



# Benchmarking produced water treatment strategies for non-toxic effluents: Integrating thermal distillation with granular activated carbon and zeolite post-treatment

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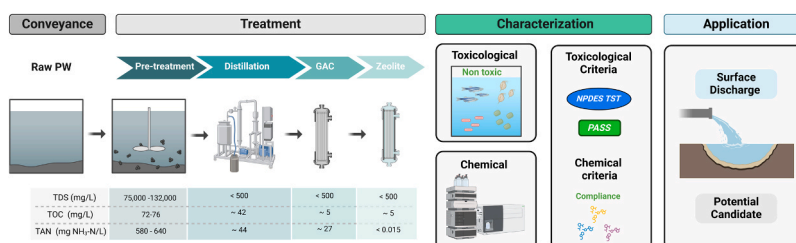
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## HIGHLIGHTS

- GAC and zeolite reduced most VOCs and ammonia to levels below detection limits.
- Removal of potential chemical stressors was consistent with toxicity reductions.
- WET tests indicated thermal distillation-GAC-zeolite treated PW to non-toxic levels.
- NPDES numeric & narrative criteria were used to assess treated PW discharge risks.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The management of produced water (PW) generated during oil and gas operations requires effective treatment and comprehensive chemical and toxicological assessment to reduce the environmental risks associated with reuse or discharge. This study evaluated a treatment train that included a low-temperature thermal distillation pilot system followed by granular activated carbon (GAC) and zeolite post-treatment for processing hypersaline Permian Basin PW. Our study provides a unique and comprehensive assessment of the treatment efficiency considering a targeted chemical scheme together with whole effluent toxicity (WET) tests across four trophic levels regarding aquatic critical receptors of concern (ROC): *Raphidocelis subcapitata*, *Vibrio fischeri*, *Ceriodaphnia dubia*, and *Danio rerio*. The distillate from the thermal distillation process met various numeric discharge standards for salinity and major ions. However, it did not meet toxicity requirements established by the United States National Pollutant Discharge Elimination System program. Subsequent post-treatment using GAC and zeolite reduced the concentration of potential stressors, including volatile organics, NH<sub>3</sub>, Cd, Cr, Zn, and Mn in the final effluent to below detection limits. This resulted in a consistent toxicity reduction across all WET tests, with no observable adverse effects for *R. subcapitata*, *C. dubia*, and *D. rerio* (no observed effect concentration >100%), and *V. fischeri* effects reduced to 19%. This study realizes the feasibility of treating PW to non-toxic levels and meeting reuse and discharge requirements. It underscores the importance of implementing integrated treatment trains to remove the contaminants of concern and provides a systematic decision framework to predict and monitor environmental risks associated with PW reuse.

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## 1. Introduction

Produced water (PW) is the wastewater generated as a byproduct during oil and gas (O&G) operations. The U.S. Ground Water Protection Council (GWPC) reported that approximately 25.9 billion barrels (bbl) ( $\sim 4.11$  billion  $\text{m}^3$ ) of PW were generated in 2021 [1–4]. PW is primarily managed through underground injection (UI), injection for enhanced oil recovery, and recycling for hydraulic fracturing [5,1–3]. UI is unsustainable on both environmental and fiscal grounds due to rising disposal costs, unavailability of disposal wells, and fluid injection-induced seismicity risks [2–4]. While reuse within the O&G sector would be the ideal management approach, PW volume far exceeds the O&G internal recycling capacity and often leads to prohibitive conveyance and storage costs [5,1–3]. Considering these challenges and the impacts that the O&G sector has on global energy, economic development, and environmental sustainability, finding alternatives to manage PW outside of O&G operations is paramount [6–8].

One of the main barriers to managing PW outside the O&G sectors is the lack of comprehensive characterization of the constituents in treated PW [9–12,1]. This constraint manifests itself in three critical issues. First, there are concerns regarding the effectiveness of PW treatment processes when the complete spectrum of its constituents remains unknown [5,1,3]. Second, the lack of exhaustive chemical and toxicological data sets hinders traditional human and environmental risk assessments [9,13,10]. Third, management guidelines and regulations for the reuse of PW beyond the O&G sector are not established due to the absence of frameworks that comprehensively assess the risk of effluents and establish feasible and protective water quality goals across different reuse scenarios [5,10,1–3,14]. Among the reuse scenarios, surface water discharge emerges as a potentially viable management strategy in major O&G-producing states like Texas, Colorado, Wyoming, and North Dakota. It has been legally sanctioned under Title 40 of the Code of Federal Regulations Part 435 (40 CFR 435) for facilities west of the 98th meridian with a National Pollutants Discharge Elimination System (NPDES) permit CFR [15]. While specific management guidelines develop in various states, this legal venue, available standardized methodologies for assessing effects on direct aquatic receptors and the potential for downstream beneficial uses, position surface water discharge as a promising short-term management strategy for PW [10,16–18].

From a treatment perspective, producing an effluent suitable for discharge is a challenging process due to the multiple organic and inorganic constituents in PW, including petroleum hydrocarbons, dissolved salts, metals, radionuclides, production chemicals, and potential transformation by-products [5,1,19]. Addressing this complex composition is further complicated by geographic and temporal variations in PW chemical composition and constituent concentration [20,5,21,22,19]. As a result, treating PW to water quality levels suitable for surface water discharge requires integrated treatment trains, including multiple treatment processes and units to remove different classes of constituents and tailored operational strategies for each geographic and temporal context [1,3,23].

Currently, PW treatment methods are tailored for onsite reuse and deep well injection, removing  $\text{H}_2\text{S}$ , suspended solids, oil, and grease using chemical oxidation, coagulation, media filtration, hydrocyclone, and dissolved air flotation [1]. The desalination of PW is required for reuse outside of the O&G field in order to meet the high water quality standards for discharge and fit-for-purpose applications. Despite composition variabilities, average total dissolved solids (TDS) concentrations in the Bakken, Permian, and Marcellus basins are reported to be 244,000, 154,000, and 166,000 mg/L, respectively [24], exceeding the upper limit for conventional membrane desalination processes. Consequently, distillation-based technologies stand out as essential for treating hypersaline PW in these regions [3,25]. Multiple distillation processes, with variable configurations and operational setups, have shown the potential to address the hypersaline content of PW. For

example, Hsieh and Malmali [26] successfully reduced the TDS levels of the Permian Basin PW from 138,000 to  $\sim 35$  mg/L using vacuum membrane distillation (MVD) and Al-Salmi et al. [27] reduced TDS levels from 135,000 to  $\sim 15$  mg/L using direct contact membrane distillation (DCMD). Using photocatalytic membrane distillation, Chen et al. reduced the TOC of Permian Basin PW by 89.7% to 4.67 mg/L in the distillate and achieved over 99.9% rejection of salts [28,29]. Although distillation processes have demonstrated to remove salts and reduce organic compounds, heavy metals, and other constituents, some pollutants susceptible to volatilization, such as volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and ammonia ( $\text{NH}_3$ ) can remain in the distillate [30,11,21,1,31,32]. Characterization studies in major basins like the Permian have consistently found VOCs, SVOCs, and  $\text{NH}_3$  at variable levels of concern. For instance, benzene ranges from 1.9 to 4.9 mg/L and  $\text{NH}_3$  levels could be up to 750 mg  $\text{NH}_3\text{-N/L}$  [19].

The presence of residual organics and  $\text{NH}_3$  in PW earmarked for surface discharge is a critical environmental issue. Residual VOCs and SVOCs can cause acute and chronic adverse effects on aquatic life and humans, ranging from mutagenic and carcinogenic effects to endocrine, neurological, and cardiovascular alterations [6,13,33,1,34–36,19].  $\text{NH}_3$  can directly harm fish and invertebrates, as well as completely disrupt ecosystems through eutrophication and depletion of dissolved oxygen levels [37]. To date, no studies have comprehensively assessed the water quality of thermally-treated PW, and the actual hazard that its organics,  $\text{NH}_3$ , and other constituents can have on direct aquatic receptors remains unknown.

Integrating distillation with targeted post-treatment units to remove the residual organic compounds and ammonia could be a strategy to minimize these pollutants and improve effluent quality for discharge and reuse. Given the complexity of water chemistry, PW requires extensive pretreatment, primary desalination, and post-treatment including multiple units and processes. For example, one recent laboratory study used the membrane bioreactor, granular activated carbon (GAC), and ion exchange resins to remove the organics, ammonia, and hardness-causing constituents before the membrane distillation process [38]. The thermal distillation followed by GAC and zeolite post-treatment provides a relatively less complex and shorter treatment train than other PW treatment processes. Among processes with demonstrated full-scale applications for municipal wastewater, adsorption with GAC and ion exchange process with zeolite offer straightforward application and operation for removing residual organics and  $\text{NH}_3$ , respectively [39,40]. GAC is a well-established technology for removing residual organics from water. Its high specific surface area and adsorption capacity make it effective for a wide range of organic contaminants, including VOCs and SVOCs. Additionally, GAC offers advantages such as commercial availability and regenerability, which have been shown to offer cost-efficient operation and maintenance in the long term [39,41,42]. Liden et al. also highlighted the value of using GAC as a pretreatment before forward osmosis desalination of PW [43]. Clinoptilolite, the most abundant natural zeolite type, provides a cost-effective approach to  $\text{NH}_3$  removal due to its high, regenerable ion exchange capacity (3 to 30 mg of  $\text{NH}_4\text{-N}$  per gram of zeolite), strong affinity, low cost, simple regeneration, and operational robustness [40,44,45].

For the first time, this study evaluated the effectiveness of integrating a low-temperature thermal distillation system with GAC and zeolite to reduce potential risks of PW for beneficial reuse. Our study provides a unique and comprehensive assessment of their integration for reusing hypersaline PW from the Permian Basin. By employing both chemical characterization and whole effluent toxicity (WET) testing across the four different trophic levels considered in chemical risk assessments – producers, primary consumers, secondary consumers, and decomposers – we establish a weight-of-evidence approach for assessing effluent hazards and the effectiveness of the treatment processes. Furthermore, to evaluate the potential of the treatments to produce effluents that would meet the water quality requirements for an NPDES permit [18,

46], this study evaluated the effluents using the NPDES test of significant toxicity (TST) approach considering established regulatory management decisions [18,46].

## 2. Materials and methods

### 2.1. Collection, pre-treatment, and treatment of PW

PW was sourced from oil and gas operations in the Permian Basin, specifically from a saltwater disposal facility near Orla, Texas, United States. PW was conveyed via high-density polyethylene (HDPE) pipelines to the pilot location. Before the main system, the raw PW was pretreated with 30% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and filtered with a basket strainer (1/16" mesh screen) to minimize the exposure risk of hydrogen sulfide ( $\text{H}_2\text{S}$ ) and reduce suspended solids, respectively. The main treatment process was a modular, pilot-scale, low-temperature distillation unit powered by waste exhaust heat from a Caterpillar 3608 gas compressor. The system incorporated four interconnected loops – heating, evaporation, condensation, and cooling – and operated under vacuum conditions. A glycol-based medium facilitated the recovery of waste heat, maintaining an average supply temperature of  $85 \pm 5^\circ\text{C}$ . The unit was operated at an average feed flow rate of 633 bbl/d ( $100 \text{ m}^3/\text{d}$ ), with a PW conductivity of  $145.1 \pm 7.07 \text{ mS/cm}$ . The system achieved an average distillate recovery rate of 238 bbl/d ( $37.8 \text{ m}^3/\text{d}$ ), constituting 38% of the feed flow rate, while the brine discharge averaged 370 bbl/d ( $58.8 \text{ m}^3/\text{d}$ ), or 58.5% of the feed flow rate.

