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Sediment Spatial Distribution and Quality Assessment of Metals in Chinook Salmon and Resident Killer Whale Marine Habitat in British Columbia, Canada

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Abstract
At-risk resident killer whale (*Orcinus orca*) populations of the northeastern Pacific, Canada, and their main prey, Chinook Salmon (*Oncorhynchus tshawytscha*), are exposed to a variety of contaminants including chemical elements from both natural and anthropogenic sources, which may be constraining their recovery. Concentrations of 36 chemical elements in subtidal surface sediments (1–435 m depth) collected from 98 sites along the British Columbia coast were used to characterize coast-wide patterns, and a subset of metals (mercury (Hg), cadmium (Cd), arsenic (As), nickel (Ni), copper (Cu), and lead (Pb)) were selected to assess Chinook Salmon and resident killer whale marine habitat quality. Principal component analysis (PCA) showed a dominance of Hg, antimony (Sb), Pb, Cu, and zinc (Zn) for Prince Rupert Harbour, Victoria Harbour, and Burrard Inlet, suggesting local sources. Based on the PCA, geochemical properties such as total organic carbon (TOC), acid volatile sulfide (AVS), and pH explained the spatial distribution of all elements in sediment ($p < 0.001$). Mercury, Cd, As, Ni, Cu, and Pb hotspots were identified along the coast of Vancouver Island, the central and north coast, in the Strait of Georgia, and Haida Gwaii. Bischof Island of Haida Gwaii and Ardmillan Bay on the central coast were most contaminated and enriched by Cd, determined by geoaccumulation index (Igeo) and enrichment factor (EF), respectively. Marine habitat quality was assessed by comparing metal concentrations to Canadian Sediment Quality Guidelines (SQGs). Chinook Salmon populations may be indirectly affected by metal toxicity (As > Cd and Cu > Ni > Hg > Pb) to lower trophic level prey species. Toxicity related impacts to benthic organisms as a result of exposure to elevated Cd and As concentrations in Northern Resident Killer Whale critical habitat and to Hg, Cd, As, Ni, Cu, and Pb concentrations in Southern Resident Killer Whale critical habitat may indirectly pose a threat to resident killer whale populations, highlighting a need for management actions to reduce risks associated with these metals.

Chemical elements can originate from natural sources, such as bedrock, volcanoes, and forest fires, as well as be enriched by anthropogenic sources, such as mines, metal smelters and refineries, landfill leachate, sewage treatment plants, and urban runoff (Grant and Ross 2002; Nriagu and Pacyna 1988). Some can undergo long-range transport via atmospheric and oceanographic processes and reach remote locations (Grant and Ross 2002). In marine geochemistry, they are generally classified as major (> 1 wt%; e.g., iron (Fe), aluminium (Al), calcium (Ca), and sodium (Na)) and trace (< 0.1 wt%; e.g., Hg, Cd, Cu, and Pb) depending on their concentrations in the environment. While some are essential/beneficial for various biochemical and physiological functions (e.g., Fe, magnesium (Mg), manganese (Mn), Cu, Zn, selenium (Se), and cobalt (Co)), others are non-essential (e.g., Hg, Cd, Pb, Ni, and As). However, both essential and non-essential elements can be toxic above a certain threshold. Amongst trace elements, metals such as Hg, Cd, Cu, and Pb are of particular concern due to their toxicity even at low concentrations (Grant and Ross 2002).

Resident killer whales (*Orcinus orca*) of the northeastern Pacific are listed as Threatened (Northern Residents) and Endangered (Southern Residents) in Canada under the *Species at Risk Act* (SARA S.C. 2002, c. 29). The Northern Resident Killer Whale (NRKW) population currently includes around 332 individuals in 15 matrilineal pods

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(Fisheries and Oceans Canada [DFO] 2022), and has a home range from Glacier Bay, Alaska to Gray's Harbor, Washington (Ford et al. 2017). The Southern Resident Killer Whale (SRKW) population includes 73 individuals in three matrilineal pods (Center for Whale Research July 1, 2022) and has a home range that extends from southeastern Alaska to central California (Ford et al. 2017). Prey availability, noise and disturbance, and environmental contaminants have been identified as primary threats for the recovery of these populations (Fisheries and Oceans Canada [DFO] 2018). While habitat loss by anthropogenic factors and climate change plays a key role in salmon population decline (Committee on the Status of Endangered Wildlife in Canada [COSEWIC] 2018), exposures to environmental pollutants are of particular concern to Pacific salmonid species, including Chinook Salmon (*Oncorhynchus tshawytscha*), which are the main prey of resident killer whales (Browne et al. 2010). In addition to organic contaminants such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), some metals have been identified as primary contaminants of concern for the recovery of resident killer whales (i.e., Hg) and as a threat to Chinook Salmon (i.e., Hg, Cd, Cu, and Pb) (Environment and Climate Change Canada [ECCC] 2020).

Accumulation of metals by marine organisms is influenced by several factors such as chemical speciation/bioavailability, water and/or air concentrations, species, diet, metal uptake and elimination kinetics, metabolic rates, age, gender, and trophic position (Das et al. 2002; Wood et al. 2011). Bioaccumulation of Cd, Cu, and Pb has been shown in Atlantic (*Salmo salar*) and Chinook Salmon (Kelly et al. 2008; Sauliute and Svecevicius 2017) as well as marine mammals (Beck et al. 1997; Gerpe et al. 2002; Hansen et al. 2016; Mackey et al. 1996), including killer whales (Endo et al. 2007). Acute and chronic exposures to Hg, Cd, Cu, and Pb in fish, including salmonids, have led to biochemical, physiological, cellular, and behavioral effects, increased mortality and reduced reproduction and growth (Wood et al. 2011). Mercury exposure caused oxidative stress and brain lesions in Atlantic Salmon parr (Berntssen et al. 2003). Chronic sublethal Cd exposure caused ionoregulatory disturbance, reducing whole-body Ca and potassium (K) in Atlantic Salmon alevins (Rombough and Garside 1984). Chronic exposure to As inhibited growth of juvenile Rainbow Trout (*Oncorhynchus mykiss*) (Speyer 1974). Nickel exposure reduced egg hatchability in Atlantic Salmon (Grande and Andersen 1983). In Chinook Salmon, Cu exposure impaired Cu avoidance behaviour due to olfactory damage (Hansen et al. 1999) and increased mortality by *Vibrio anguillarum* infection (Baker et al. 1983). Lead exposure may inhibit mitochondrial respiration by depositing Pb in the mitochondrial fraction of the kidney and liver cells of Coho Salmon (*Oncorhynchus kisutch*) (Reichert et al. 1979; Scott et al. 1971). When considering Hg, its organic form, methylmercury (MeHg), is the toxic form that has the ability to biomagnify up the food chain (Caurant et al. 1996; Holsbeek et al. 1998; Itano et al. 1984; Joiris et al. 1991; Kelly et al. 2008) leading to a variety of short- and long-term toxic responses in marine top predators such as genotoxicity, cytotoxicity, neurotoxicity, and immunotoxicity (Basu et al. 2009; Betti and Nigro 1996; Das et al. 2008; Frouin et al. 2012; Krey et al. 2015).

Anadromous Chinook Salmon have a diverse life history in both fresh and marine waters (Quinn 2005) and broad ocean habitat range (Beamish et al. 2005). Juvenile Chinook Salmon consume benthos during the rearing period in nearshore coastal areas prior to their seaward migration (Chapman and Wang 2001; Healey 1991), as food availability tends to be higher in estuarine coastal habitats than in freshwater areas (Quinn 2005). During their time in the marine environment, they undergo the majority of their growth before returning to their freshwater natal streams to spawn (Healey 1991). Fluctuations in the availability of Chinook Salmon in the coastal feeding grounds strongly influence resident killer whales' survival and reproduction (Ford et al. 2010; Ward et al. 2009), and years of poor salmon returns have been associated with poor body condition of the whales and high miscarriage rates (Wasser et al. 2017). Three areas have been identified as critical habitat (i.e., the habitat that is necessary for the survival or recovery of the listed wildlife species) for NRKW and SRKW along the British Columbia coast and are legally protected from destruction under the Canadian *Species at Risk Act* (SARA) (Fig. 1).

Sediment can act as both a sink and a source of metals in the marine environment, and upon mobilization, some metals can bioaccumulate in the organs/tissues of fish and marine mammals via direct uptake from water and/or the atmosphere and indirectly via the consumption of contaminated food (Das et al. 2002; Wood et al. 2011). Sediment can therefore provide valuable information on the quality of the marine environment and potential for metal-associated health impacts to marine organisms. In the present study, we used sediment chemical element concentrations from 98 sites along the British Columbia (BC) coast to assess the habitat quality of Chinook Salmon and resident killer whales. Sediment Quality Guidelines (SQGs) from the Canadian Council of Ministers of the Environment (CCME) and BC Ministry of Environment and Climate Change Strategy (BCMoECCS) were used to provide insight into the risk the elements found in the study may pose to the health of Chinook Salmon and resident killer whales.

