

Turbidity-associated and warm-season manganese patterns at river and canal drinking-water intakes in Hai Phong City, Vietnam: Statistical evidence and same-day alert rules from routine monitoring data

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ABSTRACT

Manganese (Mn) often has to be removed at treatment plants that draw water from lowland rivers and canals, but particle-bound Mn and dissolved Mn(II) require different treatments, and only total concentrations are reported by routine monitoring. It was examined whether records already kept by utilities can separate turbidity-associated from warm-season Mn patterns and support daily raw-water decisions. Routine data (2021–2024; 3,451 Mn and 2,022 iron determinations) from seven intakes on four sources in Hai Phong City, Vietnam, were analyzed with fixed-effects, generalized additive, and segmented regressions and gradient-boosted trees. Total Mn exceeded 0.1 mg L⁻¹ in 47.6% of samples (10.7% in February, 87.5% in September). Mn and iron (Fe) rose almost equally with turbidity, leaving the Mn/Fe ratio, on average, unchanged (standardized $\beta = +0.004$, 95% CI -0.017 to 0.023). The ratio increased instead with a 30-day water-temperature index (T_{30}) marking the warm season ($\beta = +0.036$, 0.019 to 0.055) but not with temperature anomalies, so the pattern is seasonal rather than demonstrably temperature-driven. Above a transition zone near 25 °C, Mn rose 14.2% per °C of T_{30} . Five routine variables reproduced Mn at withheld intakes, sources, and years (log-scale Nash–Sutcliffe efficiency 0.73–0.79, linear model). In leave-one-year-out tests, same-day alert rules combining a seasonal term with turbidity raised the critical success index by 0.08–0.09 over a fixed calendar. As only routine variables are needed, likely exceedance of the 0.1 mg L⁻¹ limit can be flagged in a spreadsheet on the sampling day, before the laboratory Mn result is reported.

Keywords: manganese, Mn/Fe ratio, raw-water intake, alert rule, out-of-sample validation, Red River Delta.

INTRODUCTION

Iron (Fe) and manganese (Mn) are persistent operational challenges for drinking-water treatment plants. Even at concentrations that pose no health risk, they discolor water, stain fixtures, and build up deposits in distribution networks. Within the plant, they increase oxidant demand and add to the filter load (Tobiason et al., 2016; World Health Organization, 2022). Mn is the more difficult of the two. Dissolved Mn(II) oxidizes only slowly at circumneutral pH and passes through coagulation, sedimentation, and filtration unless oxidized first (Tobiason et al., 2016). The World

Health Organization (WHO) gives a provisional health-based value of 0.08 mg L⁻¹ for Mn and notes that consumers may complain above 0.02 mg L⁻¹ (World Health Organization, 2022). The European Union (EU) sets indicator values of 0.05 mg L⁻¹ for Mn and 0.2 mg L⁻¹ for Fe (European Union, 2020). The United States (US) recommends secondary levels of 0.05 and 0.3 mg L⁻¹ (U.S. Environmental Protection Agency, 2026), and Vietnam limits the two metals in treated water to 0.1 and 0.3 mg L⁻¹ (Ministry of Health, 2024).

Removing Fe and Mn, often with ammonium, is a long-established step in treating groundwater for drinking (Tekerekopoulou et al., 2013).

In the Red River Delta (Vietnam), reductive dissolution of Fe oxides in the aquifers mobilizes Fe (Berg et al., 2007; Postma et al., 2007), and elevated groundwater Mn is predicted across the delta (Podgorski and Berg, 2026). Oxygenated surface water has received less attention, even though it still contains these metals. Microbes reduce Mn(IV) oxides before Fe(III) oxides (Froelich et al., 1979), and the Mn(II) released persists in oxic water, whereas Fe(II) is re-oxidized much faster (Davison, 1993). Wherever water or sediment turns reducing, surface water can therefore gain dissolved Mn. Resuspension of bottom sediment also mobilizes both metals (Abesser and Robinson, 2010). In rivers, much of the Fe and Mn travels on suspended particles (Baalousha et al., 2019).

Lowland rivers and canals near estuaries may be particularly prone to Mn enrichment. They are shallow and warm for most of the year and receive organic loads from settlements and drainage from paddy fields, whose flooded soils release Mn(II) (Kögel-Knabner et al., 2010). In the Red River estuaries, dissolved Mn and Fe were higher in the dry season, when salinity and residence times were greater (Duong et al., 2026). In Hai Phong City, Vietnam, at the seaward end of the Red River Delta, the public treatment plants studied here draw raw water from such channels rather than from groundwater. Mn at intakes of this kind has nevertheless received little attention. Studies in the delta have examined suspended metal fluxes in the main rivers (Roberts et al., 2022) and dissolved metals in the estuaries (Duong et al., 2026), but not the raw water that treatment plants actually receive.

Routine monitoring typically reports total metal concentrations, leaving the particulate and dissolved fractions unknown. Utilities, however, maintain long records of total Mn, total Fe, turbidity, temperature, and other routine variables, raising two questions. The first is whether these variables alone can separate statistically distinct turbidity-associated and warm-season Mn patterns. Because Fe in oxic surface water is mostly particulate, it can trace particulate input, and the Mn/Fe ratio can indicate preferential Mn mobilization; yet such indicators have rarely been examined at raw-water intakes. The second concerns data-driven models. Generalized additive models, GAMs (Wood, 2017), and tree ensembles interpreted with Shapley additive explanations, SHAP (Lundberg et al., 2020), are increasingly used in

water-quality studies (Park et al., 2022; Wang et al., 2022), but they are often validated with random splits, which leak information when data are grouped and autocorrelated (Roberts et al., 2017), and they are rarely converted into decision rules that operators can test against simple alternatives. Decision support for Mn has so far been developed for reservoir-fed plants (Bertone et al., 2015; Zhang et al., 2021), rather than for river or canal intakes with only routine laboratory records.

This study uses four years of routine records from seven intakes across four river and canal sources in Hai Phong City, Vietnam, to address both questions. Its aims are to (i) quantify the magnitude, seasonality, and spatial contrast of Mn exceedance; (ii) test whether turbidity-associated and warm-season patterns of Mn enrichment can be separated statistically; (iii) describe the nonlinear response to the water-temperature index and test how well routine variables reproduce Mn at intakes, sources, and years withheld from calibration; and (iv) derive intake-specific alert rules, test them out of sample against a fixed calendar and against the previous laboratory result, and estimate how many years of data they need. The study makes three contributions: a screening approach that separates turbidity-associated and seasonal Mn patterns using total Mn, total Fe, and turbidity alone, without filtered samples; an evaluation designed for transfer, in which whole intakes, sources, and years are withheld; and alert rules scored against two benchmarks that any utility can apply without a model.

MATERIALS AND METHODS

Study area and water sources

Hai Phong City, Vietnam, lies on the north-eastern edge of the Red River Delta, on a low-lying coastal plain crossed by rivers and a dense network of irrigation and drainage canals (Figure 1). The climate is tropical monsoon. The rainy season lasts from May to November, and the dry season from December to April. Rainfall averaged 1.637 mm yr⁻¹ across ten gauges in the city in 2023–2025 (1.240–1.937 mm among years), 88–96% of it in May–November, with a peak in August–September. Regional water temperature at the intakes averaged 19.7 °C in January and 30.1 °C in July (2021–2024). The seven intakes draw on four sources: the Re River (Quan Vinh,

QV; Hai Phong 3, HP3), the Da Do River (Cau Nguyet, CN; Hung Dao, HD), the Chanh Duong Canal, the main irrigation and drainage channel of Vinh Bao district (old) (Vinh Bao, VB1; Vinh Bao 2, VB2), and the Gia River (Ngu Lao, NL). Each sampling point is the raw-water abstraction point for the plant of the same name, where untreated water enters the plant.

Monitoring data and the regional indices

Between 1 January 2021 and 31 December 2024, Hai Phong Water Supply Joint Stock Company collected untreated grab samples at each sampling point as part of routine monitoring. Water temperature was measured on site, and samples were analyzed in the laboratory for total Mn, total Fe, turbidity (in nephelometric turbidity units, NTU), permanganate index (PI, a measure of oxidizable organic matter), ammonium ($\text{NH}_4^+\text{-N}$), nitrite ($\text{NO}_2^-\text{-N}$) and nitrate nitrogen ($\text{NO}_3^-\text{-N}$), electrical conductivity, and pH. Total Fe was determined by the 1,10-phenanthroline spectrometric method after acid digestion and reduction to Fe(II) (TCVN 6177:1996, equivalent to ISO 6332; International Organization for Standardization, 1988), total Mn by the formaldoxime spectrometric method after acid digestion (TCVN 6002:1995, equivalent to ISO 6333; International Organization for Standardization, 1986), and turbidity by nephelometry (method 2130B of Standard Methods; American Public Health Association et al., 2023); PI, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, $\text{NO}_3^-\text{-N}$, and pH by TCVN 6186:1996, 6179-1:1996, 6178:1996, 6180:1996, and 6492:2011, respectively. No value fell below the limit of quantification; the lowest reported values were 0.029 mg L^{-1} for Mn and 0.10 mg L^{-1} for Fe. The data set contains 3,717 intake-days with 3,451 Mn and 2,022 Fe determinations; every Fe value has a matching Mn value. The numbers of determinations and missing values by intake, year, month, and variable are given in Tables S1 and S2. Sampling frequency differed among intakes: the median number of Mn determinations per month was 22 at QV and HP3, 8 at CN and HD, and 4–5 at VB1, VB2, and NL. We evaluated the alert rules using laboratory turbidity on sampled days; in operation, operators' daily turbidity readings at the same point serve the same purpose.

