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Organic matter composition of gravel-stored sediments from salmon-bearing streams

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Abstract

The objective of this project was to evaluate the changing composition and structure of the sediment-associated organic matter (OM) stored in the gravel bed of highly productive salmon-bearing streams and, determine if the OM changes affect the morphology and settling rates of ne sediment. In July of 2001, a dozen in ltration gravel bags were buried in the channel bed of O'Ne-eil Creek in northern British Columbia (Canada) to collect ne

spawning period as a means of determining the role of the sh in oc formation. As well we investigate morphological characteristics (settling rates, density, size) of the gravel-stored nes to determine if any changes are associated with the activities of the returning sh.

O'Ne-eil Creek is a highly productive sockeye salmon (*Oncorhynchus nerka*) stream in the Takla Lake area of northern interior British Columbia (Canada). The lower 1.8 km of this 20 km stream is intensively used for sockeye spawning with annual returns varying between 1000 and 53 000 over the last 20 years (Petticrew, 1996). In 2001, a total of 13 893 salmon returned to spawn in O'Ne-eil Creek. Our sample rif es were located between 1400 and 1550 m from the stream mouth, where approximately 200 sh were noted on the rif es at the peak of spawn. The stream width was between 10 and 12 m and water depths were between 25 and 40 cm.

Methods

On July 13, 2001 twelve in ltration gravel bags were buried in $\sim$25 cm holes dug into the gravel bed of O'Ne-eil Creek following the methods of Lisle & Eads (1991). The folded bags were covered by cleaned gravel which was washed through a 2 mm sieve using stream water. Ropes were attached to the bag for retrieval purposes allowing collection of both gravel and in ltrated ner sediment ($<$ 2 mm). The bags were removed in pairs over the following 10 weeks to coincide with the sh activities: pre-spawn (PS) – July 17; early spawn (ES) – July 28; mid-spawn (MS) – August 3; die-off (DO) – August 12 and 16. In late September when all visible evidence of sh carcasses was gone from the stream a nal set of bags were retrieved, these are identi ed as post- sh (PF) samples.

When the in ltration bags were removed from the stream, the ner, in ltrated sediment was separated from the gravel by washing with distilled water through a 2 mm sieve. The large gravel material was kept for standard sieve size analysis. The in ltrated sediment ($<$ 2 mm), which was washed into a bucket, was stirred to re-suspend all grain sizes. The material was settled for 10 s to allow removal of sand sized material from the top layer of water. A 250 ml sub-sample of sediment was taken from this top layer of water, to allow the collection of the ne-grained particles (silt and clay) and slower settling, large composite particles (ocs or aggregates). The $<$ 2 mm sediment sample in the bucket was taken back to the laboratory and settled, dried, weighed, ashed and sieved to obtain grain size curves. The ne-grained sub-sample was returned to the lab and used for organic matter and image analysis.

Morphology and elemental composition of the organic matter

The morphology (structure) and elemental composition of the organic samples were investigated using a Philips™ XLS 30 scanning electron microscope (SEM) equipped with EDAX™ energy dispersive system (EDS). Preparation of the samples included air-drying on a SEM tin stub, and sputter-coating with Au for 60 s. The Au-coated samples were observed under the SEM for morphology of the organic matter stored in the gravel beds. The elemental composition of this organic matter was semi-quantitatively determined from an energy dispersive spectrum collected for 400 s from at least ve points on observable lms of organic matter on the surface of the mineral material. The semi-quantitative chemical composition was estimated using ZAF, a standard-less energy dispersive technique, where the estimates of the chemical composition were corrected for factors including Z (atomic number), A (absorption), and F (uorescence) for each element of interest.

We characterized the changes in organic matter composition of the gravel-stored sediments in two ways using the ZAF results. First, the apparent total acid content (ATAC) of the organic matter was calculated using Equation (1), where the ATAC equals the potential cation exchange capacity as measured by the amount of metals adsorbed onto the organic matter (McBride, 1994):

$$\text{ATAC (moles}_{+}\,\text{kg}^{-1}) = (((\text{Wt\%}_{M} * 1000)/\text{MW}_{M}) * n+), \qquad (1)$$

where Wt%$_M$ = weight percentage of the metal from SEM-EDS, MW$_M$ = atomic weight (g) of the metal, n+ = oxidation number of the metal.