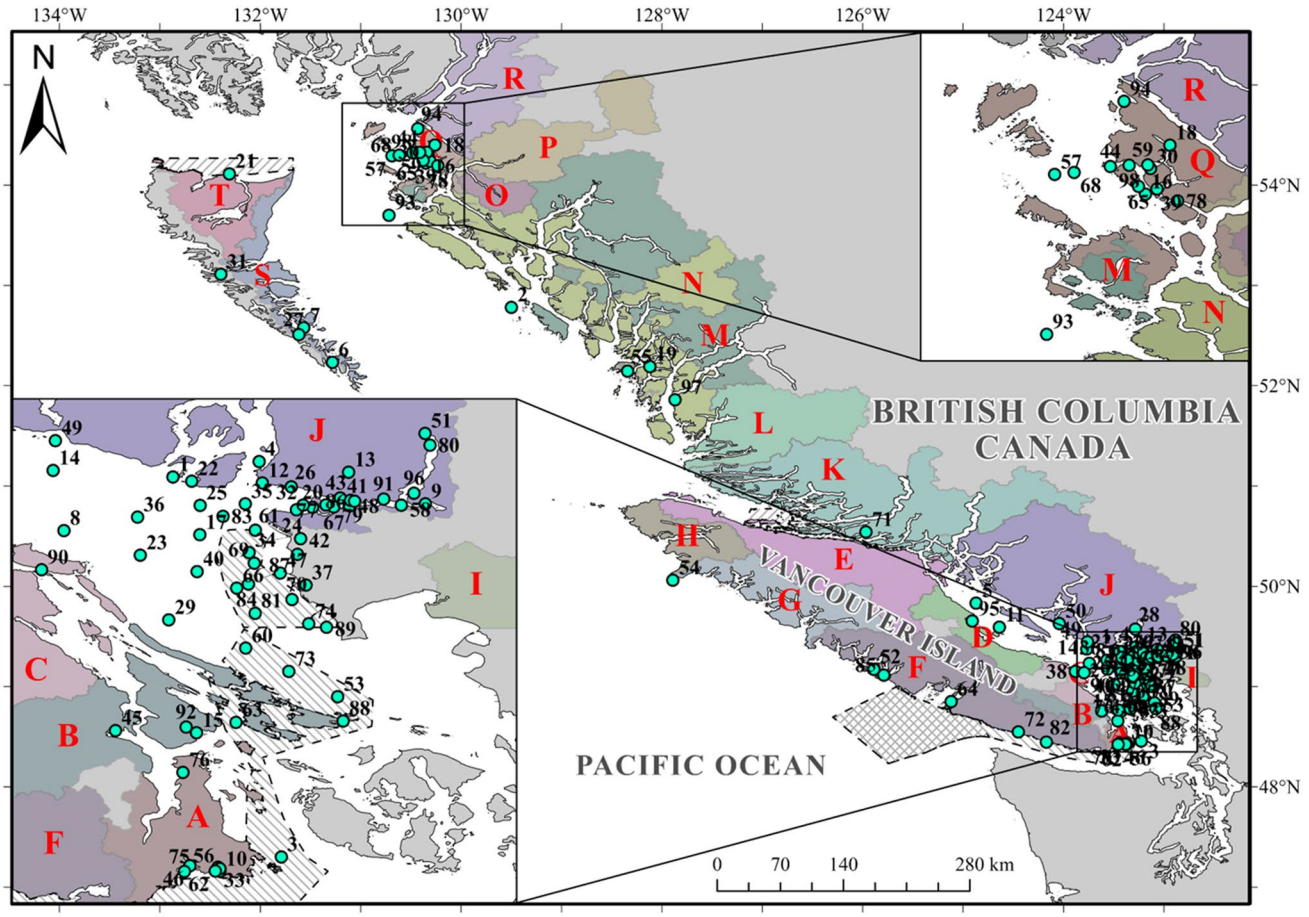

Fig. 1 Subtidal surface sediments collected from 98 sites along the coast of British Columbia, Canada. Sites were numbered with map IDs ordered from highest to lowest total element concentrations (Supporting Information, Table S1). Nearshore Conservation Units (CUs) of Chinook Salmon are shown as CU IDs A through T (Supporting Information, Table S2). Critical habitat of Northern Resident Killer Whales (///) and Southern Resident Killer Whales (\\\) are shown as hatched areas. The cross-hatched area represents shared critical habitat

Materials and Methods

Sediment Collection

Subtidal surface (~ 5–10 cm) sediments were collected from 98 sites along the BC coast (Fig. 1) between 2018 and 2020 as part of Ocean Wise Conservation Association's Pollution Tracker Program, Fisheries and Oceans Canada's Whale Contaminants Program, and Environment and Climate Change Canada's Disposal at Sea Program. A stainless-steel Petite Ponar, Smith-McIntyre, or Van Veen grab sampler was used and a minimum of two grabs were collected to make a composite sample at each site. A combination of shallow (71 samples between 1 and 55 m) and deeper (27 samples between 82 and 435 m) sediment samples were collected (Supporting Information, Table S3). Sampling effort was higher on the south coast, including the Strait of Georgia and Juan de Fuca Strait, and patchier on the central and north coast, with one site within NRKW critical habitat and 17 sites within SRKW critical habitat (Fig. 1). Among the 80 Chinook Salmon Conservation Units (CUs), 20 nearshore CUs were covered by our sampling effort (Fig. 1). Samples were stored at − 20 °C and sent to accredited laboratories for analyses.

Instrumental Analysis

All samples were analyzed for a total of 36 chemical elements by ALS Environmental Ltd. (BC, Canada). Mercury was analyzed using cold vapor atomic adsorption spectrometry (CVAAS) following US Environmental Protection Agency (EPA) methods 200.2 and 1631, and MeHg was analyzed using gas chromatography atomic fluorescence spectroscopy (GCAFS) following US EPA method 1630 and DeWild et al. (2004). All other elements were analyzed using collision/reaction cell inductively coupled

plasma mass spectrometry (CRC ICPMS) following US EPA method 6020B. Total organic carbon (TOC) was determined according to Skjemstad and Baldock (2007) by combustion using a carbon analyzer, and acid volatile sulfide (AVS) was analyzed by the methylene blue colorimetric method following US EPA method 821/R-91-100. Sediment particle size (SPS) was determined either at ALS Environmental Ltd. or at Pacific Soil Analysis Inc. (BC, Canada) based on the modified Wentworth (1922) classification system. pH was measured in accordance with procedures described in the BC environmental laboratory manual (BC 2020). For quality assurance and quality control, laboratory duplicates, method blanks, laboratory control samples, matrix spikes, and reference materials were carried out to make sure they met data quality objectives. The reference material analyzed for quality control purposes was the SS-2 standard for elements in a soil matrix supplied by SCP Science (Montreal, QC, Canada). Relative difference (%) for laboratory duplicate and recovery (%) for laboratory control sample, matrix spike, and reference material were confirmed within limits (%); i.e., less than relative difference of 30 or 40% or absolute difference of 2 × limit of reporting for laboratory duplicate, between 80 and 120% for laboratory control sample (except for MeHg, between 70 and 130%), between 70 and 130% for matrix spike, and between 70 and 130% for reference material (except for boron (B) and thallium (Tl), between 40 and 160%). Method blanks were below the limit of reporting.

Data and Statistical Analysis

All data and statistical analyses were performed using R Statistical Software (Ver. 4.0.5; R Foundation for Statistical Computing). Measured elements were classified into ten major (i.e., Fe, Ca, Al, Na, Mg, sulfur (S), K, titanium (Ti), phosphorus (P), and Mn) and 26 trace elements (i.e., strontium (Sr), Zn, vanadium (V), barium (Ba), Cu, B, chromium (Cr), Ni, lithium (Li), Pb, Co, tin (Sn), As, zirconium (Zr), molybdenum (Mo), uranium (U), Cd, Se, Sb, bismuth (Bi), silver (Ag), beryllium (Be), Tl, Hg, MeHg, and tungsten (W)) based on weight total percentage (major: between $0.5 \pm 0.0005\%$ (Mn) and $29.8 \pm 0.009\%$ (Fe) and trace: $< 0.1 \pm 0.00009\%$ (Sr)). Out of 26 trace elements, six metals (Hg, Cd, As, Ni, Cu, and Pb) were selected for further evaluation of hotspots and Chinook Salmon and resident killer whale habitat quality based on their prevalence in the samples and their exceedances of environmental Sediment Quality Guidelines (SQGs). Among those selected, one or more metals have been identified as primary contaminants of concern for Chinook Salmon (Hg, Cd, Cu, and Pb) and resident killer whales (Hg) as per the Southern Resident Killer Whale contaminants technical working group (Environment and Climate Change Canada [ECCC] 2020). Total concentrations were calculated as the sum of blank corrected major and trace element concentrations.

Data were tested for normality using the Shapiro–Wilk test, and either Pearson or Spearman's rank correlation coefficients were used to quantify the relationships among PCA projections (i.e., elements and SPSs), TOC, AVS, pH, water depth, and element density. A parametric t-test or nonparametric Mann–Whitney U test was used to compare differences in Hg, Cd, As, Ni, Cu, and Pb metals between both within and outside and Northern and Southern Resident Killer Whale critical habitat. Mean and standard error (SE) were used to describe the variability within samples. Statistical significance was set at $p < 0.05$.

Multivariate Analysis

Principal component analysis (PCA) was performed to evaluate the chemical element composition patterns in sediments from 98 sites. Only elements with > 70% detectable values were selected, and undetectable values for those elements were replaced by a random number between zero and the limit of detection (Ross et al. 2004). In total, ten major and 21 trace elements were used in the PCA. Prior to PCA, individual element concentrations were normalized to the concentration total to remove artifacts related to concentration differences among sampling sites. The centered log ratio (CLR) transformation was then applied to produce the derived compositional data unconstrained by negative bias or closure problems (Ross et al. 2004). Data were then autoscaled to give every variable equal weight. PCA was also used to evaluate sediment particle composition and similar data manipulation was done on SPS data. Since SPS analyses were conducted at two different laboratories, slightly different combinations of SPSs were reported (Supporting Information, Table S3), and 77 sites with more SPS splits were utilized.

Geoaccumulation Index and Enrichment Factor Analysis

To quantify the degree of metal contamination and anthropogenic enrichment, geoaccumulation index ($Igeo = \log_2[C_n/(1.5 \times B_n)]$, where C_n and B_n are measured and background metal concentrations, respectively) and enrichment factor ($EF = (C_x/Fe)_{sample}/(C_x/Fe)_{background}$, where C_x is measured metal concentration) were determined. Without having established baseline reference levels from cored sediment samples (Abrahim and Parker 2008), global average metal levels of the upper continental crust (UCC) including the Canadian Shield were used as background concentrations (Rudnick and Gao 2003). These background levels are within the range of metals detected at variable sediment depths along the BC coast (Harding et al. 1988;

Macdonald et al. 2008; Mariko 2013; Stantec 2013; Wojnarowicz et al. 2016) and, in particular, Hg, Cd, and As are within the lower range of unpolluted coastal sediment (Harding et al. 1988). A factor of 1.5 was used to decrease the possibility of variation in the background values for Igeo and a conservative element with low existence variability, Fe, was used for EF to identify the anomalous metal concentrations. The sediment classification is based on the Igeo value as follows: (1) < 0 = uncontaminated, (2) 0–1 = uncontaminated to moderate contamination, (3) 1–2 = moderate contamination, (4) 2–3 = moderate to strong contamination, (5) 3–4 = strong contamination, (6) 4–5 = strong to extreme contamination, (7) > 5 = extreme contamination. The elemental enrichment classification of the sediment is based on the following: (1) 0–1 = background concentration or no enrichment; (2) 1–3 = minor enrichment, (3) 3–5 = moderate enrichment, (4) 5–10 = moderately severe enrichment, (5) 10–25 = severe enrichment, (6) 25–50 = very severe enrichment, and (7) > 50 = extremely severe enrichment.

