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A systematic review of heavy metal contamination in groundwater of oil-producing regions in Nigeria: A comprehensive review of sources, fate, transport, and human health implications

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ABSTRACT

The Niger Delta is one of the world's most high-profile oil-producing regions, yet its shallow aquifers, which supply drinking water to over 20 million people, are constantly contaminated by heavy metals from both geogenic processes and decades of petroleum exploration activities. This review systematically examines the region's hydrogeological setting, natural and operational sources of metals, and the occurrence, and toxicological significance of priority metals such as lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), arsenic (As), mercury (Hg), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), barium (Ba), and vanadium (V). The review further analyzes transport pathways and hydrogeochemical controls such as pH, redox, salinity, and dissolved organic carbon that controls metal movement in the Benin Formation and Delta basin aquifers. Case studies from Ogoniland, Warri, Nembe, and other oil-bearing communities are used to evaluate the longitudinal, latitudinal, temporal contamination patterns. Human health risk assessments are appraised considerably, revealing widespread non-carcinogenic and carcinogenic risks, particularly for Pb, Cd, and As, while epidemiological evidence of elevated blood lead and urinary cadmium is also highlighted. The work also reviewed the current state of analytical monitoring, pollution indices, multivariate source apportionment, and Nigeria's regulatory framework, including the roles of National Environmental Standards and Regulations Enforcement Agency (NESREA) and Nigerian Upstream Petroleum Regulatory Commission (NUPRC). Remediation technologies such as conventional pump-and-treat to emerging phytoremediation and biochar-based approaches, are reviewed for their applicability in the region's hydrogeochemical environment. Finally, the work identified knowledge gaps concerning mixed contaminant interactions, microbial modulation of metal mobility, the legacy of artisanal refining and

orphan wells, and the compounding effects of climate change and saltwater interference, and a way forward for a sustainable groundwater management in the Niger Delta.

Keywords: Niger Delta, groundwater contamination, heavy metals, produced water, health risk assessment, environmental governance

1. INTRODUCTION

The Niger Delta, an enormous sedimentary basin in southern Nigeria, is one of the world's most significant petroleum provinces, accounting for over 90% of Nigeria's crude oil production and foreign exchange earnings [1, 2]. The region is home to approximately 20 million people, the vast majority of whom depend on surface groundwater from the Benin Formation and Deltaic aquifers as their primary source of drinking water, domestic supply, and existence agriculture [3, 4]. However, over six decades of oil and gas operations has resulted to thousands oil spills documented between 1976 and 2018, widespread produced wastewater disposal, extensive drilling activities, and the proliferation of artisanal (illegal) refineries creating a complex environmental crisis in which heavy metal contamination of groundwater has developed as a critical public health threat [5, 6]. Historically, crude oil spills, hydrocarbon pollution of surface waters, and gas flaring has been the center of environmental concerns in the Niger Delta. However, a new developing body of research demonstrates that toxic metals and metalloids, co-released with these hydrocarbons and mobilized by the biogeochemical conditions induced by petroleum contamination is an equally urgent, yet comparatively understudied dimension of water quality degradation [7, 8]. Heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), arsenic (As), mercury (Hg), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), barium (Ba), and vanadium (V) have been repeatedly detected in dug wells and boreholes across the region at high concentrations that frequently exceed the World Health Organization (WHO) drinking water guidelines and the Nigerian Standard for Drinking Water Quality [9-13].

The routes by which metals enter Niger Delta groundwaters are multiple and often superimposed. For example, the geogenic sources which primarily the reductive dissolution of iron and manganese oxyhydroxides in the organic-rich sediments, contributes a natural baseline of Fe, Mn, and adsorbed As [14, 15]. Superimposed on this matter are the operational inputs which include produced wastewater, which is co-extracted with oil and gas and frequently discharged into unlined pits, surface waters, or directly onto land, contains high concentrations of Ba, Fe, Mn, Pb, Zn, Ni, and V [16, 17]. The spent drilling fluids and barite-based drilling muds introduce Pb, Cd, Hg, and As impurities [18]. The ever corrosion of well casings and pipelines releases Fe, Ni, and Cr [19] and then leakages from aging oil infrastructure contribute crude-oil-borne metals such as V, Ni to shallow aquifers [20]. The most alarming is the rapid expansion of artisanal refining, in which stolen crude oil is distilled in open, unlined pits using scrap materials, this activity releases massive quantities of Pb, Cd, and other metals directly into the environment [21, 22].

The health implications are severe and increasingly well-over documented with Lead, leading as the potent neurotoxicant, that has been detected in groundwater at concentrations exceeding 1,500 µg/L in some communities, and blood lead levels in children in artisanal refining areas have been reported at an average of 14.2 µg/dL, far above the U.S. Centers for

Disease Control and Prevention (CDC) reference level of 3.5 µg/dL [23, 24]. Following the Lead, is the Cadmium, a known human carcinogen, followed by arsenic, a widespread geogenic carcinogen, all these occur that simply unacceptable lifetime cancer risks through drinking water ingestion [25, 26].

Despite the gravity of the problem, the scientific literature remains fragmented. Individual studies have characterized contamination in specific locations like Ogoniland, Warri, Nembe, Port Harcourt but a holistic, region-wide synthesis that integrates hydrogeology, geochemistry, toxicology, and policy has not been address. Accordingly, this review was designed to move beyond a simple catalog of concentrations. It synthesizes global evidence on heavy metal contamination in groundwater of oil-producing regions, explains contamination pathways and hydrogeochemical controls, examines health risk frameworks, assess some of the methodological weaknesses, and proposes research and policy directions This review is intended to touch light these areas in the attempt to draw attention to the people and governing bodies.

2. GROUNDWATER DEPENDENCE AND VULNERABILITY IN THE NIGER DELTA

The Niger Delta's population is mostly rural and semi-urban, with limited access to treated piped water. An estimated 70–80% of households rely on shallow groundwater from dug wells typically 2–10 m deep and boreholes of 20–60 m deep tapping the unconfined Benin Formation and the shallower Deltaic Plain aquifers [3, 4, 27]. These aquifers are composed predominantly of unconsolidated sands, silts, and gravels with high hydraulic conductivity (5–50 m/d), making them highly productive but also very vulnerable to contamination from surface and near-surface sources [28, 29].