Secondly, the af nity of organic matter for each metal was estimated from the relative metal saturation of the cation exchange sites as given by:

$$\text{Metal saturation}(\%) = (\text{m}M^{n+}/\text{ATAC}) * 100, \qquad (2)$$

where M^{n+} = metal of interest adsorbed on exchange sites, m = moles of metals expressed as single positive charge (moles$_+$)

Functional groups in the organic matter

Another technique used to assess the changes in the composition of the organic matter over the period of study involved a Centaurus™ microscope attached to a Nexus 670™ Fourier Transform Infra-red (FT-IR) spectrometer. This allowed us to investigate the changes in functional groups of the organic matter stored in the gravel beds. We used a ZnSe Attenuated Total Re ection (ATR) objective as an accessory to the microscope. The ATR technique is non-destructive and allows the analysis of a small area (10 µm $\times$ 10 µm) of a sample. The infrared beam penetrates the organic matter to a depth of 0.66–2.0 µm (at 1000 cm^{-1}) and allowed us to determine the functional groups in the lm of organic matter. Several drops of the 250 ml

Results

Structure and composition of gravel-stored organic matter

The results of the electron microscopy indicate that the morphology of the organic matter stored in gravel beds exhibits two main types of structures. The PS and PF samples exhibit a lm-like' structure while the MS samples have a ‘web-like’ structure. These structures coat the ne clay and silt-sized inorganic components of the ocs (Fig. 1a–c). The ‘ lm-like’ coating in pre-spawn samples shows a tendency to curl to strands ~1.0–5.0 μm in diameter (Fig. 1a) while the ‘ lm-like’ structure in post- sh samples is more extensive and coats larger surface areas of the inorganic ocs (~50 μm^2

Table 1. Mean (and standard deviation) of the semi-quantitative estimates* of the elemental composition (weight%) of bio lm observed on ocs collected at various stages of sh activities (n = 5)

	C	Na^{+}	K^{+}	Mg^{2+}	Ni^{2+}	Cu^{2+}	Fe^{3+}	Al^{3+}	Si^{4+}
Pre-Spawn	66.7a	1.41a	0.29b	0.20ab	2.80c	3.01b	3.61b	9.77a	0.41a
(PS)	(6.80)	(1.22)	(0.16)	(0.23)	(0.83)	(1.70)	(1.29)	(1.80)	(0.11)
Mid-Spawn	64.5a	4.16b	0.37c	1.90c	2.05b	7.40c	3.79b	1.42b	2.16c
(MS)	(1.6)	(0.63)	(0.12)	(0.46)	(0.19)	(0.85)	(0.62)	(0.33)	(0.34)

Table 3. Mean (and standard deviation) particle diameter (mm), settling rate (mm s^{-1}) and particle density (g cm^{-3}) of ocs collected at various stages of sh activities

Activities	n	Particle diameter (mm)	Settling rate (mm sec^{-1})	Particle density (g cm^{-3})	Percent weight of inorganics < 63 µm *
Pre-Spawn (PS)	92	0.332b (0.109)	2.170a (1.38)	1.047a (0.033)	5.75
Early Spawn (ES)	202	0.261a (0.112)	2.117a (0.816)	1.092b (0.068)	3.48
Mid-Spawn (MS)	102	0.244a (0.089)	2.449b (1.03)	1.116c (0.079)	1.79
Die-Off (DO)	153	0.262a (0.095)	2.122a (0.989)	1.032a (0.048)	4.34
Post-Fish (PF)	204	0.316b (0.157)	3.677b (1.59)	1.121c (0.033)	4.85

n = number of observations.
In each column, means followed by similar letter are not signi cantly different ($p > 0.05$). * Note that $n = 2$
for all samples e445395fr aer3-1(DOer)-w(r)-4.h0.8(a)enTf 3.9295 0 TD.8(3479(n)Tj /F3 1 Tf 0.7377 0 TD 0..0042 Tc 2)Tj -41.num43(

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