PREPRINT, WORKING DRAFT (EN) · \"HYDROGEOLOGY & LOGISTICS\" ARTICLE OF THE PROGRAM \"WASTE AS DYNAMICAL SYSTEMS\ · 2026-06-15

Environmental Logistics: How Preferential Flow and Redox Bistability Break the Path-Independence Axiom in Contaminant Transport

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> *Preprint, working draft (English version). Computations and figures are reproducible and openly deposited (Zenodo DOI at the first stable version). Scientific companion to the ChaoticLCA preprint (Piens 2026, Zenodo 10.5281/zenodo.20086772). No competing interests declared.*
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> *This article belongs to the research program "Waste as dynamical systems" (Piens, in preparation). Its sections are numbered independently; the few §x.y references not resolved in the text point to the companion articles, namely the theoretical Manifesto (axioms S1 to S4, theorems T1 to T4), the anaerobic digester, the toxicology of emerging contaminants, the ecology of critical transitions and public decision-making, or to the book-length manuscript.*

Abstract

Fate-and-transport models (advection-dispersion, multimedia fugacity, the distribution coefficient K_d) supply the "safety delay" and retention on which siting, monitoring and remediation decisions rest, assuming a stationary, homogeneous, linear transport substrate. We read that substrate (soils, vadose zone, aquifers, surface water, chemical fronts) as an *environmental logistics*: a dynamical system in its own right, turbulent, heterogeneous, memory-laden, threshold-driven. Two regimes break path independence head-on. With preferential flow, when the wetting front fingers, the contaminant reaches groundwater ×13 sooner (63 days versus 2.2 years; ×2 to ×28 across sweeps) than the homogeneous model predicts, so the static safety delay is wrong on timing, which is the very magnitude of risk. With redox bistability, arsenic mobility is a property of the arsenic × soil couple rather than of arsenic, and K_d jumps two orders of magnitude across a bistable redox front, so no single K_d represents the stock. The safety delay and K_d are statistical fictions masking dynamical regimes; a finite Lyapunov horizon (T1) puts the subsurface uncertainty floor at the year scale, inside the management calendar.

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1. Introduction

To decide where to store a waste, when to monitor an aquifer, how much to provision for a clean-up, assessment relies on two numbers: an arrival time and a retention factor. Both are produced by transport models that assume a well-behaved medium, stationary, homogeneous, linear, memoryless. Yet the medium is not well-behaved. We propose to name it for what it is, an *environmental logistics*, and to show, on two documented regimes, that the safety delay and the distribution coefficient K_d are statistical fictions masking a dynamics. The argument defeats the path-independence axiom (S3); it relies on the finite-horizon theorem (T1) established in the companion manifesto, of which we recall below the strict minimum.

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2. Theoretical framework (recap): path independence and finite horizon

The **path-independence axiom (S3)** posits that the consequence depends only on the present state, never on the history that led to it: no hysteresis, no amplifying feedback, a de facto reversibility. It is the assumption that allows the fate of a pollutant to be modeled by a stationary transport. It becomes false as soon as a feedback creates two basins of attraction, or a medium keeps the memory of its trappings. The theorem below, proved in the companion manifesto, also fixes the uncertainty floor proper to each transport vector.

Theorem T1 (finite prediction horizon). *Let a deterministic system have maximal Lyapunov exponent* $\lambda_{max} > 0$. *Even known exactly and started from an initial condition measured to precision* δ, *it allows an observable bounded by* L *to be predicted only up to a finite time* $t_{pred} \approx (1/\lambda_{max})\cdot\ln(L/\delta)$.