Water temperature was recorded for 71–100% of Mn samples at five intakes, but only 49 times at VB1 and 48 times at VB2 (11–14 readings per year; 17% and 22% of their Mn samples; 30 and 29 readings in the rainy season and 19 at each intake in the dry season; Table S3). Readings were spatially coherent: on 39.7% of days with two or more readings, all intakes reported the same value. We therefore built a daily regional series from the mean of all readings on each day and filled gaps of up to seven days by carrying the last value forward. When we rebuilt the series with each intake left out, it reproduced that intake's readings with a root-mean-square error of $0.15\text{--}0.34 \text{ }^\circ\text{C}$. Errors were centered near zero (bias -0.04 to $+0.05 \text{ }^\circ\text{C}$) and largest at VB1 and VB2, where readings were sparse (RMSE 0.41 and $0.37 \text{ }^\circ\text{C}$ in the rainy season and $0.17 \text{ }^\circ\text{C}$ at both intakes in the dry season, against $0.14\text{--}0.31 \text{ }^\circ\text{C}$ at the other intakes; Table S3). Because Mn was expected to follow sustained rather than day-to-day conditions, regional water temperature means were computed over the L days ending on and including the sampling day (T_L , $L = 1, 7, 14, 21, 30, 45$ and 60 d). T_{30} was used in the explanatory analyses, L was reselected within each validation loop, and T_L is interpreted as a regional warm-season index rather than the temperature at a particular intake. Antecedent rainfall P_L over the same 7- and 30-day windows was taken from a regional index, the daily median of the gauges with records from January 2022.

Sample handling, laboratory quality control and data screening

Grab samples were collected, preserved, and transported to the laboratory in accordance with the national standards for water sampling and sample handling (TCVN 6663 series, equivalent to ISO 5667) and were analyzed by the laboratory of the utility, which is accredited to ISO/IEC 17025:2017 by the Bureau of Accreditation of Vietnam (VILAS 449), using the methods described above. The scope of accreditation lists the Mn, Fe, turbidity, $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, $\text{NO}_3^-\text{-N}$, PI, and pH determinations with limits of quantification (LOQ) of 0.02 mg L^{-1} (Mn), 0.05 mg L^{-1} (Fe), 0.12 NTU , 0.03 , 0.01 , and 0.04 mg N L^{-1} , $0.6 \text{ mg O}_2 \text{ L}^{-1}$, and pH 2–12; the LOQ is the lowest reportable value, and separate limits of detection are not listed. The formaldoxime

and phenanthroline methods are applicable from 0.01 to 5 mg L⁻¹, with dilution above this range (International Organization for Standardization, 1986, 1988), which covers the observed ranges (Mn 0.029–0.898, Fe 0.10–2.92 mg L⁻¹). Both methods are calibrated against a series of standard solutions, read against a reagent blank, and include the masking of interfering ions prescribed in the standard; as an accredited laboratory, the laboratory also runs the internal and external quality checks required by ISO/IEC 17025:2017 (International Organization for Standardization, 2017). Method validation and routine control under VILAS accreditation are commonly assessed against the acceptance criteria of AOAC International (2016), which at the 0.1–1 mg L⁻¹ level require mean spiked recoveries of 80–110% and a repeatability relative standard deviation of at most 15% (0.1 mg L⁻¹) to 11% (1 mg L⁻¹); by the usual 3 σ /10 σ convention, the limits of detection are about 0.3 $\times$ LOQ,

that is, about 0.006 mg L⁻¹ for Mn and 0.015 mg L⁻¹ for Fe. The sensitivity of the results to analytical error within and beyond these limits was tested by perturbing every Mn and Fe value with independent random errors with coefficients of variation of 10% and 20% (200 replicates) and by excluding values below twice the LOQ (81 Mn values, 2.3%; no Fe value): the regression coefficients, the breakpoint, and the exceedance frequency moved by less than their bootstrap uncertainty (Table S12). The lowest reported values (0.029 mg L⁻¹ Mn; 0.10 mg L⁻¹ Fe) exceed the LOQ, so no censored values entered the log transformations or ratios; Mn is reported to three decimals and Fe to two (Table S4). Because 12.3% of the Mn values lie within $\pm 10\%$ of the 0.1 mg L⁻¹ limit, the classification of individual samples near the limit is sensitive to analytical error, whereas the pooled exceedance frequency varied only between 46.4% and 48.2% under the simulated errors. Screening of the records as

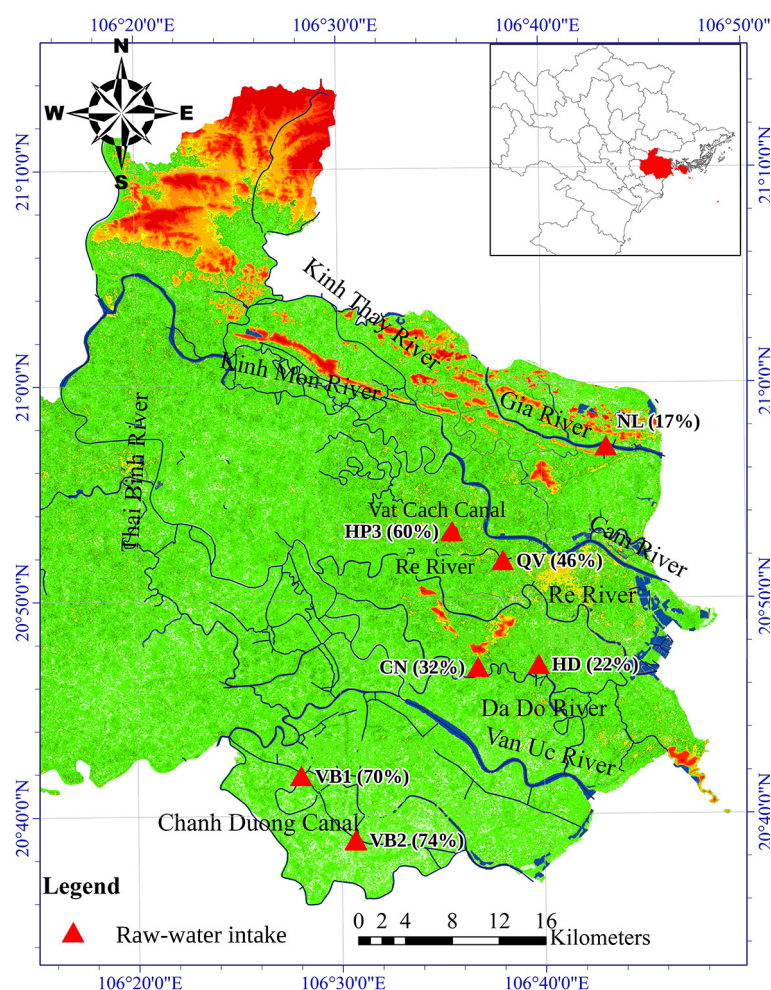


Figure 1. The seven raw-water intakes on the four sources in Hai Phong City, Vietnam; the percentage beside each code is the share of samples with total Mn > 0.1 mg L⁻¹ (2021–2024)

received (duplicate intake-days, non-numeric or non-positive entries, implausible pH, robust $z > 4$ on the log scale within each intake) found no duplicates or invalid entries; the five flagged values (one Mn, two Fe, two turbidity) were physically plausible and retained (Table S4).

Analytical framework

The analysis rests on three expectations, which describe statistical signatures rather than proof of mechanism. First, particles delivered by runoff or resuspension carry Mn and Fe together, so a turbidity-associated increase should shift $\log(\text{Mn}/\text{Fe})$ depending on the material delivered: lithogenic particles would lower the ratio, whereas particles with Mn-enriched oxide coatings, or pore-water Mn(II) released with them, would leave it unchanged or raise it. Because total Fe after acid digestion combines several phases, an unchanged ratio is compatible with, but does not prove, a common particulate carrier. Second, reductive mobilization, whether in bed sediments, flooded soils, or inflowing groundwater, releases Mn before Fe (Froelich et al., 1979), and Fe(II) is removed from oxic water much faster than Mn(II) (Davison, 1993); an increase driven by reductive mobilization should therefore raise Mn more than Fe and increase the ratio. Third, purely lithogenic Mn is not expected to exceed Fe multiplied by a crustal Mn/Fe mass ratio. We used 0.0169, from the crustal abundances of Mn (950 mg kg⁻¹) and Fe (5.63%) reported by Taylor (1964), and tested the upper-crust ratios of Wedepohl (1995; 0.0171) and Rudnick and Gao (2003; 0.0198) and the ratio of Mn to Fe fluxes on suspended matter of the Red River (0.022–0.026; Roberts et al., 2022) as basin-relevant alternatives. No measurements of the Mn and Fe content of the bed sediments or suspended matter of the Hai Phong channels were available, so the Red River ratios are the nearest basin-specific reference, and the bound is indicative only. Mn above it is described as Mn in excess of the assumed crustal proportions, not as proven non-lithogenic Mn, and no conclusion about the terrigenous or non-terrigenous origin of the Mn is drawn from it. Because acid digestion recovers Mn oxides more completely than silicate-bound Fe, the bound is approximate; we therefore evaluated it for each dry-season sample with all five ratios and, as a further check, with twice and three times the Taylor (1964) ratio (Table S5).

Statistical analyses

We $\log_{10}$ -transformed Mn, Fe, turbidity, NH_4^+ -N, NO_2^- -N, and conductivity (Helsel et al., 2020). We compared sources with the Kruskal–Wallis test (η^2 as effect size) and compared the two seasons at each intake with the Mann–Whitney test and Cliff's δ (Cliff, 1993). The timing of seasonal maxima was estimated on the 2,020 samples with Mn, Fe, and turbidity by fitting a first-order harmonic with intake-specific intercepts:

$$y_{it} = a_i + b \cdot \sin(2\pi d_t/365.25) + c \cdot \cos(2\pi d_t/365.25) e_{it} \quad (1)$$

where: i denotes the intake and d_t the day of the year. The peak day, $365.25 \cdot \text{atan2}(b, c)/(2\pi)$ (modulo 365.25), was expressed as a lag relative to the peak of the daily regional temperature.

Lagged Spearman correlations were computed between de-seasonalized anomalies of log Mn and temperature (lags 0–90 d) and, at the near-daily intakes QV and HP3, between log Mn or log Fe and turbidity (lags 0–30 d).

