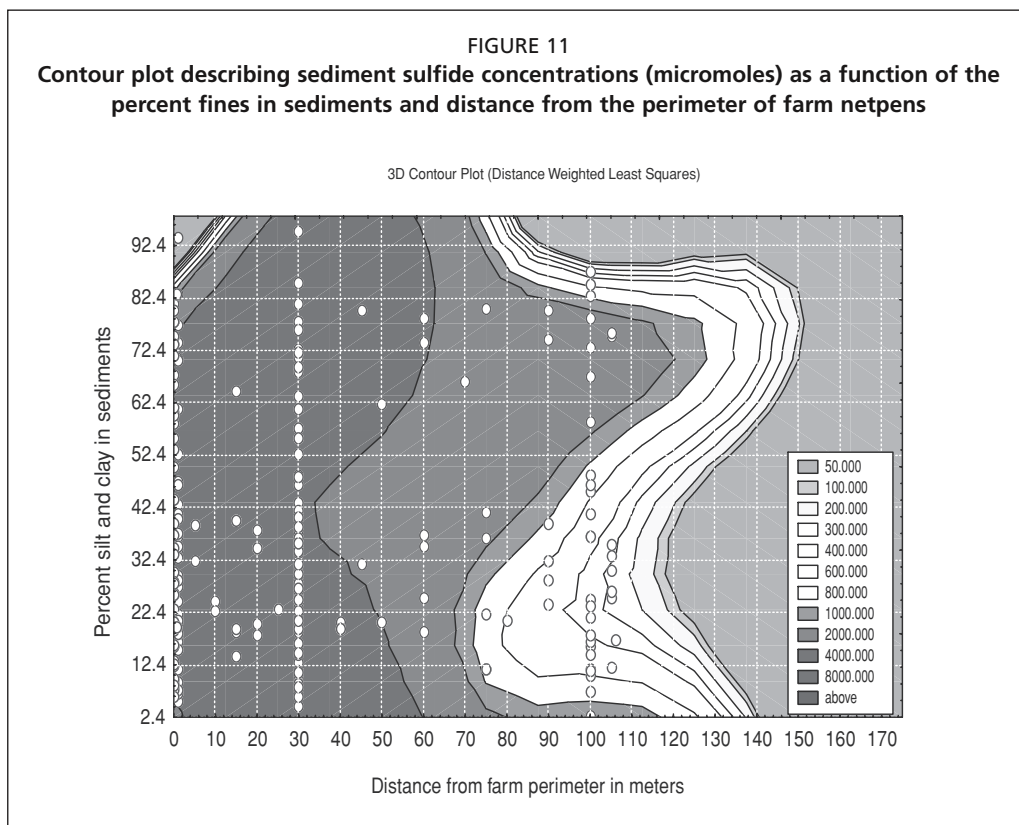The capacity of the various pathways illustrated in Figure 10 depends on a number of factors including the availability and supply of divalent cations, including iron (Fe^{2+} and Fe^{3+}), plus sulfate and oxygen in sediments. Heijs *et al.* (1999) provides a methodology for partitioning sulfide along some of these pathways. Seawater and marine sediments typically contain sufficient amounts of sulfate to fuel the catabolism of natural organic compounds. Cranston (1994) determined the concentration of ammonium, sulfate and organic carbon as a function of depth in deep (200 meter long) cores from Halifax Harbor. Cores containing low concentrations of organic carbon (<0.4 percent) also contained significant quantities of sulfate (>10 to 20 mM SO_4) to depths of at least 200 metres. These cores contained small concentrations of ammonium (NH_4^+) suggesting that sulfate reduction was responsible for most of the catabolism. Sediments containing intermediate quantities of organic carbon (0.4 percent <TOC<2.5 percent) demonstrated sulfate depletion beginning 20 centimetres below the surface with zero sulfate at 80 m below the surface. These cores contained up to 2.5 to 3.0 mM of NH_4 indicating the increasing importance of methanogenic pathways in the presence of increasing organic content that depleted the sulfate pool. Lastly, cores containing 5.0 to 6.0 percent organic carbon were depleted of SO_4 below a depth of 20 cm where HN_4^+ concentrations were 2.5 to 6.0 mM. Consistent with this pattern, organic carbon was exhausted at depth in the lightly loaded sediments but persisted at all depths where carbon concentrations were 5 to 6 percent. These observations are important to the fate of organic carbon at salmon farms where surface sediment accumulations of 25 to 35 percent percent are not uncommon. At these organic carbon concentrations, particularly in fine-grained sediments, which inhibit the intrusion of oxygen to re-oxidize sulfide to sulfate, the supply of sulfate to fuel *Disulfovibrio* catabolism of organic carbon may become depleted. Under these circumstances, the system would essentially stall. Sulfides would be converted to iron sulfide and pyrite. When the supply of Fe^{2+} and Fe^{3+} ions is exhausted, soluble sulfide in the sediments would essentially remain at a static level and further carbon degradation would occur only along energetically more expensive and therefore slower methanogenic pathways. This hypothesis would explain the long chemical remediation times and persistence of elevated sulfide concentrations at a few farms located over fine-grained sediments (Brooks *et al.*, 2004). This hypothesis would also suggest that increasing the flow of sulfate and oxygen into these sediments would restart the aerobic and perhaps more importantly the sulfate-sulfide engines resulting in reduced remediation times. This hypothesis should be explored by evaluating the entire sulfur pool in sediments at slowly remediating sites to determine if sulfate is exhausted and if the pool of dissociated Fe^{2+} and Fe^{3+} ions has been depleted.