### 2.2. Distillate post-treatment

Conceptually, the post-treatment processes in the present study were designed to reduce the residual harmful constituents in the distillate to non-toxic levels. Based on preliminary chemical characterization, several organic compounds,  $\text{NH}_3$ , and heavy metals were identified in the distillate, which were the targets for removal in the bench-scale post-treatment processes. Three distinct post-treatment setups were evaluated. The first process focused on reducing organics and metals using GAC, the second targeted  $\text{NH}_3$  using zeolite, and the third combined both GAC and zeolite to address all identified targets: organics, metals, and  $\text{NH}_3$ . The selection of GAC for the removal of organics and metals in the present study was based on its high adsorption capacity, regeneration potential, and promising results for the removal of PW organics recently documented [23,43,38]. Factors considered in the selection of natural clinoptilolite for the removal of ammonia in the distillate included its high  $\text{NH}_4^+$  exchange capacity, regeneration potential, and low cost due to large regional deposits near O&G operations in Wyoming, New Mexico, and Texas [40,47–51].

Reduction of the refractory organics and heavy metals was accomplished by processing the distillate through a packed GAC column (Aqua-Tech, Spectrum Brand, Inc.). The GAC media had a particle size range of 425–710  $\mu\text{m}$  and a pore volume of 11%. The dimensions of the column included 30 cm in height and an internal diameter of 2.5 cm. The GAC bed volume (BV) was 0.147 L, and the system was operated in an up-flow mode with a flow rate (Q) of 0.12 liters per hour. This setup allowed for an empty bed contact time (EBCT) of 1.23 h.

$\text{NH}_3$  reduction was achieved by passing the distillate through a column filled with zeolite media (Clinoptilolite, Double Eagle, Casper WYO). The zeolite particle size distribution was 280–860  $\mu\text{m}$ , with a pore volume of 7%. The dimensions, Q, and operating mode conditions of the zeolite column were identical to those previously described for the GAC column. After packing, the column had a zeolite BV of 0.147 L and an EBCT of 1.23 h.

During the third treatment, the combination of GAC and zeolite as post-treatment was investigated to evaluate whether the integration of both treatments could offer complementary performances in a unified treatment train. To explore this, the distillate underwent sequential processing through a series of columns – initially passing through the

GAC column, followed by the zeolite column. To prevent cross-contamination between tests and maintain reproducibility, new GAC and zeolite media were utilized for every individual experiment, and operational conditions were meticulously maintained for consistency across all experimental setups.

### 2.3. Chemical and toxicological characterization

In this study, we take the selection and evaluation of treatment trains as an iterative process, where the overall performance of the treatment processes is evaluated by integrating chemical characterization and WET assessments considering specific receptors of concern (ROC) across the four trophic levels considered in aquatic environmental risk assessments (ERA).

#### 2.3.1. Chemical characterization

The chemical characterization of the PW effluents included conventional water quality parameters such as TDS, electrical conductivity (EC), pH, hardness, and alkalinity. Beyond these measurements, parameters of special interest such as volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), total organic carbon (TOC), total petroleum hydrocarbons (TPH), nitrogenous compounds such as  $\text{NH}_3$ , nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ), and selected ions and metals were analyzed in effluents. Details of the specific methods and protocols used during the chemical characterization are presented in Table S1 in the supplementary information.

#### 2.3.2. Toxicological assessment

The toxicological assessment was conducted across four trophic levels to assess the ecological impact of all PW effluents on freshwater aquatic ecosystems. The evaluation included *Raphidocelis subcapitata* (alga) as the producer, *Ceriodaphnia dubia* (invertebrate) as the primary consumer, *Danio rerio* (zebrafish) as the secondary consumer and *Vibrio fischeri* (bacteria) as the decomposer. *R. subcapitata* (UTEX 1648) tests adhered to U.S. EPA guidelines for chronic WET tests (EPA-821-R-02-013) [17], considering static nonrenewal exposures and measuring growth inhibition endpoints at 24-hour intervals during a static four-day test. *R. subcapitata* tests included four replicates per concentration and control. Acute WET tests for *C. dubia* followed the U.S. EPA WET guidelines (EPA-821-R-02-012) [52] and were conducted considering a 48-hour static, nonrenewal exposure to monitor survival endpoints. *C. dubia* tests were conducted considering 20 replicates for each concentration and control. Neonates (<24 h) were divided into 4 groups of 5 and exposed in open chambers containing 20 mL of test solution. Acute toxicity tests of zebrafish embryos followed the Organisation for Economic Co-operation and Development (OECD) Method 236 guidelines [53]. Daily survival endpoints (coagulation, absence of somite formation, non-detachment of the tail, and absence of heartbeat) were assessed using an inverted microscope throughout a 96-hour exposure, considering a semi-renewal (48-hour) regimen. A total of 24 embryos per condition (1 embryo per well) with 3 mL of test solution were exposed. All experiments involving zebrafish adhered to ethical guidelines regarding experimentation animals and were approved by the New Mexico State University Institutional Animal Care and Use Committee (IACUC), proof/certificate of approval is available upon request. Toxicity against the marine bioluminescent bacterium *Vibrio fischeri* (Strain NRRL B-11177) was conducted on a Model 500 Analyzer (Azur Environmental, DE, USA), considering luminescence inhibition as an endpoint after 5 and 15 min of exposure following the 81.9 % Screening Test Protocol, as delineated previously [54]. A total of 3 replicates were conducted for each concentration and control. Methods used for test organisms maintenance, diet, and endpoints measurements followed standard protocols [16,52,17,55,53,56].

All effluents underwent acute and chronic toxicity testing following standard protocols. Dose-response assessments utilized a dilution series based on the U.S. EPA WET guidelines, with PW concentrations ranging

from 0% to 100% at specific intervals (0%, 3.125%, 6.25%, 12.5%, 25%, 50%, 100%). Organism maintenance and test dilutions employed moderately hard reconstituted water (MHRW), prepared from deionized water and reagent-grade salts to achieve final concentrations of 96 mg/L NaHCO<sub>3</sub>, 60 mg/L CaSO<sub>4</sub>·2H<sub>2</sub>O, 60 mg/L MgSO<sub>4</sub>, and 4 mg/L KCl. During testing, MHRW parameters were as follows: pH 7.4–7.8, hardness 80–100 mg/L (as CaCO<sub>3</sub>), alkalinity 57–64 mg/L (as CaCO<sub>3</sub>), and dissolved oxygen (DO) 7–9 mg/L. Control experiments were conducted to verify the potential toxicity caused by the compounds released from the GAC and zeolite columns themselves; MHRW was passed through the GAC and zeolite columns, and then the effluents were tested for toxicity and metals.

### 2.3.3. WET data analyses

Acute and chronic toxicity endpoints were derived in line with the U.S. EPA's Technical Support Document (TSD) for Water Quality-based Toxics Control and the EPA's Test of Significant Toxicity (TST; EPA 833-R-10-003, June 2010) [18,57]. In compliance with federal and state regulations, WET data validity and reliability were evaluated using the U.S. EPA WET Analysis Spreadsheet v2.1. Only data adhering to the test acceptability criteria (TAC) were considered in the present study. The no observed effect concentration (NOEC) and the lowest observed effect concentration (LOEC) were determined through hypothesis testing employing either Dunnett's or Steel's Many-One Rank tests. The effluent concentrations resulting in 25% inhibition (IC<sub>25</sub>) and 50% lethality (LC<sub>50</sub>) were calculated using linear interpolation, Spearman–Karber, Trimmed Spearman–Karber, or Probit techniques. For a detailed description of the TAC, toxicity endpoints, and statistical analysis used, readers are directed to review the U.S. EPA guidelines for conducting WET data analysis [17,52].

### 2.3.4. Test of significant toxicity (TST)

The TST is a statistical tool deployed within the WET NPDES Program framework to evaluate toxicity narrative criteria. Designed specifically to categorize effluents as either toxic or non-toxic by evaluating low-risk and high-risk Regulatory Management Decisions (RMDs) [18]. Non-toxic effluents align with low-risk RMD benchmarks (<10% effects), while toxic effluents have effects ≥ 20% for acute and ≥ 25% chronic tests. Depending on the test design and variability, hypothesis tests using either Student's t-test or Welch's t-test are employed to categorize effluents according to the NPDES criteria [18,46]. In the present study, we employed the WET Analysis Spreadsheet v2.1 for the TST analysis and determination if the different treated PW effluents were toxic under the NPDES guidelines considering the most stringent IWC scenario with 100% effluent.

## 3. Results and discussion

### 3.1. Distillate chemical and toxicological characterization

For discharge purposes, the distillation process effectively generated water with TDS ~ 475 mg/L that meet the salinity requirements of different beneficial reuse scenarios, including surface water discharge (TDS 500 mg/L) ([1,58]). However, the basal toxicity tests (Fig. 1) showed that pre-polished effluent produced by the pilot thermal distillation unit was toxic and caused adverse effects on organisms at the four trophic levels studied. Specifically, at critical concentration (100% effluent), the effluent inhibited *V. fischeri* bioluminescence by ~ 42% and *R. subcapitata* growth by ~ 50% as well as caused 100% mortality in neonates of *C. dubia* and embryos of *D. rerio* at a concentration of 50% PW distillate. To better illustrate the impact of distillate exposure on the embryonic development of zebrafish, Fig. 2-C depicts embryos exposed to 100% distillate. Notably, at 48 hpf (hours post-fertilization), these embryos exhibited undifferentiated somites and presented with pericardial and yolk sac edemas. Simultaneously, at 48 hpf, all embryos exposed to 100% and 50% distillate displayed an absence of heartbeat, a

finding that was confirmed at 72 hpf. Collectively, these observations underscore the significant developmental disruptions caused by the PW distillate and highlight that multiple phenotypic and physiological alterations are taking place in early morphogenetic development. The detailed results regarding the dose-response assessment of the distillate exposure on *V. fischeri*, *R. subcapitata*, *C. dubia*, and *D. rerio* can be found in Table S2 (supplementary material).