Geostatistical Analysis

To further explore metal levels in sediment in nearshore Chinook Salmon CUs and in and around resident killer whale critical habitat, spatial interpolation of measured concentrations was conducted using Kernel interpolation with barrier (KB), available in the Geostatistical Wizard of ArcGIS Pro Software (Ver. 2.4.3; Environmental Systems Research Institute). Prior to interpolation, total concentrations of metals were log transformed for normal distributions among sites. The KB model was chosen for the validity of breaklines (i.e., western continental coastline of BC, Vancouver Island, Queen Charlotte Islands, etc.), considering the shortest non-Euclidean distance between two points within the defined search neighborhood. Exponential was selected for the Kernel function based on the selection criteria of mean error (ME) close to 0 and smaller root-mean-square error (RMSE). ME provides an estimate of the bias (i.e., overestimate [+value] or underestimate [−value]) and RMSE represents an estimate of the deviation. Default bandwidth was used. Following the interpolation, the KB model was re-employed to generate probability maps to assess the probability of a given point to exceed a pre-defined threshold. For this purpose, measured values were converted to a probability of either 1 or 0 to indicate whether values were over or under the CCME and BCMoECCS Sediment Quality Guidelines (SQGs). To ensure the accuracy of the probability maps with a higher number of samples, extracted interpolated values, over the SQGs, were utilized by converting to a probability of 0.75. The rationale to use a probability of 0.75 was to give a medium weighted probability between 0.5 and 1. To identify hotspots of metals including organic mercury, relative (centered log ratio (CLR)) and actual (total in mg/kg) concentrations were subject to the KB model by the same procedure, and overlapped heatmaps of relative and actual concentrations with 1:1 weighted ratio were used. Overlapped regions of hotspots are proposed to be the areas of greatest environmental concern (Kim et al. 2022). Previously, CLR transformed data were employed to identify hotspots of underlying compositional metals in terrestrial soils and river sediment of nearby mining sites (Horák and Hejcman 2016; Neiva et al. 2019). To quantify the degree of metal contamination and anthropogenic enrichment at hotspots, geoaccumulation index (Igeo) and enrichment factor (EF) were again subject to the KB model by the same procedure.

Results and Discussion

Sediment Concentration of Chemical Elements

Thirty-six elements were measured in sediments collected from 98 sites (Supporting Information, Table S1). Total concentrations ranged from 20,500 to 289,320 mg/kg. While the highest total element concentrations were found at Popham Island (HS1 $_{(\text{map ID: } 1)}$) on the south coast, the lowest levels were reported at Dundas Point (NWC3 $_{(98)}$) on the north coast (Fig. 1). For major elements, Fe levels were the highest (24,250 ± 968 mg/kg for all sites), followed by Ca (16,526 ± 3,144 mg/kg), Al (15,046 ± 593 mg/kg), Na (12,392 ± 958 mg/kg), Mg (9,729 ± 389 mg/kg), S (4,301 ± 435 mg/kg), K (2,366 ± 133 mg/kg), Ti (860 ± 32 mg/kg), P (832 ± 32 mg/kg), and Mn (434 ± 76 mg/kg). Trace elements were ranked according to concentration as follows: Sr (105 ± 15 mg/kg for all sites) > Zn (81 ± 9 mg/kg) > V (54 ± 2 mg/kg) > Ba (51 ± 3 mg/kg) > Cu (47 ± 10 mg/kg) > B (32 ± 3 mg/kg) > Cr (30 ± 1 mg/kg) > Ni (25 ± 1 mg/kg) > Li (17 ± 1 mg/kg) > Pb (14 ± 2 mg/kg) > Co (9 ± 0.5 mg/kg) > As (8 ± 1 mg/kg) > Zr (5 ± 0.3 mg/kg) > Mo (2 ± 0.4 mg/kg) > U (1 ± 0.2 mg/kg) > Cd (0.8 ± 0.2 mg/kg) > Se (0.7 ± 0.1 mg/kg) > Sb (0.5 ± 0.05 mg/kg) > Be (0.3 ± 0.01 mg/kg) > Tl (0.2 ± 0.01 mg/kg) > Hg (0.1 ± 0.01 mg/kg). Tin, Ag, and Bi were detected at only a few sites, and W was below analytical detection limit at all sites. Methylmercury (0.0004 ± 0.0001 mg/kg) was only detected at 1/1000 the level of Hg. Similar average concentrations of major (i.e., Fe, Al, and Mn) and trace elements (i.e., Zn, Ba, Cu, Cr, Ni, Pb, Co, As, Mo, U, Cd, and Hg) were reported previously in surficial sediment of comparable water depths from Vancouver Island, the Strait of Georgia, Burrard Inlet, and Prince Rupert along the coast of BC (Grieve and Fletcher 1976; Harding et al. 1988; Macdonald et al. 2008; Mariko 2013; Stantec 2013; Wojnarowicz et al. 2016). Undetected W may suggest limited natural (i.e., W-bearing minerals) and local anthropogenic (i.e., metallic

W^0) sources, pH-related desorption (pH ≥ 8) from Fe(III)/Mn(IV) oxides/oxyhydroxides to seawater, or deeper sediment deposition and transport of monomeric and polymeric tungstate oxyanions (WO_4^{2-}) (Hobson et al. 2020).

Calcium had the most variation among the sites, and exceptionally high levels of Ca were detected at Popham Island (HS1 $_{(1)}$), as well as at Aristazabal Island (SRKW20-5 $_{(2)}$) on the north central coast and at Finnerty Cove (FC1 $_{(3)}$) on southeastern Vancouver Island. By excluding Ca, total element levels at these three sites were 2 to threefold higher than the totals at Dundas Point (NWC3 $_{(98)}$), compared to 7 to 14-fold higher by including Ca. High Ca concentrations at Popham Island, Aristazabal Island, and Finnerty Cove may be linked to historical uses of large quantities of limestone and lime by the construction industry for production of Portland cement, builders' lime, and building stone; in agriculture for soil amendment purposes; in metallurgical plants as a flux in smelting; and, in pulp and paper mills during the extraction of lignins from wood and in solutions for bleaching pulp (Mathews and McCammon 1957). On Canada's Atlantic coast, elevated Ca concentrations were observed in sediment in the vicinity of a gypsum loading pier and adjacent to a thermal generating plant from accidental releases (Buckley and Winters 1992). For comparison, the highest Ca concentration measured in the current study (at Popham Island (HS1 $_{(1)}$)) was approximately fivefold higher than the highest reported concentration (54,100 mg/kg Ca) on Canada's Atlantic coast (Buckley and Winters 1992).

Characterization of Chemical Element Patterns

Site-specific element profiles were established, demonstrating spatial heterogeneity (Fig. 2). Levels of major elements accounted for a total average of 99.4 ± 0.02% across all sites, whereas trace elements accounted for an average of 0.6 ± 0.02% with NWC1 $_{(30)}$ having the highest contribution (2% of total elements), where Zn and Cu accounted for 37% and 39% of trace element levels, respectively. A large portion of metals in non-polluted sediment present in the crystal lattice of minerals (Zhang et al. 2014), and higher proportions of Zn and Cu are suggestive of outer source origins based on indistinguishable proportions of major elements at NWC1 $_{(30)}$ compared to other sites (Fig. 2).

PCA was used to further characterize element patterns (Fig. 3). The principal components (PCs), PC1 and PC2, accounted for 38% and 16% of variation, respectively (Fig. 3). Major elements Mg, Ti, Al, and Fe were positively associated with PC1, along with trace elements V and Co, while major elements S and Na were negatively associated with PC1, along with Mo, Se, Cd, U, and B. Major elements P and Ca were positively associated with PC2, correlating with trace element Sr. Strontium appeared to be controlled by biogenic calcium carbonate ($CaCO_3$) (Rubio et al. 2000). Trace elements Hg, Sb, Pb, Cu, and Zn were negatively associated with PC2 without any associated major elements (Fig. 3a).

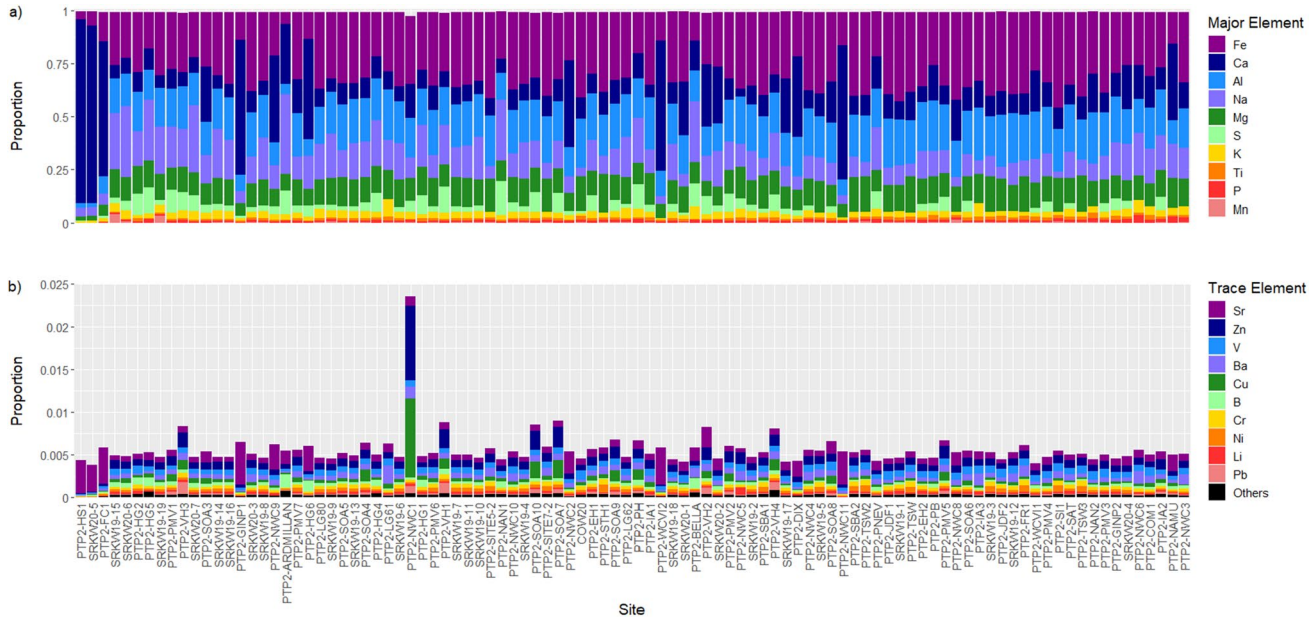

Fig. 2 Proportions of ten **a** major elements and **b** trace elements with a total of 16 trace elements remaining (Others) for sediment samples collected from 98 sites. Sites are ordered from highest (left) to lowest (right) total element concentration, which correspond to map IDs 1 through 98 (Fig. 1 and Supporting Information, Table S1). Major elements accounted for an average of approximately 99.4 ± 0.02% of total elements, and trace elements accounted for an average of approximately 0.6 ± 0.02% across all sites