Proof (sketch). Two trajectories δ apart at the initial instant separate as $\delta\cdot e^{\lambda_{max}\cdot t}$ while the dynamics stays in its linearized regime. Prediction loses its meaning when this gap reaches the amplitude L of the observable, that is $\delta\cdot e^{\lambda_{max}\cdot t} \approx L$, hence $t_{pred} \approx (1/\lambda_{max})\cdot\ln(L/\delta)$. ∎

The whole lesson is in the *form* of the result. The horizon does not grow in proportion to the measurement effort; it grows as its **logarithm**. To divide δ by a thousand adds only $(1/\lambda_{max})\cdot\ln(1000) \approx 6.9/\lambda_{max}$ to the horizon: a handful of characteristic times, never infinity. This is what grounds, rigorously, the claim of the companion manifesto about the one-hectare field. The canonical example is the atmosphere. Lorenz (1963) showed that an exponent $\lambda_{max} \approx 0.05\ d^{-1}$ imposes a weather-predictability horizon on the order of two weeks, a bound that fifty years of progress have not pushed back, precisely because it is not a limit of means. Any pollutant transport coupled to meteorology, or to a heterogeneous subsurface flow, inherits a finite horizon of the same nature; we quantify these horizons by medium below, then examine the vectors one by one in §3.

It remains to say *where* T1's floor really bites, for the horizon t_{pred} depends on the medium through its exponent λ_{max}. The orders of magnitude below bound deterministic prediction (perfect model included) for the main transport vectors, which §3 will then examine one by one.

Medium	λ_{max} (order)	t_{pred} (order)	Origin of the estimate
Free atmosphere	~0.05 d^{-1}	~2 weeks	Lorenz (1963), convection model
Heterogeneous vadose soil	~0.003–0.01 d^{-1}	~1–4 years	front instability, fingering (§3.2)
Soil redox systems	~0.001–0.002 d^{-1}	~3–5 years	oxidation-reduction kinetics (§3.5)
Lakes / surface waters	~0.01–0.1 d^{-1}	~1–5 months	seasonal mixing, stratification

The reading matters more than the decimals: for the subsurface, the dynamic floor sits at the year scale, that is, well inside the horizons over which storage and remediation decisions are made, which count in decades.

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3. Environmental logistics

We propose the term **environmental logistics** for the apparatus of physical transport that actually moves substances once released: infiltration into soils, the flow of aquifers, the runoff of sub-catchments, rivers, the atmosphere. The word "logistics" is chosen deliberately. In industrial management, logistics is never a mere matter of conveyance: it decides what arrives, where and when, and a logistics breakdown undoes the best of plans. The same holds here, with one added difficulty: the transport vector is not a passive conveyor belt but a *dynamical system* in its own right, turbulent in the atmosphere, heterogeneous and memory-laden in the subsurface, threshold-driven in redox chemistry. The *when* and *where* of a pollutant's arrival therefore inherit the irreducible uncertainty established in the companion manifesto, which the stationary, linear model writes off. Let us examine the five major vectors; each illustrates a distinct regime and prepares a vignette of the program.

3.1 The atmosphere: chaos in the strict sense

The atmosphere is the only vector where the word "chaos" is used in the strong, proven sense: positive Lyapunov exponent, finite prediction horizon (Lorenz, 1963). An atmospheric emission (an incinerator plume, a dust uplift, a volatile compound released from a cell) is caught in a turbulent field whose individual trajectory is unpredictable beyond about two weeks (companion manifesto). One predicts its *statistics* (wind rose, mean deposition), never the detail of a distant episode. For assessment, the consequence is that the arrival position of an atmospheric contaminant is by nature a tailed distribution, not a point; and that tail, unlike a log-normal margin, is a dynamic fact, not a measurement defect one would resolve.

3.2 The vadose zone: unstable wetting fronts and fingering

Below the surface, before the aquifer, water crosses a partially saturated soil: the vadose zone. The image of a planar wetting front descending steadily is false as soon as the soil is dry and poorly wettable, or stratified: the front destabilizes and fragments into moisture *fingers* that short-circuit the matrix (Glass, Steenhuis & Parlange, 1989; Hendrickx & Flury, 2001). The calculation of the effect is simple and brutal. If a fraction φ of the water flux rushes into fingers occupying only a fraction a of the section, the velocity in the fingers is $v_{finger} = v_{mean} \cdot \varphi/a$. With $\varphi \approx 0.8$ and $a \approx 0.06$ (values common in fingered soil), one obtains $v_{finger} \approx 13 \cdot v_{mean}$: the contaminant reaches the aquifer thirteen times sooner than the homogeneous model announces. This is not chaos in the strict sense but a *front instability*; the effect, for its part, is decisive, for it is on the "safety delay" computed in the homogeneous regime that intervention decisions rest (§4).