Groundwater vulnerability in the Niger Delta has been assessed using standard index-overlay methods such as DRASTIC and GOD, which indicate moderate to high vulnerability across large swathes of Rivers, Bayelsa, and Delta States due to shallow water tables often around 3 m, high recharge rates 1,500–3,000 mm/yr, and permeable vadose zones [30, 31]. However, these generic indices do not incorporate the specific contaminant loading associated with oil infrastructure. To address this, Okafor et al., [32] developed a modified DRASTIC index for the Niger Delta that integrates well density, pipeline proximity, and wastewater disposal sites, revealing that high-vulnerability zones closely coincide with major oil fields and flow-station clusters. The concept of “wellbore vulnerability” has recently gained massive attention with over 6,000 oil wells been drilled in the Niger Delta, many are now abandoned and poorly sealed wellbores which represent vertical conduits for metal-rich brine migration into potable aquifers [33, 34]. The Niger Delta regions and other nearby oil producing countries associated with this pollution are diagrammatically shown in the map of Figure 1.

3. HYDROGEOLOGICAL CHARACTERISTICS OF THE NIGER DELTA

The Niger Delta is a relapsing sedimentary basin formed during the Tertiary to Quaternary, consisting of three major lithostratigraphic units which include the deep marine Akata Formation (source rocks), the paralic Agbada Formation (main hydrocarbon reservoirs),

and the continental Benin Formation (the primary freshwater aquifer) [35, 36]. The Benin Formation is a thick sandy unit with minor clay intercalations, grading upward to 2,000 m from coastal plain sands to fluvial sands and gravels. It constitutes both unconfined and semi-confined aquifer system that provides excellent yields of 10-50 L/s [28, 37]. The hydrogeochemistry of the Benin Formation is characterized by fresh to slightly brackish water usually with total dissolved solid (TDS) of 50-500 mg/L, a low pH of 4.5-6.5 due to the dissolution of organic acids from the extensive peat and mangrove deposits, and predominantly reducing conditions often <100 mV owing to abundant organic matter [14, 38]. These conditions of low pH and high dissolved organic carbon (DOC) exert a first-order control on heavy metal speciation and mobility. The Agbada Formation hosts the region's oil and gas reservoirs, which are interbedded with aquitards and contain formation waters with salinities ranging from 10,000 to over 200,000 mg/L TDS, rich in Ba, Fe, Mn, Pb, Zn, and occasionally As and Hg [39, 40]. Where these formations are hydraulically connected to the Benin Formation through faults, fracture zones, or poorly completed wells, metal-rich brines can invade freshwater aquifers [33].

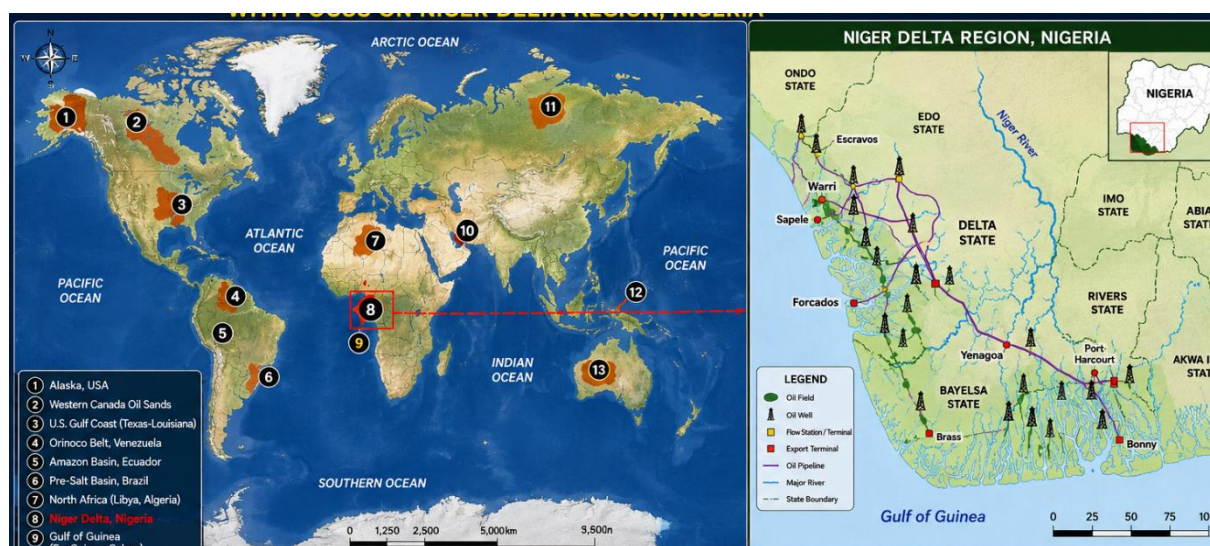


Figure 1. Map of oil producing regions.

4. SOURCES OF HEAVY METAL CONTAMINATION IN GROUNDWATER

4. 1. Geogenic sources

The Niger Delta's Quaternary sediments are naturally enriched in Fe and Mn due to the reductive dissolution of Fe(III) and Mn(IV) oxyhydroxides in the organic-rich, anoxic subsurface environment [14, 41]. The background of Fe concentrations in uncontaminated Benin Formation groundwater typically range from 0.1 to 5 mg/L, but values exceeding 10 mg/L are common even in areas remote from oil operations, driven by microbial iron reduction and abundant natural organic carbon [15]. Arsenic, which strongly adsorbs to iron oxyhydroxides, is mobilized under these same reducing conditions. Studies in the eastern Niger Delta have documented geogenic As concentrations up to 45 µg/L in groundwater, with the highest values in areas of thick peat accumulation and intense sulfate reduction [42, 43].

Barium is also naturally present due to barite dissolution in low-sulfate groundwater, though concentrations that are generally below 0.5 mg/L in uncontaminated areas [44]. Nickel and chromium concentrations in baseline groundwater are both low (<5 µg/L), reflecting the paucity of ultramafic rocks in the Niger Delta catchment [9]. The geogenic baseline is thus dominated by more Fe, Mn, and As, a signature that can be overprinted by anthropogenic inputs.

4. 2. Oil and gas operational sources

Wastewater is the most significant operational source of heavy metals with over 1.5 million barrels estimate of wastewater generated daily in the Niger Delta, a substantial portion of which is discharged to unlined pits, surface water, or directly onto land without treatment [17, 45]. Studies of this wastewater from Niger Delta wells has reportedly spike concentrations of Ba of up to 480 mg/L, Fe of up to 85 mg/L, Mn of up to 12 mg/L, Pb of up to 5 mg/L, Ni of up to 1.2 mg/L, Cd of up to 0.2 mg/L, and V of up to 3.5 mg/L [16, 46]. The practice of surface discharge was officially banned in the 1990s, particularly from aging facilities and marginal fields. Drilling operations generate large volumes of spent drilling mud and cuttings, historically disposed of in unlined reserve pits. Barite (BaSO₄), used as a weighting agent in drilling muds, often contains impurities of Pb, Cd, Hg, and As. Analysis of Nigerian barite samples shows Pb concentrations up to 120 mg/kg, Cd up to 15 mg/kg, and Hg up to 0.8 mg/kg [18]. Leachate from abandoned reserve pits has been shown to elevate Ba, Pb, and Cd concentrations in adjacent shallow groundwater for decades way after the pit closure [46].