We used three analyses to separate the two patterns. First, within each season and after removing intake means, we computed partial Spearman correlations of log Mn and log Fe with T_{30} at fixed log turbidity and with log turbidity at fixed T_{30} . Second, station fixed-effects regressions were fitted to log Mn, log Fe, and $\log(\text{Mn}/\text{Fe})$ on days with both metals:

$$\log_{10} Y_{it} = \alpha_i + \sum_k \beta_k z_{k,it} + \varepsilon_{it} \quad (2)$$

where: α_i is an intake fixed effect (seven levels are too few to estimate a variance component) and z_k are the standardized predictors T_{30} , log turbidity, PI, $\log \text{NH}_4^+$ -N, and pH.

An extended ratio model added $\log \text{NO}_2^-$ -N and log conductivity; we tested a continuous $T_{30} \times$ turbidity interaction in the ratio model and checked collinearity using within-intake variance inflation factors (VIF). Residuals were autocorrelated and shared regional forcing, so we obtained 95% confidence intervals (CIs) from 1,000 bootstrap resamples of whole calendar months (48 year-month clusters), following Cameron et al. (2008). We also refitted Equation 2 with each T_L . Third, we compared the coefficient of determination (R^2) among models that included intake effects and log turbidity, T_L , the harmonic terms of Equation 1, or both.

We ran four robustness checks: adding antecedent rainfall (2022–2024); replacing T_{30} with its anomaly relative to the day-of-year climatology, with harmonics added; weighting intakes equally; and resampling two-month blocks. Inference rests on effect sizes and CIs. The p-values for rank and likelihood-ratio tests assume independent samples and are therefore nominal. Rule comparisons were not adjusted for multiplicity, so differences whose intervals lie close to zero are treated as indicative only.

We described nonlinear responses with GAMs that included penalized regression splines for T_{30} , log turbidity, PI, log $\text{NH}_4^+\text{-N}$, and pH, plus an intake factor, with 12 basis functions per spline and smoothing selected by generalized cross-validation (Wood, 2017). The breakpoint in T_{30} was quantified with a segmented regression (Muggeo, 2003):

$$\log_{10}\text{Mn}_{it} = \alpha_i + \gamma \log_{10}\text{Turb}_{it} + \beta_1 T_{30,it} + \beta_2 (T_{30,it} - \psi)_+ + \varepsilon_{it} \quad (3)$$

where: $(x)_+ = \max(x, 0)$ and ψ was located by grid search between 17.5 and 30.5 °C in steps of 0.1 °C. We converted slopes to percentage change per °C as $100 \cdot (10^b - 1)$.

We compared the model with linear and quadratic fits using the Akaike information criterion (AIC), which we report descriptively because the residuals are autocorrelated. We repeated the analysis for log Fe, with PI, log $\text{NH}_4^+\text{-N}$, and pH as additional controls, and for 2022–2024, with antecedent rainfall. To test whether the uneven sampling frequency biased the Mn breakpoint, we refitted Equation 3 with each intake weighted equally, without the canal intakes, with each intake left out in turn, and with QV and HP3 thinned at random to at most five samples per month (200 draws).

Estimation models, validation and interpretation

Five models were used to estimate $\log_{10}$ Mn across 2916 intake-days using all predictors: a climatological baseline (monthly median); a seasonal baseline (the harmonic of Equation 1 plus log turbidity); multiple linear regression; random forest (Breiman, 2001); and XGBoost (Chen and Guestrin, 2016). The last three used T_L , log turbidity, PI, log $\text{NH}_4^+\text{-N}$, and pH, without intake identity in the spatial schemes. To avoid optimism from random shuffling (Roberts et al., 2017), we calibrated each model on all years of

the remaining intakes or sources and validated it on one withheld intake (7 folds) or source (4 folds). In rolling-origin tests, we calibrated models on 2021–2022 and validated on 2023 (1,443 and 719 samples), and on 2021–2023 and validated on 2024 (2,162 and 754 samples). Within each calibration set, we selected the window L and XGBoost hyperparameters using grouped inner cross-validation ($L \in \{1, 7, 14, 30, 45, 60\}$ d; depth 2–4; 300 or 600 trees; learning rate 0.05). Because the regional temperature series includes readings from the withheld intake, we repeated the leave-one-intake-out validation with T_L rebuilt from the other intakes only. Because the predictors are measured in the same sample as Mn, the models estimate Mn concurrently rather than forecast it; they test whether the relations transfer across intakes, sources, and years.

Skill was measured using the Nash–Sutcliffe efficiency, NSE (Nash and Sutcliffe, 1970), on the log and concentration scales, with back-transformation via a smearing factor (Duan, 1983); the coefficient of determination (R^2 , the squared Pearson correlation) on the log scale; the Kling–Gupta efficiency, KGE (Gupta et al., 2009); the root-mean-square error (RMSE) and the percent bias, PBIAS (Moriassi et al., 2015), all three on the concentration scale because the bias term of KGE depends on the origin of the log scale; and, for $\text{Mn} > 0.1 \text{ mg L}^{-1}$, the probability of detection (POD) and the false-alarm ratio (FAR). We averaged calibration skill across the folds of each scheme and computed validation skill on the pooled withheld predictions, with 95% CIs from 1,000 bootstrap resamples of year-months; skill in each of the 13 outer folds, with the selected L and hyperparameters, is reported in Table S9, and all settings and software versions in Table S7. We interpreted a final XGBoost model ($L = 45$ d, depth 2, 300 trees) with TreeSHAP (Lundberg et al., 2020; Lundberg and Lee, 2017). We located the SHAP breakpoint as in Equation 3 and checked it on the seven leave-one-intake-out models and with T_{30} in place of T_{45} ; because it is derived from the same data and predictors, it describes the fitted model and is not independent evidence of a threshold.

Operational triggers and rules, and their evaluation

For each intake, the probability that Mn exceeds 0.1 mg L^{-1} was modeled as a logistic function of the water-temperature index:

$$\text{logit } P(\text{Mn}_{\text{it}} > 0.1) = a_i + b_i T_{30,\text{it}} \quad (4)$$

We compared intake-specific slopes with a common slope using a likelihood-ratio test. We defined two triggers for each intake: $\theta_{50,i}$, the T_{30} value above which exceedance becomes more likely than not, and a precautionary $\theta_{20,i}$ at 20% probability. A day belongs to the “Mn season” of intake i when $T_{30} \geq \theta_{50,i}$, and the number of such days per year gives the length of the season. By convention in this study, we classified intakes as chronic (≥ 240 d yr⁻¹), seasonal (60–239 d yr⁻¹), or episodic (< 60 d yr⁻¹, or θ_{50} above the observed range), and used the bootstrap share of each class as a robustness measure. We then validated triggers calibrated on 2021–2023 in 2024. Six intake-specific daily rules were compared in a leave-one-year-out test, calibrated on three years and validated on the fourth: a fixed calendar (months whose exceedance frequency in the training years reached the decision level p^* defined below); the T_{30} rule (Equation 4); a turbidity-only rule; a harmonic-plus-turbidity rule; a T_{30} -plus-turbidity rule (Equation 4 with log turbidity added); and persistence, which flags a sample when the previous sample at the same intake, whatever the interval, exceeded 0.1 mg L⁻¹. The model-based rules flag a sample when the modeled probability reaches $p^* = 0.5$ or 0.2, a choice that trades missed exceedances against unnecessary dosing; persistence does not depend on p^* . Rules were scored by the critical success index, CSI = hits/(hits + false alarms + misses) (Schaefer, 1990), both pooled and averaged over intakes, with 95% CIs from the same-year-month bootstrap applied to the rule decisions. The 2021–2023 folds are trained partly on later years, so only the 2024 fold is a strict forward

test. Because exceedance frequency differs widely among intakes (16.8–74.1%), pooled scores can overstate skill (Hamill and Juras, 2006); conclusions therefore rest on paired differences and intake-weighted scores. Persistence assumes the previous result is known before the next sample is taken, which favors near-daily intakes, and all rules predict raw-water exceedance, not treated-water Mn. Finally, we calibrated the T_{30} and T_{30} -plus-turbidity rules on one, two, or three years and applied them to 2024. All analyses used a fixed random seed, and the scripts that regenerate every number, table, and figure are available with the data (see Data availability).

The rules are same-day classifications (nowcasts), not forecasts. In the monitoring records, turbidity and Mn are reported for the same sampling day. On that day, T_{30} is available from the readings of the preceding 30 days and turbidity is a direct instrumental reading, whereas total Mn requires acid digestion and spectrometric determination in the laboratory; a rule can therefore be evaluated before the Mn result is available.

RESULTS

Magnitude and seasonality of manganese

Total Mn had a median of 0.096 mg L⁻¹ (interquartile range 0.063–0.159 mg L⁻¹) and reached 0.898 mg L⁻¹. It exceeded 0.1 mg L⁻¹ in 47.6% of samples and the EU and US value of 0.05 mg L⁻¹ in 88.1% (Table 1), while Fe exceeded 0.3 mg L⁻¹ in 89.3% (Table 1), while Fe exceeded 0.3 mg L⁻¹ in 89.3%. Log Mn differed among sources (Kruskal–Wallis $H = 375.4$, $p < 0.001$, $\eta^2 = 0.11$). Exceedance was most frequent at the Chanh Duong

Table 1. Total manganese and iron in raw water at the seven intakes, 2021–2024

Source	Intake	n (Mn)	Mn median, mg L ⁻¹	Mn Q1–Q3, mg L ⁻¹	Mn P90, mg L ⁻¹	Mn > 0.05, %	Mn > 0.1, %	n (Fe)	Fe media, mg L ⁻¹	Fe > 0.3, %	δ Mn rainy–dry
Re River	QV	1.042	0.094	0.062–0.148	0.208	89.1	46.0	418	0.44	86.8	0.83
	HP3	1.010	0.129	0.067–0.206	0.294	87.7	59.7	626	0.58	94.7	0.72
Da Do River	CN	396	0.083	0.063–0.110	0.150	91.7	31.8	246	0.44	94.3	0.74
	HD	367	0.067	0.048–0.095	0.140	72.8	22.1	287	0.39	78.7	0.85
Chanh Duong Canal	VB1	281	0.127	0.095–0.191	0.323	98.9	69.8	205	0.57	96.6	0.63
	VB2	170	0.143	0.099–0.209	0.290	98.8	74.1	160	0.55	96.3	0.36
Gia River	NL	185	0.071	0.054–0.091	0.120	81.1	16.8	80	0.30	48.8	0.46
All intakes	–	3.451	0.096	0.063–0.159	0.232	88.1	47.6	2,022	0.47	89.3	0.68

Note: One sample per intake day. Q1–Q3, interquartile range; P90, 90th percentile. Mn limits: 0.05 mg L⁻¹ (EU, US) and 0.1 mg L⁻¹ (Vietnam); Fe limit: 0.3 mg L⁻¹ (US, Vietnam). δ, Cliff’s delta of Mn, rainy (May–November) versus dry (December–April) season; all $p < 0.001$.