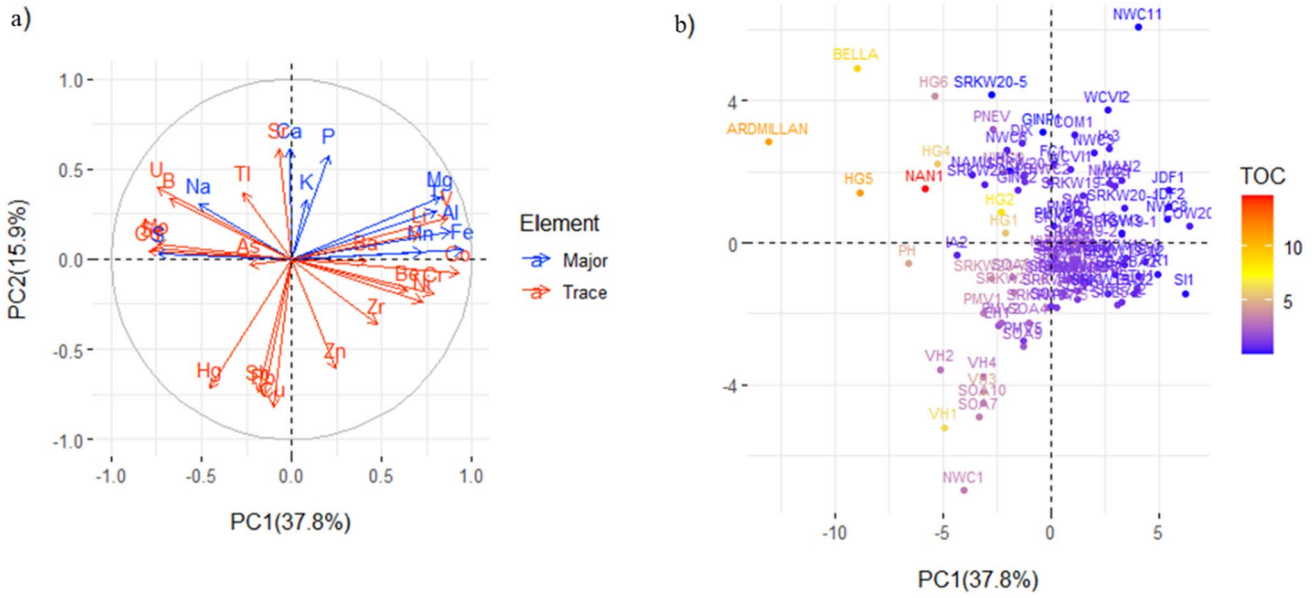

Fig. 3 A principal component analysis (PCA) for mean-adjusted element concentrations at 98 sites, **a** loading and **b** score plots. All points are color coded based on **a** element types (i.e., major and trace) and **b** total organic carbon (TOC in %). Trace elements, in particular, Hg, Sb, Pb, Cu, and Zn were negatively associated with PC2 without any correlating major elements for Prince Rupert Harbour (NWC1 $_{(30)}$), Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, VH4 $_{(62)}$), and Burrard Inlet (SOA7 $_{(43)}$ and SOA10 $_{(41)}$)

The PCA score plot showed that numerous sites shared similar element profiles, clustering in the center (Fig. 3b). The main sites that diverged from the center cluster were (1) Ardmillan Bay (ARDMILLAN $_{(19)}$), Bella Bella (BELLA $_{(55)}$), and Bischof Island (HG5 $_{(7)}$), which were on the negative side of PC1 and therefore associated with a dominance of S, Na, Mo, Se, Cd, U, and B, and (2) Prince Rupert Harbour (NWC1 $_{(30)}$), Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, VH4 $_{(62)}$), and Burrard Inlet (SOA7 $_{(43)}$ and SOA10 $_{(41)}$) which were on the negative side of PC2 and therefore associated with a dominance of Hg, Sb, Pb, Cu, and Zn. Without having associated with any major elements, Hg, Sb, Pb, Cu, and Zn would suggest common external sources. Urbanization and population growth in coastal areas have increased the number of sources that contribute metals, such as Hg, Pb, Cu, and Zn, to harbour environments, including industrial and urban discharges from shipyards, bulk loading facilities, and sewage outfalls (Garrett and Ross 2010). Motor vehicle wear particles (i.e., tire and brake lining) are a major source of Sb, Pb, Cu, and Zn in stormwater runoff, mostly from paved roads and tunnels and parking lots (Cameron and Miller 2001; Lough et al. 2005). Combined sewer overflows may contain high levels of Hg (Garrett and Ross 2010). Lead, Cu, and Zn are used in the construction of water pipelines, tanks, and reservoirs and may dissolve and become incorporated in the urban sewage effluents (Guerra-García et al. 2005). Washout of antifouling and anticorrosive paints used on vessels may contribute to elevated concentrations of Cu and Zn in harbour areas (Guerra-García et al. 2005; O'Regan et al. 2018). Atmospheric deposition of Pb from vehicle emissions may represent a major source of Pb to marine sediment (Guerra-García et al. 2005).

Factors Governing Distribution of Chemical Elements

In addition to potential local sources influencing element distribution along the coast, total organic carbon (TOC), along with sediment particle size (SPS), acid volatile sulfide (AVS), and pH, are well known factors influencing element partitioning and distribution in sediment (Chapman et al. 1999; Simpson et al. 2012; Strom et al. 2011). As shown in the PCA score plot (Fig. 3b), the majority of sites at the center shared TOC values below 5%, while the divergent sites had higher TOC at ranges between 6 and 15%. PC1 was explained by TOC ($R = -0.66$, $p < 0.001$), AVS ($R = -0.52$, $p < 0.001$), and pH ($R = 0.37$, $p < 0.001$), while PC2 was significantly correlated with SPS ($R = -0.49$, $p < 0.001$), TOC ($R = -0.36$, $p < 0.001$), and pH ($R = 0.25$, $p < 0.05$). Water depth and element density were also considered but did not affect PC1 nor PC2 (Table 1), confirming spatial elemental distributions are primarily governed by geochemical properties of sediment (Zhang et al. 2014).

Sites with divergent element patterns on the negative side of PC1 were therefore characterized by higher TOC and AVS along with lower pH and were dominated by trace elements Mo, Se, Cd, U, B, Hg, Sb, Pb, Cu, and Zn. Metals in polluted sediment mainly exist in the forms of soluble,

Table 1 Correlation coefficients to quantify the relationships among PCA projections (i.e., elements and SPSs), TOC, AVS, pH, water depth, and element density

	PC1 (37.8%)	PC2 (15.9%)
SPS PC1 (69.3%)	$R = -0.22$; $p > 0.05$	$R = -0.49$; $p < 0.001$
TOC	$R = -0.66$; $p < 0.001$	$R = -0.36$; $p < 0.001$
AVS	$R = -0.52$; $p < 0.001$	$R = -0.11$; $p > 0.05$
pH	$R = 0.37$; $p < 0.001$	$R = 0.25$; $p < 0.05$
Depth	$R = 0.13$; $p > 0.05$	$R = -0.19$; $p > 0.05$
Density	$R = -0.27$; $p > 0.05$	$R = -0.35$; $p > 0.05$

Statistical significance was set at $p < 0.05$

AVS, Acid volatile sulfide (µmol/g); PCA, Principal component analysis; SPS, Sediment particle size; TOC, Total organic carbon (%)

For SPS, PC1 derived from PCA (Supporting Information, Fig. S1) was used

ion-exchangeable, organic matter/sulfides, Fe–Mn oxides, and carbonates (Hou et al. 2013), and Hg, Sb, Pb, Cu, and Zn at Prince Rupert Harbour (NWC1 $_{(30)}$), Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, and VH4 $_{(62)}$), and Burrard Inlet (SOA7 $_{(43)}$ and SOA10 $_{(41)}$) may largely be deposited onto sediment surfaces and immobilized through precipitation by forming insoluble fractionation with organic matter/sulfides (Salomons et al. 1987; Yang et al. 2010). Moreover, efficient binding of Hg, Sb, Pb, Cu, and Zn is expected from their significant association with smaller particle sizes, as the fine-grained fraction in sediment provides larger surface area and higher cation exchange capacity than coarse particles (Fernandes et al. 2011; Lu et al. 2005; Zhao et al. 2010). This suggests that high contributions of Hg, Sb, Pb, Cu, and Zn may be the result of a combination of local sources and favorable environmental conditions for precipitation.

Hotspots of Toxic Metals

Six toxic metals (Hg, Cd, As, Ni, Cu, and Pb) were selected for further evaluation of hotspots along the BC coast and to help determine Chinook Salmon and resident killer whale habitat quality based on their prevalence in samples and their exceedance of environmental Sediment Quality Guidelines (SQGs). Mercury, Cd, Cu, and Pb and Hg have been identified as primary contaminants of concern for Chinook Salmon and resident killer whales, respectively.

Hotspot overlaps identified using relative (centered log ratio (CLR)) and actual (total in mg/kg) concentrations (Supporting Information, Fig. S2) are proposed to be the areas of greatest environmental concern (Kim et al. 2022). The cross-validation results of KB showed a better interpolation for the relative (CLR) than actual (total in mg/kg) concentrations for six toxic metals with lower RMSE and overestimation with positive ME for both CLR and total Cd, Cu, and Pb (Supporting Information, Table S4). Regardless of the overall overestimation, CLR and total Cd, Cu, and Pb were constantly underestimated at Prince Rupert Harbour (NWC1 $_{(30)}$) on the north coast with the largest margin of error (Supporting Information, Fig. S2). A default bandwidth used for KB appears to have resulted in an oversmoothed density estimate that hides some underlying structures (Yin 2020).