Table 1 presents conventional water quality parameters and the results of key analytes detected in the distillate. Chemical analysis identified a diverse range of residual constituents, including concerning levels of certain organics, ammonia (NH<sub>3</sub>), and metals. For detailed data on the complete chemical characterization and toxicity endpoints, please refer to Tables S4–S6 in the supplementary material. Regarding organics, measurable and unmeasurable constituents may act as stressors [1,13]. Therefore, when toxic effects coincide with the presence of organics, accounting for measurable and unmeasurable fractions is crucial, not only to associate adverse effects to the organic fractions but also to identify specific organics potentially contributing to observed toxicity. Concerning the measurable constituents, several VOCs and SVOCs were detected in the distillate. Specifically, detected VOCs comprised benzene (0.501 mg/L), toluene (0.548 mg/L), ethylbenzene (0.0214 mg/L), and xylenes (0.377 mg/L); and identified SVOCs include acenaphthene (0.00043 mg/L), fluorene (0.00147 mg/L), naphthalene (0.0131 mg/L), phenanthrene (0.00145 mg/L), phenol (0.026 mg/L), and 2-nitrophenol (0.007 mg/L). Although all these identified organics have been reported to cause adverse effects on the organisms tested (Table S3, supplementary material), species-specific toxicity endpoints suggest only benzene, toluene, and phenol may have contributed directly to the adverse effects observed in *D. rerio* (100% embryos mortality), as the detected levels are in range with the reported LC<sub>50</sub> for benzene (0.05 mg/L), toluene (0.1 mg/L) and phenol (0.036 mg/L) [59, 60]. Regarding unknown and unmeasurable organics, the presence of other potentially toxic constituents cannot be completely ruled out, especially considering the residual levels of TOC of ~ 42 mg/L and the total petroleum hydrocarbons (TPH) of ~ 3 mg/L with carbon chains in the range of C6 through C35 (C<sub>6</sub> to C<sub>35</sub>). These basic water parameters, while not definitive in associating organics as stressors, show significant levels of unidentified organics that may potentially play a role as stressors for the organisms tested, albeit remaining beyond our analytical reach [1,13]. Ammonia (~46 mg NH<sub>3</sub>-N/L) exceeded all recommended aquatic life Ambient Water Quality Criteria (AWQC) (chronic: 17 mg NH<sub>3</sub>-N/L, acute: 1.9 mg NH<sub>3</sub>-N/L) [37] and likely contributed to the observed toxicity in *V. fischeri*, *C. dubia*, and *D. rerio*. This claim is supported by the fact that NH<sub>3</sub> levels exceeded the reported EC<sub>50</sub> values for *V. fischeri* (0.57 to 1.75 mg NH<sub>3</sub>-N/L) [61,62], LC<sub>50</sub> values for *C. dubia* (0.09 to 1.18 mg NH<sub>3</sub>-N/L) [63,64], and LC<sub>50</sub> values for *D. rerio* (0.05 to 0.1 mg NH<sub>3</sub>-N/L) [65]. Notably, despite NH<sub>3</sub> levels exceeding the EC<sub>50</sub> values for *V. fischeri* several times, the measured inhibition was only 42%, suggesting the presence of potential agonistic processes influencing the observed toxicity (Fig. 1) [61,62]. When comparing the characterization results of specific regulated element constituents with the AWQC for aquatic life, the effluent is found to comply with the established criteria for zinc (0.12 mg/L), lead (0.0025 mg/L), chloride (230 mg/L), boron (5 mg/L), cadmium (acute: 0.0018 mg/L), chromium (0.011 mg/L), and iron (1 mg/L). Although the detected Cd concentration of 0.0011 mg/L is below the AWQC acute criterion recommended for aquatic life, the effluent exceeds the Cd chronic criterion of 0.00072 mg/L. Likewise, data suggests that Cu (0.0095 mg/L) could have played a role in the observed toxicity in *C. dubia* and *R. subcapitata*, as the residual Cu levels are higher than LC<sub>50</sub> values reported for *C. dubia* (0.00557 mg/L) [66], and EC<sub>50</sub> ranges documented for *R. subcapitata* (0.0016 to 0.048 mg/L) [67,68] under similar WET setups.

Based on the chemical and toxicological assessment of the distillate, although the pilot unit provided water quality that met the salinity requirements for surface discharge applications and satisfied the



recommended AWQC for the protection of aquatic life of multiple constituents of concern, the distillation system alone was not entirely successful in reducing all the constituents of PW to non-toxic levels. Therefore, to achieve a non-toxic effluent, it is hypothesized that reducing the residual concentrations of organics,  $\text{NH}_3$ , Cd and Cu could mitigate the toxicity observed in WET testing of the distillate.

### 3.2. Individual effects of GAC and zeolite as post-treatment units

As outlined in the previous section, reducing residual levels of organics,  $\text{NH}_3$ , Cd, and Cu could potentially mitigate the adverse effects observed in exposed organisms. For this, post-treatments using GAC and zeolite were employed.

#### 3.2.1. Distillate toxicological assessment after the GAC and zeolite individual post-treatment

The outcomes of the acute and chronic toxicity tests for the distillate after the individual GAC or zeolite treatments are presented in Fig. 1. Further, the results of the statistical analyses and the toxicity endpoints determined for each organism in the dose-response assessment are summarized in Table 2.

To assess the impact of constituents released from the materials themselves, MHRW was passed through the GAC and zeolite columns as negative controls. As confirmed by t-tests ( $P > 0.05$ ), MHRW control did not introduce additional toxicity in *V. fischeri* and *R. subcapitata* WET tests. Therefore, the observed adverse effects are solely attributable to the chemical constituents in the distillate. For detailed results of the statistical analysis performed on the MHRW controls, please refer to Tables S7-S10 in the supplementary material.

All toxicity tests (Fig. 1A-F) revealed a significant reduction in the overall toxicity of the distillate following GAC and zeolite treatments. As shown in Table 2, the GAC treatment mitigated the adverse effects on *V. fischeri* and *R. subcapitata* by ~16.7% and ~35.2%, respectively, with  $\text{IC}_{25}$  values of 56.0% for *V. fischeri* and 46.7% for *R. subcapitata*. In comparison, the zeolite treatment resulted in toxicity reductions of 61.2% for *V. fischeri* and 18.2% for *R. subcapitata*, with  $\text{IC}_{25}$  values of >100% for *V. fischeri* and 64.7% for *R. subcapitata*. Furthermore, it significantly reduced the mortality rates of the *C. dubia* and *D. rerio* tests (Fig. 1E, F). Initially, 100% mortality was observed in both WET tests with 50% distillate concentration. After zeolite treatment, mortality rates were reduced to 63.2% for *C. dubia* and 54.1% for *D. rerio* with 100% effluent. The dose-response assessment also showed increases in the  $\text{LC}_{50}$  for both tests, with increases from 31.9% to 48.2% for *C. dubia* and from 16.7% to 70.7% for *D. rerio* (Table 2). These results collectively suggest a substantial reduction of toxicity as a result of both treatments.

The acute and chronic toxicity assessment demonstrated that both post-treatments alone effectively reduced the adverse effects in all toxicity tests. However, the effluents still exerted a significant adverse impact on the exposed organisms. At critical concentration (100% effluent), the GAC treatment inhibited bioluminescence in *V. fischeri* by 35.3% and *R. subcapitata* growth by 32.1%. Furthermore, the zeolite treatment, although reducing *V. fischeri* inhibition to 16.4%, caused 40.5% growth inhibition in *R. subcapitata*, and mortality rates of 63.2% and 54.1% for *C. dubia* neonates and *D. rerio* embryos, respectively. Also, as presented in Fig. 2D, it was observed that the survivor zebrafish embryos experienced marked developmental delays and abnormalities such as delayed hatching time (72 hpf), and pericardial and yolk sac edemas (48, 72 and 96 hpf).

These findings highlight the presence of residual stressors in the post-treated distillate when GAC and zeolite post-treatments are used as an individual treatment process. The next section will investigate potential contributors to the observed effects, focusing on the chemical composition of the effluents from the individual GAC and zeolite post-treatment.

#### 3.2.2. Distillate chemical characterization after the GAC and zeolite independent post-treatment

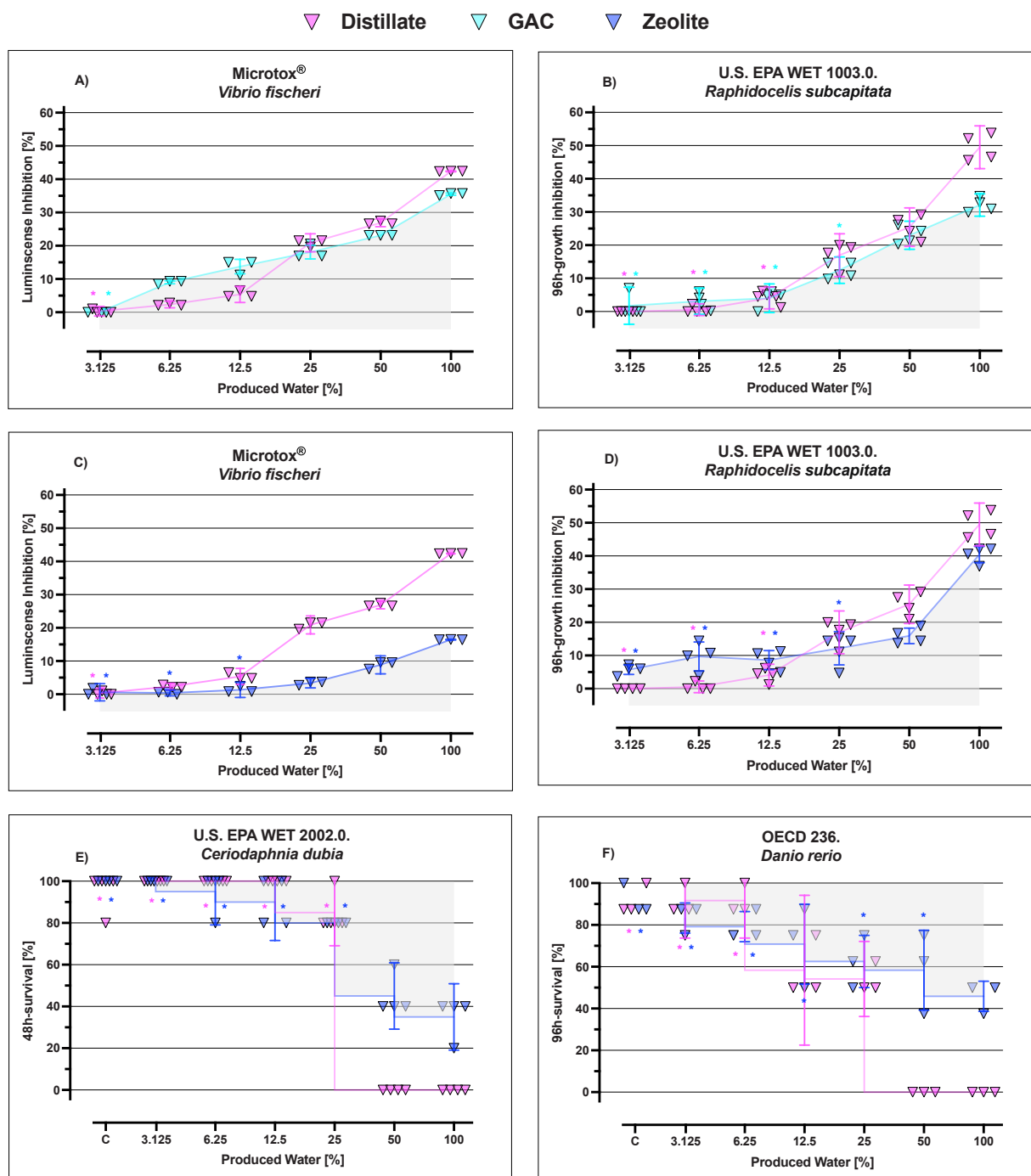
Chemical characterization of the treated effluents was carried out in parallel with toxicity tests to identify the specific residual constituents that contributed to the observed adverse effects after the GAC or zeolite post-treatment and to determine how these treatments reduced the overall concentration of toxicants. Characterization of the effluents encompassed a suite of 45 analytes, which included conventional water quality parameters, metals, nitrogenous compounds, and selected ions. Additionally, the post-GAC treatment analysis was extended to include a detailed profile of VOCs and SVOCs.

The performance of the treatment units involved a comparative analysis between the post-treatment concentrations of each constituent against their initial levels in the distillate. To assess the performance of each treatment on specific constituents in the distillate, the water quality parameters were classified into three categories: constituents that increased in concentration, those that decreased, and those that remained unaltered after each post-treatment process. Table 1 presents the results of key analytes, such as select organics, metals, and  $\text{NH}_3$ . For the complete analysis of the chemical characterization data, readers are referred to Tables S4-S6 in the supplementary material.

**3.2.2.1. GAC treatment.** The ability of GAC to remove a broad spectrum of organics and metals, including VOCs such as benzene, toluene, ethylbenzene, and xylene (BTEX), and SVOCs like fluorene, anthracene, and phenanthrene, is well documented in industrial and municipal wastewater applications [69-71]. This capability and recent applications to reduce organics on PW made it a suitable candidate to target and eliminate these specific contaminants from the distillate [38,43].

