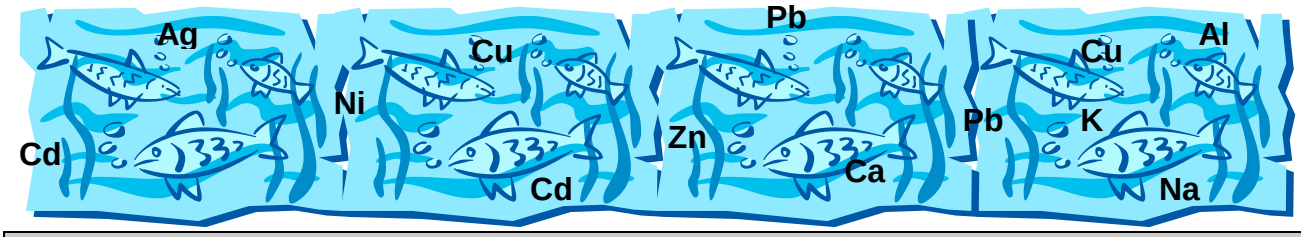
NSERC – Industry Project on Metal Bioavailability
Research Newsletter



Vol. 15: No. 1 Wilfrid-Laurier/*McMaster University* Nov. 2011

NEWS

First and foremost, I'd like to say a big 'thank you' to the Wood lab at McMaster for keeping this newsletter going for so long. Many distinguished scientists, past and present (e.g. Natasha Franklin, Patricia Gillis, Sunita Nadella, Tania Ng and Erin Leonard to name but a recent few), have had editorship of this newsletter and it really has been a great way of keeping everyone informed. It is now Wilfrid-Laurier University's turn, so the reins have been handed over to me, Chris Cooper, and I'll try my best to live up to the high standards set by previous editors. This is the first newsletter in awhile so it is a bit long but the plan is to distribute more frequent and shorter newsletters in the future.

The aim of this newsletter is to keep everyone up-to-date with regards to personnel, publications and presentations on all things related to aquatic metal toxicity. As usual, at the end of each newsletter will be a 'hot off the press' morsel of cutting edge science, this time it's from Rachael Diamond, Wilfrid-Laurier University. Well, it's been a year since the last newsletter and members of the Metals Bioavailability Group have been busy little bees…

Comings and goings (2010-2011):

As always, McMaster University has been a hive of activity. Ph.D. students **Lygia Noguiera** and **Mariana Basso Jorge** (from the laboratory of Dr. Adalto Bianchini, Federal University of Rio Grande, Brazil) spent a year (April 2010 - April 2011) working in the labs of Dr. Chris Wood at McMaster University and Dr. Patty Gillis at Environment Canada, Burlington. During this time, they performed several studies on the effects of Cu and salt on the physiology and toxicology of freshwater mussels. Visiting professor Dr. **Vania Loro** of the Federal University of Santa Maria, Brazil, has also left after spending a sabbatical year (September 2010 - September 2011) working in the lab of Dr. Chris Wood. Vania contributed to a number of metal-related projects, and led a detailed study on the ionoregulatory and oxidative stress responses of the killifish to sublethal Zn exposure as a function of salinity. Visiting Ph.D. student **Kassio Rios da Silva** from the Federal University of Rio Grande spent 3 months (January 2010 - March 2010) working with the other Brazilian team members in Dr. Chris Wood's lab, and contributed to a number of metral-related projects during that period.

However, fear not, the Brazilian invasion continues at McMaster University! Visiting Ph.D. student **Marianna Lauer**, and visiting M.Sc. students **Marina Giacomin** and **Abel Machado** (also from Dr. Adalto Bianchini's lab) are currently spending 8 months (May 2011 - December 2011) again with Dr. Chris Wood, Dr. Patty Gillis, and Dr. Grant McClelland. They are carrying out several studies on the effects of Cu, DOC, and non-point source pollution on the physiology and toxicology of freshwater mussels, on the impact of Cu and salinity on the blue crab, and on the impact of Cu and salinity on the

killifish. Travelling in the other direction was McMaster Ph.D. student **Alex Zimmer**, from Dr. Chris Wood's lab. He spent 5 months (March 2011 - July 2011) in Dr. Adalto Bianchini's lab, where he studied the interactive effects of Cu and salinity on ammonia toxicity to a native guppy species. All of this research has been part of the IDRC-CRC International Research Chair Program awarded to Drs. Bianchini and Wood.