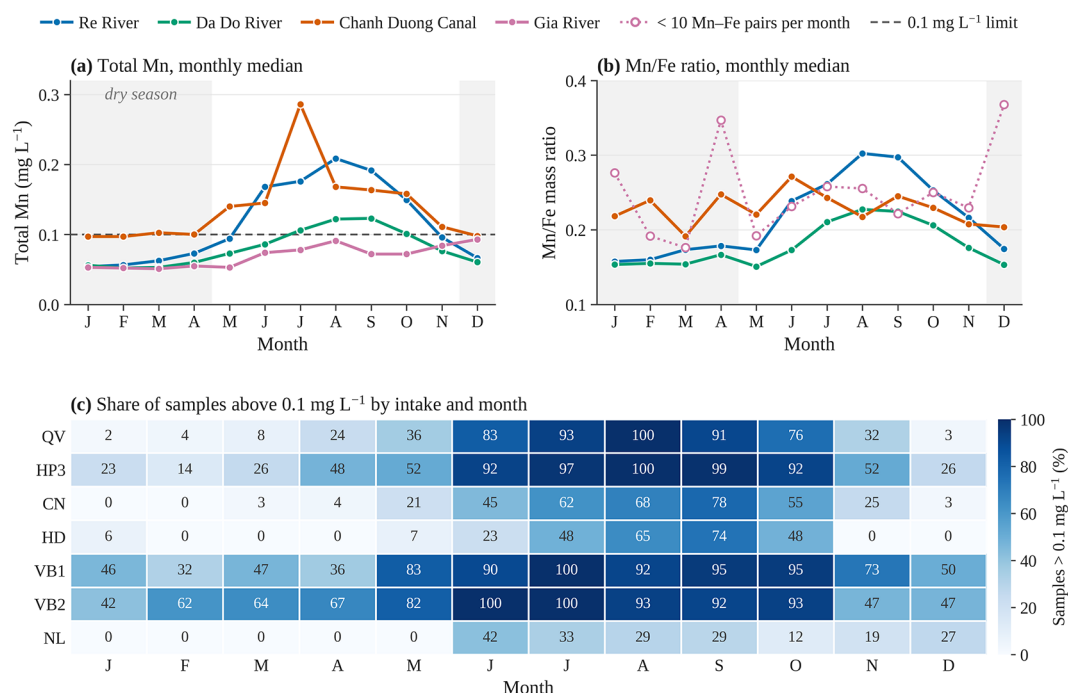


Figure 2. Seasonal regime of Mn, 2021–2024: monthly median of (a) total Mn and (b) the Mn/Fe ratio by source (dotted, < 10 pairs per month); (c) share of samples with Mn > 0.1 mg L⁻¹ by intake and month. Gray shading in (a, b), dry season

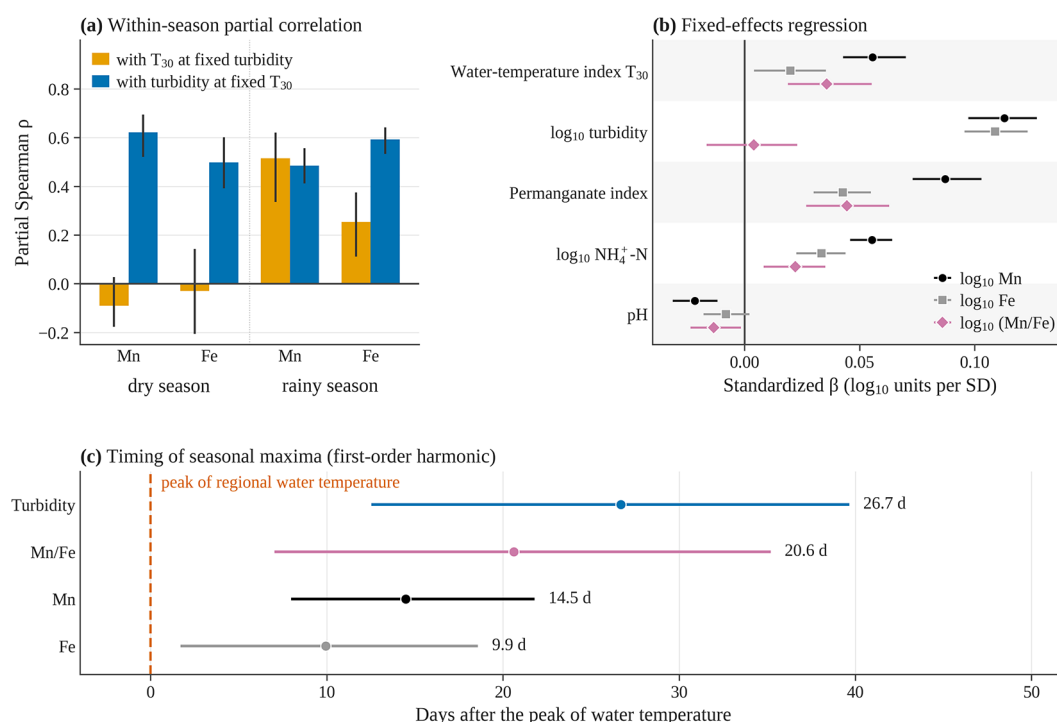


Figure 3. Turbidity-associated and warm-season patterns: (a) within-season partial Spearman correlations; (b) standardized coefficients of the fixed-effects regressions ($n = 1,942$; SD, standard deviation); (c) timing of seasonal maxima relative to the peak of regional water temperature. Bars, 95% bootstrap CIs

Canal intakes (VB2 74.1%, VB1 69.8%) and least frequent at NL on the Gia River (16.8%).

Mn followed a pronounced seasonal cycle (Figure 2a). Rainy-season Mn exceeded

dry-season Mn at every intake (Cliff's δ from 0.36 at VB2 to 0.85 at HD), but at the canal intakes Mn remained close to or above the limit even in the dry season. The median Mn/Fe ratio rose from

0.165 in January to 0.260 in September (Figure 2b). This seasonal rise was pronounced at the Re and Da Do intakes ($\delta = 0.37$ – 0.62) but small at VB1, VB2, and NL ($\delta = -0.09$ to 0.12). System-wide exceedance rose from 10.7% in February to 87.5% in September (Figure 2c). All 836 dry-season samples exceeded the crustal bound with each of the five reference ratios. The median share of Mn in excess of crustal proportions was 90% with the Taylor (1964) ratio, 85–90% with the alternative crustal and Red River ratios, and 80% and 70% when the Taylor bound was doubled or tripled (Table S5); the median Mn/Fe ratio (0.171 in the dry season, 0.228 in the rainy season) was ten to fourteen times the crustal ratio.

Turbidity-associated and warm-season patterns

Within each season, Mn related differently to turbidity and T_{30} (Figure 3a). In the dry season ($n = 792$), Mn correlated with turbidity at fixed

T_{30} (partial $\rho = 0.62$, 95% CI 0.52–0.69) but not with T_{30} at fixed turbidity ($\rho = -0.09$, -0.18 to 0.03). In the rainy season ($n = 1,185$), an association with T_{30} appeared ($\rho = 0.52$, 0.34–0.62), while the association with turbidity remained ($\rho = 0.49$, 0.41–0.56). Fe showed the same pattern, with a weaker rainy-season association with T_{30} ($\rho = 0.25$, 0.11–0.38).

The fixed-effects regressions quantified this contrast in matched samples ($n = 1,942$; Table 2, Figure 3b). Per standard deviation of log turbidity, log Mn and log Fe increased almost equally ($\beta = 0.113$ and 0.109), and the Mn/Fe ratio did not change ($\beta = +0.004$, 95% CI -0.017 to 0.023). Per standard deviation of T_{30} , by contrast, log Mn increased by 0.056 and log Fe by only 0.020, and the Mn/Fe ratio increased ($\beta = +0.036$, 0.019 to 0.055). The ratio also increased with PI and NH_4^+ -N and decreased with pH. In the extended model, it increased with NO_2^- -N and conductivity, and the T_{30} coefficient remained positive. The T_L coefficient of the ratio

Table 2. Station fixed-effects regressions (panel A) and segmented regressions on the 30-day water-temperature index (panel B)