Hotspots of six toxic metals were identified (Fig. 4): 1. Hg at Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, and VH4 $_{(62)}$) and Esquimalt Harbour (EH1 $_{(46)}$) on Vancouver Island, Hardwood and Hornby Islands (SRKW20-6 $_{(5)}$ and SRKW20-7 $_{(11)}$) in the Strait of Georgia, and Bischof Island (HG5 $_{(7)}$) and Armentieres Channel (HG1 $_{(31)}$) in Haida Gwaii; 2. Cd at Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, and VH4 $_{(62)}$), Esquimalt Harbour (EH1 $_{(46)}$), and Dixon Island (DIX $_{(64)}$) on Vancouver Island, Pender Harbour (PH $_{(50)}$) in the Strait of Georgia, Ardmillan Bay (ARDMILLAN $_{(19)}$) and Bella Bella (BELLA $_{(55)}$) on the central coast, Banks Island (SRKW20-4 $_{(93)}$) on the north coast, and Bischof Island (HG5 $_{(7)}$), Haswell Bay (HG4 $_{(27)}$), and Wiah Point (HG6 $_{(21)}$) in Haida Gwaii; 3. As at Pender Harbour (PH $_{(50)}$) in the Strait of Georgia, Ardmillan Bay (ARDMILLAN $_{(19)}$) and Bella Bella (BELLA $_{(55)}$) on the central coast, Smith Island (SRKW20-3 $_{(16)}$) and Porpoise Harbour (NWC10 $_{(39)}$) on the north coast, and Bischof Island (HG5 $_{(7)}$) in Haida Gwaii; 4. Ni at various locations adjacent to the Metro Vancouver area (STH1 $_{(47)}$, SITE5-2 $_{(37)}$, SITE7-2 $_{(42)}$, TSW2 $_{(70)}$, and SRKW19-7 $_{(34)}$) in the Strait of Georgia; 5. Cu at Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, and VH4 $_{(62)}$) on Vancouver Island and Pender Harbour (PH $_{(50)}$), Hardwood Island (SRKW20-6 $_{(5)}$), and Hornby Island (SRKW20-7 $_{(11)}$) in the Strait of Georgia; and 6. Pb at Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, and VH4 $_{(62)}$) and Esquimalt Harbour (EH1 $_{(46)}$) on Vancouver Island and Pender Harbour (PH $_{(50)}$) in the Strait of Georgia.

Hotspots of MeHg were identified and aligned with Hg hotspots (CLR: $R = 0.23$, $p = 0.03$ and total in mg/kg: $R = 0.48$, $p < 0.001$ at 63 detected sites). Common hotspots were shared around southern Vancouver Island at Victoria and Esquimalt Harbours (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, VH4 $_{(62)}$, and EH1 $_{(46)}$) and in the Strait of Georgia around Hardwood and Hornby Islands (SRKW20-6 $_{(5)}$ and SRKW20-7 $_{(11)}$) (Supporting Information, Fig. S3). While MeHg levels vary widely, the overall concentrations of MeHg are related to the total levels of Hg in sediment. Rates of biomethylation of Hg to MeHg are a function of environmental variables affecting the bioavailability of inorganic Hg (II) as well as the productivity of anaerobic microbes, such as methanogenic, iron-reducing, and sulfate-reducing bacteria (Hsu-Kim et al. 2013). Low pH and high concentrations of organic matter enhance biomethylation by increasing Hg (II) availability and stimulating microbial populations, respectively

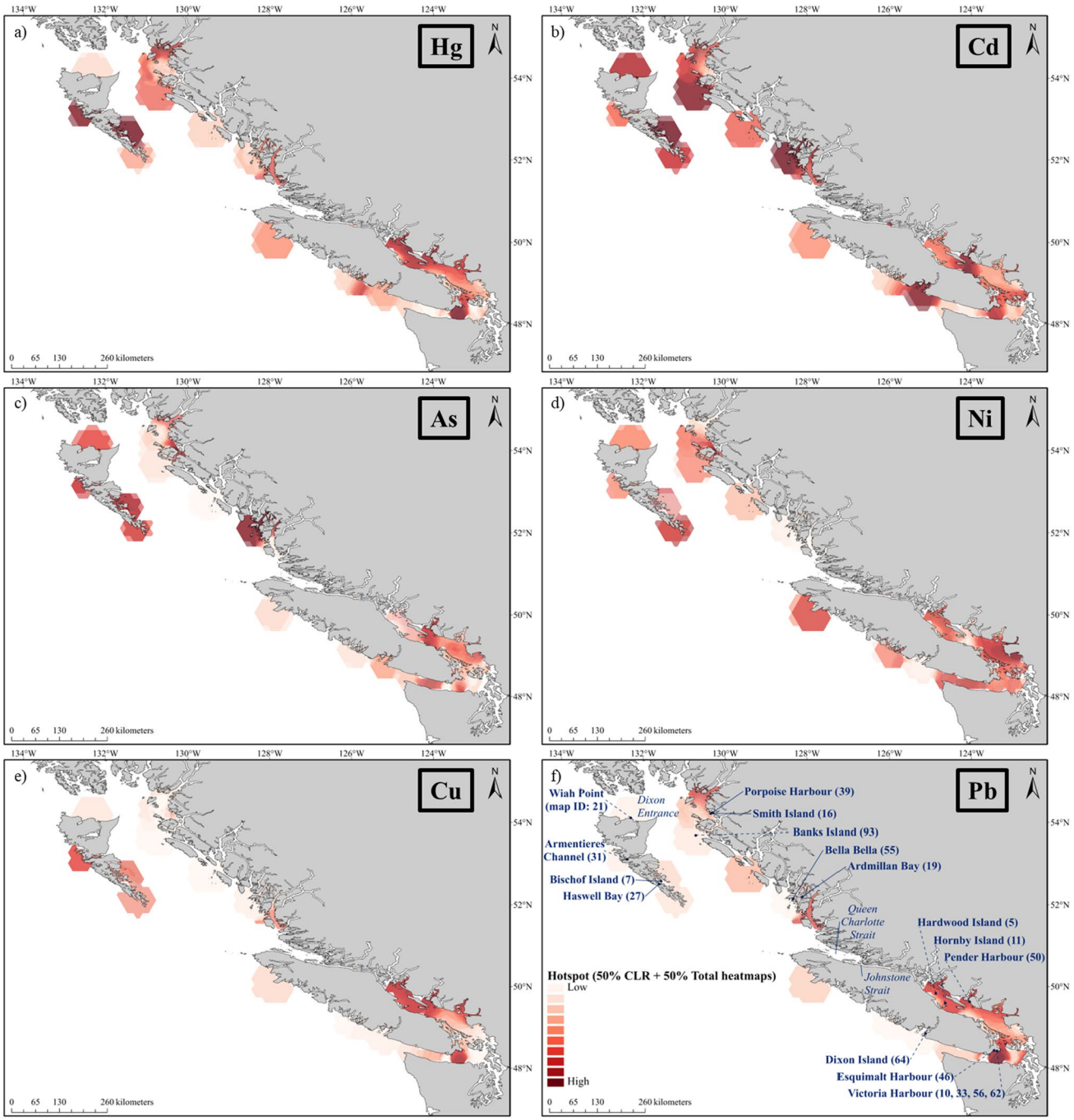

Fig. 4 Overlapped contour maps of relative (CLR) and actual (total in mg/kg) concentrations (Supporting Information, Fig. S2) with 1:1 weight are presented for **a** mercury (Hg), **b** cadmium (Cd), **c** arsenic (As), **d** nickel (Ni), **e** copper (Cu), and **f** lead (Pb)

(Government of Canada 2013). With lower pH and higher TOC, the formation of MeHg would have readily occurred, particularly at Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, and VH4 $_{(62)}$). At these sites, active sulfate reduction by sulfate-reducing bacteria in anaerobic sediment might have led to the formation of higher AVS (Zhang et al. 2014).

Metal Contamination and Anthropogenic Enrichment

To quantify the degree of metal contamination and anthropogenic enrichment at hotspots (Fig. 4), Kernel interpolated heatmaps of geoaccumulation index (Igeo) and enrichment

factor (EF) were generated (Fig. 5). Igeo and EF are used to analyze the degree of contamination and the impact of anthropogenic sources in marine sediment, respectively (Perumal et al. 2021). By imposing metal concentrations at hotspots to their respective background concentrations, environmentally relevant comparison can be achieved and are commonly used to assess the extent of metal pollution in aquatic systems, including river, reservoir, and marine environments (Abdullah et al. 2020; Abrahim and Parker 2008; Saikia et al. 2014). Overall, the cross-validation results of KB showed a better interpolation for EF than Igeo for the six toxic metals. In addition, results showed overestimations for