The GAC treatment effectively removed both measurable and unmeasurable organics. All initially detected BTEX were reduced to concentrations below their respective method detection limits (MDL) (benzene < 0.000214 mg/L, toluene < 0.000500 mg/L, ethylbenzene < 0.000515 mg/L, and xylene < 0.000330 mg/L). Similarly, all SVOCs except phenol (post-GAC concentration: 0.000693 mg/L) were removed to undetectable levels (acenaphthene < 0.000102 mg/L, fluorene < 0.000103 mg/L, naphthalene < 0.0000990 mg/L, phenanthrene < 0.0000866 mg/L, and 2-nitrophenol < 0.00167 mg/L). Additionally, the GAC treatment reduced TPH to levels below MDL (< 0.840 mg/L) and led to an 88% reduction in TOC (~5 mg/L). Please refer to Table S3 in the supplementary material for the detailed characterization of organic compounds. These results are consistent with previous studies using activated carbon for the reduction of organics in pre-treated produced waters. Hildenbrand et al. [23] obtained comparable TOC removals (~82%) in PWs from the Eagle Ford Shale region after ozonation and filtration processes. Additionally, the removal of individual constituents is consistent with these findings, as this study showed a reduction of ~64% in individual volatile species as well. In terms of metals and other inorganics, B, Ba, Cd, Cr, Cu, Fe, Mn, P, Sr, Zn, and  $\text{NH}_3$  displayed marked decreases in concentration, aligning with the recognized effectiveness of GAC in adsorbing a wide range of compounds [42, 69]. Specifically, significant reductions in Sr (~91%), Mn (~61%), Ba (~44%), Cu (~42%), and  $\text{NH}_3$  (~42%) were determined along with reductions to non-detectable levels of Cd, Fe, Zn, and P.

The reduction of VOCs and SVOCs was significantly higher than that of certain metals. Previous studies showed differences in the adsorption capacity of GAC for organics such as phenanthrene and acenaphthylene, and metals such as Cd, Cu, and Zn [42]. Our results confirm that when organics and metals are present, organics exhibit a higher affinity for GAC compared to heavy metals due to different adsorption mechanisms [42]. Specifically, organic adsorption involves hydrophobic interactions and Van der Waals forces, which are more dominant than ion exchange, chelation, and complexation mechanisms used by heavy metals [42,72]. When polar organics and metals coexist in the water matrix, they compete for GAC adsorption sites, reducing the adsorption of both [42,



**Fig. 1.** Toxicological assessment: impact of GAC and zeolite treatments on distillate toxicity. *V. fischeri*: 3 experimental replicates, 15 min of exposure time; *R. subcapitata*: 4 experimental replicates, 96 h of exposure time; *C. dubia*: 20 experimental replicates grouped in 4 groups of 5 replicates (4 × 5), 48 h of exposure time; *D. rerio*: 24 experimental replicates grouped in 3 groups of 8 replicates (3 × 8), 96 h of exposure time; Luminescence (%) and growth inhibition (%) endpoints were calculated with respect to their respective controls; Survival (%) was calculated with respect to the initial population exposed; Error bars: 95% confidence upper and lower intervals; gray areas: correspond to residual toxicity of the post-treated effluents across the concentration range; \*: effects not significantly different from the control.

73]. In this study, most identified organics were removed below MDL, and metal removals varied, from complete removals of Cd and Zn to increases in Cr concentration from 0.0003 mg/L to 0.003 mg/L. Based on these results, the presence of organics and metals did not affect GAC performance significantly. Our findings suggest that the low concentrations of the specific metals (<0.01 mg/L) and identified organics (<1 mg/L) in the distillate did not lead to significant competition for adsorption sites. Previous studies have documented competition

occurred at concentrations of 5, 20, and 50 mg/L of various metals [42, 73]. Therefore, the low concentration of these constituents in the distillate may explain the observed performance. Considering that competition for adsorption sites among the multiple constituents of PW may hinder the application of GAC, further research should explore adsorption dynamics and competition processes in long-term operations to evaluate the feasibility of GAC application for the treatment of PW distillates.

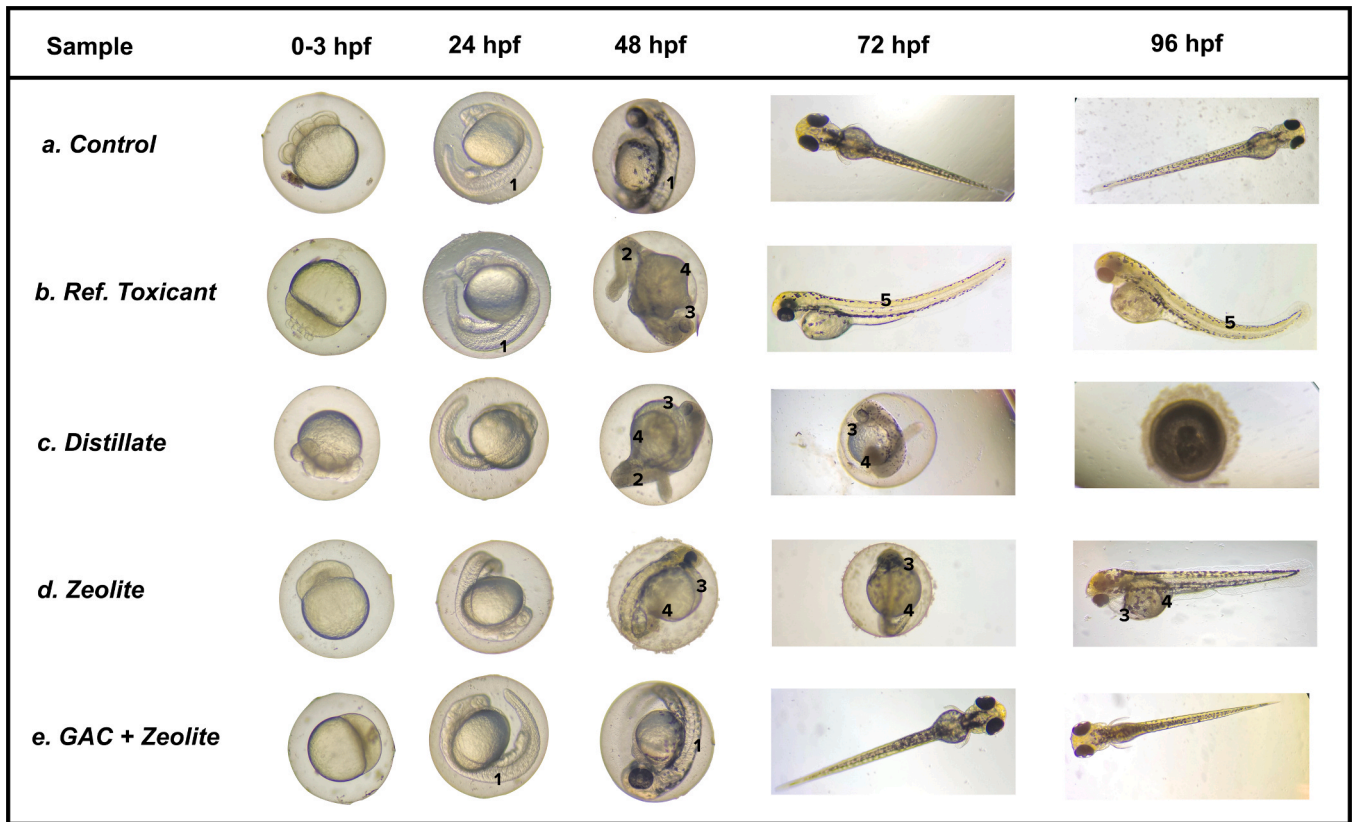


Fig. 2. Development of *D. rerio* embryos during FET test. hpf: hours post fertilization; 1: formation of well-differentiated somites; 2: lack of somites formation; 3: pericardial edema; 4: yolk sac edema; 5: scoliosis.

Table 1  
Impact of the Treatments on Distillate Chemical Composition.

| Analyte                                  | Distillate    | GAC           |               | Zeolite       |               | GAC+zeolite   |               |
|------------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                                          | Value<br>mg/L | Value<br>mg/L | Change<br>(%) | Value<br>mg/L | Change<br>(%) | Value<br>mg/L | Change<br>(%) |
| EC <sup>S</sup>                          | 288.0         | 172.0         | -40.3         | 237.0         | -17.7         | 171.0         | -40.6         |
| Hardness <sup>C</sup>                    | 0.52          | 15.02         | 2788.5        | 15.56         | 2892.3        | 15.82         | 2942.3        |
| Alkalinity <sup>C</sup>                  | 0.00          | 18.39         | NA            | 146.82        | NA            | 148.55        | NA            |
| pH <sup>U</sup>                          | 8.4           | 7.9           | - N/A         | 6.7           | N/A           | 7.4           | N/A           |
| TOC                                      | 42.30         | 5.25          | -87.6         | 45.07         | 6.5           | 5.40          | -87.2         |
| TPH (C <sub>6</sub> to C <sub>35</sub> ) | 3.04          | < 0.84        | -100.0        | N/A           | N/A           | N/A           | N/A           |
| Benzene                                  | 0.5010        | < 0.000214    | -100.0        | N/A           | N/A           | N/A           | N/A           |
| Toluene                                  | 0.5480        | < 0.000500    | -100.0        | N/A           | N/A           | N/A           | N/A           |
| Phenanthrene                             | 0.0014        | < 0.00142     | -100.0        | N/A           | N/A           | N/A           | N/A           |
| Phenol                                   | 0.0260        | 0.000693      | -97.3         | N/A           | N/A           | N/A           | N/A           |
| Cd                                       | 0.0011        | 0.0000        | -100.0        | 0.0014        | 27.3          | 0.0000        | -100.0        |
| Cu                                       | 0.0095        | 0.0055        | -42.1         | 0.0173        | 82.1          | 0.0163        | 71.6          |
| Cr                                       | 0.0003        | 0.0030        | 900.0         | 0.0000        | -100.0        | 0.0000        | -100.0        |
| Zn                                       | 0.0031        | 0.0000        | -100.0        | 0.0000        | -100.0        | 0.0000        | -100.0        |
| Mn                                       | 0.0115        | 0.0044        | -61.7         | 0.0000        | -100.0        | 0.0000        | -100.0        |
| Na                                       | 1.19          | 1.58          | 31.9          | 64.86         | 5332.0        | 62.34         | 27692.0       |
| NH <sub>3</sub> <sup>N</sup>             | 46.35         | 27.10         | -41.5         | < 0.015       | -100.0        | < 0.015       | -100.0        |

S: units  $\mu\text{S}/\text{cm}$ ; C: mg  $\text{CaCO}_3/\text{L}$ ; N: mg  $\text{N-NH}_3/\text{L}$ ; U: unitless; Change (%): - percentage reduction with respect to distillate; + percentage increment with respect to distillate

WET tests are designed to measure the aggregate toxic effects of all constituents on water. Therefore, considering all the constituents removed by the GAC column, the reduction in adverse effects observed after the treatment is the result of the decrease of multiple toxicants rather than the mitigation of any single constituent [17,74,75].