Term	$\log_{10}$ Mn	$\log_{10}$ Fe	$\log_{10}$ (Mn/Fe)	$\log_{10}$ (Mn/Fe), extended
A. Standardized coefficients β [95% CI], same samples				
Water-temperature index T_{30}	+0.056 [0.043, 0.070]	+0.020 [0.004, 0.035]	+0.036 [0.019, 0.055]	+0.051 [0.029, 0.072]
$\log_{10}$ turbidity	+0.113 [0.097, 0.127]	+0.109 [0.096, 0.123]	+0.004 [−0.017, 0.023]	+0.001 [−0.020, 0.017]
Permanganate index	+0.087 [0.073, 0.103]	+0.043 [0.030, 0.055]	+0.044 [0.027, 0.063]	+0.035 [0.013, 0.059]
$\log_{10}$ NH_4^+ -N	+0.055 [0.046, 0.064]	+0.033 [0.022, 0.044]	+0.022 [0.008, 0.035]	+0.009 [−0.004, 0.021]
pH	−0.022 [−0.031, −0.012]	−0.008 [−0.018, 0.002]	−0.013 [−0.024, −0.002]	−0.016 [−0.025, −0.002]
$\log_{10}$ NO_2^- -N	—	—	—	+0.022 [0.010, 0.035]
$\log_{10}$ conductivity	—	—	—	+0.029 [0.008, 0.045]
n	1.942	1.942	1.942	1.941
R ² (within intake)	0.79 (0.75)	0.66 (0.58)	0.30 (0.25)	0.33 (0.28)
Residual lag-1 autocorrelation	0.31	0.18	0.33	0.31
Maximum within-intake VIF	1.77	1.77	1.77	2.52
GAM deviance explained	0.81	0.67	—	—
B. Segmented regression on T_{30}				
ψ , °C [95% CI] — controls: intake, turbidity	25.4 [23.2, 26.4]	22.4 [21.8, 27.7]	—	—
Slope below ψ , % per °C	+0.9 [−3.6, 2.8]	−4.6 [−11.9, 1.6]	—	—
Slope above ψ , % per °C	+14.2 [10.3, 18.7]	+4.5 [3.5, 11.3]	—	—
ΔAIC vs linear / vs quadratic	276 / 32	65 / 5	—	—
n	3.034	1.977	—	—

Note: A: least squares with intake fixed effects; β , change in $\log_{10}$ units per standard deviation of the predictor; “extended” adds nitrite and conductivity. B: controls, intake and $\log_{10}$ turbidity; slopes as % change per °C, $100 \cdot (10^b - 1)$; the fits with PI, NH_4^+ -N, and pH as additional controls are in Table S6. 95% CIs from 1,000 bootstrap resamples of year-months.

was positive for every window from 7 to 60 d ($\beta = 0.030\text{--}0.042$, all CIs excluding zero).

Daily regional water temperature peaked on day 212 (Figure 3c). Fe peaked 9.9 d later, Mn 14.5 d later, the Mn/Fe ratio 20.6 d later, and turbidity 26.7 d later. The Mn peak coincided with that of T_{30} (day 227). The 95% CIs of these lags overlapped. At QV and HP3, Mn and Fe correlated most strongly with turbidity at zero lag ($\rho = 0.61\text{--}0.73$), whereas de-seasonalized temperature anomalies were only weakly related to Mn anomalies at lags of 0–90 d (ρ between -0.11 and 0.06 , $n = 3.377$).

The turbidity coefficient of the ratio did not vary detectably with T_{30} (interaction $\beta = -0.011$, -0.023 to 0.004). After accounting for intake and turbidity effects, $\log(\text{Mn/Fe})$ increased with $\log \text{NO}_2^- \text{-N}$ (partial $\rho = 0.24$, 0.15 to 0.32). Monthly median $\text{NO}_2^- \text{-N}$ rose from $0.030 \text{ mg N L}^{-1}$ in January to $0.085 \text{ mg N L}^{-1}$ in August, while nitrate varied only between 0.76 and 0.83 mg N L^{-1} . Mn also showed seasonal hysteresis. At nearly the same monthly mean daily water temperature (27.7°C in May and 27.3°C in October), median Mn was 0.091 mg L^{-1} in May but 0.131 mg L^{-1} in October. T_{30} , which lags daily temperature, averaged 26.1°C in May and 28.5°C in October.

Adding T_{30} to intake effects and log turbidity raised R^2 for log Mn from 0.49 to 0.65 ($n = 2.960$).

A first- or second-order seasonal harmonic raised it to 0.68 or 0.69 , and the first-order harmonic plus T_{30} gave 0.68 . As a predictor of Mn level, therefore, T_{30} added nothing to a seasonal harmonic.

Nonlinear response to the water-temperature index

The GAMs explained 81% of the deviance in log Mn and 67% in log Fe. For both metals, the partial effect of turbidity was steep and nearly linear on the log-log scale. The partial effect of T_{30} on Mn was much weaker below about 25°C than above it, whereas its effect on Fe remained weak throughout (Figure 4a, b). Segmented regression placed the statistical change-point of the Mn response to the index at 25.4°C (95% CI $23.2\text{--}26.4^\circ\text{C}$), with a slope near zero below it and $+14.2\%$ per $^\circ\text{C}$ above it, and was preferred over linear and quadratic fits (Table 2, Figure 4c). The residual sum of squares stayed within 1% of its minimum between 23.5 and 26.6°C , so the breakpoint is better read as a transition zone than as a sharp threshold; because T_{30} also marks the time of year, it describes when Mn rose in the seasonal cycle and is not a demonstrated physicochemical temperature threshold. The breakpoint was insensitive to the uneven sampling: it

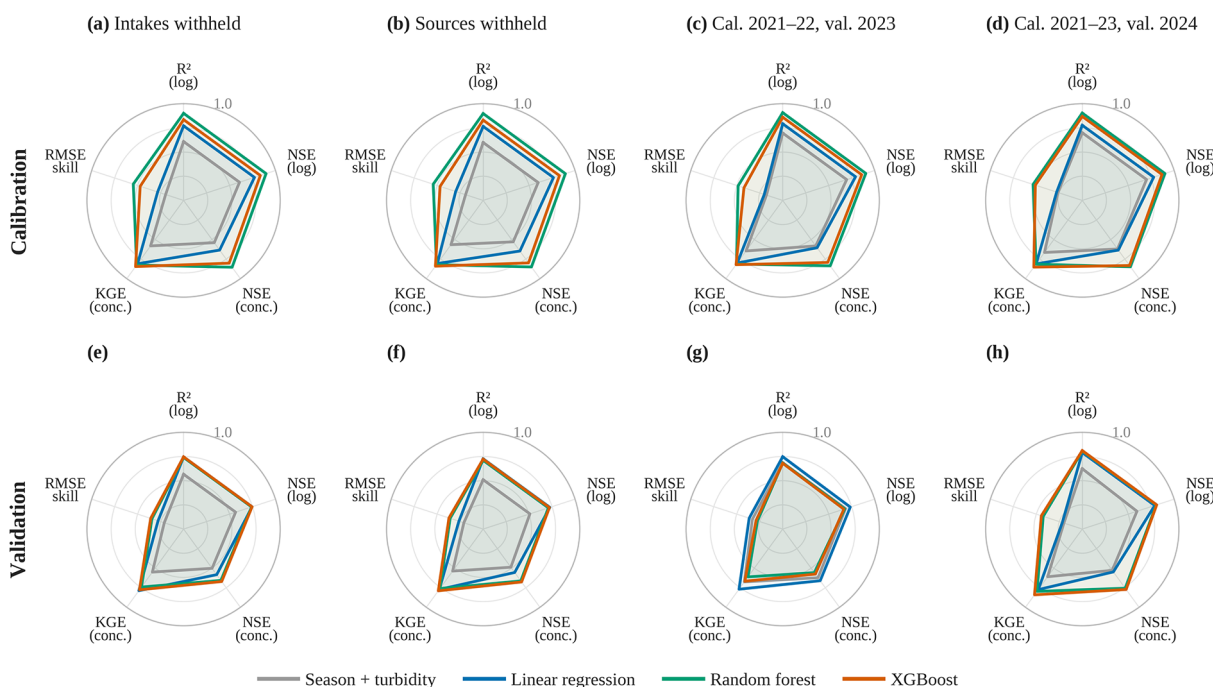


Figure 4. Nonlinear responses of Mn and Fe: GAM partial effects of (a) T_{30} and (b) turbidity (bands, 95% CI); (c) segmented regression on binned partial residuals (median and interquartile range); dashed line and band, Mn breakpoint ψ and its 95% CI

was 26.0 °C (95% CI 22.8–27.5 °C) with intakes weighted equally, 25.4 °C without the canal intakes, 25.2–25.5 °C with each intake left out in turn, and 25.5 °C (25.2–26.0 °C over 200 draws) with QV and HP3 thinned to at most five samples per month (Table S6). T_{30} rose above 25.4 °C between 3 and 16 May in every year. With PI, NH_4^+ -N, and pH as additional controls, the breakpoint was similar but less precise, and the upper slope was smaller, because these covariates share part of the warm-season signal; for Fe, the breakpoint was poorly constrained (Table S6).

Robustness to rainfall, the seasonal cycle and sampling density

Antecedent rainfall was associated with higher Mn and Fe (7-day rainfall: $\beta = +0.018$ and $+0.025$) but not with a higher Mn/Fe ratio (-0.007 , -0.024 to 0.009). In 2022–2024, the CI of the T_{30} coefficient for Fe included zero, with or without rainfall, whereas those for Mn ($+0.045$, 0.030 to 0.061) and the ratio ($+0.049$, 0.024 to 0.072) excluded it. Once the seasonal cycle was absorbed by harmonics, however, T_{30} anomalies (standard deviation 0.62 °C) were not associated with Mn (-0.001 , -0.011 to 0.010), Fe, or the ratio. With rainfall added (2022–2024), the

breakpoint was 25.9 °C (23.3–28.6 °C). When intakes were weighted equally, the CI of the T_{30} coefficient for the ratio still excluded zero ($+0.030$, 0.011 to 0.050), and the turbidity coefficient remained close to zero. Two-month blocks left the intervals almost unchanged.