The combination of acidic groundwater, corrosive formation brines rich in CO₂ and H₂S, and aging infrastructure promotes the corrosion of steel casings and degradation of cement sheaths. Studies in the western Niger Delta have identified elevated Fe, Mn, Ni, and Cr in groundwater within 50 m of abandoned wellheads, attributed to casing corrosion and leakage [33, 47]. The use of lead-based thread compounds in older wells, a practice that discontinued in the 1990s, has left a legacy of Pb contamination around well pads. Over 13,000 oil spills were officially recorded between 1976 and 2018, releasing an estimated 12–13 million barrels of oil into the environment [5]. Crude oil naturally contains Ni, V, Fe, and Cu in organometallic complexes so when spilled, these metals are released into soils and subsequently leach into groundwater [20]. In areas of chronic spillage, such as Bodo, Ogoniland, and Nembe, soil and groundwater samples show strong correlations between total petroleum hydrocarbon (TPH) concentrations and dissolved Pb, Ni, and V [5, 49].

The most acute source of heavy metal contamination in recent years is artisanal which is illegal refining. An estimated 100,000–150,000 barrels per day of crude oil are processed in makeshift on an open-pit distillation unit across the region [21, 22]. The process involves heating crude oil in metal drums over open fires, often using scrap materials that include lead-acid batteries, lead-soldered tanks, and Pb-contaminated scrap metal. This release enormous quantities of Pb, Cd, Cr, and Ni into adjacent soils and shallow groundwater. Groundwater Pb concentrations exceeding 1,500 µg/L have been measured within 200 m of artisanal refining sites in Rivers State, with soil Pb concentrations up to 150,000 mg/kg [23, 50].

4. 3. Co-occurring anthropogenic sources

Urbanization, agriculture, and industrial activities further compound the metal load, for example, phosphate fertilizers, widely used in the region's intensive agriculture, contain 60 mg/kg of Cadmium and 20 mg/kg of Arsenic as impurities, contributing to diffuse groundwater

contamination [51]. Municipal solid waste dumpsites, particularly in Port Harcourt and Warri, leach Pb, Cd, Cr, and Ni into shallow aquifers [52]. Artisanal gold mining in neighboring states like Zamfara and Osun state is a known source of Pb and Hg, though its direct impact on Niger Delta groundwater is limited. The widespread atmospheric deposition of Pb from leaded gasoline, phased out in Nigeria only in 2006, has left a legacy of Pb in urban soils that continues to leach into groundwater [53].

4. 4. Priority heavy metals in oil-impacted groundwater systems

4. 4. 1. Lead (Pb)

Lead is the most extensively documented heavy metal contaminant in Niger Delta groundwater. Studies across the region has reported Pb concentrations ranging from $<0.1 \mu\text{g/L}$ in remote control sites to over $1,500 \mu\text{g/L}$ in areas impacted by artisanal refining or leaded gasoline contamination [9, 23]. The WHO and Nigerian Standard for Drinking Water Quality guideline value for Pb is $10 \mu\text{g/L}$.

In a systematic survey of 112 hand-dug wells across Ogoniland, UNEP [5] found that 42% exceeded the WHO guideline, with a maximum of $980 \mu\text{g/L}$ of which much higher concentrations are consistently associated with artisanal refining sites. Dooyema et al. [23] reported groundwater Pb of $200\text{--}1,500 \mu\text{g/L}$ in communities in Rivers and Bayelsa States, directly linked to open-pit distillation operations. The health impacts are well-documented: Mahapatra et al. [24] measured mean blood Pb of $14.2 \mu\text{g/dL}$ in children living within 2 km of artisanal refining clusters, compared to $4.1 \mu\text{g/dL}$ in control communities, with associated neurodevelopmental deficits.

4. 4. 2. Cadmium (Cd)

Cadmium concentrations in Niger Delta groundwater are generally lower than Pb, typically in the range $<0.1\text{--}12 \mu\text{g/L}$, but occasionally reaching $85 \mu\text{g/L}$ near large oil flow stations [9, 10]. The WHO guideline value is $3 \mu\text{g/L}$. Cadmium is primarily sourced from produced water, phosphate fertilizers, and corrosion of galvanized well components. A meta-analysis by Ezekwe et al. [25] showed that over twenty-five groundwater samples in the Niger Delta found that 35% of sampled wells exceeded the WHO Cd limit. Cadmium is particularly a concerning issue because of its long biological half-life (10-30 years) and renal toxicity of which urinary Cd levels in adults in oil-impacted communities have been reported at $2.5\text{--}4.8 \mu\text{g/g}$ creatinine, indicating significant chronic exposure [24].

4. 4. 3. Chromium (Cr)

Total chromium in Niger Delta groundwater ranges from <1 to $280 \mu\text{g/L}$, with Cr(VI) concentrations up to $180 \mu\text{g/L}$ in specific locations [9, 12]. The Nigerian standard is $50 \mu\text{g/L}$ for total Cr. Both geogenic and anthropogenic sources contribute to naturally occurring Cr(III) in aquifer sediments which can be oxidized to Cr(VI) under the slightly acidic, toxic conditions of shallow and seasonal recharge zones [54].

Historical use of chromium lignosulfonate drilling additives has left residual contamination around legacy well sites. In the Warri area, Onyema et al. [10] reported mean Cr concentrations of $42 \mu\text{g/L}$, with several wells exceeding $100 \mu\text{g/L}$, attributed primarily to industrial effluents and drilling waste.

4. 4. 4. Nickel (Ni)

Nickel concentrations in Niger Delta groundwater range from 1 to 320 µg/L and in a median around 15-40 µg/L [10]. The WHO guideline is 70 µg/L. Ni is abundant in crude oil as nickel porphyrins and is co-released in produced water during spills. It is also a corrosion product from stainless steel components in well completions and pipelines. In the Nembe area, Ni concentrations up to 220 µg/L have been measured in boreholes within 100 m of abandoned flow stations [48].