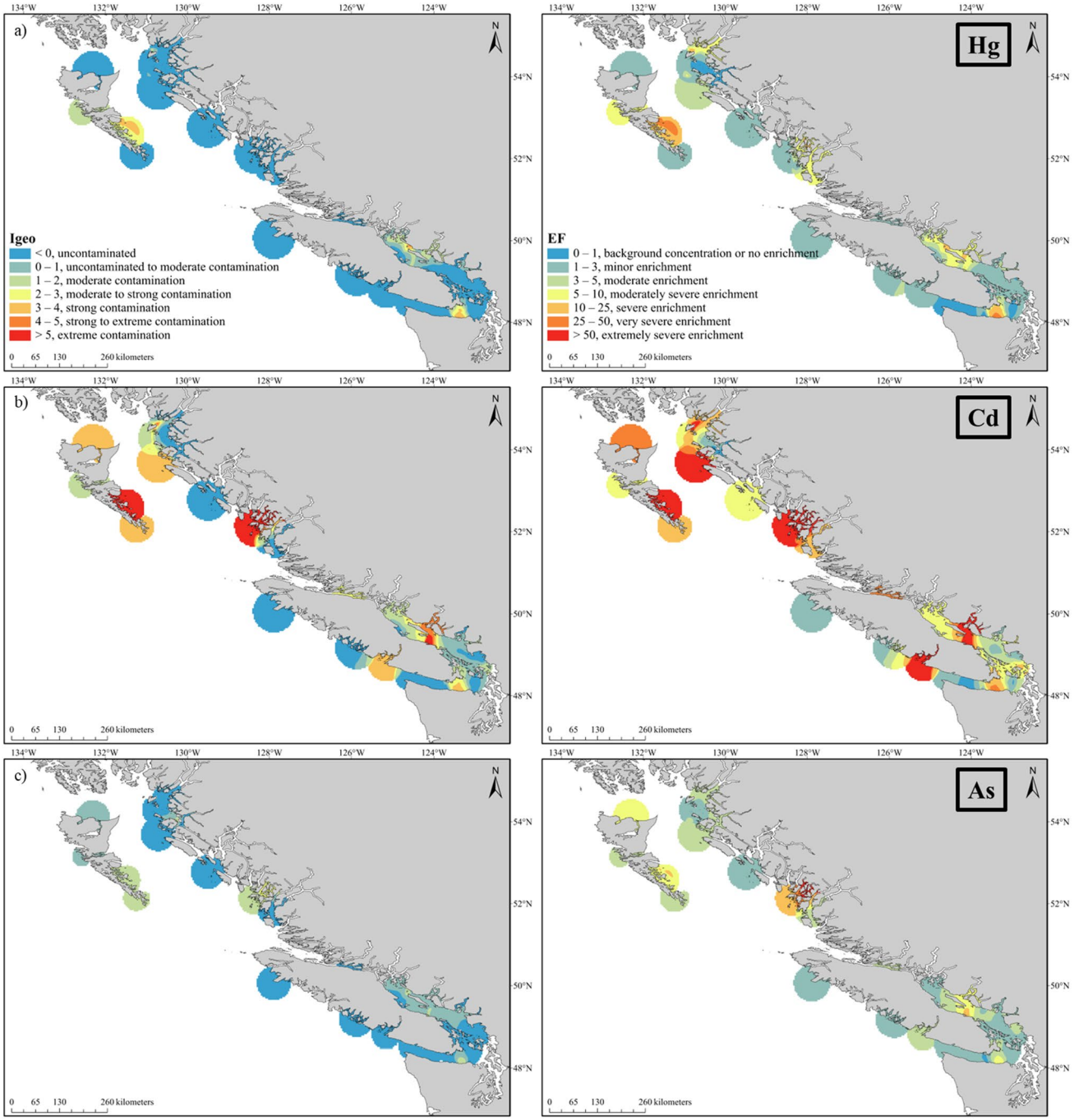

Fig. 5 Contour maps of geoaccumulation index (Igeo, left) and enrichment factor (EF, right) are presented for **a** mercury (Hg), **b** cadmium (Cd), **c** arsenic (As), **d** nickel (Ni), **e** copper (Cu), and **f** lead (Pb). Kernel interpolation with barrier (KB) in ArcGIS Pro geostatistical package was used

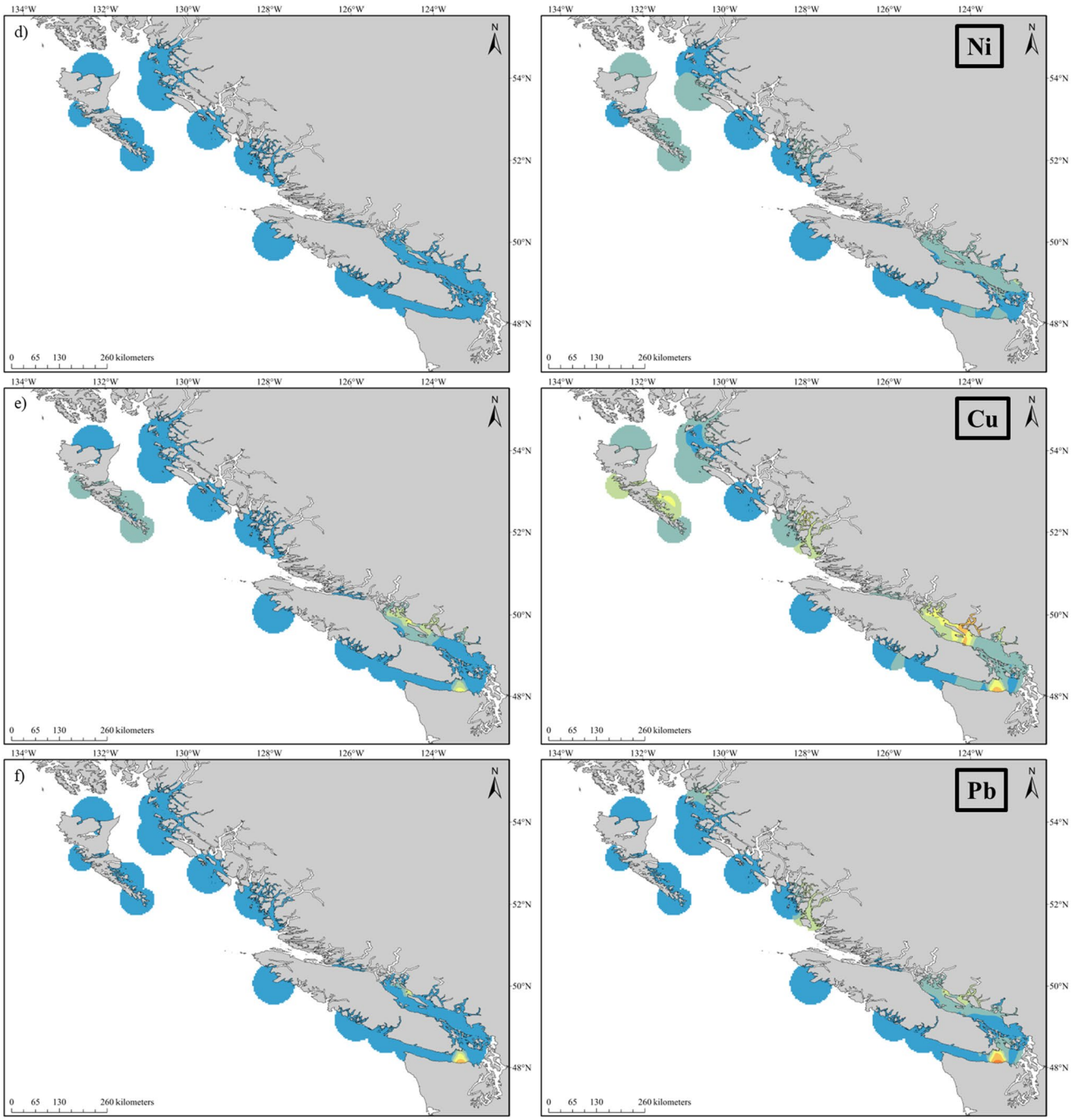

Fig. 5 (continued)

both Igeo and EF for Cd, Cu, and Pb (Supporting Information, Table S4).

Igeo and EF were quantified on the identified hotspots of six toxic metals (Fig. 5) and ordered by EF: 1. Hg at VH3 $_{(10)}$ (Igeo: 3.45; strong contamination and EF: 23.75; severe enrichment) > HG5 $_{(7)}$ (2.86, 23.29) > VH1 $_{(33)}$ (2.92, 20.60) > VH2 $_{(56)}$ (2.13, 17.40) > VH4 $_{(62)}$ (2.29, 16.97) > EH1 $_{(46)}$ (2.30, 14.98) > HG1 $_{(31)}$ (1.78, 9.25) > SRKW20-7 $_{(11)}$ (0.75, 4.88) > SRKW20-6 $_{(5)}$ (0.94; uncontaminated to moderate, 4.74; moderate); 2. Cd at ARDMILLAN $_{(19)}$ (5.47; extreme, 523.36; extremely severe) > HG5 $_{(7)}$ (6.99, 409.87) > BELLA $_{(55)}$ (5.42, 311.77) > HG4 $_{(27)}$ (6.35, 278.73) > PH $_{(50)}$ (4.59, 114.10) > SRKW20-4 $_{(93)}$ (3.44, 94.95) > DIX $_{(64)}$ (3.78, 67.27) > HG6 $_{(21)}$ (3.08, 45.28) > VH1 $_{(33)}$ (3.22, 25.38) > VH3 $_{(10)}$ (3.47, 24.14) > VH2 $_{(56)}$ (2.50,

22.49) > EH1 $_{(46)}$ (2.76, 20.56) > VH4 $_{(62)}$ (2.35; moderate to strong, 17.62; severe); 3. As at ARDMILLAN $_{(19)}$ (2.41; moderate to strong, 62.48; extremely severe) > BELLA $_{(55)}$ (1.40, 19.18) > HG5 $_{(7)}$ (1.55, 9.43) > PH $_{(50)}$ (0.94, 9.06) > SRKW20-3 $_{(16)}$ (1.25, 4.14) > NWC10 $_{(39)}$ (0.66; uncontaminated to moderate, 3.44; moderate); 4. Ni at all identified hotspots (− 0.59 to 0.03; uncontaminated to moderate, 1.41–2.39; minor); 5. Cu at PH $_{(50)}$ (1.18; moderate, 10.71; severe) > VH4 $_{(62)}$ (1.25, 8.26) > VH1 $_{(33)}$ (1.55, 7.96) > VH3 $_{(10)}$ (1.66, 6.88) > VH2 $_{(56)}$ (0.67, 6.33) > SRKW20-6 $_{(5)}$ (0.97, 4.82) > SRKW20-7 $_{(11)}$ (0.57; uncontaminated to moderate, 4.32; moderate); and 6. Pb at VH3 $_{(10)}$ (2.70; moderate to strong, 14.14; severe) > VH1 $_{(33)}$ (2.25, 12.90) > VH2 $_{(56)}$ (1.20, 9.11) > VH4 $_{(62)}$ (1.39, 9.06) > PH $_{(50)}$ (−0.46, 3.45) > EH1 $_{(46)}$ (−0.06; uncontaminated, 2.91; minor). Overall, Cd pollution by Igeo at Bischof Island (HG5 $_{(7)}$) and by EF at Ardmillan Bay (ARDMILLAN $_{(19)}$) were quantified as the top classifications (Igeo > 5; EF > 50), while Ni had one of the bottom classifications (Igeo < 0 and 0–1; EF = 1 − 3) at identified hotspots.

Some discrepancies can be expected when using average metal levels of the upper continental crust (UCC) as norms for evaluating enrichments of regions with varied background concentrations (Abrahim and Parker 2008). Potential sources of Cd for extremely severe enrichment (EF > 50) at Pender Harbour (PH $_{(50)}$) are docks (O'Regan et al. 2018) and industrial activities, paper mills and recycling plants, at Dixon Island (DIX $_{(64)}$) (Mariko 2013). An increasing trend of Cd northward along the BC coast has been observed previously (Haggarty et al. 2003). Historical and current marine disposal of mine tailings and ocean dumping might have contributed to extremely severe anthropogenic enrichment of Cd at Bella Bella (BELLA $_{(55)}$) and Ardmillan Bay (ARDMILLAN $_{(19)}$) on the central coast, Banks Island (SRKW20-4 $_{(93)}$) on the north coast, and Bischof Island (HG5 $_{(7)}$) and Haswell Bay (HG4 $_{(27)}$) in Haida Gwaii (Haggarty et al. 2003; Johannessen et al. 2007). Wood preservatives and arsenical pesticides might have contributed elevated As enrichment at ARDMILLAN $_{(19)}$ (Haggarty et al. 2003).