Differences in species sensitivity were observed after the GAC and zeolite post-treatment, which indicates that test organisms have differential tolerance to the treated effluent constituents. This statement is supported by the differences in toxicity reductions between the algal

(Fig. 1-B) and the bacteria (Fig. 1-A) toxicity tests. As shown in Table 2, the algae *R. subcapitata* test showed that GAC post-treatment could reduce toxicity by 35.2%, while only a 16.7% toxicity reduction was observed in bacteria *V. fischeri* tests. This difference in WET tests is likely attributed to the residual  $\text{NH}_3$  concentration after GAC treatment (27 mg  $\text{NH}_3\text{-N}/\text{L}$ ), which was significantly higher than the reported  $\text{EC}_{50}$  ranges for *V. fischeri* (0.57–1.75 mg  $\text{NH}_3\text{-N}/\text{L}$ ) [61,62], likely contributing to the lower observed toxicity reduction in the *V. fischeri* test. In contrast, while some studies suggest that ammonia may contribute to

growth inhibition in *R. subcapitata* [76,77], ammonia cannot be considered a stressor to the algae, as establishing a definitive relationship between the  $\text{NH}_3$  levels with the observed effects on the chronic algal test is hindered by a lack of comprehensive toxicological data. Additionally, an interesting phenomenon was observed during the dose-response assessment (Fig. 1A), where the effluent post-GAC showed higher inhibitions toward *V. fischeri* than the distillate at 12.5% and 6.25% concentrations. While a more linear or continuous dose-response relationship is anticipated for unique substances, during WET assessments, the presence of multiple stressors with different toxic potentials (different dose-response slopes), water matrix effects, and synergistic and agonistic interactions can influence dose-response evaluations [17,74,75]. Although identifying the specific factors is out of the scope of this research, the previous factors and the complex chemistry of PW may account for this phenomenon.

The results highlight the limitations of GAC treatment alone in completely removing the distillate toxicity and emphasize the importance of considering specific contaminants and their differential effects on organisms when associating adverse effects with specific constituents in the treated PW.

The GAC process had no effect on certain constituents measured in the chemical characterization, including Al, As, Be, Bi, Br, Co, Li, Ni, Pb, Se, and Tl. However, several constituents, including Ca, Cl, Cr, K, Mg, Mo, F, and Na, increased in concentration after GAC treatment. Notably, Ca, which can adsorb in GAC, showed a net increase of almost 5 mg/L, likely due to the displacement of calcium ions from the activated carbon surface as a result of competitive adsorption dynamics with the multiple distillate constituents [78,79]. It is noteworthy that Cr concentration in the distillate increased tenfold to 0.003 mg/L after GAC treatment. Although the total Cr concentration is lower than the maximum contaminant level of 0.1 mg/L in the U.S. EPA National Primary Drinking Water Regulations, considering that this concentration is in the range of the reported Cr  $\text{EC}_{50}$  range for *R. subcapitata* (0.0036 mg/L) [67], it is possible to consider Cr as another stressor that potentially contributes to the 35% growth inhibition observed in the chronic *R. subcapitata* test.

Although GAC treatment successfully reduced most of the characterized organic compounds, Cd, Cu, and Zn, it was insufficient to fully mitigate the toxicity of the distillate. This is evidenced by the lingering adverse effects observed in both *R. subcapitata* and *V. fischeri* WET tests. Based on reported toxicity endpoints,  $\text{NH}_3$  and Cr could be potential contributors to the remaining toxicity. In particular, the post-treatment concentrations of  $\text{NH}_3$  and Cr remain within the reported  $\text{EC}_{50}$  ranges for *V. fischeri* and *R. subcapitata*, respectively. These findings indicate that

GAC treatment alone was insufficient for fully addressing the complex mixture of concerning compounds in the distillate. This observation underscores the need for further exploration of alternative or combined treatment strategies to achieve a non-toxic effluent.

**3.2.2.2. Zeolite treatment.** The ability of clinoptilolite for  $\text{NH}_3$  removal is well documented and  $\text{NH}_3$  was the main target of the zeolite treatment [45,49]. This study showed 100% removal of  $\text{NH}_3$  and  $\text{NH}_4^+$ , specifically with  $\text{NH}_3$  levels below MDL ( $<0.015$  mg  $\text{NH}_3\text{-N/L}$ ). Zeolite can remove  $\text{NH}_4^+$  ions through ion-exchange and adsorption by electrostatic interactions [80]. The ammonium ions present in the distillate (46.4 mg  $\text{NH}_3\text{-N/L}$ ; 3.3 meq/L) were mainly removed by ion exchange with sodium ions as  $\text{Na}^+$  concentration increased by 62 mg/L (2.7 meq/L) in the effluent. In addition, electrostatic interactions also played a role. Clinoptilolite is negatively charged at the distillate pH of 8.4 since it has an isoelectric point  $< 2$  [81]. Therefore, positively charged ammonium ions can adsorb on clinoptilolite.

Consistent with previous observations, the zeolite treatment significantly reduced the adverse effects in *V. fischeri* (luminescence inhibition reduced from 42% to 16%, Fig. 1C), *C. dubia* neonates (mortality reduced from 100% to 63%, Fig. 1E), and *D. rerio* embryos (mortality reduced from 100% to 54%, Fig. 1F). Initially,  $\text{NH}_3$  was considered one of the major stressors in the distillate, as its concentration ( $\sim 46$  mg  $\text{NH}_3\text{-N/L}$ ) significantly exceeded established toxicity thresholds for these species (*V. fischeri*  $\text{EC}_{50}$ : 0.57–1.75 mg  $\text{NH}_3\text{-N/L}$ , *C. dubia*  $\text{LC}_{50}$ : 0.09–1.18 mg  $\text{NH}_3\text{-N/L}$ , *D. rerio*  $\text{LC}_{50}$ : 2.07 mg  $\text{NH}_3\text{-N/L}$ ) [63,61,64,65,62]. Considering that the zeolite treatment effectively reduced  $\text{NH}_3$  concentrations to below MDL, both chemical characterization and reported toxicity endpoints suggest that  $\text{NH}_3$  removal played a major role in the observed toxicity reductions.

The toxicity reduction in *R. subcapitata* (growth inhibition reduced from 50% to 40%, Fig. 1D) was significantly smaller compared to the other organisms tested. This observation suggests that ammonia played a minor role in the toxicity of the distillate toward the algae and is consistent with previous studies, which have indicated that although  $\text{NH}_3$  can affect the growth of *R. subcapitata*, its effects are limited and are often associated with co-exposure to other stressors such as oxidants, surfactants, or hydrophobic compounds [76,77].

The zeolite treatment also reduced Cr, Fe, Mn, and Zn to levels below MDL and removed  $\sim 90\%$  of Sr from the distillate. It indicates that in addition to  $\text{NH}_4^+$ , other cations were exchanged as well. This observation is in agreement with previous studies that reported the sorptive capacity of zeolite to remove several heavy metals [82–85]. While Cr, Mn, and Zn have been identified as stressors in previous studies, their concentrations

**Table 2**  
Dose-response Assessment of the post-GAC and post-Zeolite effluents.

| Sample ID                                                                | NOEC [%] | LOEC [%] | $\text{IC}_{25} - \text{LC}_{50}$ [% 95% C.I.] | Hypothesis test (S – NS) | Point estimate test | Effect at 100% | Toxicity reduction [%] <sup>TR</sup> |
|--------------------------------------------------------------------------|----------|----------|------------------------------------------------|--------------------------|---------------------|----------------|--------------------------------------|
| <b>Microtox® <i>V. fischeri</i> Acute Toxicity Test</b>                  |          |          |                                                |                          |                     |                |                                      |
| Distillate                                                               | 3.125    | 6.25     | 40.4 (36.3 – 43.4) <sup>IC</sup>               | S <sup>DT</sup>          | LI                  | 42.4           | -                                    |
| GAC                                                                      | 3.125    | 6.25     | 56.0 (55.5 – 56.7) <sup>IC</sup>               | S <sup>DT</sup>          | LI                  | 35.3           | 16.7                                 |
| Zeolite                                                                  | 12.5     | 25       | > 100 (NA – NA)                                | S <sup>DT</sup>          | LI                  | 16.4           | 61.2                                 |
| <b>U.S. EPA WET 1003.0 <i>R. subcapitata</i> Chronic Toxicity Test</b>   |          |          |                                                |                          |                     |                |                                      |
| Distillate                                                               | 12.5     | 25       | 34.9 (27.9 – 41.9) <sup>IC</sup>               | S <sup>DT</sup>          | LI                  | 49.5           | -                                    |
| GAC                                                                      | 25       | 50       | 46.7 (31.2 – 68.9) <sup>IC</sup>               | S <sup>SMORT</sup>       | LI                  | 32.1           | 35.2                                 |
| Zeolite                                                                  | 25       | 50       | 64.7 (55.0 – 71.0)                             | S <sup>SMORT</sup>       | LI                  | 40.5           | 18.2                                 |
| <b>U.S. EPA WET 2002.0 <i>Ceriodaphnia dubia</i> Acute Toxicity Test</b> |          |          |                                                |                          |                     |                |                                      |
| Distillate                                                               | 25       | 50       | 31.9 (28.5 – 35.6) <sup>IC</sup>               | S <sup>DT</sup>          | SK                  | 100            | -                                    |
| Zeolite                                                                  | 25       | 50       | 48.2 (41.3 – 56.3) <sup>IC</sup>               | S <sup>SMORT</sup>       | TSK                 | 63.2           | 36.8                                 |
| <b>OECD 236. <i>D. rerio</i> Fish Embryo Acute Toxicity (FET) Test</b>   |          |          |                                                |                          |                     |                |                                      |
| Distillate                                                               | 6.25     | 12.5     | 16.7 (13.2 – 20.1) <sup>IC</sup>               | S <sup>DT</sup>          | P                   | 100            | -                                    |
| Zeolite                                                                  | 50       | 100      | 70.7 (70.7 – 70.7) <sup>IC</sup>               | S <sup>SMORT</sup>       | TSK                 | 54.1           | 45.9                                 |

<sup>IC</sup>: concentration causing 25% inhibition ( $\text{IC}_{25}$ ); concentration causing 50% lethality ( $\text{LC}_{50}$ ); 95% CI: 95% confidence upper and lower intervals; S: 100% sample concentration is statistically different from the control; NS: 100% sample concentration is not statistically different from the control; DT: Dunnett's Test.; SMORT: Steel's Many-One Rank Test; LI: Linear interpolation.; SK: Spearman-Kärber; TSK: Trimmed Spearman-Kärber; <sup>TR</sup>: reduction in toxicity (%) with respect to the distillate. *V. fischeri*: n = 3; *R. subcapitata*: n = 4; *C. dubia*: n = 20; *D. rerio*: n = 24



in the distillate (Cr: 0.00030 mg/L, Mn: 0.0155 mg/L, Zn: 0.031 mg/L) were below the toxicity endpoints previously reported for *V. fischeri* [86,87], *R. subcapitata* [88,68,89], *C. dubia* [87,90,91], and *D. rerio* [92,93]. Therefore, the observed toxicity reductions following the zeolite treatment cannot be directly attributed to the removal of these specific metals. Other constituents, such as Al, As, Be, Bi, Br<sup>-</sup>, Co, Mo, Ni, Pb, S, Se, and Tl, did not show noticeable changes after zeolite treatment, maintaining undetectable levels before and after the process. However, previously undetected constituents such as lithium (Li<sup>+</sup>), fluoride (F<sup>-</sup>), and potassium (K<sup>+</sup>) became detectable after the zeolite treatment, introduced from the zeolite media. Furthermore, there was a notable increase in the levels of sodium (Na<sup>+</sup>), calcium (Ca<sup>2+</sup>), and silicon (Si) after post-treatment. Considering that zeolites are naturally comprised of Ca, Na, and K, these increases can be directly attributed to the ion exchange process of the clinoptilolite [49,85].

