because boron remains dissolved irrespective of redox conditions, natural self-attenuation processes can be ruled out. Consequently, passive expectations of concentration decline or mitigation measures focused exclusively on the river channel are ineffective and unlikely to yield measurable improvements.

An effective management strategy must therefore focus on controlling contaminant fluxes and the conditions governing their migration, which can only be achieved through a combination of engineering controls and geochemically informed interventions.

Source stabilization as a mandatory first step

Stabilization of technogenic sludge storage facilities represents a necessary and sufficient condition for achieving a substantial reduction in contaminant inputs to groundwater. Engineering measures aimed at limiting infiltration—including capping, diversion of surface runoff, and localized hydraulic isolation—directly reduce the leaching rates of Cr(VI) and boron, thereby decreasing the contaminant mass flux transported toward the river.

From both environmental and economic perspectives, this stage is the most efficient intervention. It requires moderate capital investment, avoids the risks of secondary contamination associated with excavation, and provides a rapid and measurable effect in the form of reduced groundwater loading. Implementation of source stabilization establishes a robust foundation for subsequent remedial actions and prevents the recurrent formation of contaminant fluxes.

Thermodynamically guided immobilization of Cr(VI)

For chromium, the key management action is the intentional shift of the system from the Cr(VI) stability field to that of Cr(III), fully consistent with the thermodynamic analysis presented above. This is achieved by creating localized reducing conditions and promoting the immobilization of Cr(III) within the solid phase [10,35].

In practice, this objective is commonly accomplished through the application of Fe(II)-bearing materials or iron-based reactive media, which induce the reduction of Cr(VI) followed by the precipitation of $Cr(OH)_3$ or mixed Fe–Cr solid phases. This approach is neither experimental nor conceptual, it is based on well-established in situ remediation technologies that have been extensively applied for the management of Cr(VI)-contaminated groundwater systems [38,47-48].

From an economic standpoint, in situ immobilization is markedly more favorable than complete sludge excavation. It requires lower capital costs, is scalable, allows phased

implementation, and ensures long-term reduction of the toxic and mobile chromium fraction without the need to remove the entire technogenic mass.

Interception of groundwater flow as a system-level solution

Because groundwater has been identified as the dominant transport pathway for contaminants, interception of this flow constitutes a core element of sustainable management. Permeable reactive barriers or other interception systems installed along the “sludge storage facility–river” transect can effectively reduce Cr(VI) inputs to the river by promoting its reduction and immobilization within a controlled zone.

For boron, which does not respond to changes in redox conditions, such systems function primarily as hydraulic barriers, limiting advective transport and creating opportunities for localized extraction or concentration. Consequently, groundwater interception provides a simultaneous reduction in contaminant loading for both Cr(VI) and boron, even when dissolved forms persist within parts of the system.

From an operational perspective, these solutions are characterized by low maintenance requirements, passive operation, and high long-term reliability, making them particularly suitable for environments affected by chronic secondary contamination.

Overall environmental and economic effectiveness

The proposed strategy—based on source stabilization, thermodynamically guided immobilization of Cr(VI), and interception of groundwater flow—provides a robust and reproducible reduction of contamination in the river system. In contrast to cost-intensive and high-risk full excavation scenarios, this integrated approach minimizes both capital and operational expenditures while maximizing environmental benefits [16].

Accordingly, the management of Cr(VI) and boron contamination in technogenically impacted river systems should be regarded not as a collection of isolated measures, but as a coherent, thermodynamically grounded framework of actions capable of delivering guaranteed positive outcomes over the medium and long term.

Conclusions

This study demonstrates that the persistent contamination of a river system by hexavalent chromium and boron is governed not by random or episodic factors, but by fundamental thermodynamic and hydrogeological controls. Under the characteristic pH and Eh conditions, Cr(VI) represents a thermodynamically stable and highly mobile species, whereas boron remains dissolved regardless of redox conditions. Consequently, natural self-attenuation of the system is not feasible.

The results show that technogenic sludge storage facilities function as long-term secondary sources of contamination, while groundwater constitutes the dominant transport pathway delivering contaminants to the river network. This explains both the chronic nature of the contamination and the limited effectiveness of mitigation measures focused solely on surface-water manifestations.

Based on thermodynamic analysis, a management strategy is substantiated that includes source stabilization, targeted immobilization of Cr(VI) via reduction to Cr(III), and interception of groundwater flow. This approach ensures a sustained reduction in contaminant mass fluxes and represents an environmentally and economically sound alternative to complete excavation of technogenic deposits.

The conclusions of this study have broader applicability and can be transferred to other technogenically disturbed river systems with legacy environmental damage, where contaminant persistence is controlled by thermodynamic constraints and secondary sources.

