Protectiveness of Water Quality Criteria for Copper in Western United States Waters Relative to Olfactory Responses in Juvenile Pacific Salmon as Predicted by an Olfactory-Parameterized Biotic Ligand Model

David K DeForest,[1]* Robert W Gensemer,[2] Eric J Van Genderen,[3] Joseph W Gorsuch[4]

[1]Windward Environmental LLC, Seattle, WA; [2]GEI Consultants, Denver, CO; [3]International Zinc Association, Durham, NC; [4]Copper Development Association Inc., New York, NY

Abstract

At elevated levels copper can impair olfaction in salmonid fishes, thus inhibiting the ability of salmonids to avoid elevated copper concentrations and/or predators. Several salmonid species are listed as threatened or endangered in the western US, including many in urban watersheds. Because copper is commonly elevated in stormwater runoff in urban environments, storm events may result in elevated copper concentrations in salmon-bearing streams. Accordingly, there is concern that existing copper criteria, which were not derived using data for olfactory-related endpoints, may not be adequately protective of salmonids. However, a reparameterized olfactory-based biotic ligand model (BLM) was recently proposed as a modification of the US Environmental Protection Agency's ionoregulatory-based BLM for deriving site-specific copper criteria. This revision, based on olfactory inhibition in coho salmon (*Oncorhynchus kisutch*) exposed to copper in various combinations of pH, hardness, alkalinity, and dissolved organic carbon (DOC) levels, was used to derive copper IC20 values for 133 stream locations in the western US. The olfactory BLM-based criteria were compared to the existing hardness-based copper criteria for western US states and the US Environmental Protection Agency's (USEPA's) BLM-based copper criteria. Of the 133 sampling locations, hardness-dependent acute and chronic copper criteria were below the olfactory BLM-based IC20 in 122 (92%) and 129 (97%) of the waters, respectively (i.e., < 20% olfactory impairment would have been predicted at the hardness-based copper criteria concentrations). Waters characterized by high hardness and very low DOC are most likely to have hardness-based copper criteria that are not lower than the olfactory-based IC20, as DOC strongly influences copper bioavailability in the BLM. In all waters the USEPA's current BLM-based criteria were less than the olfactory-based IC20 values, indicating that adoption of the USEPA's BLM-based criteria by western states should ensure protection of salmonids from olfactory impairment.

Study Objective

Evaluate whether existing hardness- and biotic ligand model (BLM)-based ambient water quality criteria (AWQC) for copper are protective against predicted olfactory impairment in juvenile Pacific salmon based on the water chemistry of western United States (US) streams

Background

- Olfactory-based effects data for juvenile coho salmon (*Oncorhynchus kisutch*) exposed to copper and a natural odorant (L-serine) were presented in McIntyre et al. (2008a, 2008b).
  - Olfactory response prior to and during copper exposure was measured using electro-olfactogram (EOG) recordings.
  - Olfactory impairment tests were conducted in waters with varying levels of hardness, alkalinity, and dissolved organic carbon (DOC).
- Meyer and Adams (2010) parameterized an olfactory-based BLM for calculating IC20 (concentration required for 20% inhibition of an effect) values for olfactory impairment in juvenile Pacific salmon.[1]
- Meyer and Adams (2010) determined that changing the sensitivity term in the rainbow trout BLM (HydroQual 2010, Version 2.2.3) from 3.70 to 0.1988 nmol/g wet weight resulted in the target geometric mean ratio of 1.00 based on the BLM-predicted IC50 (concentration required for 50% inhibition of an effect) values, versus the corrected IC50 values reported in McIntyre et al. (2008b), and that the predicted versus reported IC50 ratios ranged from 0.32 to 2.74.
  - The predicted IC50 value for olfactory impairment can then be multiplied by 0.315 to estimate the IC20 value for olfactory impairment.

[1] See Platform 510, 10:40 AM on Wed.