Ola Dr. **Paula Sanchez-Marin**, who is a postdoctoral fellow from the laboratory of Dr. Peter Campbell at INRS, Université du Québec. She's visiting Dr. Chris Wood's lab at McMaster for 2 months (October 2011 - November 2011) to conduct studies on silver transport in cultured gill epithelia of rainbow trout.

Dr. Grant McClelland has also welcomed 3 new students to McMaster. M.Sc **Victoria Ransberry** started in May and comes from Brent Sinclair's Lab at Western. She is currently working on oxidative stress effects of combined Cu and hypoxia in killifish. B.Sc **Daniel Li** started in September and he will be examining the effects of Cu and hypoxia on killifish gill ion transporter gene expression and gill morphometry. Finally, B.Sc **Narina Jabari** is examining the expression of HIF1a and HIF-regulating genes with Cu and hypoxia in killifish.

Back at Bamfield Marine Sciences Centre, British Columbia, for another season (June and July 2011) was Dr. **Adalto Bianchini**, his Ph.D. student **Marianna Lauer** (Federal University of Rio Grande, Brazil), Dr. **Chris Wood** and Research Assistant **Sunita Nadella**, (McMaster University). The team studied the impact of Zn, Pb, Cu, and Ni exposure, and the interactive effects of DOC, on the physiology and toxicology of early life stages of blue mussel and purple sea urchin larvae.

Now on to Laurier, **Rachael Diamond** won the best poster award at the CSC in Montreal (2011) and **Emily-Jane Costa** won the best undergraduate oral presentation at SETAC in Portland (2010) – Congrats to both!

Dr. Scott Smith also has a few new additions to the laboratory. Dr. **Chris Cooper** (the good-looking English chap), has recently joined the team as a postdoctoral fellow, all the way from the University of Guelph. After doing a PDF with Dr. Patricia Wright on ammonia transport in fish, he is now working on the affects of salinity and DOC on metal toxicity to rotifers (*Brachionus plicatilis*). New M.Sc student **Tara Tait**, who did her B.Sc in Biomedical Toxicology also at Guelph, will be focusing on Cu speciation in marine waters and how this affects bioavailability and subsequent toxicity. Undergraduate students **Jocelyn Schaefer** and **Amanda Johnston**, will be testing Pb ion selective electrode in saltwater, and investigating Cu interactions with channel blocker drugs amiloride and furosemide (thus having implications for future channel blocker experiments), respectively.

Down the hallway at Laurier in Dr. Jim McGeer's lab, we'd like to welcome **Rabia Nasir**, who did her B.Sc in Biology at Ryerson University in Toronto. Her M.Sc work will be on the effects of salinity on metal toxicity to mysid shrimp. **Shawn Hudes** has an undergrad degree in Biology from Brock University. His project is on the relationship between subcellular distribution of Cu in tissues and whole organism behavior and performance. After doing her B.Sc in biology at Laurier, **Kelly Livingstone** obviously liked the place. She's now doing an M.Sc focusing on the importance of NOM source on mitigating chronic Cu toxicity to *Hyalella azteca* in the context of the recovery of damaged ecosystems.

New Funding:

- **Scott Smith (P.I.), Chris Wood, Grant McClelland,** and **Jim McGeer** received a NSERC CRD 2011-2014, "Research towards BLM for saltwater systems: chemical and biological perspectives" - $493,640 (NSERC) $322,180 from ICA, CDA, ILZRO, IZA, Teck Resources, Xstrata, Vale, NiPERA.

- **Scott Smith** was awarded a NSERC Discovery $100,000 grant, 2010-2015, "Organic matter variability and implications for metal bioavailability in urban watersheds".

- **Jim McGeer** and **Scott Smith** have just finished compiling a database on the toxicology of the lanthanides, the goal was to identify gaps in our understanding of the chemistry, bioavailability, and toxicity potential of the lanthanides to aquatic organisms. Environment Canada supported the project via the CNTC and a final report and reference database was produced (see below "Ng, T., Smith, D.S., Straus, A. and J.C. McGeer. 2011").