Nickel mobility is enhanced under the region's acidic conditions of pH 4.5-6.0 and is attenuated only under strongly sulfidic conditions, which are not pervasive in the shallow, seasonally recharged Benin Formation aquifer.

4. 4. 5. Arsenic (As)

Arsenic in Niger Delta groundwater presents a dual geogenic and anthropogenic origin where baseline geogenic concentrations range from <0.5 to 45 µg/L, with the highest values in the peaty, reducing aquifers of the eastern delta [14, 42]. The WHO guideline is 10 µg/L. Produced water from Niger Delta fields contains As up to 3 mg/L, and when discharged into the reducing, organic-rich shallow aquifer, it drives further reductive dissolution of iron oxides and release of adsorbed As [9].

Consequently, As concentrations in groundwater near oil spill sites are significantly elevated around mean value of 22 µg/L compared to control sites with mean values of 2.5 µg/L [14]. In Ogoniland, UNEP [5] recorded As up to 85 µg/L in groundwater below a large waste pit. The concurrent presence of As and other carcinogens raises serious long-term cancer risk concerns.

4. 4. 6. Mercury (Hg)

Mercury is among the least studied metals in Niger Delta groundwater, but available data indicate concentrations up to 5.2 µg/L in proximity to gas flaring sites and artisanal gold processing areas that occasionally overlap with oil operations [55]. The WHO guideline is 6 µg/L. Hg in crude oil and natural gas that has elemental Hg can be released to the atmosphere and subsequently deposited, or discharged in produced water. Methylation of inorganic Hg by sulfate-reducing bacteria in anoxic, organic-rich groundwater plumes is a potential but unquantified risk in the Niger Delta, where Hg in edible fish from deltaic rivers already exceeds international consumption advisory levels [56].

4. 4. 7. Iron (Fe) and Manganese (Mn)

Iron and manganese are the most abundant metals in Niger Delta groundwater, with Fe concentrations frequently exceeding 50 mg/L and Mn exceeding 12 mg/L in areas impacted by oil activities and in natural reducing zones [9, 15]. The Nigerian Standard for Drinking Water Quality sets aesthetic limits of 0.3 mg/L for Fe and 0.1 mg/L for Mn, and a health-based guideline for Mn of 0.4 mg/L.

High Fe and Mn cause severe aesthetic problems such as red-brown staining and metallic taste, promote bacterial growth in wells, and are associated with potential neurodevelopmental effects in children after a chronic Mn exposure [57]. The sources include natural reductive dissolution, produced water intrusion, and corrosion of steel casings and pipelines.

4. 4. 8. Copper (Cu), Zinc (Zn), Barium (Ba), and Vanadium (V)

Copper (Cu) and Zinc (Zn) concentrations in Niger Delta groundwater are generally within WHO guidelines 2,000 µg/L and 3,000 µg/L, respectively, but localized elevations occur due to corrosion of brass and bronze fittings, and from agricultural runoff [9]. Zn is often correlated with TPH, suggesting co-mobilization during oil spills [48] while Barium (Ba) is a definitive tracer of produced water contamination. Background Ba in the Niger Delta is <0.5 mg/L, but concentrations exceeding 15 mg/L have been reported in groundwater directly impacted by produced water disposal, far above the WHO guideline of 1.3 mg/L [44, 46]. Ba-rich brines mixing with sulfate-bearing shallow water cause barite precipitation, but residual dissolved Ba remains high. 150 mg/kg of Vanadium (V) is enriched in Niger Delta crude oils and to 3.5 mg/L in produced water [16, 20]. Groundwater V concentrations up to 210 µg/L have been documented in spill-impacted areas, with no current Nigerian standard. V's embryotoxicity and probable carcinogenicity make it an emerging contaminant of concern.

Table 1. Range and mean of heavy metal concentrations (µg/L, except Fe and Mn in mg/L) in groundwater from selected Niger Delta states, compared with Nigerian/WHO drinking water standards.

Metal	NIS/WHO Guideline (µg/L)	Rivers State [9, 10]	Bayelsa State [48]	Delta State [12]	Akwa Ibom [58]	Ogoniland (UNEP) [5]
Pb	10	15-1200	1-800	2.2-998	0.6-200	5-980
Cd	3	12-81	0.2-32	0.5-44	0.1-9	0.5-12
Cr	50	4-220	1.7-64	3-180	0.8-25	1-120
Ni	71	4-312	5-222	2-99	1.5-31	5-160
As	12	0.5-45	0.9-42	1.2-29	0.3-13	2-86
Hg	6	0.01-5.5	0.02-3.8	0.05-4.5	<0.5	0.1-3.9
Fe	0.3	0.7-99	1.3-56	0.9-87	0.4-13	2.1-79
Mn	0.1	0.05-18	0.1-8.5	0.08-7.7	0.02-4	0.5-9.9
Ba	1300	15-9000	20-9000	10-1200	8-1212	50-18000

5. TRANSPORT PATHWAYS AND FATE OF HEAVY METALS IN GROUNDWATER

The transport of heavy metals in Niger Delta aquifers occurs through advection, dispersion, and diffusion, with advection dominating in the high-permeability sands of the Benin Formation [29, 59]. Contaminant plumes from surface spills, reserve pits, and artisanal refining sites migrate vertically through the unsaturated zone this process accelerates by the high rainfall particularly between 1,500-3,000 mm/yr and then laterally along groundwater flow paths, which generally trend southward toward the Atlantic coast. The position of metals during transport is strongly influenced by sorption onto iron oxyhydroxides, clay minerals, and organic

matter, which are abundant in the Benin Formation [59, 60]. However, the low pH of 4.5-6.0 and high DOC of the groundwater reduce metal sorption, particularly for cations such as Pb^{2+} , Cd^{2+} , and Ni^{2+} , which compete with H^+ for surface sites.

The distribution coefficients (K_d) for Pb, Cd, and Zn are therefore lower in Niger Delta groundwater than in neutral-pH temperate aquifers, leading to greater mobility [61].

Colloid-facilitated transport is a significant yet understudied mechanism which occurs when produced water discharge and oil spills introduce colloidal phases nanoparticulate Fe and Mn oxides, clay minerals, and natural organic matter that can transport strongly sorbing metals such as Pb, V, Cr(III) over distances far exceeding predictions based on dissolved-phase K_d values [62]. The high ionic strength of brine-impacted water can cause colloid aggregation and deposition, but transient low-salinity conditions during rainy-season recharge can remobilize colloids and associated metals [63]. Density-driven flow occurs where dense, saline wastewater plumes sink through the less dense freshwater of the Benin Formation. This phenomenon is observed in the coastal Niger Delta which creates complex, three-dimensional plume geometries that cannot be captured by conventional horizontal flow models. In the Bonny area, electrical resistivity surveys have imaged brine plumes extending over 100 m vertically into the freshwater aquifer, with associated metal enrichment [64]. An overview image of the environmental fate of this menace is as shown in Figure 2.