Chanton *et al.,* 1987 observed seasonal changes in dissolved sulfide flux with large summer increases annually for four years in North Carolina sediments not associated with aquaculture. They observed hydrogen sulfide concentrations as high as 2 000 μM at sediment depths of 1.0 cm during summer with a peak of 5 000 μM $S^=$ during August at a depth of 7.0 cm. Sulfide concentrations were significantly lower in winter with less than 200 μM $S^=$ at depths to 8.0 cm. Sulfides then increased to approx. 1 000 μM $S^=$ at 13 cm depth in May. Similar seasonal summer increases were observed by Kristensen *et al.* (2000) in Wadden Sea sediments who ascribed them to changes in temperature. Vosjan (1975 cited in Kristensen *et al.,* 2000) observed that sulfate reduction was ten times higher at 18°C than at 4°C in Wadden Sea sediments. If temperature is the driving factor, then the relatively constant (8 to 10°C) temperatures found in deep British Columbia water under most salmon farms should mediate the seasonal changes, which could otherwise present a significant problem for regulatory programs.

Several authors (Brooks, 1999; Johnsen, Grahl-Nielson and Lunestad, 1993) have organoleptically (smell) evaluated sediments for the presence of hydrogen sulfide. As reported by Brooks (2001), biologically significant concentrations of free sulfide (>450 μM) are frequently undetected using this sensory technique and it is not recommended.

Sediment concentrations of total sulfide (S$^=$) collected between 1996 and 2000 (Brooks, 2000b) and are summarized in Figure 11. It should be emphasized that the sulfide probes used in collecting this data measure the total soluble sulfide (HS$^-$, H$_2$S, and S$^=$) available in sediments – they do not measure FeS$^-$ or FeS$_2$ concentrations. Sulfide concentrations exceeding 4 000 µmoles were restricted to distance importance, sediment sulfide concentrations exceeding 600 micromoles were observed as far as 135 m from the perimeter of netpens. Note that higher sulfide concentrations were observed at greater distances (130 to 140 m) from farms located in depositional areas characterized by fine-grained sediments, than from farms located in erosional areas. Sediment sulfide data has been reported by Kristensen *et al.* (2000) and Holmer and Kristensen (1992) for sediments close to commercial netpens in the Wadden Sea. Hargrave *et al.* (1995) reported sulfide concentrations at 2.0 cm depth intervals in Bay of Fundy sediments from under salmon farms and at reference stations. All reference station sediments contained > 800 to 1 000 µmoles S$^=$ at sediment depths >14 cm and more generally at sediment depths >4.0 cm. Surficial sediment (0 to 2.0 cm depth) concentrations of sulfide were less than 280 µmoles. This is consistent with the previous review indicating that anaerobic conditions should be expected in fine-grained reference stations at sediment depths greater than 1.0 to 2.0 cm. It is only the surficial sediments that are typically aerobic.

In contrast to reference conditions, Hargrave *et al.* (1995) recorded mean ($\pm$ 95 percent confidence interval) surficial sediment sulfide concentrations of 1 084 $\pm$ 475 with a range of 180 and 4 200 µm adjacent to salmon farms. Wildish *et al.* (1999) reported 1998 surficial (2.0 cm depth) sediment concentrations of sulfide at Bay of Fundy salmon farms that averaged 2.3 times higher at 3 280 $\pm$ 472 µmoles with a range of 20 to 36 000 µmoles. The differences may have attributable to different salmon production levels during the two studies or to slight differences in analytical technique. Wildish *et al.* (1999) also report sulfide concentrations in surficial sediments under intensive mussel cultures that averaged 11 476 $\pm$ 3 046 µmoles with a range of 180 to 57 000 µmoles and