3.3 Aquifers: anomalous dispersion and long memory

Once in the aquifer, transport is often modeled by a Fickian advection-dispersion, which produces well-behaved Gaussian plumes. But in real geological media, strongly heterogeneous, transport is *anomalous*, non-Fickian: it develops early arrivals and long tails that classical dispersion cannot generate, described by continuous-time random walks (Berkowitz et al., 2006). Concretely, part of the contaminant races through the most permeable channels while another stays trapped for a very long time in dead zones, whence a release spread over decades. This "long memory" of the aquifer is the exact opposite of path independence (S3): the present state of the plume encodes the history of its trappings.

3.4 Surface waters: flood thresholds and episodic transport

In rivers and catchments, the bulk of particulate transport does not happen in the mean regime but during rare high-flood events: a few days a year can carry most of the annual flux of sediments and of the contaminants associated with them. Transport is *episodic*, governed by mobilization thresholds, and its statistics are heavy-tailed rather than Gaussian. An assessment calibrated on mean flow structurally under-estimates the dose delivered by the episode, the same asymmetry as for PFAS persistence (§7.1), but carried here by hydrology.

3.5 Redox and pH fronts: chemistry as logistics

There remains a vector one forgets because it does not move in space: local chemistry. The redox potential (Eh) and the pH of a soil decide the *form* in which an element exists, hence its mobility. The same stock of arsenic is mobile in its oxidized form As(V) and nearly immobile in its reduced form As(III); the passage from one to the other follows a redox front that moves with moisture and organic matter. Redox chemistry thus functions as a logistics in its own right: it opens or closes the valves of mobility without any mass first having to move. And because these fronts are bistable (two stable regimes for intermediate conditions), they fall under categorical invariance defeated (S4) and under the redox switch (§5).

These five logistics can be summarized, each with its regime, its signature and the vignette that quantifies it:

Vector	**Dominant regime**	**Observable signature**	**Axiom / vignette**
Atmosphere	chaos ($\lambda > 0$)	~2-week horizon, deposition tail	S1, companion manifesto (T1)
Vadose zone	front instability	early arrival ×13	S3, §4
Aquifer	anomalous dispersion (non-Fickian)	early arrivals + long tails	S3, §3.3
Surface waters	episodic transport	flux carried by rare floods	S1, §7.1
Redox/pH fronts	bistability	mobility jump (K_d)	S4, §5

In all five cases, the vector imposes its own dynamics on the waste, and it is that dynamics (not the emitted quantity alone) that decides real exposure. Environmental logistics is not the background of assessment: it is, most often, its determining factor.

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4. Agricultural soil: preferential flow, safety delay over-estimated by ×13

The transport of a pollutant toward the aquifer is commonly modeled by a homogeneous advection-dispersion, which produces a smooth front arriving in years. But, as we saw in §3.2, the real soil often fragments this front into moisture fingers (Hendrickx & Flury, 2001; Glass et al., 1989), and the contaminant arrives in days. On a representative case, the homogeneous model (Ogata-Banks solution) announces a first arrival at 2.2 years, where fingered transport places it at 63 days: a factor of **13**, robust between **×2 and ×28** over the range of plausible finger parameters. This is not chaos in the strict sense (it is a front instability, which puts S3 at fault), but the effect on the decision is decisive, for it is the homogeneous delay that serves as a "safety delay."