Methods

- Compiled water chemistry data from the US Geological Survey's National Water-Quality Assessment (NAWQA) Program database (USGS 2009) for western US streams. The only sites considered were those that measured the following BLM parameters: DOC, pH, calcium, magnesium, sodium, potassium, sulfate, chlorine, alkalinity, and temperature.
- Calculated copper IC20 values for olfactory impairment in juvenile Pacific salmon using the olfactory-based copper BLM derived from Meyer and Adams (2010) and summarized in the Background section above.
- Calculated the US Environmental Protection Agency's (USEPA's) BLM-based copper criteria (EPA 2007).
- Calculated hardness-based copper criteria (slopes, intercepts, and conversion factors for each state are provided in Table 1) as follows:

$$\text{Copper criterion } (\mu g/L) = e^{(\text{Slope} \times \ln(\text{Hardness, mg/L}) + \text{Intercept})} \times \text{Conversion factor}$$

- Compared hardness- and BLM-based copper criteria with copper IC20 values for olfactory impairment to evaluate whether copper criteria are protective against olfactory impairment.

Table 1. Summary of current water quality criteria for copper in Alaska, California, Idaho, Montana, Oregon, and Washington

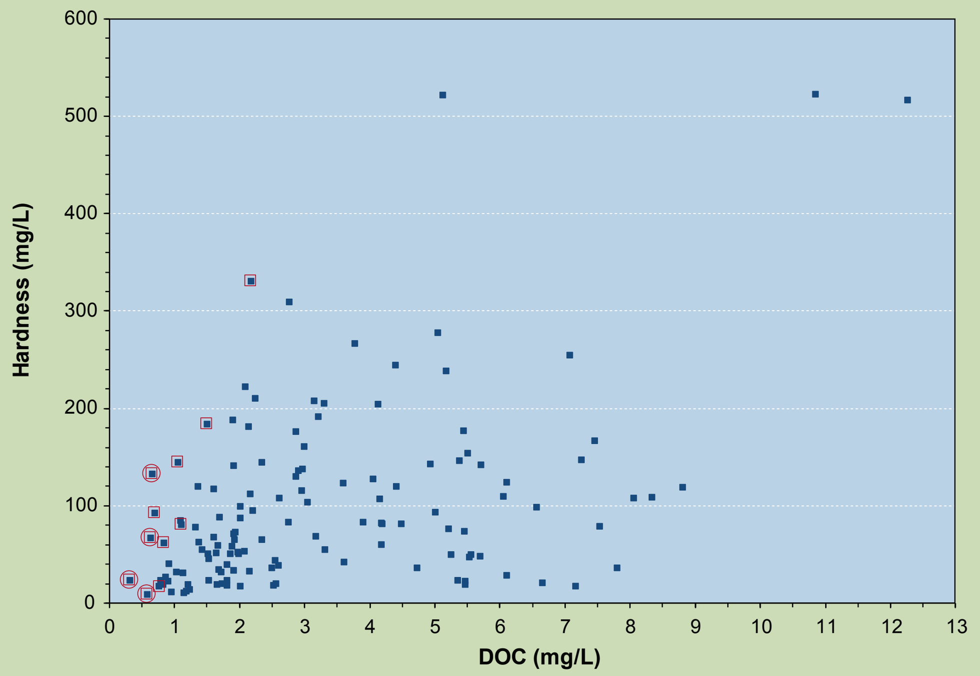
State	Type	Slope	Intercept	Conversion Factor[a]	Dissolved Copper Criteria (µg/L) at Hardness of 50 mg/L
Alaska	acute	0.9422	-1.700	0.96	7.0
	chronic	0.8545	-1.702	0.96	5.0
California	acute	0.9422	-1.700	0.96	7.0
	chronic	0.8545	-1.702	0.96	5.0
Idaho[b]	acute	0.9422	-1.464	0.96	8.9
	chronic	0.8545	-1.465	0.96	6.3
Montana	acute	0.9422	-1.700	1.00	7.3
	chronic	0.8545	-1.702	1.00	5.2
Oregon	acute	0.9422	-1.464	0.96	8.9
	chronic	0.8545	-1.465	0.96	6.3
Washington	acute	0.9422	-1.464	0.96	8.9
	chronic	0.8545	-1.465	0.96	6.3

[a] The conversion factor was used to convert the criterion from a total recoverable copper basis to a dissolved copper basis.

[b] If the actual hardness of a water body is less than 25 mg/L as calcium carbonate, copper is assumed to be no more toxic than at a hardness of 25 mg/L as calcium carbonate, and the minimum hardness used in the criteria equations is 25 mg/L. Similarly, the maximum hardness used in criteria is 400 mg/L as calcium carbonate.