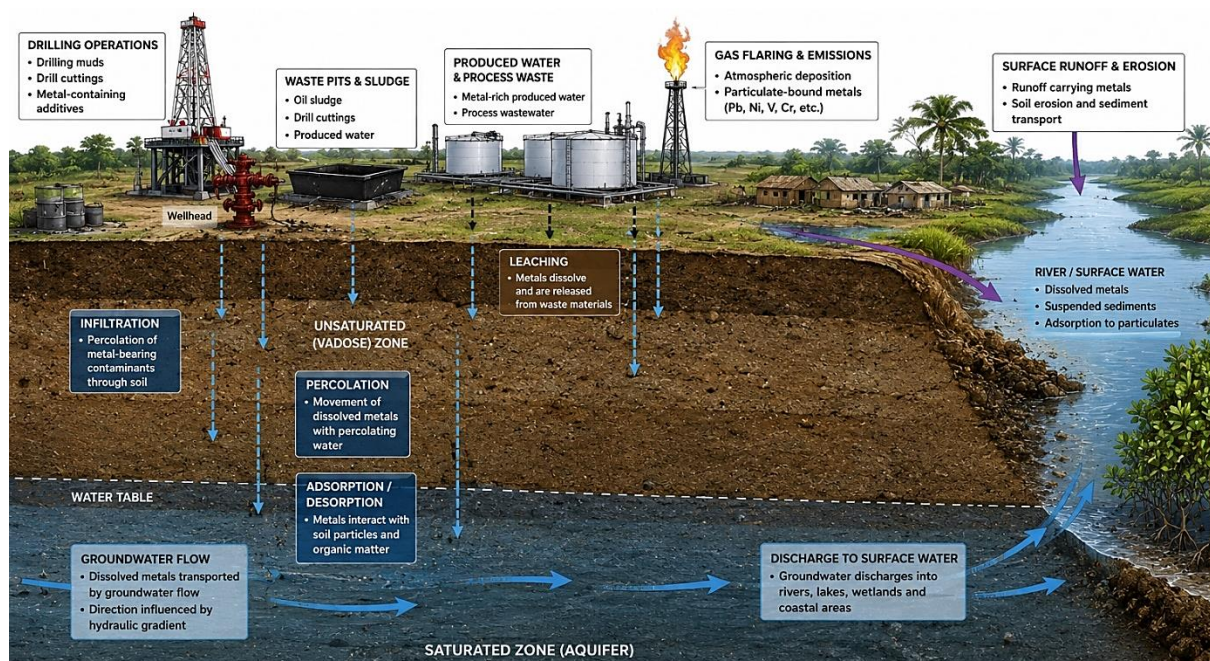


Figure 2. Pathways of transport and transfer mechanism of groundwater contamination.

6. HYDROGEOCHEMICAL CONTROLS ON HEAVY METAL MOBILITY AND PERSISTENCE

The mobility of heavy metals in Niger Delta groundwater is governed by pH, redox potential (Eh), dissolved organic carbon (DOC), and the availability of sulfide and carbonate.

The Benin Formation aquifer is naturally acidic with pH ranging from 4.5–6.5 due to the oxidation of organic matter and the dissolution of CO₂ from soil respiration [38,65]. Under acidic conditions, cationic metals like Pb, Cd, Ni, Cu and Zn are desorbed and present as free ions or chloride complexes, enhancing their mobility. Conversely, oxyanions such as arsenate (H₂AsO₄⁻) and chromate (CrO₄²⁻) exhibit lower sorption at acidic pH than at neutral to alkaline pH, but their mobility is more strongly controlled by redox.

The groundwater is predominantly reducing Eh typically from 100 to +50 mV and driven by the abundance of organic matter. Under these conditions, Fe(III) and Mn(IV) oxides reductively dissolve, releasing Fe²⁺, Mn²⁺, and adsorbed As(III). Sulfate reduction which occurs in deeper anoxic zones generates sulfide that precipitates chalcophile metals (Pb, Cd, Cu, Zn) as highly insoluble metal sulfides [66]. However, in the Niger Delta, sulfate reduction is often limited by low sulfate concentrations in the predominantly freshwater aquifer, meaning that sulfide precipitation may not be sufficient to immobilize metals. Where sulfate is introduced through wastewater which can contain 200-2,000 mg/L SO₄²⁻, sulfide generation can be stimulated, but the high DOC may complex metals and compete with sulfide precipitation [67].

Dissolved organic carbon (DOC) concentrations in the Benin Formation aquifer are high, typically around 5-30 mg/L originating from peat, mangrove detritus, and petroleum hydrocarbons [14, 67]. Low-molecular-weight organic acids such as acetate and oxalate form stable dissolved complexes with Pb, Cd, Cu, and Zn, increasing their mobility. Humic and fulvic acids can both mobilize metals through complexation and immobilize them through sorption of metal-organic complexes to mineral surfaces depending on pH and ionic strength [80]. The extensive presence of petroleum hydrocarbon plumes in many parts of the Niger Delta introduces additional organic ligands that complex metals and potentially enhance their transport. Wastewater intrusion elevates salinity from <500 mg/L to >5,000 mg/L TDS in impacted wells. The associated increase in chloride concentration enhances the formation of stable chloro-complexes of Cd, Pb, and Zn, which sorb poorly to negatively charged aquifer surfaces, thus increasing mobility [59]. Cation competition from elevated Na⁺, Ca²⁺, and Mg²⁺ in brine plumes further reduces sorption of trace metals.