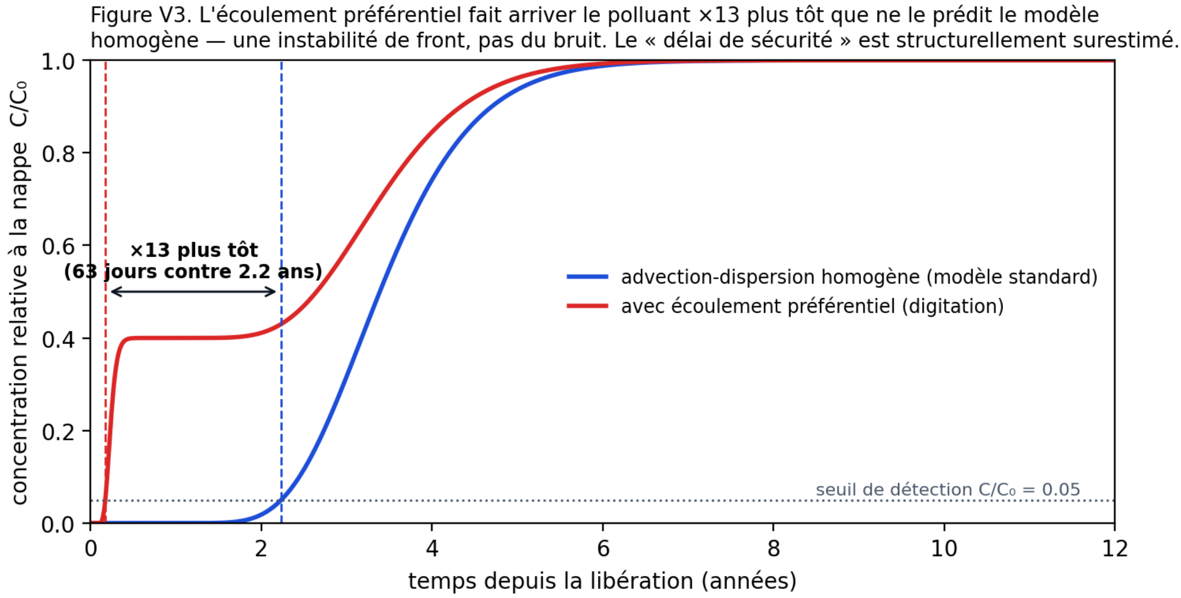

Figure V3. Preferential flow: fingering produces an early arrival that the homogeneous model does not generate. The safety delay is over-estimated by a factor of about 13.

And this delay is not just a physical quantity: it is the assumption on which the whole economy of monitoring rests. A manager who believes he has two years before arrival at the aquifer derives from it the frequency of his sampling, the lead time to install a barrier, the financial provision for a possible clean-up. If in reality he has only two months, these three decisions are taken too late. Now the error is not symmetric: to over-estimate the safety delay is to forgo the *option value* of early detection, the inexpensive possibility of acting while the contamination is still confined. And the cost of acting too late is not marginally higher: it changes scale, passing from the monitoring of a piezometer (a few thousand euros a year) to the rehabilitation of a contaminated aquifer (orders of magnitude above, over decades). A model that systematically over-estimates the delay therefore shifts the risk toward the most expensive scenario, and it does so silently. This is, in miniature, the economic argument of the whole article: it is not the central value that ruins, it is the blindness to regime that makes one arrive too late.

Falsifiable. Tracer tests on representative soils: compare the arrival time predicted by homogeneous advection-dispersion with the one imposed by the observed fingering.

5. Heavy metals and redox/pH bistability of the soil

As we saw in §3.5, local chemistry is itself a logistics: it opens or closes the valves of mobility without any mass having to move. Arsenic is its clearest illustration, and the heaviest in consequences for a storage site. Its mobility depends not so much on its quantity as on its *form*, which is fixed by the redox-potential–pH couple, the Pourbaix diagram. Under oxidizing conditions, arsenic exists as As(V), soluble and mobile; under reducing conditions, it passes to As(III), strongly sorbed and nearly immobile. The boundary between the two, in our simplified plot, follows `Eh ≈ 300 − 60·(pH − 7)` mV.