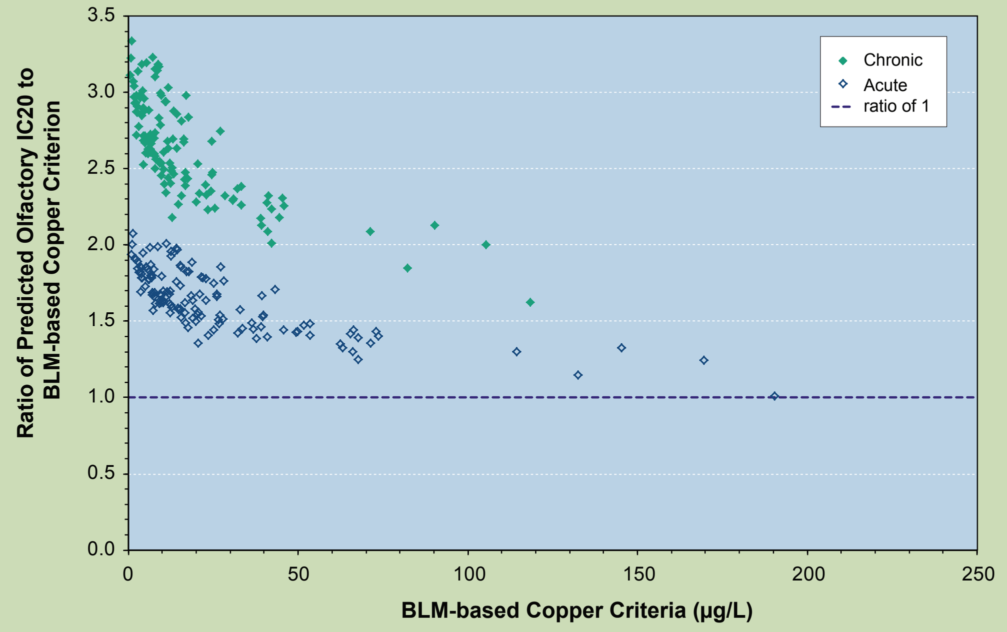
Results

- A total of 133 sampling locations with adequate water quality data for running the BLM were identified in the NAWQA database for Alaska, California, Idaho, Montana, Oregon, and Washington.
- Of the 133 sampling locations, the average hardness-dependent acute and chronic criteria were below the average olfactory-based BLM IC20 value in 122 (92%) and 129 (97%) of the locations, respectively.
  - In general, waters with the lowest DOC concentrations relative to hardness concentrations were more likely to result in hardness-based copper criteria that were higher than the olfactory-based BLM IC20 value (Figure 1).
- USEPA's acute and chronic BLM-based copper criteria, based on mean water chemistry levels, were always lower than the olfactory-based BLM IC20 values.
  - The site-specific ratios of the olfactory IC20 values to their respective acute and chronic BLM-based criteria ranged from 1.0 to 2.1 and from 1.6 to 3.3, respectively (Figure 2).
  - The ratios were higher when associated with lower BLM-based criteria (i.e., in water with conditions that favor higher copper bioavailability), indicating that although the criteria were always protective of olfactory IC20 values, the level of protection was higher when associated with water that had high copper bioavailability (Figure 2).
- Seasonal/time-varying water chemistry influenced the protectiveness of hardness- and BLM-based copper criteria relative to olfactory-based IC20 values.
  - DOC and hardness concentrations were often inversely related following storm events in the coastal western US and snow melt in the interior West (Figure 3).



Note: Open-square and open-circle symbols note waters in which state hardness-based acute or chronic criteria, respectively, exceeded the olfactory BLM-based IC20.

Figure 1. Relationship between hardness and DOC concentrations in water at 133 sampling locations



Note: The ratio increases as criterion concentrations decrease, indicating that the BLM-based criteria are more protective against olfactory impairment in waters with higher copper bioavailability.

