Supplementary Material (ESI) for Journal of Environmental Monitoring

A biogeochemical approach to understanding the accumulation patterns of trace elements in three species of dragonfly larvae: evaluation as biomonitors

Isela Lavilla *et al.* **DOI: 10.1039/b920379f**

Data of concentrations (dry weights) of trace elements in Odonata larvae from the literature.

Element	Concentration (µg.g^{-1})	Taxon	Site	Reference
Fe	912	Anisoptera	Iron and steel factory in Koverhar (Finland)	(12)
	116	Anisoptera	Control area (Finland). Unpolluted.	(12)
Mn	6.5	Anisoptera	Iron and steel factory in Koverhar (Finland)	(12)
	2.8	Anisoptera	Control area (Finland). Unpolluted.	(12)
	82.53	Benthic macroinvertebrate (Odonata)	Rhumel River and Boumerzog River (Argelia). Urban, industrial and agricultural wastes.	(14)
Zn	163	Zygoptera (*Ischnura elegans*)	Dommel River (Netherland). Polluted.	(33)
	98-106	Zygoptera (*Ischnura elegans*)	Maarsseveen (Netherland). Unpolluted lake	(33)
	91.6	Anisoptera (Libellulidae)	Lakes from three sites with different water chemistry (Canada)	(11)
	97	Anisoptera	Iron and steel factory in Koverhar (Finland)	(12)
	95	Anisoptera	Control area (Finland). Unpolluted.	(12)
	76.4 – 203.3	Odonata (Anisoptera/Zygoptera)	Stormwater treatment ponds in Maryland (USA)	(13)
Cu	29	Zygoptera (*Ischnura elegans*)	Dommel River (Netherland). Polluted	(33)
	12-13	Zygoptera (*Ischnura elegans*)	Maarsseveen (Netherland). Unpolluted lake.	(33)
	25.8	Anisoptera (Libellulidae)	Lakes from three sites with different water chemistry (Canada)	(11)
	34	Anisoptera	Iron and steel factory in Koverhar (Finland)	(12)
	37	Anisoptera	Control area (Finland). Unpolluted.	(12)
	11.3 – 62.2	Odonata (Anisoptera/Zygoptera)	Stormwater treatment ponds in Maryland (USA)	(13)
Ni	2.9	Anisoptera (Libellulidae)	Lakes from three sites with different water chemistry (Canada)	(11)
	3.0	Anisoptera	Iron and steel factory in Koverhar (Finland)	(12)
	1.0	Anisoptera	Control area (Finland). Unpolluted.	(12)
Cr	14	Benthic macroinvertebrate (Odonata)	Rhumel River and Boumerzog River (Algeria). Urban, industrial and agricultural wastes	(14)
Pb	15.34	Zygoptera (*Ischnura elegans*)	Dommel River (Netherland). Polluted	(33)
	1.2 - 5.1	Zygoptera (*Ischnura elegans*)	Maarsseveen (Netherland). Unpolluted lake	(33)
	2.5	Anisoptera (Libellulidae)	Lakes from three sites with different water chemistry (Canada)	(11)
	1.8	Anisoptera	Iron and steel factory in Koverhar (Finland)	(12)
	1.0	Anisoptera	Control area (Finland). Unpolluted.	(12)
	<0.02 - 4.81	Odonata (Anisoptera/Zygoptera)	Stormwater treatment ponds in Maryland (USA)	(13)
	34.3	Benthic macroinvertebrate (Odonata)	Rhumel River and Boumerzog River (Algeria). Urban, industrial and agricultural wastes	(14)
Cd	1.66	Zygoptera (*Ischnura elegans*)	Dommel River (Netherland). Polluted	(33)

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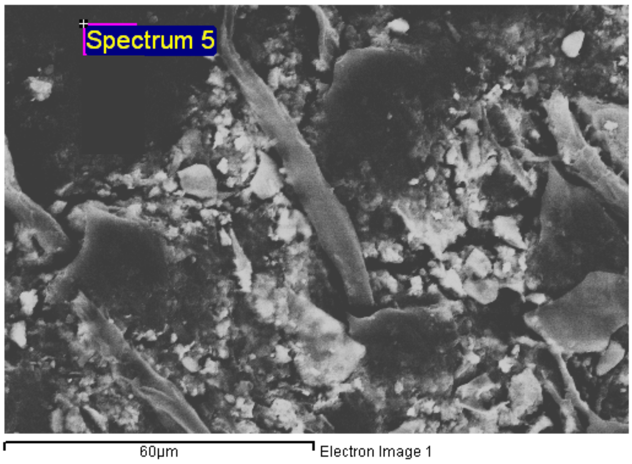
Cd	1.66	Zygoptera (*Ischnura elegans*)	Dommel River (Netherland). Polluted	(33)