FIGURE 11

Contour plot describing sediment sulfide concentrations (micromoles) as a function of the percent fines in sediments and distance from the perimeter of farm netpens

Brooks (2005c) reported sulfide concentrations between 12 800 and 15 300 µM under raft cultured mussels in Washington State. These latter findings support the hypothesis that the intensive culture of all species can result in exceeding the assimilative capacity of local sediments leading to high concentrations of sulfide. The results of Brooks (2001) are generally consistent with those of Wildish *et al.* (1999) and suggest that sediment concentrations of sulfide under and on the perimeter of intensive aquaculture operations vary with production levels and with local bathymetry and hydrodynamics and that they can reach concentrations > 20 000 µmoles. Brooks (2001), Brooks and Mahnken (2003a), Brooks *et al.* (2003c) and Brooks, Stierns and Backman (2004) are the only reports found in the literature that have examined sediment physicochemical characteristics at distances greater than 100 m from salmon farms.

Biological response to physicochemical changes in sediments

Brooks (2001) reported that both sulfides and redox potential were well correlated with nearly all endpoints describing macrobenthic communities near salmon tenures and at reference locations in British Columbia. Free sediment sulfides measured immediately in the field were the most reliable predictor of biological effects and subsequently became the focus of the British Columbia Marine Netpen Waste Regulation. Figure 12 describes the log transformed number of taxa observed by Brooks *et al.* (2004) in Carrie Bay sediments. In general, marine macrofauna are sensitive to increases in $S^=$ with a lower low effects thresholds of a few tens of micromoles. Free sulfides at reference stations are generally < approx. 350 µM. However, sulfides are elevated where ever there are large accumulations of animals including natural shellfish beds in intertidal environments and around piling, which frequently support large and diverse communities of organisms (Goyette and Brooks, 1998; 2000).

In contrast to the diversity of animals, their abundance is frequently increased near fish culture operations (Figure 13). At least eight species of annelids, mollusks and crustaceans have been identified proliferating in enriched sediments. Reference sediments in deep water typically support 50 to 60 types of organisms in an abundance
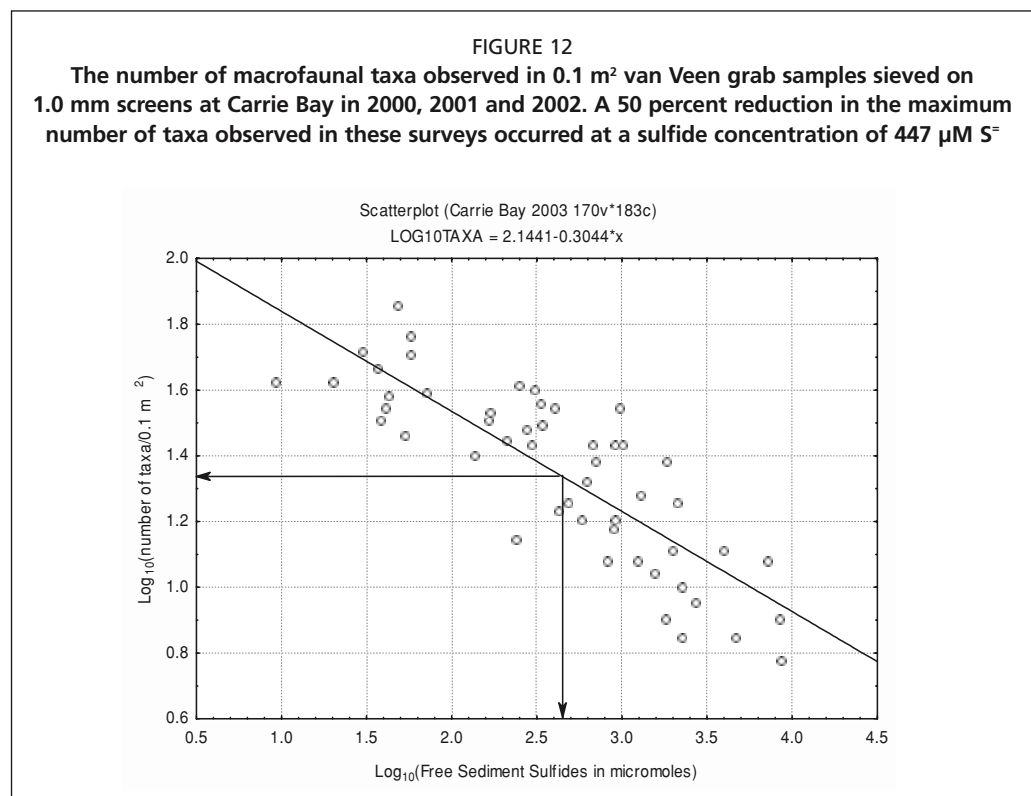