Figure 2. Ratios of predicted olfactory IC20 values to BLM-based copper criteria as a function of BLM-based criteria

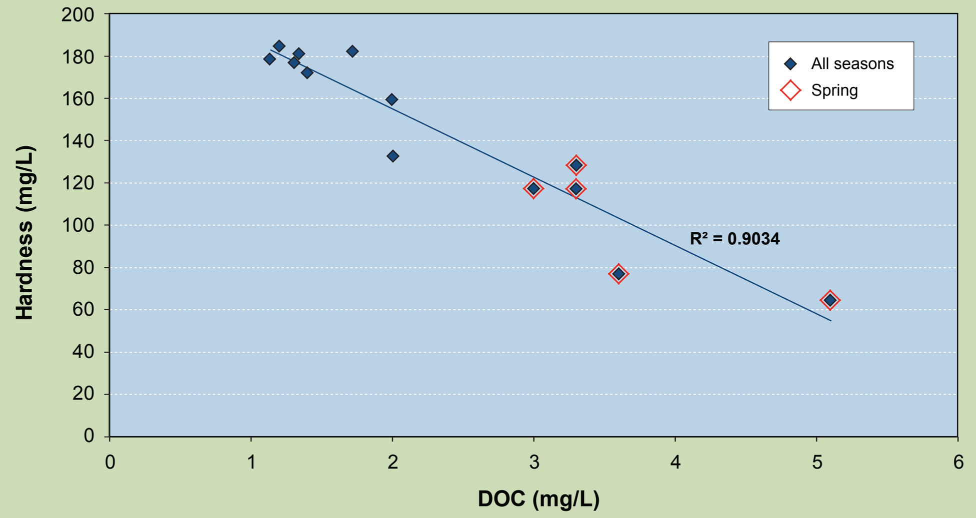
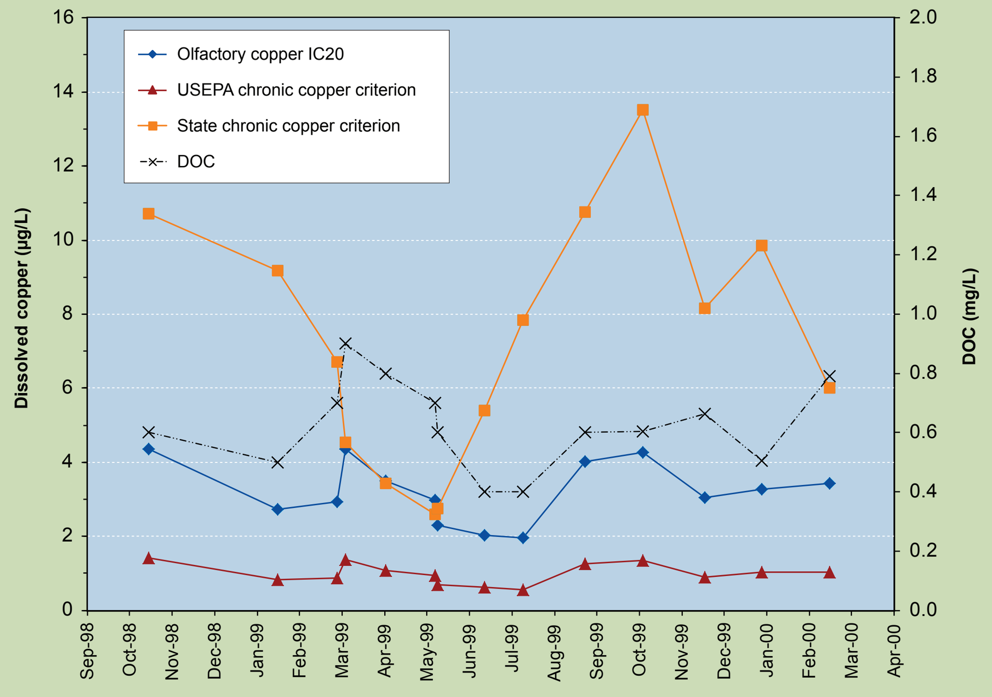


Figure 3. Example of the inverse relationship between DOC and hardness as a result of seasonal variability (Clark Fork near Bonner, Montana)

Site-Specific Example No. 1 – South Fork of the Coeur d'Alene River (Idaho)

- Site was characterized by low DOC (mean = 0.6 mg/L) and moderate hardness (mean = 68 mg/L).
- Hardness varied seasonally from 18 to 123 mg/L, with DOC concentrations being less variable, ranging from 0.4 to 0.9 mg/L.
- Hardness-based copper criteria were not protective of the olfactory IC20 value when hardness was high, but BLM-based copper criteria were always protective of the IC20 value (Figure 4).
- Because the effects of copper on olfactory impairment were more strongly influenced by DOC than to hardness and the copper BLM was likely more sensitive to DOC than to hardness, BLM-based criteria were consistently protective of the olfactory-based IC20 value.