Although zeolite treatment reduced the toxicity in the tested organisms, adverse effects persisted, as evidenced by the acute and chronic WET tests. Characterization data suggest that residual levels of organics, Cd, and Cu might be associated with persistent effects, as zeolite treatment not only failed to reduce their levels in the distillate but also appeared to have slightly increased them. Characterization data indicated a slight increase in Cd and Cu post-zeolite treatment. Specifically, Cd increased by 27% (0.0011 to 0.0014 mg/L) and Cu by 82% (0.0095 to 0.0173 mg/L). These observations can be a direct result of the lower affinities of zeolite for Cd and Cu compared to other ionic constituents present in the distillate, such as Ba<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, and Ca<sup>2+</sup> [83,94], and could explain not only the lack of removal but also the potential leaching of these metals from the zeolite itself. As previously discussed, Cu concentrations were identified at levels potentially harmful to *R. subcapitata*, as the Cu concentration in the distillate (0.0095 mg/L) falls within the reported EC<sub>50</sub> range for Cu (0.0016 to 0.048 mg/L [67, 68]). Considering the observed increases in Cu levels (0.0173 mg/L) after zeolite treatment, it is possible that Cu contributed partially to the 40% growth inhibition observed in the chronic *R. subcapitata* test, and this could also explain why the reduction in toxicity achieved in algal test (18%) was less compared to other toxicity tests. With respect to *V. fischeri*, given that the residual level of Cu (0.0173 mg/L) surpasses the reported EC<sub>50</sub> of 0.0146 mg/L [95], the increased Cu concentration after zeolite treatment, could be responsible for the residual toxicity observed in the Microtox® test albeit the complete removal of NH<sub>3</sub> achieved. Interestingly, despite Cu levels exceeding the EC<sub>50</sub>, the inhibition in the Microtox® test was only around 16%. This antagonistic response highlights the complexity of the chemical interactions in PW regarding toxicity and reinforces the value of using multiple ROCs along with comprehensive chemical characterization when evaluating the risk of PW [1,96]. After the zeolite treatment, a mortality of 63% was observed in the *C. dubia* acute WET test. Considering that the residual Cu levels (0.0173 mg/L) after the zeolite treatment fall within the range of reported mortality endpoints (LC<sub>50</sub>: 0.00557 mg/L, LC<sub>100</sub>: 0.064 mg/L) [66,90]. The results suggest that Cu could be one of the potential stressors that contribute to these lingering adverse effects.

Considering the hydrophilic nature and size exclusion properties of the aluminosilicate structure of clinoptilolite, the removal of organic molecules is not anticipated during zeolite treatment [97,44,45,85]. This conjecture was verified by the TOC characterization, which showed no removal of organic constituents. From the identified organics in the distillate, several VOCs and SVOCs were determined to be at toxic levels for *D. rerio*. Specifically, detected levels of benzene (0.501 mg/L), toluene (0.548 mg/L), and phenol (0.026 mg/L) exceeded the previously reported toxicity thresholds for embryos of *D. rerio* [98,59,60]. Given that organics were not reduced after zeolite treatment, it is possible that these constituents still contributed to the 54% mortality observed in zebrafish embryos and the embryogenic alterations depicted in Fig. 2D – delayed hatching time and pericardial and yolk sac edemas – despite the complete removal of NH<sub>3</sub>. Although no specific organic compounds were identified at toxic levels for *V. fischeri*, *R. subcapitata*,

and *C. dubia* in the distillate, the determined levels of TOC remain a significant concern, as uncharacterized organics could contribute to the cumulative adverse effects observed [11,13]. From an evidence-based perspective, definitively excluding the impact of organic compounds in PW during WET evaluations requires fulfilling at least one of the following two criteria: i) undetectable levels of organic compounds confirmed by chemical analysis, or ii) no observable adverse effects in WET assessments. Given that neither of these criteria were met in this study and the actual risk of these potential stressors remains unknown, the influence of uncharacterized organic compounds on these species cannot be neglected.

Although the zeolite treatment successfully removed NH<sub>3</sub> species to levels below MDL, as shown in the WET assessment, it was insufficient to reduce the toxicity of the distillate and caused significant adverse effects on *R. subcapitata*, *C. dubia* and *D. rerio*. Based on chemical characterization results and reported toxicity endpoints, organics and Cu could be potential contributors to the lingering toxicity. When comparing the performance of the GAC and zeolite treatments, clear distinctions emerge in terms of the removals of targeted toxicants. While GAC treatment removed organics compounds, Cu, and Cd substantially, zeolite effectively reduced NH<sub>3</sub> and Cr. Therefore, it is plausible that treatment trains considering both GAC and zeolite as post-treatment could boost the overall performance of the process and reduce the toxic effects of the distillate during WET tests.

### 3.3. Effects of the combination GAC and zeolite as post-treatment

Based on the performance of individual GAC and Zeolite treatments, we investigated the efficacy of combining these units as a post-treatment strategy. The combined treatment (GAC followed by zeolite, denoted as GAC+Zeolite) aimed to achieve synergistic effects and minimize effluent toxicity by targeting a wider range of contaminants, including organics, metals, and NH<sub>3</sub>. Subsequent sections will explore the chemical and toxicological characterization of the effluent produced by the GAC+Zeolite post-treatment.

#### 3.3.1. Toxicological assessment of the GAC+Zeolite post-treatment

Fig. 3 presents the results of the acute and chronic WET assessment of the GAC+Zeolite effluent. Statistical analyses and toxicity endpoints computed for each organism involved in the dose-response assessment are provided in Table 3.

The GAC+Zeolite treatment showed superior efficacy in reducing the toxicity of distillate. As presented in Table 3, at critical concentration (100% effluent), exposures of *R. subcapitata*, *C. dubia*, and *D. rerio* to the GAC+Zeolite effluent showed no statistically significant differences from their respective controls in the SMORT hypothesis test. Additionally, the LOEC exceeded 100% effluent for all three species. These findings highlight the superior performance of the combined treatment in reducing toxicity compared to GAC or zeolite independently. The dose-response assessment determined that IC<sub>25</sub> values for *V. fischeri* and *R. subcapitata*, as well as LC<sub>50</sub> values for *C. dubia* and *D. rerio* were > 100% of the effluent. Furthermore, with the exception of *V. fischeri* (Fig. 3-A), which showed effects of < 20% at 100% effluent, the adverse effects determined on all other organisms were not higher than 10%. Additionally, the phenotypic (pericardial and yolk sac edemas) and physiological alterations (lack of heartbeat) initially observed in zebrafish embryos exposed to the distillate were completely mitigated, as none of these responses were observed in the embryos exposed to the GAC+Zeolite effluent (Fig. 2-E) during the 96 h of exposure. Therefore, from an effects-based perspective, it was shown that the combination of GAC and zeolite units had complementary effects, as it reduced the adverse effects consistently across all ROC.

Noteworthy, at 100% effluent, the combined GAC+Zeolite treatment achieved similar bioluminescence inhibition in the Microtox® test (19.3%) compared to zeolite alone (16.4%). It raises concerns about the suitability of Microtox® for characterizing the complex composition of

PW. This concern stems from the observed discrepancies in responses between *V. fischeri* and the other tested species. For instance, while *C. dubia* and *D. rerio* exhibited significant variations in toxicity across treatments (5–100%), *V. fischeri* consistently displayed moderate inhibition (15–40%) regardless of effluent. Although dedicated studies are necessary to assess the Microtox® suitability for PW characterization, these observations, and the NH<sub>3</sub> and Cu agonistic responses discussed previously, suggest *V. fischeri* may exhibit less sensitivity to PW effluents compared to the other tested species. This may be due to the complexity of PW and the documented tolerance of *V. fischeri* to certain constituents encountered in PW [99]. Given the complex and variable composition of PW, WET assessments considering multiple aquatic ROC may be among the most practical and reliable tools for evaluating the overall water quality of PW effluents intended for surface water discharge [13,100,101].

Fig. 4 summarizes the results of the TST analysis for the acute and chronic toxicity tests conducted on the effluents. Aiming to evaluate potential discharges in the most stringent scenario (no receiving water), the TST analysis was executed considering an IWC of 100%. Given that the adverse effects of the distillate, post-GAC, or post-zeolite effluents did not meet the regulatory management decision (RMD) thresholds of 20% for acute tests and 25% for chronic tests, at the IWC studied, these effluents failed the TST and would be considered toxic under NPDES. On the other hand, as presented in Fig. 4, the GAC+Zeolite post-treatment was successful in surpassing the TST, not only meeting both acute and chronic RMD thresholds but also achieving the low-risk RMD benchmark (mean effect less than 10%) for *R. subcapitata*, *C. dubia* and *D. rerio* tests. Therefore, the GAC+Zeolite post-treatment demonstrated the capacity to effectively treat the PW and deliver an effluent with toxicity levels that would be acceptable under the NPDES program. The complete statistical results of the TST analysis can be found in Table S11 in the supplementary material.

Although designated uses, water quality criteria, effluent limitations, and antidegradation policies are specific to each receiving water and discharge scenario, the TST results suggest that combining low-temperature distillation, GAC, and zeolite units in a treatment train could meet U.S. EPA aquatic toxicity thresholds and align with narrative water quality criteria required for an NPDES permit [16,46,102,103].

### 3.3.2. Chemical characterization of the GAC+Zeolite post-treatment

The reduction of adverse responses during WET assessment is attributed to the cumulative removal of individual toxicants, and the intrinsic characteristics of the GAC+Zeolite effluent (e.g., pH, hardness, and conductivity) [52,17,74,53]. Table 1 summarizes key chemical characterization data for the GAC+Zeolite post-treatment. The characterization showed that the GAC+Zeolite process combined the benefits offered by the GAC and zeolite treatments individually. It removed NH<sub>3</sub>, Cd, Cr, Zn, and Mn to undetectable levels and successfully reduced 88% of TOC (5.2 mg/L).