Transferability to unseen intakes, sources and years

The nested selection chose a T_L window of 45–60 d in 10 of the 13 outer folds. With intakes withheld, XGBoost reached a log-scale NSE of 0.75 (95% CI 0.71–0.77), compared with 0.33 for climatology, 0.57 for the seasonal baseline, and 0.67 on the concentration scale (Table S8). With all sources withheld, it reached 0.72 (0.68–0.75), and in 2024 it reached 0.81 (0.75–0.84) on the log scale and 0.77 on the concentration scale. The linear model reached validation log-scale NSEs of 0.75, 0.73, 0.74, and 0.79 when intakes, sources, 2023, and 2024 were withheld, respectively, at most 0.06 below its calibration NSEs (0.77–0.79), whereas the calibration–validation gap was 0.06–0.19 for XGBoost and 0.09–0.23 for random forest (Table S8). R^2 , KGE, and RMSE showed a similar contrast between the linear and tree-based models (Table S8, Figure 5). For the

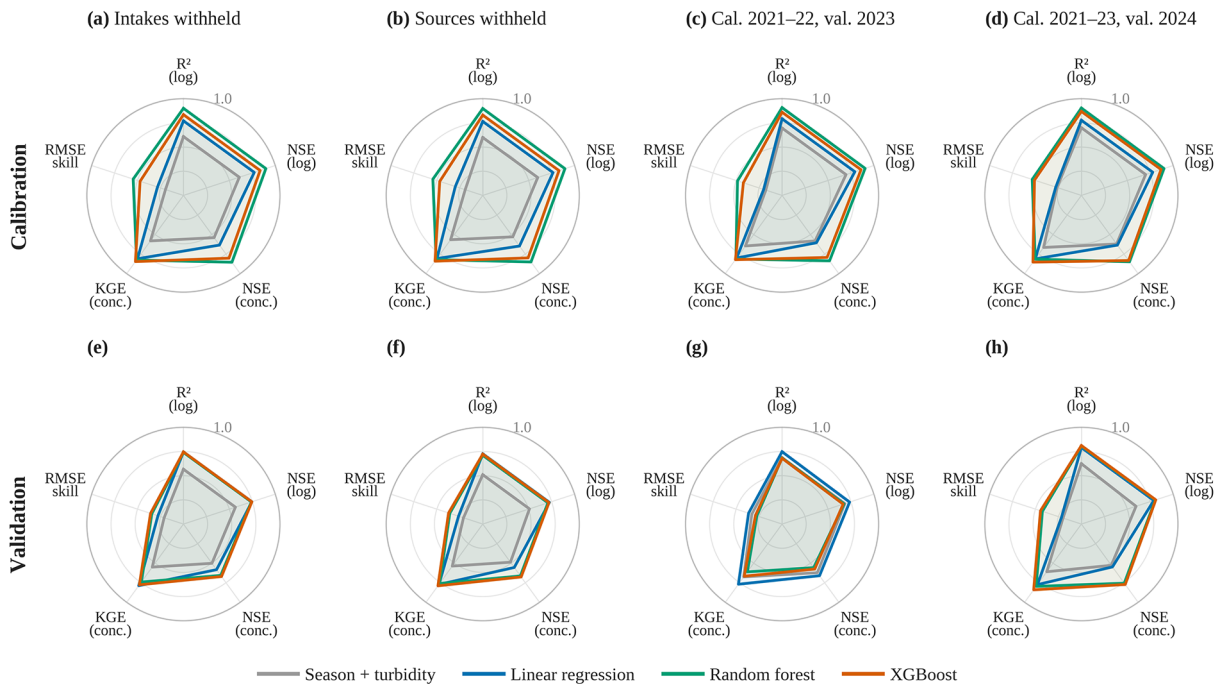


Figure 5. Skill of the seasonal baseline and the three predictor-based models in calibration (a–d; mean over folds) and validation (e–h; pooled withheld data): (a, e) intakes withheld; (b, f) sources withheld; (c, g) calibrated on 2021–2022, validated on 2023; (d, h) calibrated on 2021–2023, validated on 2024. Axes: R^2 and NSE on the $\log_{10}$ scale; NSE, KGE and RMSE skill ($1 - \text{RMSE}/\text{RMSE}$ of climatology) on the concentration scale; rings at 0.25 intervals

three predictor-based models, validation R^2 exceeded NSE by at most 0.02, and PBIAS stayed within $\pm 8\%$; the linear model reached validation KGEs of 0.77–0.79 and RMSEs of 0.051–0.060 mg L^{-1} , against 0.074–0.080 mg L^{-1} for climatology. The linear model improved on the seasonal baseline by 0.18–0.22, except in 2023, when the CI of the gain included zero (+0.05, –0.01 to 0.11). XGBoost did not improve on the linear model on the log scale (differences –0.07 to +0.02; CI below zero only in 2023) but did on the concentration scale in 2024 (+0.22, 0.02 to 0.52). Skill varied among the 13 folds (Figure 6a; Table S9). With intakes withheld, the linear model reached log-scale NSEs of 0.77 (QV), 0.81 (HP3), 0.70 (CN), 0.68 (HD), 0.59 (VB1), 0.24 (VB2), and –0.27 (NL), and XGBoost 0.79, 0.78, 0.69, 0.69, 0.61, 0.38, and –0.36; with sources withheld, 0.78 (Re), 0.69 (Da Do), 0.43 (Chanh Duong), and –0.33 (Gia) for the linear model and 0.77, 0.66, 0.45, and –0.24 for XGBoost; and in the forward tests 0.74 (2023) and 0.79 (2024) for the linear model and 0.67 and 0.81 for XGBoost. The linear model was within 0.02 of XGBoost or better in all folds but VB2 and the Gia River. At NL, and for the Gia River, which comprises only NL, every predictor-based model was worse than the seasonal baseline (NSE 0.17), so the relations learned at the other intakes did not transfer to this source. Rebuilding the temperature series without the withheld intake changed the leave-one-intake-out NSE by at most 0.004, except for XGBoost at

NL (+0.021; Table S10), so the regional series did not leak information from the withheld intake. An audit of the 13 folds confirmed that no intake-day and, in the intake and source folds, no intake appeared in both the calibration and the validation set; that every calibration date preceded every validation date in the year folds; and that L , the hyperparameters, and the smearing factor were selected or estimated within the calibration set only (Table S13).

SHAP attribution ranked PI (mean $|\text{SHAP}| = 0.079 \log_{10}$ units) and turbidity (0.078) above T_{45} (0.056), $\text{NH}_4^+\text{-N}$ (0.042), and pH (0.011). The water-temperature index accounted for 24.5% of the attribution in the dry season and 18.7% in the rainy season, with opposite signs. Because no dry-season association with T_{30} was found at fixed turbidity (Figure 3a), T_{45} also serves as a seasonal indicator in the model. The SHAP dependence on T_{45} steepened from about 0.007 to about 0.022 $\log_{10}$ units per $^{\circ}\text{C}$ at a breakpoint of 24.4 $^{\circ}\text{C}$. This breakpoint lay between 24.2 and 24.9 $^{\circ}\text{C}$ in all seven leave-one-intake-out models and was 25.9 $^{\circ}\text{C}$ with T_{30} ; as a property of the fitted model, it is not independent confirmation of the segmented-regression estimate.

Operational triggers and rules out of sample

Intake-specific logistic slopes were preferred over a common slope (likelihood-ratio statistic 57.2, 6 degrees of freedom, $p < 0.001$), and the

Table 3. Water-temperature triggers, length of the manganese season and operational class of each intake

Source	Intake	θ_{50} , $^{\circ}\text{C}$ [95% CI]	θ_{20} , $^{\circ}\text{C}$	Season, d yr^{-1} [95% CI]	Class (bootstrap share)	Exceedances in season, %	Exceedances outside season, n	Turbidity outside season, exceed / not, NTU	2024 test: detected / exceedances
Re River	QV	26.5 [25.8, 27.0]	24.4	172 [161, 189]	Seasonal (1.00)	86.4	65	19.3 / 11.6	106 / 116
	HP3	24.2 [22.6, 25.6]	21.1	228 [194, 265]	Seasonal (0.75)	81.4	112	55.2 / 12.6	128 / 206
Da Do River	CN	28.5 [28.0, 29.1]	26.1	129 [101, 139]	Seasonal (1.00)	81.0	24	29.0 / 18.5	22 / 37
	HD	29.6 [28.8, 30.8]	27.3	60 [8, 120]	Seasonal (0.54)	45.7	44	25.2 / 13.6	2 / 24
Chanh Duong Canal	VB1	22.5 [21.8, 23.3]	18.7	266 [250, 284]	Chronic (1.00)	84.4	30	16.2 / 17.1	35 / 40
	VB2	20.8 [18.6, 22.7]	15.4	308 [263, 356]	Chronic (1.00)	88.8	14	14.2 / 14.6	40 / 40
Gia River	NL	not reached ^a	27.8	0 [0, 35]	Episodic (1.00)	0.0	31	7.5 / 6.1	0 / 7

Note: θ_{50} , θ_{20} : T_{30} at which the probability of $\text{Mn} > 0.1 \text{ mg L}^{-1}$ is 50% and 20%. Season: days per year with $T_{30} \geq \theta_{50}$. Classes: chronic ≥ 240 , seasonal 60–239, episodic $< 60 \text{ d yr}^{-1}$. 2024 test: triggers fitted on 2021–2023. θ_{20} at VB2 lies below the observed T_{30} range (extrapolated) and should not be used operationally. ^a θ_{50} above the highest observed T_{30} (31.1 $^{\circ}\text{C}$).

mean within-intake area under the receiver-operating-characteristic curve was 0.84. θ_{50} ranged from 20.8 °C at VB2 to 29.6 °C at HD; at NL it exceeded the highest observed T_{30} of 31.1 °C (Table 3, Figure 7). The Mn season lasted 308 and 266 d yr⁻¹ at the two canal intakes, 129–228 d yr⁻¹ at QV, HP3, and CN, and 60 d yr⁻¹ at HD (95% CI 8–120 d yr⁻¹). The classes were robust (bootstrap share 1.00), except at HP3 (0.75) and HD (0.54). Outside the season, exceedances at the Re and Da Do intakes occurred at much higher turbidity than non-exceedances, but those at the canal intakes did not (Table 3); there, the probability of exceedance was already high at low T_{30} (Figure 7a).