7. SPATIAL AND TEMPORAL PATTERNS OF CONTAMINATION

Spatially, heavy metal contamination in the Niger Delta exhibits three distinct patterns:

- 1).** Localized hotspots around point sources: The artisanal refining sites, abandoned waste pits, flow stations, and oil spill sites. Concentrations of Pb, Cd, and Ni are extremely high within 0.5 km of these sources and decrease exponentially with distance [23, 55]. Geostatistical analysis using ordinary kriging confirm that Pb, Cd, and Ni exhibit strong spatial autocorrelation with ranges of 5-20 km, corresponding to oil field infrastructure clusters [69, 70]. In Rivers State, Pb and Cd spatial patterns are strongly correlated with proximity to artisanal refining sites exhibiting R² of >0.7 in hotspot regression models [55].
- 2).** Linear plumes following groundwater flow paths: Brine plumes from produced water disposal and pipeline leaks extend southward toward the coast with Ba, Fe, Mn, and V concentrations attenuating along the flow path due to sorption, dilution, and precipitation [68].
- 3).** Diffuse, regionally elevated concentrations in areas of high well density and chronic spillage: In the Gokana and Tai Local Government Areas of Ogoniland, Ba, Fe, Mn, and Pb

concentrations are elevated across the entire shallow aquifer, reflecting cumulative impact from decades of oil activities [5, 55]. Temporally, contamination shows pronounced seasonal variation like in the rainy season between April–October, heavy rainfall dilutes shallow groundwater metal concentrations and raises the water table into contaminated soil zones, causing complex flushing and dissolution patterns. In the dry season around November–March, concentrations increase as groundwater is concentrated by evaporation and reduced recharge [5, 71, 72].

8. COMPARATIVE EVIDENCE FROM WITHIN THE NIGER DELTA AND OTHER NIGERIAN BASINS

Within the Niger Delta, contamination severity varies significantly by state and operational history. For example, Ogoniland in Rivers State, Nigeria has a concentrated artisanal refining and when UNEP conducted its comprehensive assessment, presents the most extreme Pb, Cd, and As contamination [5]. In Delta State, industrialization around Warri and the presence of the Warri Refinery add co-occurring industrial metal sources, resulting in higher Cr and Ni levels [49, 55]. Bayelsa State, with its dense network of creeks and extensive mangrove swamps, shows widespread Ba and Fe contamination from wastewater disposal and pipeline leaks, but generally lower Pb than Ogoniland due to less artisanal refining [45]. Akwa Ibom State, which has relatively newer oil fields and less chronic spill history, exhibits lower metal concentrations, though geogenic Fe and Mn remain high [70]. Comparative evidence from other Nigerian sedimentary basins like the Anambra Basin and the Chad Basin, where petroleum operations are minimal or absent, shows baseline heavy metal concentrations significantly lower than in the Niger Delta, supporting the anthropogenic attribution of the excess metals [73, 74]. In the Anambra Basin, the Pb is $<1 \mu\text{g/L}$ and Cd $<0.2 \mu\text{g/L}$ as compared to 35–85 $\mu\text{g/L}$ and 5–15 $\mu\text{g/L}$, respectively in the Niger Delta [75].

9. HUMAN HEALTH AND ECOLOGICAL IMPLICATIONS

Human exposure to heavy metals from Niger Delta groundwater occurs predominantly through ingestion of untreated drinking water, with secondary exposure through dermal absorption during bathing and the consumption of crops irrigated with contaminated water [24, 25]. Health risk assessments applying USEPA methodology have been conducted for multiple communities. Non-carcinogenic hazard quotients (HQ) for Pb in children consuming groundwater exceed 1 which is the safety threshold, in 60–80% of sampled wells in Ogoniland, Warri, and Nembe [25, 55, 71]. For Cd, HQ exceeds 1 in approximately 30% of wells, indicating significant non-carcinogenic kidney risk. The hazard index (HI) for multiple metals routinely exceeds 5 in hotspot areas, signaling a high probability of adverse health effects.

Incremental lifetime cancer risk (ILCR) from As and Cd ingestion frequently exceeds the acceptable range of 1×10^{-6} to 1×10^{-4} . In a probabilistic Monte Carlo assessment of Ogoniland groundwater, Akaninyene et al. [26] calculated 95th-percentile ILCR values for As of 8.5×10^{-4} and for Cd of 3.2×10^{-4} , both well above the 1×10^{-4} threshold, indicating an unacceptable cancer burden for the exposed population. Epidemiological evidence, while limited, is compelling. Mahapatra et al. [24] reported that children aged 1–10 years in Gokana LGA had blood Pb levels

averaging 14.2 µg/dL, with 68% exceeding the CDC reference level of 3.5 µg/dL. Urinary Cd concentrations in adults were elevated and evaluated to have a mean of 3.2 µg/g creatinine and associated with distance to the nearest artisanal refining site. A cross-sectional study in Delta State found that residents using hand-dug wells within 500 m of flow stations had a significantly higher prevalence of proteinuria and a marker of Cd nephrotoxicity than control populations [76]. Ecologically, heavy metal discharge from groundwater baseflow into the Niger Delta's extensive network of creeks and rivers impacts aquatic life. Bioaccumulation of Hg, Pb, and Cd in fish and shellfish with higher concentrations in Tilapia and catfish from impacted rivers exceeding FAO/WHO safe consumption limits [63, 77]. Benthic macroinvertebrate community structure is severely degraded downstream of oil-impacted groundwater discharge zones, with metal-tolerant chironomids and oligochaetes dominating [78].

10. ANALYTICAL METHODS AND GROUNDWATER MONITORING APPROACHES

The analysis of heavy metals in Niger Delta groundwater relies heavily on established spectrophotometric techniques. Atomic absorption spectrometry (AAS) of both flame (FAAS) and graphite furnace (GFAAS) is commonly used method in Nigerian university and government laboratories, offering adequate sensitivity for Pb, Cd, Cr, Ni, Cu, and Zn at the µg/L level [9, 10]. Inductively coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) are increasingly employed in better-resourced institutions and international collaborations, providing multi-element capability and lower detection limits [67, 79]. However, quality assurance and quality control (QA/QC) remain a significant concern. Many published studies lack rigorous field blanks, duplicate samples, and certified reference material verification. Sample preservation in the field is often inadequate, with delays between collection and acidification potentially leading to metal precipitation or sorption onto container walls [80]. The complex matrix of Niger Delta groundwater of high Fe, high DOC, and occasionally free-phase hydrocarbons presents analytical interferences that are not always adequately addressed, particularly in older AAS-based studies.

Field-deployable technologies, such as portable X-Ray fluorescence (pXRF) for rapid metal screening, are being piloted in Ogoniland by NGOs and remediation contractors, offering the potential for cost-effective, real-time monitoring [81]. Passive diffusive samplers, which provide time-weighted average concentrations have been tested in a few research wells and show promising monitoring seasonal variability. The Nigerian Hydrological Services Agency (NIHSA) and state water agencies maintain a sparse network of monitoring boreholes mostly focused on water level and basic chemistry, with heavy metal analysis conducted infrequently and in few locations. The Niger Delta lacks a dedicated, publicly accessible groundwater quality database that integrates data from oil companies, regulatory agencies, and academic studies.