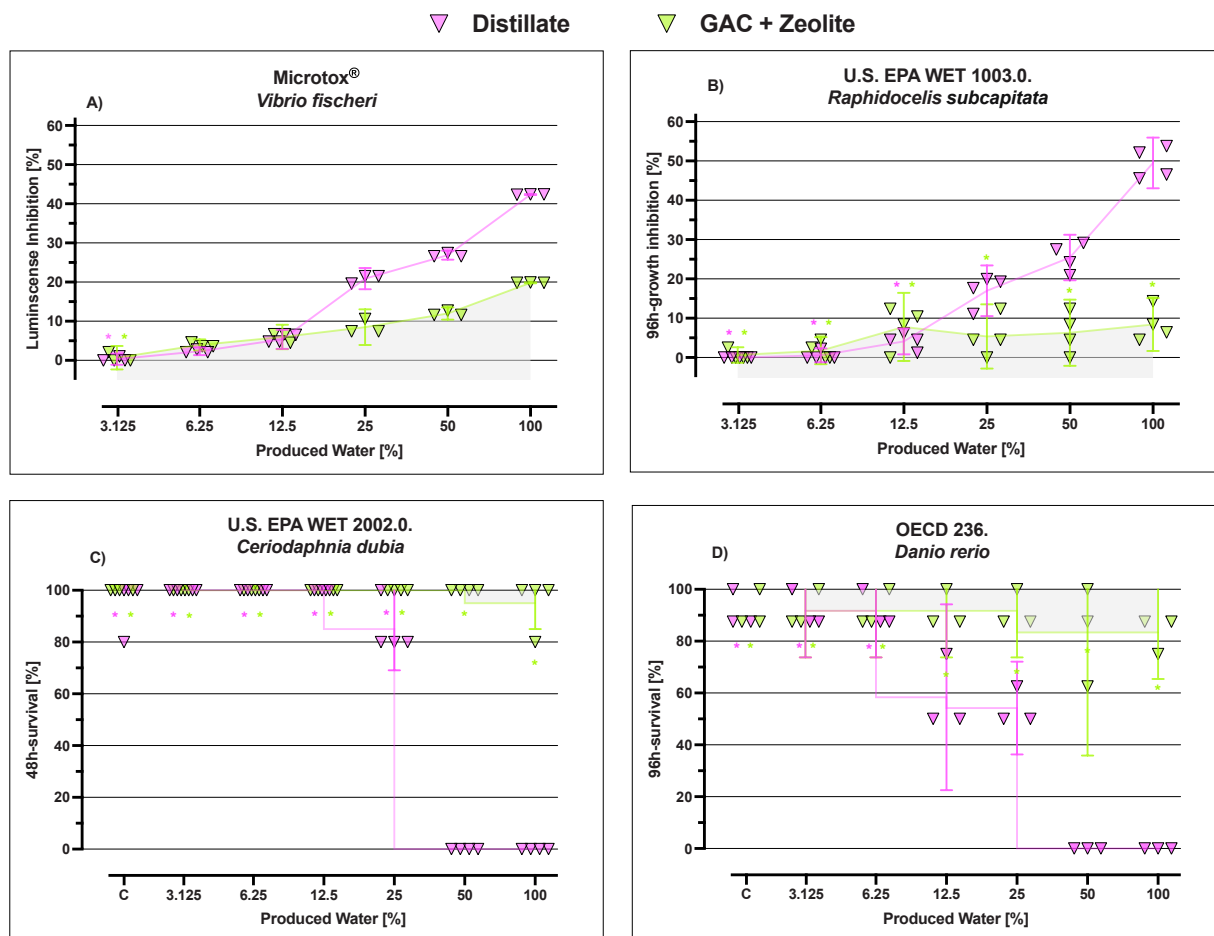
Regarding organics, as discussed above, after GAC treatment, except phenol (0.000693 mg/L), all organics identified in the distillate were reduced to levels below the MDL. Considering that benzene, toluene, and phenol were identified at levels that exceeded the reported LC<sub>50</sub> for *D. rerio* (benzene: 0.05 mg/L, toluene 0.1 mg/L, and phenol: 0.036 mg/L) [59,60], the reduction of these constituents played a major role in the > 90% reduction in the mortality of zebrafish embryos (Fig. 3-D) as well as in the complete mitigation of phenotypic alterations and toxicological endpoints studied (Fig. 2-E). Although the treatment did not achieve complete removal of the organic components (TOC 5.2 mg/L in the GAC+Zeolite effluent) and comprehensive identification and toxicological characterization of these organics are beyond our analytical reach, our findings indicate that the residual organics following the GAC+zeolite treatment have limited effects on the organisms tested. As detailed in Table 3, no significant adverse effects were observed in *R. subcapitata*, *C. dubia*, and *D. rerio* at 100% effluent concentration. Additionally, the dose-response assessment determined an IC<sub>25</sub> for

*V. fischeri* that exceeded 100% effluent. Therefore, under the conditions of the present study, the remaining organic content of the treated PW, although not fully characterized, had minimal impact on the organisms tested.

Similar to the zeolite treatment, the removal of NH<sub>3</sub> is considered one of the key factors in the toxicity reduction observed in the *V. fischeri*, *C. dubia*, and *D. rerio* WET tests. As discussed above, the concentration of NH<sub>3</sub> in the distillate (~ 46 mg NH<sub>3</sub>-N/L) was significantly higher than the reported toxicity thresholds for each organism (*V. fischeri* EC<sub>50</sub>: 0.57–1.75 mg NH<sub>3</sub>-N/L; *C. dubia* LC<sub>50</sub>: 0.09–1.18 mg NH<sub>3</sub>-N/L; *D. rerio* LC<sub>50</sub>: 2.07 mg NH<sub>3</sub>-N/L) [63,61,64,65,62]. Considering that the GAC+Zeolite treatment reduced NH<sub>3</sub> levels to below MDL (0.015 mg NH<sub>3</sub>-N/L), it is likely a determinant factor in the observed reductions in toxicity for *V. fischeri* (83%), *C. dubia* (95%) and *D. rerio* (92%) tests.

Despite NH<sub>3</sub> removal might not be a major factor influencing *R. subcapitata* toxicity after the GAC+Zeolite treatment and no specific organics were identified at toxic levels to the algae, the cumulative reduction of multiple constituents may have played a significant role in the 83% toxicity reduction observed on the *R. subcapitata* chronic test (Fig. 3B). Initially, the concentration of Cd in the distillate (0.0011 mg/L) was found to be within the 25% threshold of the reported EC<sub>50</sub> for *R. subcapitata* (0.00157 mg/L) [104]. Given that Cd was completely removed after the combined treatment, this removal likely contributed to the toxicity reduction observed on the algal WET test. This outcome reinforces the hypothesis that Cd may be one of the stressors for *R. subcapitata*, and it is consistent with the results of the zeolite treatment previously discussed, where residual Cd (0.0014 mg/L) levels were associated with 40% growth inhibition in the algal test (Fig. 1-B).

Characterization data revealed an increase in the concentration of several constituents after the GAC+Zeolite treatment, including Na, Ca, K, S, Mg, Cl, Li, P, Cu, V, Mo, NO<sub>3</sub> and SO<sub>4</sub><sup>2-</sup>. Among these, the > 70% increase in the concentration of Cu (0.0163 mg/L) is noteworthy from both water treatment and toxicological perspectives. The complete chemical characterization data are shown in Tables S4-S6 in supplementary material. Considering that Cu levels only increased when the distillate was treated with zeolite (Zeolite and GAC+Zeolite treatments), the results suggest that zeolite may have served as an external source of Cu during the treatment process. This outcome disagrees with previous studies that have reported zeolite capacity to remove Cu [84,105]. However, the moderate affinity of clinoptilolite for Cu<sup>2+</sup> in comparison with other cations in the systems such as NH<sub>4</sub><sup>+</sup>, K<sup>+</sup> and Na<sup>+</sup>, is likely to account for this result [49,105]. Despite the residual Cu levels (0.0163 mg/L) being within the ranges of reported Cu toxicity thresholds for *R. subcapitata* (EC<sub>50</sub>: 0.0016 – 0.048) [67,68], *V. fischeri* (EC<sub>50</sub>: 0.0146 mg/L) [95], and *C. dubia* (LC<sub>100</sub>: 0.0116 – 0.064 mg/L) [66], with the exception of the Microtox® test (19% inhibition), no significant adverse effects were observed in the *R. subcapitata* (Fig. 3B) and *C. dubia* (Fig. 3C) WET tests. This observation suggests that other constituents in final effluent may offset Cu toxicity in these tests. Similar to several metals, Cu toxicity has been reported to vary considerably due to various physicochemical factors, including pH, dissolved organic carbon (DOC), hardness (Ca<sup>2+</sup>, Mg<sup>2+</sup>), alkalinity (CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>), and Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> levels [106,107]. Specifically, pH can influence Cu speciation [108,109], DOC, CO<sub>3</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup> can form complexes with Cu and reduce its bioavailability [108,109], Ca<sup>2+</sup>, Mg<sup>2+</sup> ions can displace Cu species from biological receptors [106,110], and Na<sup>+</sup> can compete directly for transporters and toxic action sites on biological surfaces [106]. Although determining the specific factors that may have influenced Cu is beyond the scope of this research, this observation underscores the complexity of identifying and quantifying the hazards in PW, highlighting the need to consider both effluent and receiving water chemistry when establishing specific discharge limits. According to the Biotic Ligand Model (BLM) – U.S. EPA tool for deriving Cu site-specific water quality criteria – considering major ions, pH of 8.0, DOC of 4 mg/L, and hardness of 40 mg/L as CaCO<sub>3</sub>, the aquatic life AWQC for Cu is established at 0.0276 mg/L [107]. Although establishing the Cu criterion would be



**Fig. 3.** Toxicological assessment: impact of GAC+Zeolite treatment on distillate toxicity. *V. fischeri*: 3 experimental replicates, 15 min of exposure time; *R. subcapitata*: 4 experimental replicates, 96 h of exposure time; *C. dubia*: 20 experimental replicates grouped in 4 groups of 5 replicates (4 × 5), 48 h of exposure time; *D. rerio*: 24 experimental replicates grouped in 3 groups of 8 replicates (3 × 8), 96 h of exposure time; Luminescence (%) and growth inhibition (%) endpoints were calculated with respect to their respective controls; Survival (%) was calculated with respect to the initial population exposed; Error bars: 95% confidence upper and lower intervals; gray areas: correspond to residual toxicity of the post-treated effluents across the concentration range; \*: effects not significantly different from the control.

**Table 3**

Dose-response Assessment of the GAC+Zeolite effluent.

| Receptor              | NOEC [%] | LOEC [%] | IC <sub>25</sub> – LC <sub>50</sub> [%; 95% C.I.] | Hypothesis test (S – NS) | Point estimate test | Effect at 100% | Toxicity reduction [%] <sup>TR</sup> |
|-----------------------|----------|----------|---------------------------------------------------|--------------------------|---------------------|----------------|--------------------------------------|
| <i>V. fischeri</i>    | 3.125    | 6.25     | > 100 (NA) <sup>IC</sup>                          | S <sup>DT</sup>          | LI                  | 19.3           | 54.5                                 |
| <i>R. subcapitata</i> | 100      | > 100    | > 100 (NA) <sup>IC</sup>                          | NS <sup>SMORT</sup>      | LI                  | 8.4            | 82.9                                 |
| <i>C. dubia</i>       | 100      | > 100    | > 100 (NA) <sup>LC</sup>                          | NS <sup>SMORT</sup>      | LI                  | 5.0            | 95.0                                 |
| <i>D. rerio</i>       | 100      | > 100    | > 100 (NA) <sup>LC</sup>                          | NS <sup>SMORT</sup>      | LI                  | 8.1            | 91.9                                 |

<sup>IC</sup>: concentration causing 25% inhibition (IC<sub>25</sub>); <sup>LC</sup>: concentration causing 50% lethality (LC<sub>50</sub>); 95% CI: 95% confidence upper and lower intervals.; NA: not applicable; S: 100% sample concentration is statistically different from the control; NS: 100% sample concentration is not statistically different from the control; DT: Dunnett's Test; SMORT: Steel's Many-One Rank Test; LI: Linear interpolation; SK: Spearman-Kärber; TSK: Trimmed Spearman-Kärber; P: Probit. <sup>TR</sup>: reduction in toxicity (%) with respect to the distillate. *V. fischeri*: n = 3; *R. subcapitata*: n = 4; *C. dubia*: n = 20; *D. rerio*: n = 24

unique for each discharge scenario and residual Cu levels (0.0163 mg/L) being within the range of reported toxicity endpoints, under these conditions, the effluent would comply with the Cu aquatic life AWQC [107]. These results reiterate the potential of combined treatment to satisfy not only toxicity requirements but also recommended numeric criteria for priority pollutants such as Cu [15].

The results underscore the superior effectiveness of the GAC+Zeolite post-treatment in removing a wide range of constituents, including identified organics of concern, TOC, NH<sub>3</sub>, Cd, Zn, and Cr from the distillate. These removals had evident impacts on WET assessment, reducing the toxicity of the distillate to non-observable levels on

*R. subcapitata*, *C. dubia*, and *D. rerio*. Although further evaluations are needed, the TST analysis and available numeric water quality criteria suggest that the effluent could be a candidate for an NPDES permit. Given that all units employed in this research have demonstrated full-scale applications, these findings support further investigations to explore the treatment's long-term robustness and operational dynamics to minimize the risks associated with PW during beneficial reuse applications.