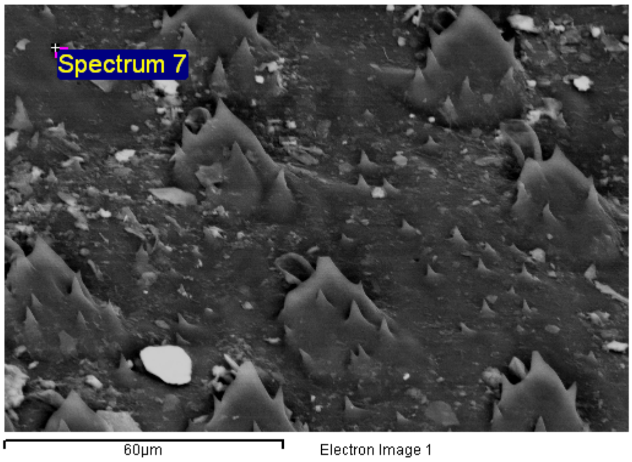
0.04 - 0.26	Zygoptera (*Ischnura elegans*)	Maarsseveen (Netherland). Unpolluted lake	(33)
0.2	Anisoptera (Libellulidae)	Lakes from three sites with different water chemistry (Canada)	(11)
0.86	Anisoptera	Iron and steel factory in Koverhar (Finland)	(12)
0.12	Anisoptera	Control area (Finland). Unpolluted.	(12)
0.46	Benthic macroinvertebrate (Odonata)	Rhumel River and Boumerzog River (Algeria). Urban, industrial and agricultural wastes	(14)

Comparing the values found for the three species with those published for Odonata larvae, it can be seen that many of the measured Fe and Mn contents are higher than the values published for a polluted area next to a steel factory.[12] When the concentration values of Cu and Zn in this study are compared with those found for *I. elegans*,[33] it can be concluded that the levels of Cu are above the reference value given for non-polluted zones and the Zn values are close to the reference value in most cases. Cd levels are below the reference values for polluted zones.[33,12] Ni values are, in most points, below the reference values for polluted zones in Nummelin *et al*.[12] with the exception of some concentrations which are up to four times higher. Pb concentrations are similar to those found by Timmermans[33] for non-polluted zones in *I. elegans*. This author found significant differences in the levels of Pb between non-polluted and polluted zones, whilst Nummelin *et al*.[12] found very small differences in dragonfly larvae for this element. Information in the literature about Cr content in Odonata is scarce. Afri-Mehennaoui *et al*.[14] determined this element in a number of different macro-invertebrates (with some Odonata). The found value in this reference is greater than those found in the present work.

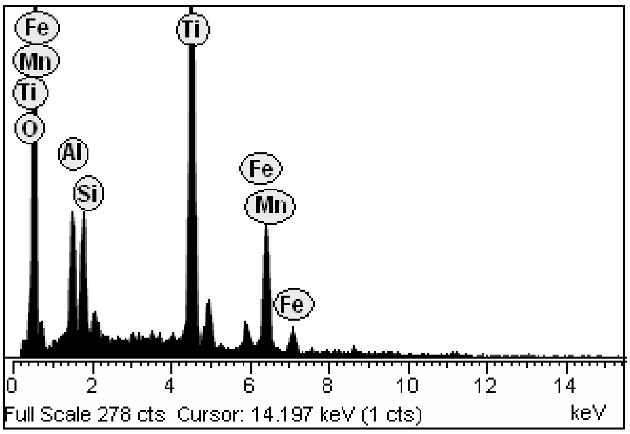
(a)