11. POLLUTION INDICES, RISK ASSESSMENT MODELS, AND SOURCE APPORTIONMENT TECHNIQUES

A range of quantitative tools has been applied to interpret heavy metal data in the Niger Delta, some of those tools include;

Pollution indices: The heavy metal pollution index (HPI), metal index (MI), contamination factor (CF), and degree of contamination (Cdeg) are routinely used to classify groundwater quality for regulatory and public communication purposes [83, 98]. Eyankware et al. [69] applied HPI to groundwater from Abia and Rivers States, finding that over 70% of samples had HPI >100, categorizing them as critically polluted. The Nemerow pollution index, which emphasizes the most offending metal, highlights Pb and Cd as the dominant contributors to overall pollution [82].

Health risk assessment models: The deterministic USEPA model calculating chronic daily intake (CDI) via ingestion, dermal, and inhalation pathways, then deriving HQ and ILCR is standard [25]. Increasingly, probabilistic Monte Carlo simulations are used to characterize uncertainty and variability in exposure factors such as body weight, ingestion rate, and exposure duration [26]. These models consistently identify ingestion as the dominant exposure pathway (>90% of risk), but dermal absorption of lipophilic metal-organic complexes in produced water-affected wells may be underestimated.

Source apportionment techniques: Principal component analysis (PCA) and hierarchical cluster analysis (HCA) are widely applied to groundwater chemistry datasets to group metals by source [9, 83, 84]. In the Niger Delta, PCA typically extracts 3 to 4 factors: a geogenic factor of Fe, Mn, As, a produced water/brine factor of Ba, Cl, TDS, V, an artisanal refining/spill factor of Pb, Cd, TPH, and an agricultural/urban factor of Cd, Zn, NO₃. Positive matrix factorization (PMF) has been used less frequently but offers advantages in non-negative source resolution and uncertainty weighting; a recent PMF study in Delta State resolved sources including geogenic (28%), oil operations (42%), artisanal refining (22%), and agriculture (8%) [85]. Lead isotopes (²⁰⁶Pb/²⁰⁷Pb, ²⁰⁸Pb/²⁰⁶Pb) have been used to distinguish between lead from Nigerian crude oil, leaded gasoline (historical), and natural Pb in Benin Formation sediments [54, 86]. Cadmium and zinc isotopes ($\delta^{114}\text{Cd}$, $\delta^{66}\text{Zn}$) have been tested in a few research studies to differentiate produced water from fertilizer sources, but are not yet routine [87].

12. REGULATORY STANDARDS AND ENVIRONMENTAL GOVERNANCE

The regulatory framework for groundwater quality protection in the Niger Delta involves multiple, often overlapping, institutions.

National standards: The Nigerian Standard for Drinking Water Quality (NSDWQ, 2007, revised 2015), administered by the Standards Organization of Nigeria (SON) and the Federal Ministry of Water Resources, sets maximum permissible limits for heavy metals largely aligned with WHO guidelines [87]. The National Environmental (Drinking Water Quality) Regulations, enforced by NESREA, provide legal backing for monitoring and enforcement, but compliance is very weak, particularly in rural areas.

Petroleum sector regulation: The Nigerian Upstream Petroleum Regulatory Commission (NUPRC, formerly the Department of Petroleum Resources, DPR) issues environmental guidelines and standards for the petroleum industry (EGASPIN), which include limits for produced water discharge quality and requirements for environmental impact assessments (EIAs) and environmental evaluation reports (EERs) [88]. However, enforcement has been historically inconsistent; UNEP's [5] assessment of Ogoniland found that none of the major oil companies fully complied with their own stated waste management procedures.

The UNEP Environmental Assessment of Ogoniland (2011) was a watershed moment, providing the most comprehensive scientific assessment of environmental contamination in the region and making over 300 recommendations, including the establishment of a Hydrocarbon Pollution Restoration Project (HYPREP) and a groundwater monitoring authority [5]. Implementation has been slow: as of 2024, only a fraction of the recommended remediation has been completed, and the proposed groundwater monitoring network is not yet operational [86].

Governance challenges: Key challenges include fragmented institutional mandates with poor coordination between water, environment, and petroleum agencies; grossly insufficient funding for groundwater monitoring and laboratory analysis; lack of a publicly accessible, centralized groundwater quality database; limited technical capacity at state and local government levels; and the difficulty of establishing legal liability for contamination in a context of multiple operators, artisanal refining, and community complicity. The Petroleum Industry Act (2021) provides for an Environmental Remediation Fund, but its operationalization and disbursement remain unclear [89].

13. REMEDIATION TECHNOLOGIES AND MANAGEMENT STRATEGIES

Remediation of heavy metal-contaminated groundwater in the Niger Delta is in its infancy. Most efforts to date have focused on surface oil spill cleanup, with little attention to subsurface metal plumes:

Pump-and-treat (P&T): The few implemented groundwater remediation projects, such as those by Shell in the Raminfusk and Diebu Creek areas, have utilized pump-and-treat with above-ground chemical precipitation and filtration. However, P&T is energy-intensive, requires disposal of metal-rich waste streams, and has proven ineffective in achieving cleanup goals in the highly transmissive Benin Formation, where plumes are quickly replenished from residual contamination in the unsaturated zone [90].

Permeable reactive barriers (PRBs): PRBs using zero-valent iron (ZVI) or biochar have been tested at the laboratory scale for Niger Delta groundwater, demonstrating >90% removal of Pb, Cd, and Cr(VI) in column studies [91,92]. Field-scale deployment has not occurred, primarily due to cost, lack of technical expertise, and the challenge of installing barriers in the region's unconsolidated, high-permeability sands.

Phytoremediation and constructed wetlands: These are widely promoted for their low cost and community acceptance. Pilot projects in Ogoniland and Bayelsa have used *Eichhornia crassipes* (water hyacinth), *Typha latifolia* (cattail), and *Pistia stratiotes* (water lettuce) to remove metals from shallow groundwater discharge zones and contaminated surface water [93, 94]. The plants accumulate Pb, Cd, and Ni in their tissues, which are then harvested and incinerated. While effective as a polishing step, phytoremediation cannot treat deep contamination or high-concentration source zones.

In-situ stabilization: Injection of phosphates such as apatite and bone char to stabilize Pb as insoluble pyromorphite has been proposed for soil and shallow groundwater at artisanal refining sites, but field trials are yet to be reported [95].

Emerging approaches: Biochar produced from locally available agricultural waste (palm kernel shells, cassava peels) is being investigated as a low-cost adsorbent for metal

removal in both PRBs and point-of-use filters [96, 97]. Sulfidated nanoscale zero-valent iron (S-nZVI) has shown high reactivity for Pb and Cd in simulated Niger Delta groundwater in laboratory studies, but field delivery and longevity remain unresolved [98].