### 3.3.3. Limitations and future research

While the findings of this study are promising and suggest a potential

alternative for treating hypersaline oilfield PW to levels suitable for surface water discharge, there are significant limitations that must be acknowledged. These limitations pertain to both the treatment process and the characterization of the effluents. The performance of GAC and zeolite in post-treatments was assessed in short-term experiments. Long-term operational studies on GAC and zeolite within the integrated treatment train are essential to assess the performance, robustness, regeneration capacity of the materials, and safe disposal of all the wastes (e.g., spent GAC and zeolite) during the operation. These studies are necessary not only to optimize operation but also to generate data for conducting a techno-economic analysis (TEA) of the treatment approach, considering regeneration and disposal costs. The current research predominantly utilized acute WET tests and measured standard toxicity endpoints. Future studies should incorporate chronic WET tests to evaluate the long-term biological effects of treated PWs. Additionally, the inclusion of sublethal and more subtle toxicity endpoints should be

considered. Overcoming these limitations would provide a deeper understanding of the safety of the effluents for reuse applications. While this study has extensively characterized VOCs, SVOCs, metals, and major ions, employing a more robust chemical characterization scheme that considers both targeted and non-targeted approaches could enable a more comprehensive characterization of the treated effluents and generate more data for conducting environmental risk assessments [11].

### 3.4. Decision framework for PW beneficial reuse after treatment

As PW management guidelines and predictive risk assessment frameworks continue to develop, our results emphasize the need for a systematic approach to predict and monitor environmental risks associated with PW reuse. Based on the insights gained in this research, a pioneering framework is presented to guide PW beneficial reuse efforts, specifically in PW earmarked for surface water discharge and reuse

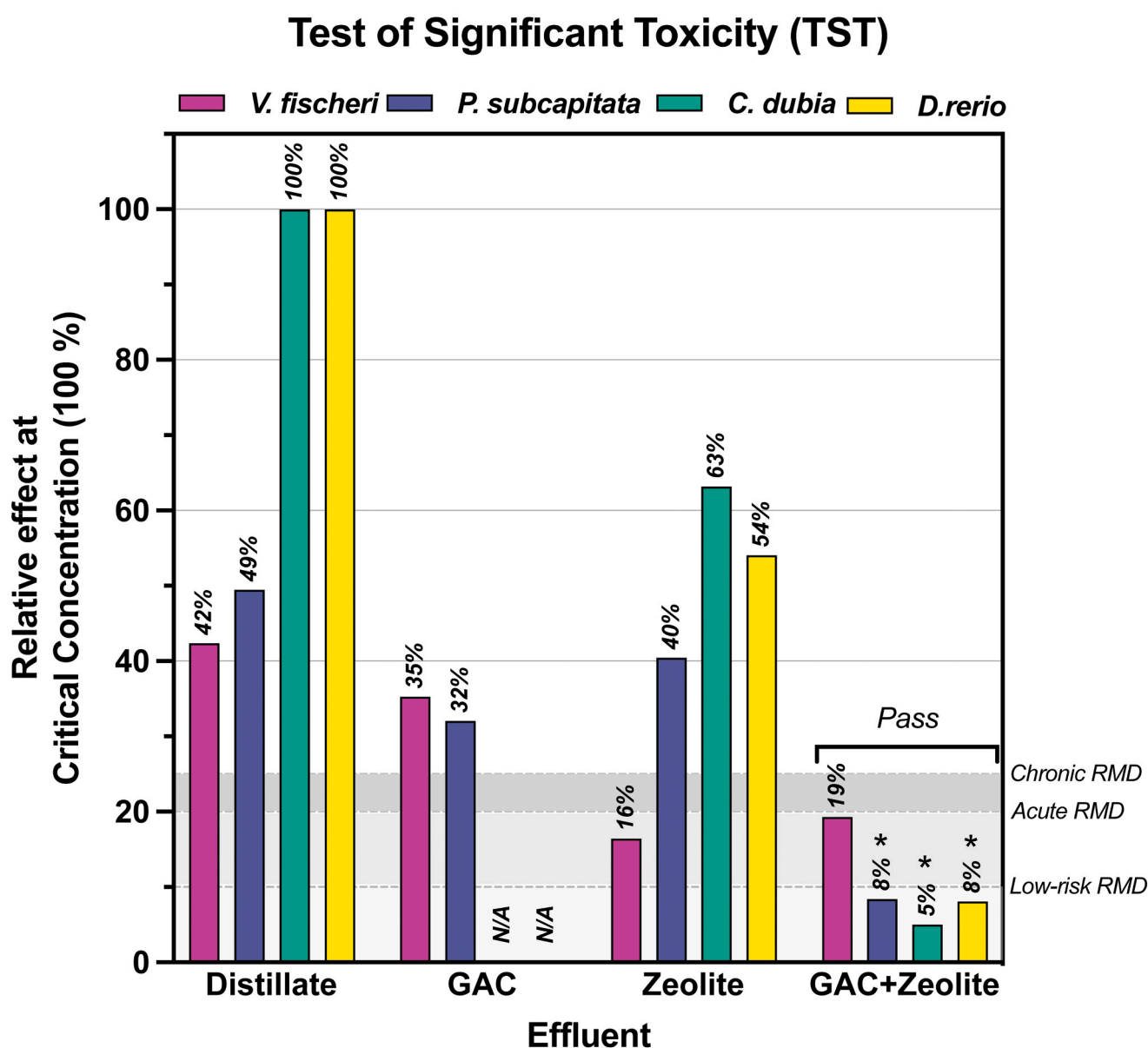


Fig. 4. Test of Significant Toxicity (TST) analysis of the effluents. Instream Waste Concentration (IWS) of 100; \*: effects not significantly different from the control. Acute RMD: Acute TST regulatory management decision (20% effect); Chronic RMD: chronic TST regulatory management decision (25% effect); Low-risk RMD: Low-risk regulatory management decision (10% effect); Pass: toxicity levels in the effluent are considered acceptable.



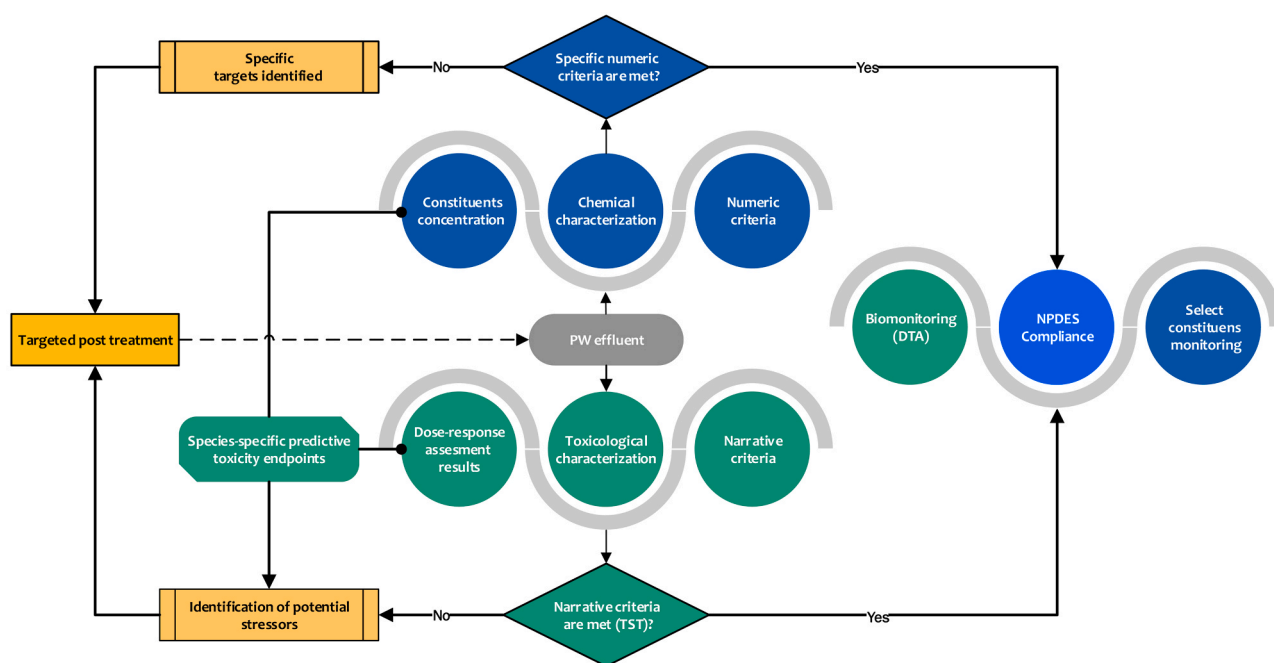


Fig. 5. Decision framework for the beneficial reuse of treated PW in surface discharge applications.

(Fig. 5). Before reuse applications, predictions based on specific chemical, toxicological, and available risk characterization tools are essential for informed decisions and meeting specific numeric and narrative criteria required in the NPDES program. This framework also suggests the application of post-treatment processes to target analytes that either do not comply with specific numeric criteria or are identified as potential stressors based on available toxicological data. For instance, further polishing is needed for the scenario that the effluent i) meets available specific numeric criteria, ii) fails to meet toxicity narrative criteria (TST), and iii) has residual uncharacterized organics (e.g., TOC, DOC, TPH, HEM). Given the potential risks and the limitations associated with its characterization, the uncharacterized fraction of organics should be considered a "potential stressor", and a treatment unit aiming to remove organics should be considered as the next step.

In this framework, the predictive tools and methods presented, although fundamental, are not spared of uncertainties, subjective errors, and bias, as well as may not fully capture the complex interactions influencing pollutant behavior and toxicity in real aquatic environments [96,111,112]. Therefore, to address these limitations and ensure environmental safety in the long term, incorporating monitoring strategies that focus on actionable and practical measures such as acute and chronic direct toxicity assessment (DTA) and monitoring of select analytes on receiving waters should be considered [112]. The holistic approach presented in this framework would be science-based and conservative before reuse, practical during monitoring activities, and ultimately, can be an alternative to advance PW reuse while protecting water resources through risk-based decisions [111]. For detailed information about the process and subprocesses proposed in the framework, please refer to Table S12 in the supplementary information.

#### 4. Conclusions

This study comprehensively assesses the capability of a pilot-scale low-temperature thermal distillation system, combined with bench-scale GAC and zeolite post-treatments, to produce an effluent suitable for surface discharge from the Permian Basin oilfield PW. The evaluation of treatment performance was based on comprehensive chemical and toxicological characterization, considering critical aquatic receptors. Implementing GAC and zeolite post-treatments, both individually and in

tandem, improved overall water quality and reduced the adverse effects on aquatic test organisms. Combining thermal distillation, GAC, and zeolite proved to be the optimal setup, reducing most identified organics,  $\text{NH}_3$ , Cd, Cr, Zn, and Mn concentrations below the method detection limit. This led to a maximum reduction in toxicity, fulfilling the NPDES toxicity criteria. Considering the protection of aquatic life as a potential designated use, we propose a treatment strategy that could potentially achieve the NPDES program's numeric and narrative water quality criteria. Finally, given the findings of this work, we propose a decision framework to inform evidence-based management strategies and foster the development of effective treatment trains for the alternative management of PW in major O&G-producing regions.

#### CRediT authorship contribution statement

**Mike Hightower:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Haoyu Bradley Wang:** Investigation, Formal analysis, Writing – review & editing. **Yeinner Mauricio Tarazona:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yanyan Zhang:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Pei Xu:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

#### Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Pei Xu reports financial support was provided by US Bureau of Reclamation. Yanyan Zhang reports financial support was provided by New Mexico Produced Water Consortium. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2024.135549](https://doi.org/10.1016/j.jhazmat.2024.135549).

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