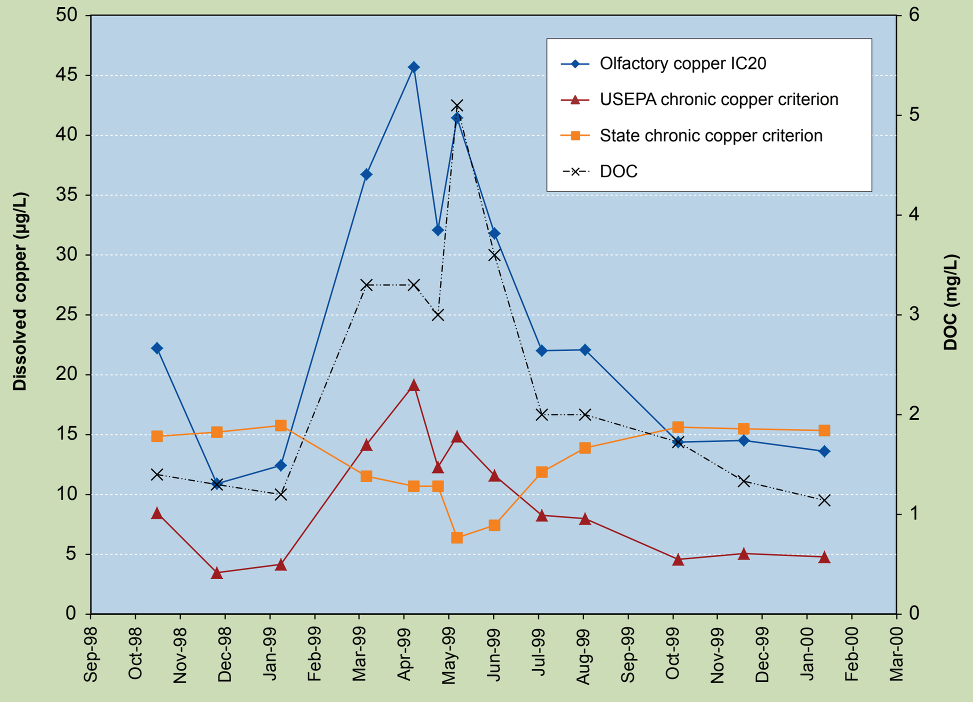


Note: State water quality criteria are hardness-dependent and therefore directly reflective of temporally variable hardness levels. The BLM-based olfactory IC20 values and chronic criteria are more strongly influenced by DOC than by hardness.

Figure 4. Changes in calculated chronic water quality criteria and olfactory IC20 values over time in the South Fork of the Coeur d'Alene River, Idaho

Site-Specific Example No. 2 – Clark Fork (near Bonner, Montana)

- Site was characterized by low to moderate DOC (mean = 2.3 mg/L) and high hardness (mean = 144 mg/L).
- Both hardness (64 to 185 mg/L) and DOC (1.1 to 5.1 mg/L) varied seasonally.
- Seasonal variability in hardness and DOC resulted in periods when hardness-based copper criteria were lower than BLM-based copper criteria, and vice versa (Figure 5).
- During periods of low hardness and high DOC, hardness-based copper criteria were approximately 70 to 85% lower than olfactory-based BLM IC20 values; during winter periods with low snow melt and high hardness concentrations, hardness-based copper criteria were higher than olfactory-based BLM IC20 values (Figure 5).
- BLM-based copper criteria also varied seasonally but are consistently protective of the olfactory-based IC20 value (Figure 5).



Note: State water quality criteria are hardness-dependent and therefore directly reflective of temporally variable hardness levels. The BLM-based olfactory IC20 values and chronic criteria are more strongly influenced by DOC than by hardness.

Figure 5. Changes over time in calculated chronic water quality criteria and olfactory IC20 values in the Clark Fork (near Bonner, Montana)

Discussion

Copper AWQC Derivation and Protectiveness Relative to Olfactory Effects

- USEPA AWQC are derived using a species sensitivity distribution approach.
- USEPA's copper criteria are driven by the sensitivity of invertebrate taxa, with the nine most sensitive taxa being invertebrates (Table 2).
- Although olfactory impairment is a more sensitive endpoint than acute lethality in coho salmon, the greater sensitivity of several invertebrate taxa results in criteria that are protective against olfactory impairment.