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ЕЛЕК ӨЗЕНІ МЫСАЛЫНДА ӨЗЕН ЖҮЙЕСІНДЕГІ АЛТЫВАЛЕНТТІ ХРОМ МЕН БОРДЫҢ ҚОЗҒАЛМАЛЫЛЫҒЫНЫҢ ТЕРМОДИНАМИКАЛЫҚ БАҚЫЛАНУЫ

Аңдатпа. Өзен жүйелерінің бейорганикалық ластағыштармен тұрақты ластануы көбінесе белсенді нүктелік төгінділерден гөрі екінші реттік көздер мен жер асты арқылы тасымалдану процестерімен байланысты. Бұл жұмыста техногендік бұзылған өзен жүйесіндегі алтывалентті хром (Cr(VI)) мен бордың (B) қозғалмалылығын анықтайтын термодинамикалық және гидрогеологиялық факторлар Ілек өзені (Қазақстан) мысалында зерттелді.

Далалық зерттеулер нәтижесінде жерүсті және олармен гидравликалық байланысқан жерасты суларының бейтарап–сілтілі орта (pH 7,2–9,0) және тұрақты тотығу жағдайларымен (Eh +300…+600 мВ) сипатталатыны анықталды. Eh–pH жүйесіндегі термодинамикалық талдау бұл жағдайлардың Cr(VI)-дің тұрақтылық аймағына сәйкес келетінін көрсетеді, яғни оның Cr(III)-ке табиғи түрде тотықсыздануы термодинамикалық тұрғыдан тиімсіз. Ал бор тотығу-тотықсыздану жағдайларына тәуелсіз болып келеді және оның судағы түрлері H_3BO_3 пен $B(OH)_4^-$ арасындағы қышқыл-негіздік тепе-теңдікпен анықталады.

Гидрогеологиялық талдау ластағыштардың негізгі тасымалдану жолы жерасты сулары екенін көрсетеді, олар аллювиалды шөгінділерде тұрақты шлейфтер түзеді. Табиғи өзін-өзі тазарту механизмдерінің жеткіліксіздігі өзеннің созылмалы ластануын және тек жерүсті суларына бағытталған шаралардың тиімсіздігін түсіндіреді.

Зерттеу нәтижелері негізінде ластаушы көздерді тұрақтандыруды, Cr(VI)-ді Cr(III)-ке дейін тотықсыздандыру арқылы иммобилизациялауды және жерасты сулары ағынын бақылауды қамтитын термодинамикалық негізделген басқару тәсілі ұсынылды. Алынған нәтижелер ұқсас техногендік жүйелердегі екінші реттік ластануды басқаруға қолданылуы мүмкін.

Кілт сөздер: алтывалентті хром (Cr(VI)); бор; Eh–pH термодинамикасы; жерасты және жерүсті суларының өзара әрекеттесуі; екінші реттік ластану; аллювиалды сулы горизонт; өзеннің ластануы; «көз–таралу жолы–қабылдаушы» тұжырымдамасы; табиғи әлсіреу шектері.

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ТЕРМОДИНАМИЧЕСКИЙ КОНТРОЛЬ ПОДВИЖНОСТИ ШЕСТИВАЛЕНТНОГО ХРОМА И БОРА В РЕЧНОЙ СИСТЕМЕ НА ПРИМЕРЕ РЕКИ ИЛЕК

Аннотация. Устойчивое загрязнение речных систем неорганическими поллютантами часто обусловлено вторичными источниками и подповерхностным переносом, а не действующими точечными сбросами. В данной работе исследованы термодинамические и гидрогеологические факторы, определяющие подвижность шестивалентного хрома (Cr(VI)) и бора (B) в техногенно нарушенной системе на примере реки Илек (Казахстан).

Полевые данные показывают, что поверхностные и связанные с ними подземные воды характеризуются нейтрально-щелочным pH (7,2–9,0) и устойчиво окислительными условиями (Eh +300…+600 мВ). Термодинамический анализ в системе Eh–pH свидетельствует, что данные условия соответствуют области устойчивости Cr(VI), что исключает его самопроизвольное восстановление до Cr(III). Бор, напротив, не зависит от окислительно-восстановительных условий и определяется кислотно-основным равновесием между H_3BO_3 и $B(OH)_4^-$.

Гидрогеологический анализ показывает, что основным путём переноса загрязнителей являются подземные воды, формирующие устойчивые шлейфы в аллювиальных отложениях. Отсутствие эффективных механизмов естественного самоочищения объясняет хронический характер загрязнения и низкую эффективность мер, направленных только на поверхностные воды.

Предложена термодинамически обоснованная схема управления, включающая стабилизацию источников, восстановление Cr(VI) до Cr(III) и контроль потоков подземных вод. Результаты могут быть использованы для управления вторичным загрязнением в аналогичных системах.

Ключевые слова: шестивалентный хром (Cr(VI)); бор; Eh–pH термодинамика; взаимодействие подземных и поверхностных вод; вторичное загрязнение; аллювиальный водоносный горизонт; загрязнение рек; концепция «источник–путь переноса–рецептор»; ограничения естественного самоочищения.