Habitat Quality Assessment of Toxic Metals

A habitat quality assessment was conducted by comparing Hg, Cd, As, Ni, Cu, and Pb concentrations measured in sediments collected from 98 sites to the available Canadian SQGs (Hg: 0.13 mg/kg, Cd: 0.7 mg/kg, As: 7.24 mg/kg, Cu: 18.7 mg/kg, and Pb: 30.2 mg/kg [CCME]; Ni: 30 mg/kg [BCMoECCS]). Although current SQGs are only protective of lower trophic level organisms (i.e., benthos), they were used to provide insight into the habitat quality of higher trophic level organisms, such as Chinook Salmon and resident killer whales. Benthos, such as gammarid amphipods, polychaete worms, harpacticoid copepods, and tanaids, are also largely targeted by juvenile Chinook Salmon (Healey 1991; Kennedy 2016); therefore, a healthy benthic community is crucial for Chinook Salmon success and, consequently, healthy resident killer whale populations.

Across all 98 sites, Cu levels exceeded SQGs at the most sites (58%) followed by As (50%), Ni (36%), Cd (20%), Hg (19%), and Pb (8%) (Fig. 6). Average concentrations for Hg, Cd, Cu, and Pb were lower within resident killer whale critical habitat compared to outside (Hg: 0.03 ± 0.004 and 0.11 ± 0.02 mg/kg, Cd: 0.18 ± 0.06 and 0.98 ± 0.28 mg/kg, Cu: 17.35 ± 1.95 and 53.19 ± 12.21 mg/kg, and Pb: 5.17 ± 0.50 and 16.05 ± 2.87 mg/kg for within and outside, respectively; Mann–Whitney U test, $p < 0.05$), and only the average concentrations outside critical habitat exceeded the SQGs for Cd and Cu (~ 1- and threefold higher, respectively). Concentrations of As and Ni did not differ within and outside critical habitat (As: 5.96 ± 0.32 and 8.53 ± 0.63 mg/kg and Ni: 29.27 ± 2.69 and 24.04 ± 1.66 mg/kg for within and outside, respectively; Mann–Whitney U test, $p > 0.05$). Moreover, considering sites located within resident killer whale critical habitat, Ni surpassed SQGs at the most sites (8/18; 44%) followed by Cu (33%), As (22%), and Cd (6%) (Fig. 6). Mercury and Pb levels were below SQGs for sites within killer whale critical habitat. All of the sites with exceedances were within SRKW critical habitat for Ni and Cu and within NRKW and SRKW critical habitat for As. Cadmium had a single site, Wiah Point (HG6 $_{(21)}$), that was above the SQG and was located within NRKW critical habitat (Fig. 6). When two nearby sites, Port Neville (PNEV $_{(71)}$) and Dixon Island (DIX $_{(64)}$), were considered as part of the NRKW critical habitat, higher concentrations at sites within SRKW critical habitat for Ni (NRKW 11.91 ± 3.60 and SRKW 28.62 ± 2.91 mg/kg; t-test, $p = 0.04$) and NRKW critical habitat for Cd (NRKW 1.30 ± 0.28 and SRKW 0.22 ± 0.10 mg/kg; Mann–Whitney U test, $p = 0.02$) were determined.

For further evaluation of habitat quality as it relates to Chinook Salmon and resident killer whales, measured and estimated concentrations of the six toxic metals were used to generate probability maps by comparing levels to SQGs using KB (Fig. 7).

Overlapping with resident killer whale critical habitat, our results suggest that the northern part of the NRKW critical habitat, located in western Dixon Entrance, is adversely affected by both Cd and As, while the portion in Johnstone Strait and southeastern Queen Charlotte Strait is affected by Cd (Fig. 7). Southern Resident Killer Whale critical habitat appeared to be affected by all six toxic metals, in particular, areas around Victoria Harbour by Hg, Cd, As, Cu, and Pb. In addition, both shared critical habitat, located off of southwestern Vancouver Island, appeared to be impacted by Cd. This suggests that NRKW and SRKW populations

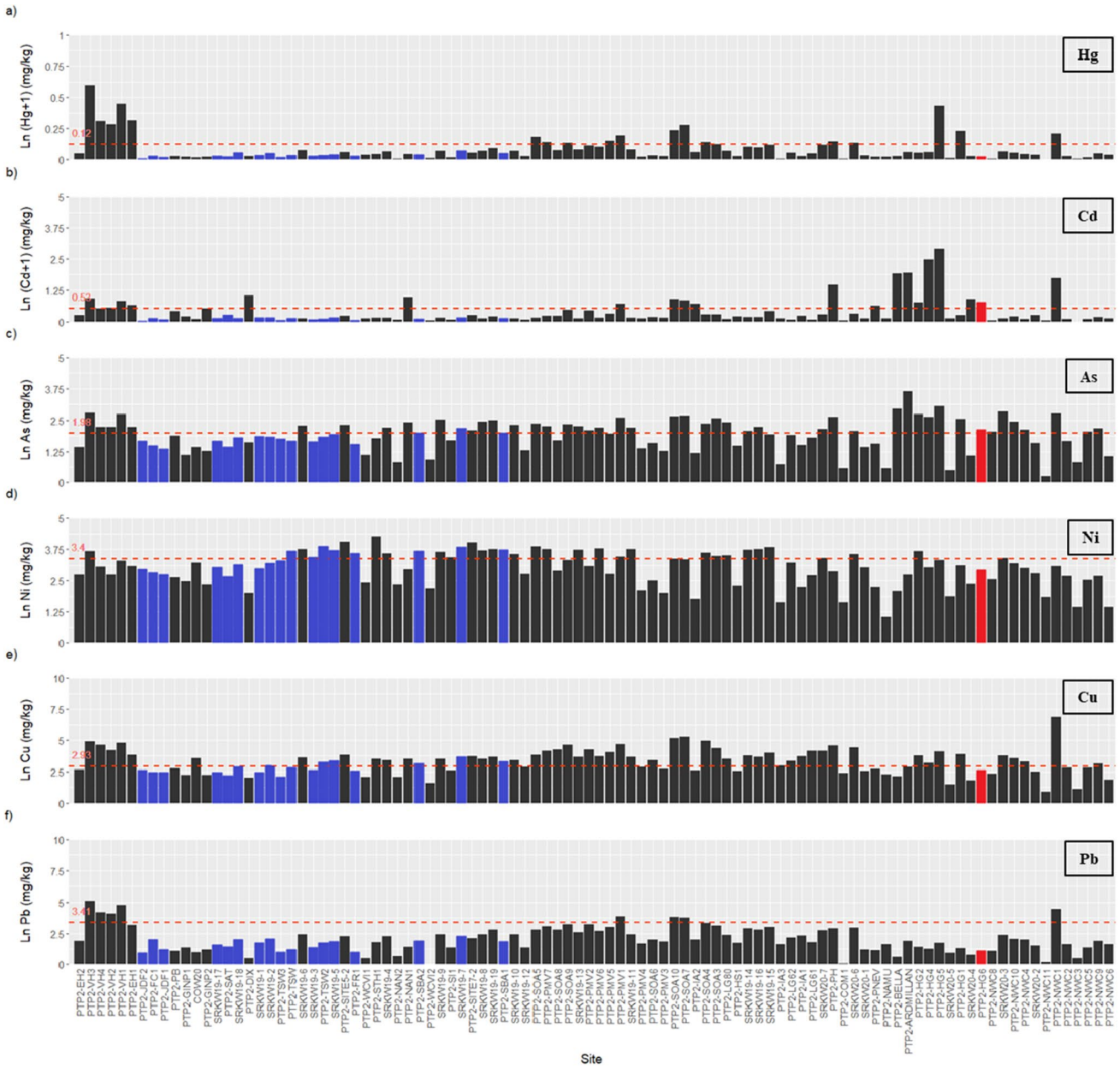

Fig. 6 The ln transformed **a** mercury (Hg), **b** cadmium (Cd), **c** arsenic (As), **d** nickel (Ni), **e** copper (Cu), and **f** lead (Pb) concentrations are presented for 98 sediment samples, including one and 17 samples within Northern Resident Killer Whale (NRKW) and Southern Resident Killer Whale (SRKW) critical habitat (red and blue bars), respectively. Sites are arranged by geographic region from south (left) to north (right). When two nearby sites, Port Neville (PNEV $_{(71)}$) and Dixon Island (DIX $_{(64)}$), were considered as part of the NRKW critical habitat, significantly higher concentrations at sites within SRKW critical habitat for Ni and NRKW critical habitat for Cd were determined. The ln transformed CCME and BCMoECCS Sediment Quality Guidelines (SQGs) are shown as dotted lines

could be impacted indirectly via impacts to Chinook Salmon food web toxicity due to elevated Cd and As concentrations in NRKW critical habitat and Hg, Cd, As, Ni, Cu, and Pb concentrations in SRKW critical habitat (Fig. 7). Moreover, indirect effects are expected to be severe in SRKW critical habitat around Victoria Harbour (VH1 $_{(33)}$, VH2 $_{(56)}$, VH3 $_{(10)}$, and VH4 $_{(62)}$), as benthos bioaccumulation and toxicity effects of Hg, Pb, and Cu will be higher where they are bound to sediment characterized by higher TOC and fine-grained fractions (De Jonge et al. 2009; Méndez-Fernández et al. 2014; Strom et al. 2011) and from a synergistic mixture toxicity (Rebolledo et al. 2021).

