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Measurement of Low Levels of Molybdenum in the Environment by Using Aquatic Insects[1]

Theo Colborn

Western State College of Colorado, Gunnison, CO 81230 and Rocky Mountain Biological Laboratory, Gothic, CO 81224

In the near future, the Gunnison River, Gunnison County, Colorado (Fig. 1) may be affected by mining and milling operations for both molybdenum and uranium (USDA 1979; USDA 1979a; AMAX). At present, little molybdenum has been documented in the aquatic systems of the county (EPA 1971-1977). However, levels of molybdenum in the environment can increase with the mining and milling, RUNNELLS (1975) found that areas that are highly mineralized and physically disturbed have significantly more molybdenum in the environment than similarly mineralized areas that are undisturbed. Historically, the release of molybdenum into the surrounding ecosystem has been exacerbated by the mining of coal, molybdenum, and uranium (LE GENDRE & RUNNELLS 1975). In the milling of both molybdenum and uranium, the ores are reduced to a fine powder (HOMESTAKE 1980; AMAX). During the milling process of both metals, an alkaline flotation system precipitates out most metals, but increases the solubility of molybdenum (LE GENDRE & RUNNELLS 1975). Both the ore reduction and flotation processes redistribute molybdenum in the environment. Potable water supplies are limited in Colorado and thus increases the possibility of livestock and human beings consuming molybdenum-contaminated water in areas of pertubation. Already, cases of molybdenosis in livestock have been documented in Colorado downstream from a molybdenum mine (KABACK 1976). As the mining of the molybdenum and uranium lodes commences, a technique to monitor the relocation of molybdenum in the aquatic environment of Gunnison County is needed.

Aquatic insects concentrate certain metals, such as cadmium, from the surrounding ecosystem by two to four orders of magnitude (COLBORN 1981). This study was initiated to test the idea that insects could reflect levels of molybdenum in an ecosystem before the molybdenum was detectable by standard methods of

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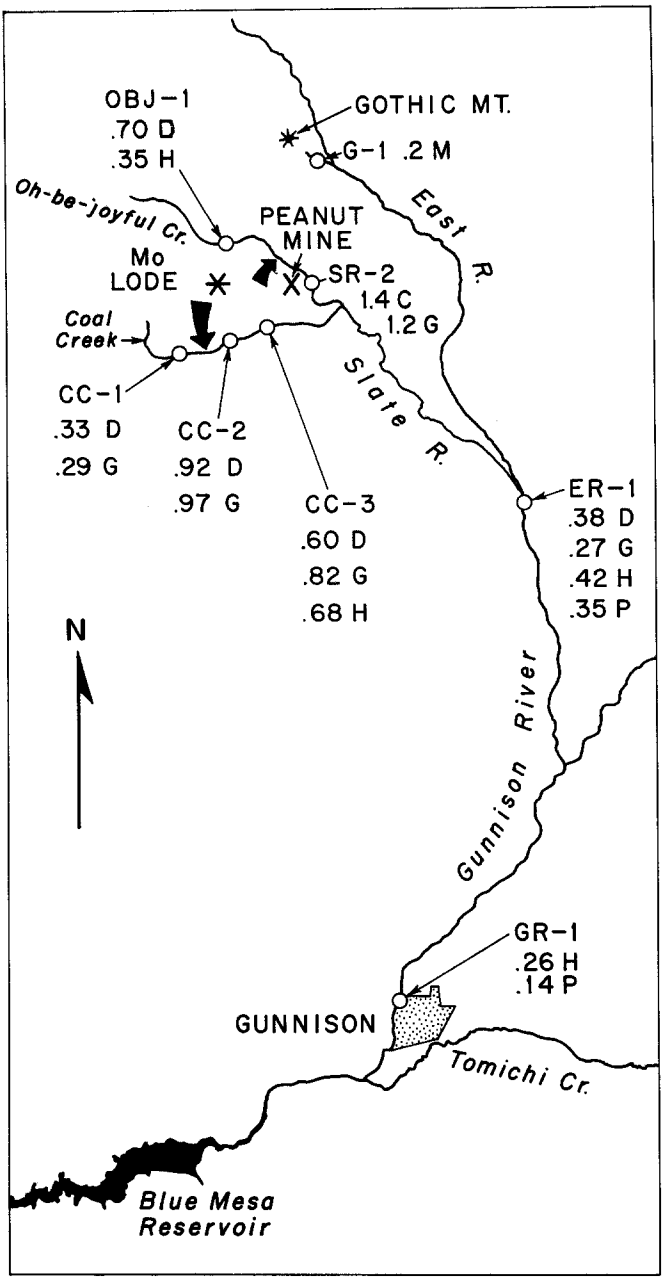

Fig. 1. East River - Upper Gunnison River, Gunnison County, Colorado showing the location of the molybdenum ore body. Insect molybdenum concentrations for each sampling station are listed. KEY: C = Cinygmula sp.; D = Drunella doddsi; G = Drunella grandis; H = Hydropsyche; M = Megarcys signata; P = Pteronarcella badia.

water analysis (APHA-AWWA-WPCC 1975). The research establishes background levels of molybdenum in insects in the East River - Upper Gunnison River drainage before significant mining commences.