Now the redox potential of a soil is not a constant: it depends on moisture, organic matter, aeration, and it can oscillate between two stable regimes, this is *redox bistability*. Three soils of the same arsenic content give the measure of the gap. An oxidizing, aerated soil (Eh +400 mV, pH 7) keeps arsenic as mobile As(V); a balanced soil (Eh +200 mV, pH 6.5) and a reducing soil, moist or anaerobic (Eh −50 mV, pH 7), keep it as immobile As(III) (Figure V7a). The distribution coefficient `K_d`, which measures retention, then jumps by two orders of magnitude on either side of the redox front, from about 1 L/kg in the immobile regime to 0.01 L/kg in the mobile regime (Figure V7b). This is not a continuum one would interpolate: it is a switch.

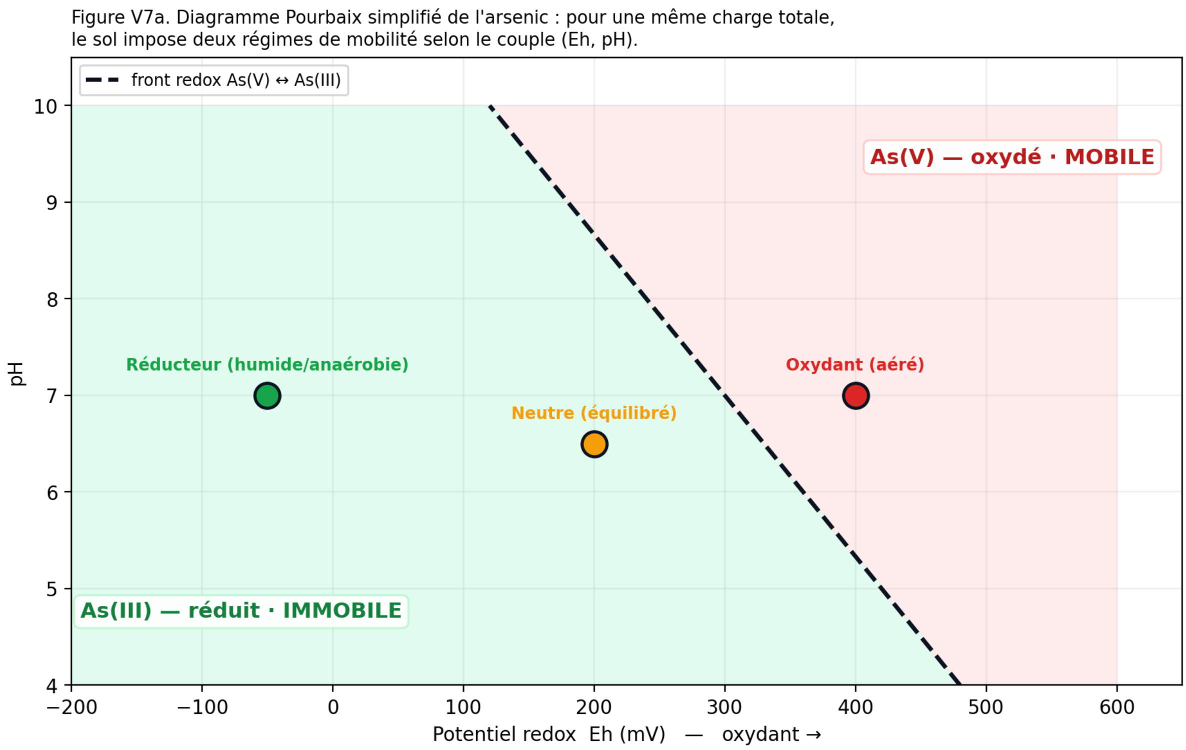

Figure V7a. Simplified Pourbaix diagram of arsenic: for the same total load, the soil imposes two mobility regimes depending on the (Eh, pH) couple. The three points figure three soils of the same content, oxidizing (mobile), neutral and reducing (immobile).