FIGURE 12
The number of macrofaunal taxa observed in 0.1 m² van Veen grab samples sieved on 1.0 mm screens at Carrie Bay in 2000, 2001 and 2002. A 50 percent reduction in the maximum number of taxa observed in these surveys occurred at a sulfide concentration of 447 µM $S^=$

Scatterplot (Carrie Bay 2003 170v*183c)
LOG10TAXA = 2.1441-0.3044*x

X-axis: Log_{10}(Free Sediment Sulfides in micromoles)
Y-axis: Log_{10}(number of taxa/0.1 m²)

FIGURE 13
Abundance of macrofauna as a function of free sediment sulfides (µM) at seven British Columbia salmon farms reported in Brooks (2001)

Infaunal abundance versus sediment free sulfides
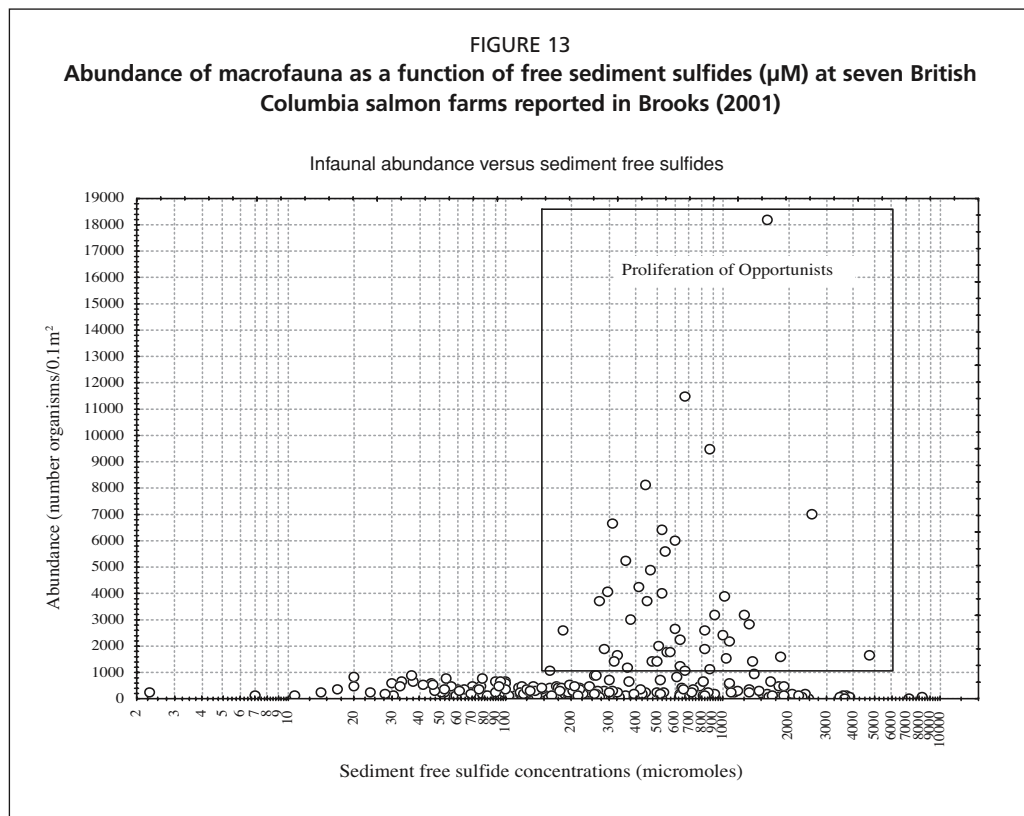
of about 4 500 animals/m² (WDOE, 1996). Macrofaunal abundance reached 189 000 animals/m² at some farms in Clayoquot Sound, British Columbia (Brooks, 2001). The most abundant organism was the crustacean *Nebalia pugettensis*, which has also been found proliferating around piling in Puget Sound (Brooks, 2004). Figures 14 and 15

FIGURE 14
Number of taxa observed in 0.1 m² modified van Veen grab samples at the Upper Retreat salmon farm in British Columbia as a function of distance (m) from the netpen's perimeter

Log(Taxa + 1) versus distance at Focused Study Farm F

Log(Taxa + 1) = 0.51 + 1.20*(1-exp(-0.029*distance)) R^2 = 0.90