METHODS

Starting at high altitudes and extending down the valley, near and below the molybdenum mine, aquatic insects and water samples were collected for atomic absorption spectrophotometric analysis for molybdenum. Eight stations were sampled in the East River - Upper Gunnison River drainage, Gunnison County, Colorado (Fig. 1). Five water samples were collected at each station by using resin column extraction of ions (COLBORN 1981; RILEY & TAYLOR 1968). Ions in the water were concentrated 40 times by eluting with 25 mL of 4 N HNO_3 followed by 25 mL 4 N NH_4OH, stored in 25-mL polyethylene bottles, and chilled until analysis. At the time of water collection, aquatic insects were collected, washed with 10 mL deionized distilled water, air-dried, stored in plastic bags and kept in a freezer until analyzed. Approximately 100 mg dry weight per sample of the common larger larvae were used (Table 1). At the time of analysis, insect samples were dried to constant weight and digested in 5 mL 10 N HCl. Both water and insect samples were assayed by atomic absorption spectrophotometry, flame mode. In addition, APDC-MIBK organic extraction for molybdenum was used (DAVIES 1975).

RESULTS

No molybdenum was found above the detectable level of 1 ug/L in any of the water samples, even after concentrating the ions in the water 40 times. The insects reflected trace amounts of molybdenum in different degrees. The stonefly, Perlodidae *Megarcys signata* at C-1 held 0.20 ppm molybdenum. On the north side of the molybdenum lode (Fig. 1) the mayfly, (Ephemerellidae) *Drunella doddsi* at OBJ-1 held twice as much molybdenum as the caddis fly, Hydropsyche; 0.70 to 0.35 ppm. To the east and just below the molybdenum lode, the Slate River *D. doddsi* assayed for 1.2 ppm molybdenum and the mayfly, Heptageniidae *Cinygmula* sp., 1.4 ppm. On the south side of the molybdenum lode, CC-1 insects held the least amount of molybdenum of all the stations on Coal Creek (0.33 ppm). CC-2 insects concentrated three times more than CC-1. CC-3, with twice as much molybdenum in the insects as CC-1, decreased a little over CC-2. Farther downstream, away from the ore body, ER-1 invertebrates show approximately the same molybdenum content as CC-1.

Table 1. Station Insect Sampling Data for the East River-Upper Gunnison River Drainage.

Station[a]	1980 Sampling Data	Species	$\bar{X}$ Insects Per Sample	N	$\bar{X}$ Insect {Mo} ppm	Range Insect {Mo} ppm	S.D.
Gothic-1 G-1	18 July	Megarcys signata	10	5	0.20	0.11-0.33	0.09
Oh-be-joy-ful-1 OBJ-1	12 August	Drunella doddsi	27	5	0.70	0.56-0.85	0.13
		Hydropsyche	36	1	0.35		
Slate River-2 SR-2	29 August	Cinygmula sp.	40	3	1.40	0.95-1.65	0.39
		Drunella doddsi	8.5	2	1.18	0.94-1.41	0.33
Coal Creek-1 CC-1	21 July	Drunella doddsi	10	5	0.33	0.21-0.57	0.13
		Drunella grandis	13	1	0.29		
Coal Creek-2 CC-2	26 July	Drunella doddsi	18.6	5	0.92	0.69-1.41	0.30
		Drunella grandis	19	1	0.97		
Coal Creek-3 CC-3	8 August	Drunella doddsi	10	5	0.60	0.35-0.89	0.20
		Hydropsyche	9	1	0.68		
		Drunella grandis	25	1	0.82		
East River-1 ER-1	28 July	Hydropsyche	43.6	5	0.42	0.33-0.66	0.12
		Pteronarcella badia	7.4	5	0.35	0.25-0.49	0.10
		Drunella grandis	21	1	0.27		
		Drunella doddsi	12	1	0.38		
Gunnison River-1 GR-1	24 July	Pteronarcella badia	8.8	5	0.14	0.09-0.18	0.03
		Hydropsyche	19.7	3	0.26	0.18-0.30	0.05

[a]Site Locations: Gothic-1, T 12 S; R 86 W; on a stream west to east directly between NE ¼ and SE ¼ of NE ¼ of Sect. 4 at an elevation of 3505m. Oh-be-joy-ful-1, T 13 S; R 87 W; NE ¼ of SE ¼ of Sect. 24 at an elevation of 2926m. Slate River-2, T 13 S; R 86 W; NE ¼ of SW ¼ of Sect. 34 at an elevation of 2682m. Coal Creek-1, T 14 S; R 87 W; SW ¼ of NE ¼ of Sect. 7 at an elevation of 2956m. Coal Creek-2, T 14 S; R 87 W; between the NE ¼ and SE ¼ of NE ¼ of Sect. 7 at an elevation of 2915m. Coal Creek-3, T 14 S; R 86 W; SE ¼ of NE ¼ of Sect. 5 at an elevation of 2820m. East River-1, T 14 S; R 85 W; center point of SW ¼ of Sect. 27 at an elevation of 2602m. Gunnison River-1, T 50 N; R 1 W; center point of Sect. 24 at an elevation of 2365m.