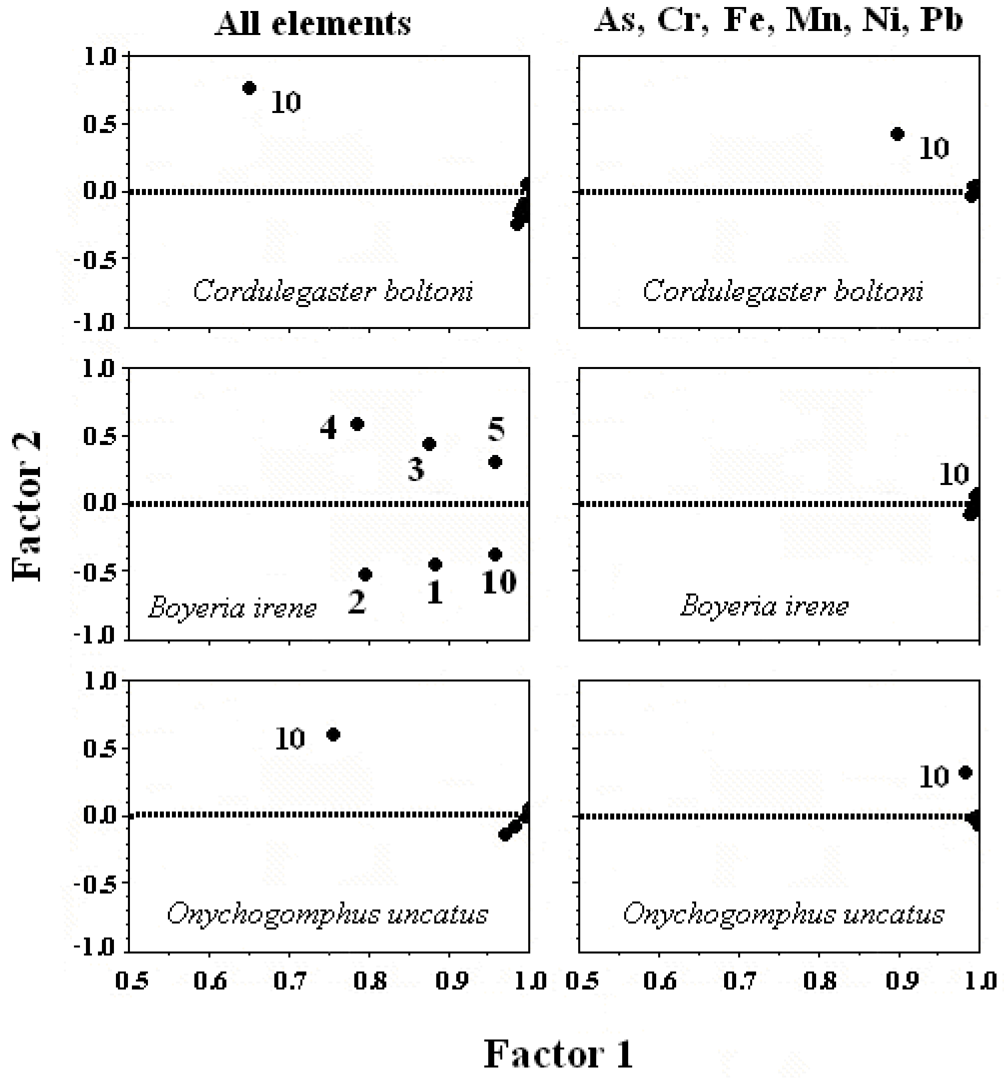
(b)



(c)



(a) Scanning electron micrograph of the surface of a specimen of *C. boltoni* collected from point 10 in the Louro River, washed with water (b) Scanning electron micrograph of the surface of a specimen of *C. boltoni* collected from point 10 in the Louro River, washed with EDTA-HCl. (c): Energy dispersive X-ray analysis of particles? of the surface of the specimen washed with water.



PCA loading plots of the concentrations of all elements and As, Cr, Fe, Mn, Ni and Pb for the three species in the different sampling points.

SOME NUMERICAL RESULTS

- ✓ **Section "Total heavy metals and Arsenic in Dragonfly larvae: Chemometric interpretation of results":**

Coefficients of variation (CVs, %) for Cu and Zn in Odonata

	Cu	Zn	Molar fraction Cu	Molar fraction Zn
C. boltoni	24.0	29.6	9.8	2.8
B. irene	15.5	33.3	21.0	4.0
O. uncatus	24.0	31.0	5.6	1.9

Pearson correlation coefficients (CCs, %) in Odonata

	Zn-Cu	Cd-Cu	Cd-Zn
C. boltoni	0.882	0.646	0.489
B. irene	0.800	0.729	0.821
O. uncatus	0.982	0.850	0.870

- **Section "Accumulation patterns of trace elements in dragonfly larvae":**

Mean value removed by washing (%)

	As	Fe	Mn	Cd	Ni	Cr	Pb
C. boltoni	98	70	73	50	45	50	38
B. irene	99	68	69	52	47	35	54
O. uncatus	98	71	70	52	50	20	80

Concentration ratios in sediments and larvae

	Al/Si	Fe/Si	Mn/Si
Sediments	0.3-0.5	0.06-0.1	0.001
Larvae	0.7-1.5	0.3-9.6	0.02-0.04

- **Section "Relations with geochemistry: trace elements in sediments and dragonfly larvae":**

Pearson correlation coefficients (CCs, %) between Odonata and sediments

	As (V)	Total Pb	Cr
C. boltoni	0.840	0.603	First fraction, 0.961
			Second fraction, 0.882
			Third fraction, 0.889
			Total, 0.852
B. irene	0.907	0.717	Second fraction, 0.895
			Third fraction, 0.686
O. uncatus	0.950	0.938	--------

✓ **Section "Dragonfly larvae as biomonitors of concentration by trace element":**

Mean concentration of different element in Hydropsyche (µg g^{-1})

As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
3.2	1.0	2.9	160	3.8	938	81	3.2	203

Hydropsyche larvae have been extensively used as biomonitors of heavy metals in fresh water ecosystems due to their high tolerance to metals.[9] Levels of trace elements in the sample of *Hydropsyche* taken from the Louro River were, in many cases, of the same order as those found in dragonfly larvae (Table 1), with the exception of Cu, Ni and Fe (contents of these elements were highest in this genus). *Hydropsyche* larvae were only found in the first four sampling points, because many of the species cannot tolerate the organic pollution in the water, and moreover, they need an abundance of pebbles and gravel in the river bed. Dragonfly larvae appear as possible biomonitors as opposed to *Hydropsyche* in the Louro River because they are more abundant along the course of this river, the time for larval development is longer, the species is easy to identify and its body size is suitable.