Table 2. Summary of the USEPA's BLM-based copper criteria and the sensitivity of representative taxa

Rank	GMAV (µg copper/L)[a]	Species	SMAV (µg copper/L)[a]
19	69.63	*Pimephales promelas* (fathead minnow)	69.63
17	68.31	*Salvelinus confluentus* (bull trout)	68.31
10	31.39	*Oncorhynchus apache* (Apache trout)	32.54
		Oncorhynchus clarki (cutthroat trout)	32.97
		Oncorhynchus gorbuscha (pink salmon)	40.13
		Oncorhynchus kisutch (coho salmon)	22.93
		Oncorhynchus mykiss (rainbow trout)	22.19
		Oncorhynchus nerka (sockeye salmon)	54.82
		Oncorhynchus tshawytscha (Chinook salmon)	25.02
9	20.41	*Physa integra* (snail)	20.41
8	12.31	*Juga plicifera* (snail)	12.31
7	12.07	*Hyalella azteca* (amphipod)	12.07
6	11.33	*Actinonaias pectorosa* (freshwater mussel)	11.33
5	9.73	*Scapholeberis* sp. (cladoceran)	9.73
4	9.60	*Gammarus pseudolimnaeus* (amphipod)	9.60
3	6.67	*Lithoglyphus virens* (snail)	6.67
2	5.93	*Ceriodaphnia dubia* (cladoceran)	5.93
1	4.05	*Daphnia magna* (cladoceran)	6.00
		Daphnia pulicaria (cladoceran)	2.73
Total number of GMAVs			**27**
Final acute value (µg/L)			**4.674**
Criterion maximum concentration (µg/L)			**2.337**
Acute-chronic ratio			**3.22**
Criterion continuous concentration (µg/L)			**1.452**

[a] SMAVs and GMAVs are BLM-normalized based on the following physical-chemical characteristics: temperature = 20 °C, pH = 7.5, dissolved copper = 1.0 µg/L, DOC = 0.5 mg/L, humic acid = 10%, calcium = 14.0 mg/L, magnesium = 12.1 mg/L, sodium = 26.3 mg/L, potassium = 2.1 mg/L, sulfate = 81.4 mg/L, chlorine = 1.9 mg/L, alkalinity = 65.0 mg/L, sulfur = 0.0003 mg/L (EPA 2007).

BLM – biotic ligand model
USEPA – US Environmental Protection Agency
GMAV – genus mean acute value (geometric mean of SMAVs for a given genus)
LC50 – concentration that is lethal to 50% of an exposed population
SMAV – species mean acute value (geometric mean of LC50s for a given species)

Recent Studies with Non-Salmonid Fish Species

Recent studies with non-salmonid fish species include the following:

- Green et al. (2010) – Examined the influence of copper on olfactory response and behavior in fathead minnows (*Pimephales promelas*).
  - BLM-based copper criteria were lower than the copper concentration that did not result in a statistically significant ($p > 0.05$) effect on the EOG response and approximately an order of magnitude below the copper concentration of 10 µg/L that affected the EOG response and the fathead minnow behavioral response to food stimulus.
- Linbo et al. (2009) – Examined the influence of copper on the lateral line of larval zebrafish (*Danio rerio*).
  - Lateral line is a mechanosensory system that influences fish behavior, such as predator avoidance and numerous other behaviors.
  - Toxicity endpoint was measured as hair cell death.
  - EC50 (concentration that causes a non-lethal effect in 50% of an exposed population) values for hair cell death were 2.6 to 62 times higher than USEPA's BLM-based acute criteria and 4.2 to 101 times higher than USEPA's BLM-based chronic criteria.

Summary and Conclusions

- Existing acute and chronic hardness-based copper criteria were lower than the olfactory IC20 in 92 and 97%, respectively, of the 133 western US sampling locations evaluated.
- USEPA's current BLM-based acute and chronic copper criteria were lower than the olfactory IC20 in all locations evaluated.
- The margin of protection is greater in waters with high copper bioavailability (e.g., low DOC).

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