At the lower end of the valley, GR-1 drops as low as 0.26 and 0.14 ppm, much like G-1.

DISCUSSION

The insect molybdenum levels were lowest at G-1 and GR-1, the uppermost and lowest stations under study. Since these insects were the most removed from the molybdenum lode, perhaps their molybdenum content represents the intrinsic requirement of molybdenum in aquatic insects.

The fact that CC-1 insects held the least amount of molybdenum in the Coal Creek drainage, suggests that CC-1 lies far enough upstream to be above the watershed influence of the molybdenum lode. On the other hand, the high level of insect molybdenum at SR-1 might reflect the impact from an old abandoned mine which tunnels under the mountain which harbors the molybdenum lode.

The geographical profile of insect-molybdenum in the East River - Upper Gunnison River drainage starts very low at Gothic, increases at all stations around the molybdenum lode, peaks at SR-2, and then decreases as the riverine system flows farther away from the main ore body. The plotting of the insect molybdenum concentrations on the continuum graph (Fig. 2) correlated with a known lode of molybdenum. Molybdenum-insect data sets should be collected above, near, and below other suspected molybdenum lodes to prove the feasibility of using aquatic insects to prospect for molybdenum.

As the ore body in Gunnison County becomes disturbed, more water-insect-molybdenum data sets should be collected. Any increase in insect molybdenum concentration over the results of this study would indicate new releases of molybdenum into the Gunnison County environment. This is important because the detectable limit for molybdenum in water using present standard methods of analyses is 1 ug/L. In this case, aquatic insects will provide a more sensitive measurement of a toxic metal in the aquatic systems of the County, allowing trends to be determined before the metal reaches detectable limits by standard water analysis methods.

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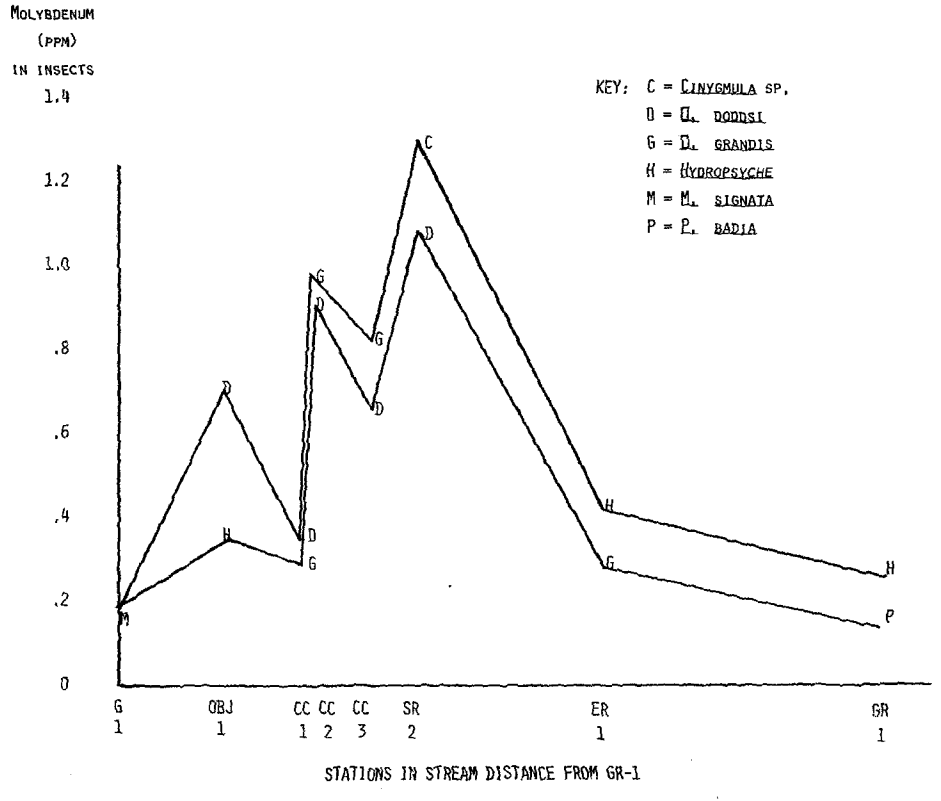

Fig. 2. Distribution of Mo through the river continuum from headwaters at G-1 and OBJ-1 to GR-1. Graph shows lowest and highest mean Mo insect values (per species) for each station. KEY: C = Cinygmula sp.; D = D. doddsi; G = D. grandis; H = Hydropsyche; M = M. signata; P = P. badia.

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