Critical habitat for Chinook Salmon has not been defined, as Chinook Salmon are not listed under SARA, despite many populations having been designated as Threatened or Endangered by COSEWIC (Committee on the Status

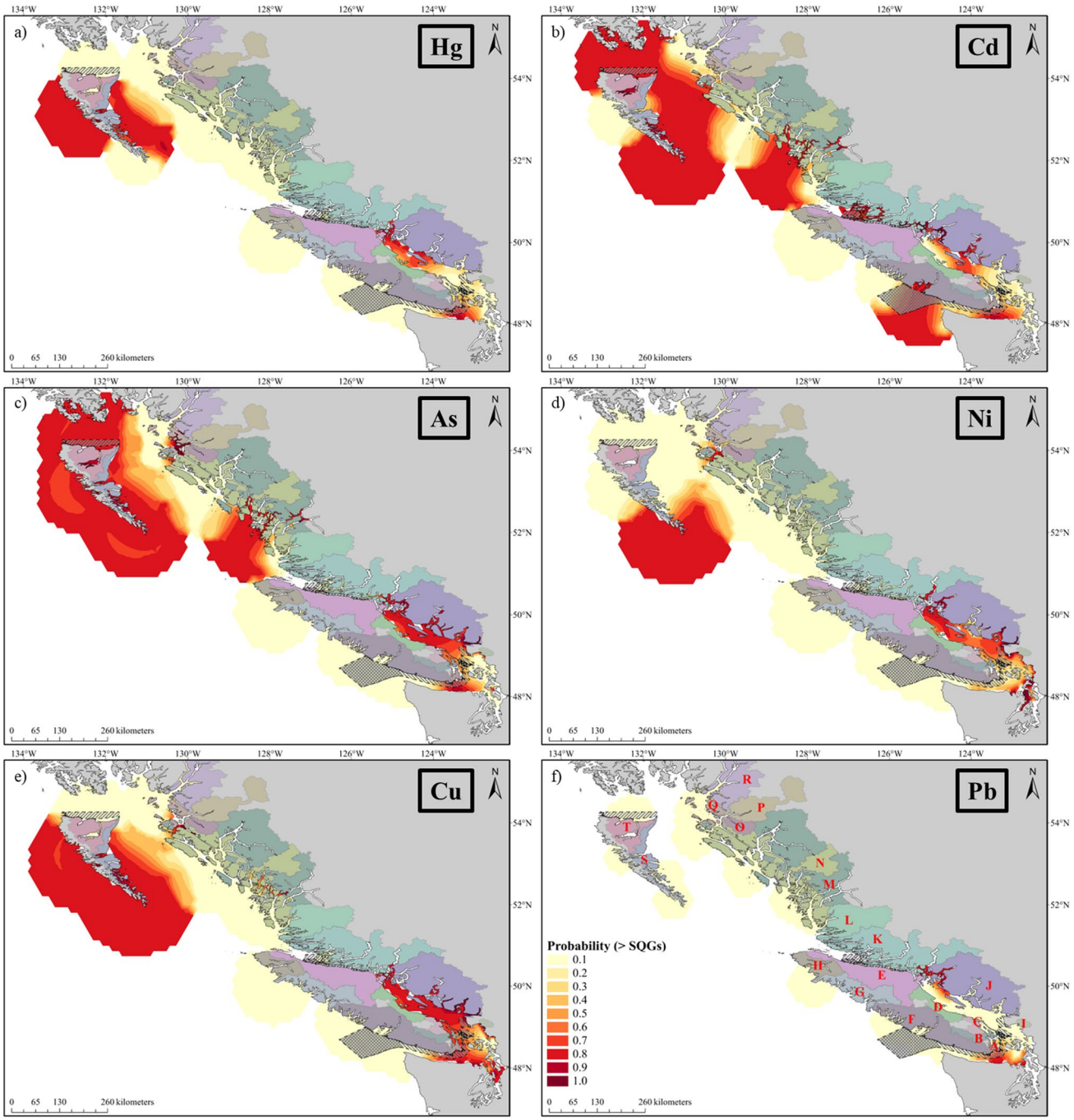

Fig. 7 Contour maps for probability of exceeding established sediment-derived thresholds are shown for **a** mercury (Hg), **b** cadmium (Cd), **c** arsenic (As), **d** nickel (Ni), **e** copper (Cu), and **f** lead (Pb). Kernel interpolation with barrier (KB) was used to predict probabilities of given points to exceed pre-defined thresholds (CCME and BCMoECCS Sediment Quality Guidelines (SQGs)). Nearshore Conservation Units (CUs) of Chinook Salmon are shown as CU IDs A through T (Fig. 1 and Supporting Information, Table S2). Critical habitat of Northern Resident Killer Whales (///) and Southern Resident Killer Whales (\\\) are shown as hatched areas. The cross-hatched area represents shared critical habitat. SQGs = Sediment Quality Guidelines. Results of interpolation are shown in Supporting Information, Table S4

of Endangered Wildlife in Canada [COSEWIC] 2018). The potential impact of metals to coastal Chinook Salmon habitat was evaluated using areas around their Conservation Units (CUs). CUs have been specified for Chinook Salmon along the BC coast and are defined as "a group of wild Pacific salmon sufficiently isolated from other groups

that, if extirpated, is very unlikely to recolonize naturally within an acceptable timeframe" (Fisheries and Oceans Canada [DFO] 2009). Out of 80 total CUs, 20 nearshore CUs were examined (Fig. 1 and Supporting Information, Table S2). Arsenic may pose a threat to Chinook Salmon, as 18 of the 20 (90%) nearshore CUs assessed (CU ID: A, B, C, D, E, F, H, I, J, K, M, N, O, P, Q, R, S, and T) had > 0.5 probability of exceeding the SQG, followed by Cd and Cu both with 13 of 20 (65%) CUs (Cd: A, C, D, E, F, H, J, K, M, N, Q, S, and T Cu: A, B, C, D, E, F, I, J, K, M, N, Q, and S), Ni with 11 of 20 (55%) CUs (B, C, D, E, I, J, K, M, N, Q, and S), Hg with 7 of 20 (35%) CUs (A, D, E, F, J, K, and S), and Pb with 5 of 20 CUs (25%) (A, E, F, J, and K) (Fig. 7). At nearshore CUs, Chinook Salmon populations may be indirectly threatened by a reduction in prey availability and diversity caused by metal toxicity in species at lower trophic levels, including individual species of gammarid amphipod (Campana et al. 2012; McGee et al. 1993) and communities of harpacticoid copepod (Amorri et al. 2022). In particular, Chinook Salmon populations at nearshore CUs of southwestern Vancouver Island (F) and Johnstone Strait and southeastern Queen Charlotte Strait (E and K) may be severely impacted by high Cd levels in sediment, as these CUs contain sites with a red integrated CU status designation by Wild Salmon Policy (WSP), considered at risk of extinction by COSEWIC. Moreover, these CUs (E, F, and K) correspond to 43% of total nearshore CUs (A, B, E, F, K, S, and T) in NRKW and SRKW critical habitat, and therefore, relatively more impacts to resident killer whales may be expected by the indirect loss of Chinook Salmon populations from Cd toxicity.

Most of the regions with metal concentrations above the SQGs were also identified as hotspots (Fig. 4), and Chinook Salmon and resident killer whales may be vulnerable to combined direct and indirect effects in these regions, in particular, by the priority contaminants, Hg, Cd, Cu, and Pb which are known to affect salmon health and, in the case of Hg, resident killer whale health. Special consideration needs to be given to MeHg as modeling under a high carbon emission climate change scenario predicts significant increase in exposure and bioaccumulation by 2100 therefore increasing risks to Chinook Salmon and SRKW in the northeastern Pacific (Alava et al. 2018). Conversely, aside from MeHg with its biomagnification potential, direct metal effects may not be as severe in mid to high trophic organisms such as Chinook Salmon and resident killer whales, respectively, with developed mechanisms either to control the internal concentration of certain elements or to mitigate their toxic effects. Such examples are excreting mechanisms and various detoxification processes such as tiemmanite (i.e., mercury selenide (HgSe)) storage and binding to metallothioneins (MT) (Das et al. 2002; Roch and McCarter 1984). Nevertheless, bioaccumulation and toxicity effects of metals can not be overlooked.

Conclusion

Our coast-wide dataset for chemical elements provides a strong baseline to characterize patterns and better understand sources, transport, and fate, as well as to identify hotspots and assess marine habitat quality for potential impacts of the following priority metals (Hg, Cd, As, Ni, Cu, and Pb) to Chinook Salmon and resident killer whale populations. Our findings strengthen the understanding of local sources and geochemical properties of sediment (TOC, AVS, and pH) as the primary factors governing the divergent spatial distributions and profiles of chemical elements in the marine environment. Current levels of sediment Hg, Cd, As, Ni, Cu, and Pb may pose a threat to Chinook Salmon and resident killer whale populations both directly and indirectly. Chinook Salmon and resident killer whales may be most vulnerable to the combined direct and indirect effects at hotspots with metal concentrations above the SQGs. Metals were enriched by anthropogenic sources to varying degrees at these hotspots, highlighting a need for management actions such as source controls and clean-up operations (removal and/or capping) to reduce risks to migratory Chinook Salmon and resident killer whale populations.

Current Sediment Quality Guidelines (SQGs) for metals approved by the CCME and BCMoECCS have been developed to protect invertebrate aquatic life, specifically benthic communities. Therefore, the use of current SQGs as benchmarks to protect Chinook Salmon and resident killer whale populations remains unknown. However, the use of these SQGs in habitat quality assessments is justifiable, as effects on the benthic community will indirectly affect Chinook Salmon, and subsequently, resident killer whale populations through a reduction in the availability and/or quality of their primary prey.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00244-023-01013-1.

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bioaccumulation, and the relative health risks of Southern Resident Killer Whales. The results will inform chemical regulations and best practices to reduce the exposure of Southern Resident Killer Whales to contaminants. Other financial support from Fisheries and Oceans Canada (DFO)'s *Whale Contaminants* Program; Environment and Climate Change Canada (ECCC)'s *Disposal at Sea* Program; and Ocean Wise Conservation Association (OWCA)'s *PollutionTracker* Program partners (Funders: Association of Denman Island Marine Stewards, Capital Regional District (Victoria BC), DFO, ECCC, Metro Vancouver, Metlakatla First Nation, Neptune Terminals, Port of Prince Rupert, Tsleil-Waututh Nation, and Vancouver Fraser Port Authority; In-kind supporters: Bamfield Marine Sciences Centre, Comox Valley Project Watershed Society, Marine Planning Program of the Council of the Haida Nation, Heiltsuk Integrated Resource and Management Department, K'ómoks First Nation, Lax Kw'alaams Fisheries Biologist and Technicians, Musqueam Indian Band, Nuu-chah-nulth Tribal Council, Saturna Island Marine Research and Education Society, Tlowitsis Guardian Watchmen, Tsawwassen First Nation, and Pender Harbour Ocean Discovery Station) is gratefully acknowledged.

Data Availability All relevant data (chemical element concentration, sediment particle size, total organic carbon, acid volatile sulfide, pH, water depth, and geographical coordinate) are available from the *PollutionTracker* database of Ocean Wise Conservation Association on reasonable request and Canadian Data Report of Fisheries and Aquatic Sciences (Cat. No. Fs97-13/1346E-PDF and ISBN 978-0-660-40619-0, https://publications.gc.ca/site/eng/9.505124/issues.html).

Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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