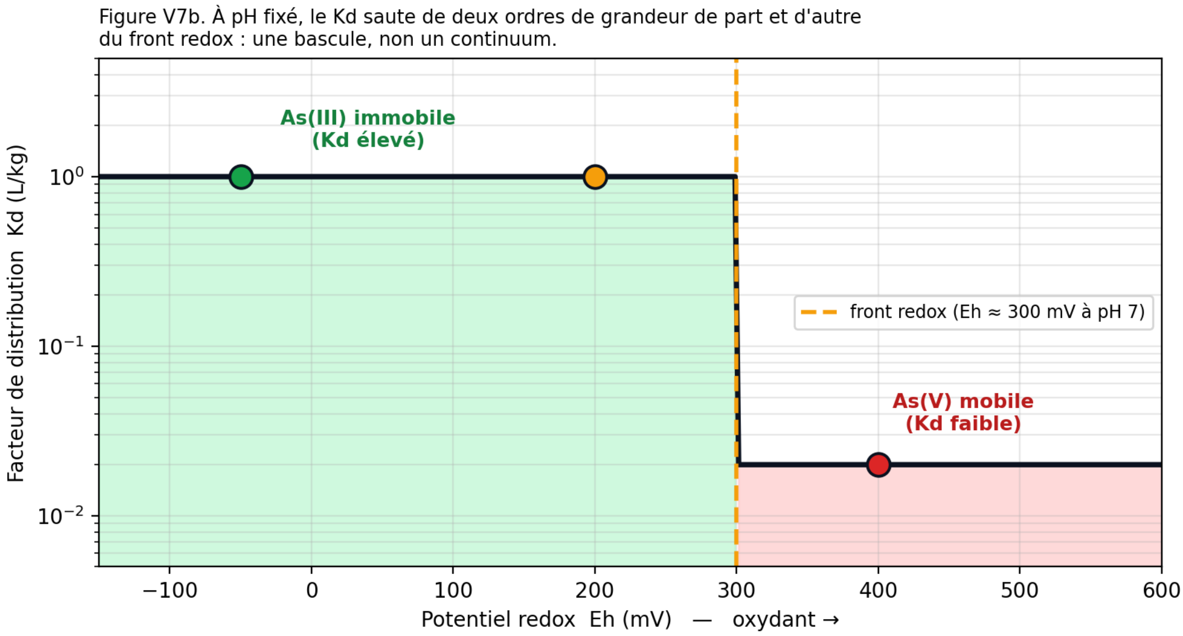

Figure V7b. At fixed pH, the distribution coefficient K_d jumps by two orders of magnitude on either side of the redox front: a switch, not a continuum.

The consequence for assessment is direct, and it is again axiom S4 that falls: no single release factor can represent this arsenic, because its mobility is not a property of the arsenic but of the couple arsenic × soil. There is here a kind of sleeping poison. The same stock, judged harmless because the soil is reducing today, becomes mobile again as soon as a drainage, a drought or an earthworks lets the soil breathe and tips the front. To assess the content without assessing the redox regime is to photograph a system that can change state; and the day it changes, half the conclusions tip with it. The quantity, here, says almost nothing: everything is in the soil's disposition to release it.

Falsifiable. On representative soil columns, impose cycles of aeration and saturation and measure the K_d of arsenic: the regime reading predicts two distinct values depending on the direction of the redox front, not a single value.

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6. Conclusion

The transport substrate is not the inert background of assessment: it is, most often, its determining factor. Read as a dynamic logistics, it reveals what stationary models write off: an arrival thirteen times too early, a retention factor that jumps by two orders of magnitude when a redox front tips. The safety delay and the K_d are not slightly uncertain quantities;

they are statistical fictions that freeze a regime. For media liable to finger or to tip, assessment would gain by reporting the transport regime, and the finite horizon that bounds it, rather than a single number set on the assumption of a memoryless medium.

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Supplement

Code and figures are reproducible (Python; numpy/scipy/matplotlib) and openly deposited (Zenodo DOI at the first stable version). The factors quoted are not cherry-picked points but representative values over a plausible parameter space, with robustness sweeps.