Management strategies must prioritize source control: Cessation of produced water surface discharge, proper plugging of abandoned wells, decommissioning of unlined waste pits, and most critically, addressing the artisanal refining crisis through alternative livelihood programmes and environmental remediation. Long-term institutional capacity for groundwater monitoring and remediation, funded through the Petroleum Industry Act's remediation provisions, is essential but not yet realized [98].

Table 2. Suitability and status of remediation technologies for heavy metal-contaminated groundwater in the Niger Delta.

Technology	Stage of Development	Effectiveness	Challenges
Pump-and-treat	Limited field deployment	Low long-term efficiency	High cost, energy, waste disposal
ZVI Permeable Reactive	Barrier Laboratory only	High for Pb, Cd, Cr(VI)	Installation complexity, cost
Biochar (adsorption)	Laboratory and small-scale field	Moderate to high	Saturation, variable feedstock
Phytoremediation	Pilot field projects	Moderate for shallow water	Slow, land requirement, seasonal
In-situ phosphate stabilization	Proposed only	Potentially high for Pb	May mobilize As, delivery challenges
Constructed wetlands	Pilot field projects	Moderate for surface water	Requires land, maintenance
Point-of-use filters (biochar/clay)	Community pilots	Moderate	Social acceptance, maintenance

14. KNOWLEDGE AND RESEARCH PRIORITIES

Despite significant research efforts, critical knowledge gaps impede effective management of heavy metal contamination in Niger Delta groundwater.

- 1) Mixed contaminant dynamics: The interaction between heavy metals, petroleum hydrocarbons, and their degradation by-products is poorly understood. Hydrocarbon biodegradation generates organic acids that complex metals, while simultaneously driving redox conditions that mobilize or immobilize metals. The net effect on metal mobility remains largely unquantified.
- 2) Microbial modulation: The role of indigenous aquifer microbial communities in metal transformation for example, Hg methylation, As redox cycling, metal sulfide precipitation is virtually unknown. Metagenomic studies of Niger Delta aquifers could

reveal the functional potential for microbial metal processing and inform bioremediation strategies.

- 3) Vadose zone storage and release: The vast majority of spilled metals reside in the unsaturated zone, yet the long-term release of metals from oil-contaminated soils to groundwater recharge has not been systematically studied. This is critical for predicting future contamination trends as rainfall patterns shift with climate change.
- 4) Legacy and orphan wells: The number, location, and integrity status of abandoned oil wells in the Niger Delta are not publicly available. A systematic programme to identify, prioritize, and monitor orphan wells for groundwater impacts is urgently needed.
- 5) Health impact quantification: Epidemiological studies with robust exposure assessment (personal groundwater sampling, biomarker measurement) and health outcome data are exceedingly scarce. Longitudinal cohort studies in hotspot communities are required to establish causal links between metal exposure and adverse health outcomes.
- 6) Climate change and saltwater intrusion: Sea level rise is projected to accelerate saltwater intrusion into the Benin Formation aquifer along the Niger Delta coastline. The interaction between intruding seawater, geogenic metals, and remnant produced-water plumes could create complex, synergistic contamination scenarios that are entirely unexplored.
- 7) Remediation scalability: Locally appropriate, low-cost remediation technologies—such as biochar-based PRBs, enhanced natural attenuation, and community-managed phytoremediation—require field-scale piloting and life-cycle assessment to demonstrate long-term effectiveness and safety.
- 8) Integrated data systems: The establishment of an open-access Niger Delta Groundwater Quality Database, incorporating data from regulators, operators, academia, and NGOs, is a prerequisite for evidence-based management. This should be accompanied by a fit-for-purpose monitoring network with real-time sensors in strategic locations.

15. CONCLUSIONS AND RECOMMENDATIONS

Heavy metal contamination of groundwater in the Niger Delta is a pervasive, multi-source environmental health crisis that has been allowed to accumulate over six decades of petroleum operations and inadequate environmental governance. Lead, cadmium, arsenic, chromium, nickel, barium, iron, manganese, and vanadium are routinely present in drinking water sources at concentrations that pose unacceptable non-carcinogenic and carcinogenic risks to the region's 30 million inhabitants. The sources are geogenic iron, manganese, and arsenic released under the delta's natural reducing conditions, produced water and drilling waste discharged without adequate treatment, legacy and ongoing spills, corroding infrastructure and the catastrophic expansion of artisanal refining, which has introduced extreme lead levels into shallow aquifers.

Hydrogeochemical conditions such as low pH, reducing redox, high dissolved organic carbon, and the saline brines collectively enhance the mobility of many metals, making the contamination plumes persist and spread through the highly permeable Benin Formation. Spatial patterns are dominated by intense localized hotspots around artisanal refining and oil infrastructure, superimposed on a diffuse elevation in areas of chronic oil activity. Health risk

assessments consistently indicate significant non-carcinogenic risks for lead and cadmium and unacceptable lifetime cancer risks from arsenic and cadmium, with epidemiological evidence of elevated blood lead and urinary cadmium in exposed communities. Regulatory frameworks exist on paper but are crippled by fragmentation, under-resourcing, and lack of enforcement. Remediation efforts are nascent and heavily skewed toward surface oil spill response, with subsurface metal contamination largely unaddressed. The UNEP Ogoniland assessment provided a scientific blueprint for action, but implementation has been critically slow.

Based on this review, it is recommended that:

- (i) There is an immediate establishment of a dedicated Niger Delta Groundwater Management Authority, adequately funded through the Petroleum Industry Act, to coordinate monitoring, data management, and remediation
- (ii) A region-wide baseline survey of heavy metals in all potable groundwater sources, using standardized QA/QC protocols and including speciation analysis for As and Cr;
- (iii) A prioritized source control including complete cessation of produced water surface discharge, inventory and safe plugging of orphaned wells, and urgent intervention in artisanal refining hotspots through provision of alternative livelihoods and environmental cleanup
- (iv) An investment in field-scale pilots of biochar-based PRBs and phytoremediation systems, with community participation
- (v) An initiation of a longitudinal epidemiological cohort study in hotspot communities; and
- (vi) An integration of climate change projections into groundwater vulnerability assessments, particularly regarding saltwater intrusion and altered recharge.

The Niger Delta's groundwater is both a critical resource and a chronic health threat. Bridging the gap between scientific evidence and decisive action is the defining challenge for the region's environmental and public health future.

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