When we validated triggers calibrated on 2021–2023 in 2024, θ_{50} detected 71% of

exceedances (Table 3), with a FAR of 0.14, and θ_{20} detected 85%, with a FAR of 0.27. In the leave-one-year-out comparison (Figure 6b; Table S11), the T_{30} rule performed about as well as a fixed calendar (CSI 0.64 versus 0.62 at $p^* = 0.5$; difference +0.020, −0.009 to 0.053), and turbidity alone did no better (0.58). Combining a seasonal term with same-day turbidity improved on the calendar: CSI rose to 0.72 with a calendar harmonic and 0.71 with T_{30} , gains of 0.092 (0.050 to 0.141) and 0.081 (0.039 to 0.133), or 0.075 and 0.063 with intakes weighted equally. Persistence reached a CSI of 0.68. The harmonic-plus-turbidity rule slightly exceeded it (+0.036, 0.008 to 0.068), and the T_{30} -plus-turbidity rule matched it (+0.025, −0.003 to

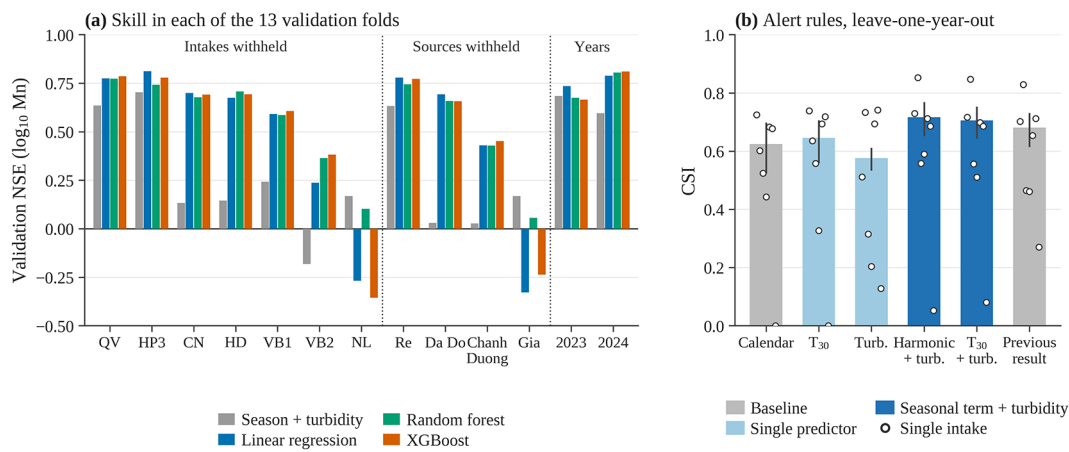


Figure 6. Skill in every validation fold and by alert rule: (a) validation NSE of log₁₀ Mn in each of the 13 outer folds (seven intakes, four sources, and two years withheld) for four models; (b) critical success index (CSI) of six daily alert rules at $p = 0.5$ in leave-one-year-out tests (bars, pooled CSI with 95% bootstrap CI; circles, single intakes). Full results in Tables S8, S9, and S11

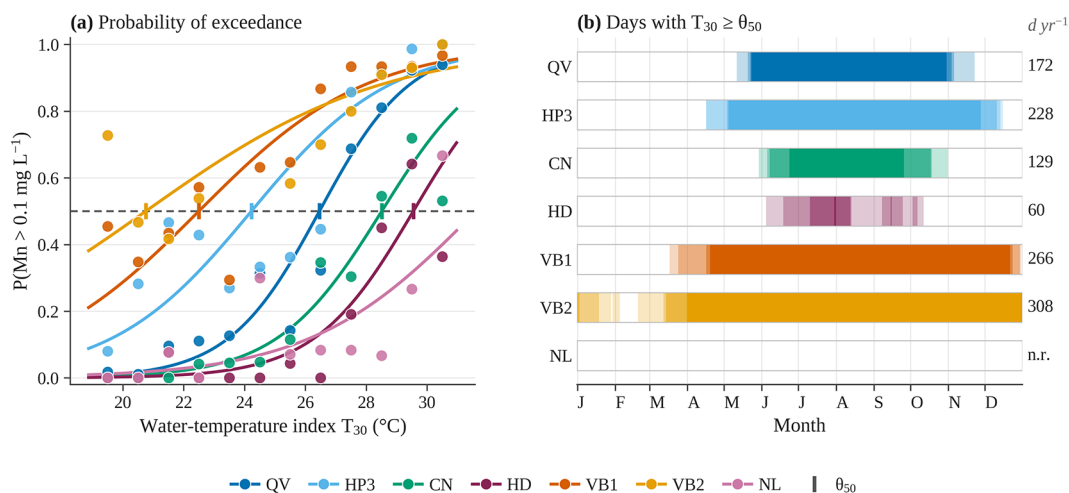


Figure 7. (a) Probability of Mn > 0.1 mg L⁻¹ versus T_{30} : intake-specific logistic fits (lines), observed frequencies (symbols), and θ_{50} (vertical ticks); (b) days with $T_{30} \geq \theta_{50}$ (shading, share of years; right, mean days per year; n.r., not reached)

0.056). By intake, the combined rules matched or exceeded persistence except at VB2 (−0.03) and NL (−0.19 to −0.22), and their gain over the calendar was concentrated at HP3 (+0.25) and HD (+0.07 to +0.15), the intakes with the largest turbidity-driven excursions (Table S11). With T_{30} plus turbidity, rules calibrated on a single year reached a CSI of 0.61–0.69 in 2024, compared with 0.69 (0.58–0.78) for two years and 0.69 for three years.

DISCUSSION

What routine records can and cannot show

Routine records of total Mn, total Fe, and turbidity are sufficient to separate two statistically distinct patterns of Mn variation without filtered samples, but not to identify the processes behind them. The turbidity-associated pattern is associated with proportional increases in Mn and Fe, on average leaves their ratio unchanged, is strongest at zero lag, and operates in both seasons. If the particles were purely lithogenic, the ratio would fall as turbidity rose. An unchanged ratio is therefore consistent with particles rich in authigenic Fe–Mn oxyhydroxides, such as resuspended bed fines (Abesser and Robinson, 2010), or with pore-water Mn(II) released with them; because total Fe combines several phases, it does not prove that Mn and Fe share the same particles. Because dry-season Mn tracked turbidity but not T_{30} , and 70–90% of the Mn in the median dry-season sample exceeded crustal proportions under all reference ratios tested, the turbidity-associated Mn would be largely in excess of crustal proportions if the reference ratios apply to the local source material, whose composition has not been measured; the origin of this Mn therefore remains open.

The warm-season pattern shows three signatures that turbidity-associated transport does not explain at fixed turbidity. Its T_{30} coefficient is larger for Mn than for Fe, so the Mn/Fe ratio coefficient is positive for every window from 7 to 60 d. It strengthens sharply above a water-temperature index of about 25 °C, which was reached between 3 and 16 May each year (25.4 °C by segmented regression; the SHAP dependence of the fitted XGBoost model on the same index changed slope at 25.9 °C). It persists when antecedent rainfall is controlled.

Putative mechanisms and alternative explanations

One putative mechanism is Mn(IV) reduction under mildly reducing conditions; the data are consistent with it but cannot confirm it. The ratio increases with PI and $\text{NH}_4^+\text{-N}$ and decreases with pH (Table 2). Microbial Mn(IV) and Fe(III) reduction is coupled to the oxidation of organic carbon (Lovley, 1991), and Fe(III) reduction in wetland soils had an average temperature coefficient (Q_{10}) of 3.5 (range 1.5–8.9) between 6 and 18 °C (Schilling et al., 2019). Lower pH slows Mn(II) re-oxidation (Davison, 1993), whereas warming accelerates biotic Mn(II) oxidation (Pearl et al., 2025), so a warm-season rise would imply, if Mn(II) dominates, that its supply outpaces its removal. The ratio also increased with nitrite, an intermediate of both nitrification and nitrate reduction, which peaked in late summer while nitrate stayed nearly constant. Because nitrate persisted in the water column, where it acts as a redox buffer that protects Mn oxides from reduction (Rudolf von Rohr et al., 2014), any Mn(IV) reduction would more plausibly occur in sediments, soils, or groundwater than in the channel water itself. The hysteresis between May and October and the selection of 45–60-day windows are consistent with Mn following conditions that accumulate over the season. PI, $\text{NH}_4^+\text{-N}$, and nitrite all share the seasonal cycle; however, these associations are consistent with reduction but cannot, by themselves, separate it from seasonality. The increase in the ratio with conductivity suggests that slower water exchange may also contribute, consistent with the dry-season enrichment of dissolved metals, including Mn, at higher salinity and longer residence times in the Red River estuaries (Duong et al., 2026); the Re River, which supplies QV and HP3, is among the northern rivers affected by salt intrusion (Dat and Huyen, 2025), so conductivity at these intakes also reflects tidal influence. Whether Mn(II) or particulate Mn dominates in either season remains a hypothesis, because no speciation was measured.

Three hypothetical sources of reduced Mn can be considered: bed sediments in slow-flowing reaches, where weak water exchange during the warm season can create reducing conditions, as in reservoirs (Krueger et al., 2020); drainage from flooded paddy fields, whose soils release Mn(II) within weeks of flooding (Haque et al., 2015; Kögel-Knabner et al., 2010), although flooding

of the spring crop (about February–May) coincides with low Mn; and exfiltration of reducing groundwater, which carries dissolved Fe on the Red River floodplain (Postma et al., 2007) and is predicted to be rich in Mn across the delta (Podgorski and Berg, 2026). Faster removal of Fe(II) than of Mn(II) (Davison, 1993) or settling of coarse, Fe-rich particles could also raise the ratio, but settling alone does not explain why the ratio rises with T_{30} at fixed turbidity.

The water-temperature index is best interpreted as a seasonal marker. The enrichment survived control for rainfall and equal weighting of intakes, but it did not track 30-day temperature anomalies and added nothing to a seasonal harmonic. The data thus do not show that temperature itself drives the enrichment. The most parsimonious explanation is a seasonal process that builds up over the warm, rainy months, possibly through reduction of warm channel-bed sediments, field drainage, or accumulated organic loading.

Limitations

These interpretations remain hypotheses. Without DO, ORP or Eh, alkalinity or dissolved inorganic carbon, dissolved and particulate Mn and Fe, sulfide, or Fe(II) and Mn(II), neither the redox mechanism nor the share of dissolved Mn(II) can be confirmed. Because T_{30} also marks the time of year and its anomalies did not explain Mn, the transition zone near 25 °C cannot be read as a physiological or chemical threshold. The regional temperature series cannot resolve local differences between intakes, and direct readings at VB1 and VB2 are few (Table S3); the crustal bound depends on a reference composition that has not been verified locally (Table S5); and the Mn and Fe values carry the analytical uncertainty of routine spectrometric determinations, although the results were insensitive to simulated analytical error (Table S12). All results refer to raw-water total Mn at one utility, without jar-test, pilot, or treated-water data. Paired filtered and unfiltered samples, DO and ORP readings, and pore-water measurements would be needed to test the putative mechanisms.

Contrasting sources: the Chanh Duong Canal and the Gia River

The canal intakes behaved differently. Mn was close to or above the limit every month; the

Mn/Fe ratio varied little between seasons ($\delta = 0.03$ – 0.12), and exceedances outside the Mn season were not linked to high turbidity. The canal carried the highest $\text{NH}_4^+\text{-N}$ (median over both intakes 0.31 mg N L^{-1}) and a high PI ($3.36 \text{ mg O}_2 \text{ L}^{-1}$). As the main irrigation and drainage channel of an agricultural district, it may combine long residence times, organic-rich sediments, and field drainage, which could sustain Mn-mobilizing conditions for most of the year. The Gia River at NL is the opposite case: clear water (median turbidity 6.1 NTU), higher pH (7.84) and conductivity ($407 \text{ }\mu\text{S cm}^{-1}$), and rare exceedances. The models' failure there indicates that relations learned from turbid, organic-rich sources do not transfer to a chemically distinct source.

Estimation skill in context

The best model achieved a log-scale NSE of 0.73 – 0.81 across validation schemes, reflecting concurrent estimation rather than forecasting. The loss of skill for withheld sources and the failure at NL parallel the lower skill of global groundwater-Mn models under spatial cross-validation (Podgorski and Berg, 2026) and support the use of grouped validation to assess transferability (Roberts et al., 2017). That a linear model matched or exceeded XGBoost on the log scale at most intakes and folds (Table S9) and lost less skill from calibration to validation suggests largely additive, log-linear controls; the tree ensemble served mainly to describe the steeper warm-season response, and, because its predictors are correlated, its SHAP values describe the fitted model rather than causal effects (Aas et al., 2021).

Practical value and transferability

Four results show how records utilities already hold can support raw-water management at river and canal intakes. First, the alert rules need only T_{30} (or the date) and same-day turbidity, both available on the sampling day before the laboratory Mn result is reported, and both can be combined in ordinary spreadsheet formulas (Figure 8). Second, out-of-sample, rules combining a seasonal term with same-day turbidity improved on a fixed calendar and, pooled over intakes, matched or exceeded the previous laboratory result. Most of the gain came from adding same-day turbidity: the T_{30} rule alone barely outperformed the calendar (Figure 6b), so the contribution lies in

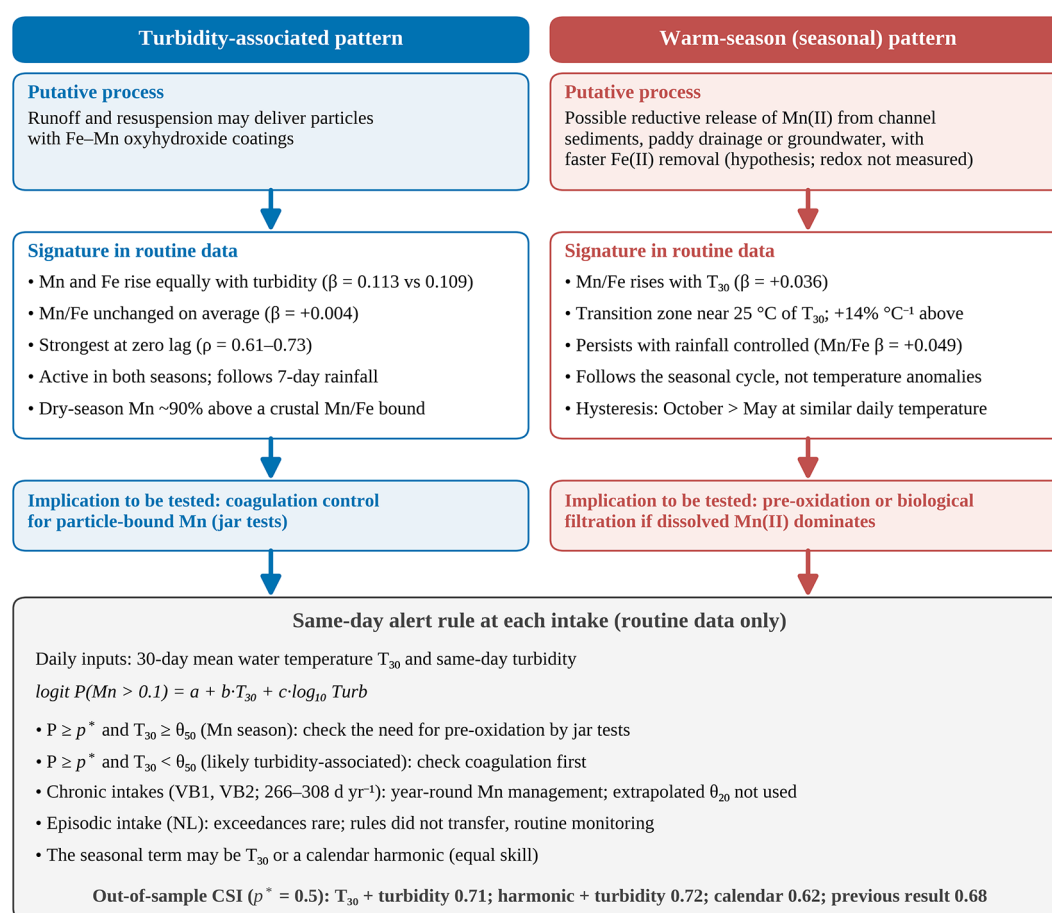


Figure 8. Conceptual summary of the turbidity-associated and warm-season Mn patterns: putative processes, signatures in routine data, implications to be tested, and the same-day alert rule

combining a seasonal indicator with turbidity rather than in an independent diagnostic value of T_{30} . Third, rules calibrated on a single year were less consistent in the forward test than those calibrated on two or three years. Fourth, skill held when a whole source was withheld but failed at the one chemically distinct source, which indicates that rules for such sources, and for intakes with persistently high Mn such as VB2, depend on local calibration. At VB2, the extrapolated θ_{20} (15.4°C) should not be used operationally; VB2 is better treated as a chronic intake. The procedure is general in its inputs and steps but local in its coefficients, which should be refitted from more than one year of local records and re-evaluated against local calendar and persistence baselines.

Possible implications for treatment

If the two patterns correspond to particulate and dissolved Mn, as hypothesized, they would call for different treatment responses; because no speciation, jar-test, pilot, or treated-water data

were analyzed, the following implications are assumptions, to be tested in jar, pilot, or full-scale trials at each plant before any change in operation (Figure 8). Turbidity-associated Mn can be removed with coagulated solids to the extent that it is particulate (Tobiason et al., 2016), so out-of-season exceedances at the Re and Da Do intakes, which occur at high turbidity, may respond first to coagulation control. Warm-season enrichment may indicate a larger share of dissolved Mn(II), which passes conventional treatment unless oxidized (Tobiason et al., 2016). Ammonium (intake medians 0.07 – 0.38 mg N L^{-1}) complicates chlorination: chloramines inhibit Mn(II) oxidation, as shown in distribution pipes (Li et al., 2022), and ammonia-induced breakpoint chlorination raised trihaloacetaldehyde yields, with trihalomethane formation depending on the organic matter (Chen et al., 2025); in coastal surface water, where salt intrusion supplies bromide, brominated trihalomethanes exceeded guideline values in pilot tests once residual chlorine exceeded 0.4 – 0.8 mg L^{-1} (Dat et al., 2024). At the seasonal intakes (QV,

HP3, CN, and HD), an alert within the Mn season ($T_{30} \geq \theta_{50}$) may indicate conditions under which the need for pre-oxidation should be checked by jar tests, which were not performed here, whereas an alert outside it is more likely to be turbidity-driven. At the chronic canal intakes, where the Mn season lasts more than eight months, whether a permanent Mn removal stage would outperform seasonal dosing is an assumption that only pilot tests can settle. A lower decision level, $p^* = 0.2$, raised POD to 0.94–0.95 at the cost of more false alarms (Table S11); the choice depends on the relative costs of missed exceedances and unnecessary treatment.

CONCLUSIONS

Four years of routine raw-water records from seven intakes on four river and canal sources in Hai Phong City, Vietnam, show that manganese is a widespread and strongly seasonal treatment problem: total Mn exceeded 0.1 mg L^{-1} in 47.6% of samples and in nearly nine of ten samples in late summer. Using Fe as a particle tracer, the Mn/Fe ratio and a crustal mass balance separated two statistically distinct patterns without filtered samples. A turbidity-associated pattern, present year-round, is associated with proportional increases in Mn and Fe and, on average, leaves their ratio unchanged, although even dry-season Mn exceeds the crustal Mn/Fe proportions assumed here, a bound not yet verified against local sediment composition. A warm-season pattern is associated with larger increases in Mn than in Fe, strengthens above a transition zone of the 30-day water-temperature index centered near 25°C , and persists after rainfall is controlled. Because it does not follow temperature anomalies beyond the seasonal cycle, the index marks the warm season rather than driving it, and the redox processes and Mn species behind this pattern remain hypotheses. Five routine variables reproduced Mn at unseen intakes, sources, and years (log-scale NSE 0.73–0.79, linear model). Out of sample, same-day alert rules combining a seasonal term with turbidity improved the critical success index over a calendar schedule by 0.08–0.09 and matched or exceeded the previous Mn result. The treatment implications drawn from the two patterns are assumptions, because treatment performance was not evaluated.

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