Conference presentations:

The following papers are going to be presented by the Metals Bioavailability Group in the 32nd Annual SETAC North America Meeting, Boston, Massachusetts. Sunday the 13th to Thursday the 17th of November, 2011.

- **Al-Reasi, H., Wood, C.M., Smith, D.S.** Absorbance and fluorescence properties of natural organic matter as quality measures predicting protective effect against Cu toxicity to *Daphnia magna*.
  Platform, Ballroom C, Wednesday 8:00 AM

- **Alsop, D., Chowdhury, J., Wood, C.M.** Evaluating the relative contributions of dietary and waterborne lead to toxicity in rainbow trout.
  Poster, Exhibit Hall, Wednesday 8:00 AM

- **Alsop, D., Wood, C.M.** Sodium loss is the acute toxic mechanism of metals and other contaminants in zebrafish: implications for additive toxicity.
  Poster, Exhibit Hall, Wednesday 8:00 AM

- **Blewett, T., MacLatchy, D., Wood, C.M.** Environmental influences on the accumulation of ethynylestradiol in marine teleosts.
  Poster, Exhibit Hall, Wednesday 8:00 AM

- **Chan, K., McGeer, J.C.** The effects of Ca^{2+}, Mg^{2+}, and natural organic matter quantity and quality on Ni Toxicity to *Hyalella azteca*.
  Poster, Exhibit Hall, Wednesday 8:00 AM

- **Costa, E., McGeer, J.C.** Acute and chronic toxicity of nanoparticle and ionic forms of silver to *Daphnia pulex.*
  Platform, Room 208, Monday 3:10 PM

- **Cunningham, J., McGeer, J.C.** The effect of Cd on repeated swim performance in relation to metabolic recovery in rainbow trout (*O. mykiss*) during sublethal waterborne exposure.
  Platform, Ballroom C, Wednesday 11:05 AM

- **Lauer, M., de Oliveira, C., Cagnin, R., Cantarela, B., Loureiro, L., Bianchini, A.** Copper effects on energy metabolism in the sea cucumber *Trachythyone crassipeda*.
  Poster, Exhibit Hall, Wednesday 8:00 AM

- **Leonard, E.M., Banerjee, U., D'Silva, J.J., Wood, C.M.** Nickel bioaccumulation, sub-cellular fractionation and essential ion disruption in two teleosts: the round goby and the rainbow trout.
  Platform, Ballroom C, Wednesday 4:10 PM

- **Livingstone, K., McGeer, J.C.** Effect of natural organic matter quantity and quality on the acute toxicity of Cu to the aquatic amphipod *Hyalella azteca*.
  Poster, Exhibit Hall, Wednesday 8:00 AM

- **Loro, V.L., Wood, C.M.** Effects of waterborne zinc exposure on oxidative stress parameters and antioxidant enzymatic response of the killifish (*Fundulus heteroclitus*) acclimated to different salinities.
  Poster, Exhibit Hall, Monday 8:00 AM

- **Machado, A.A.S., Cardozo, J.G., Gomes, E.G., Hoff, M.L.F, Bianchini, A.** Biomarkers to assess metal exposure in estuarine fish.
  Poster, Exhibit Hall, Tuesday 8:00 AM

- **Martins, C., Jorge, M., Giacomin, M., Wood, C.M., Bianchini, A.** Copper uptake by sodium transporters and its distribution in the blue crab *Callinectes sapidus* acclimated to low salinity.
  Platform, Ballroom C, Wednesday 4:35 PM

- **Moustafa, A.M., Kang, S., Smith, D.S., Wang, J., El-Din, M.G.** A comparison between carboxyl groups quantifications for different naphthenic acids using the linear programming technique and the FT-IR spectroscopy.
  Platform, Room 311, Wednesday 5:00 PM

- **Nadella, S.R., Smith, S., Bianchini, A., Tellis, M., Diamond, R., Wood, C.M.** Pb and Zn toxicity to mussel and echinoderm larvae: effects of salinity and DOC.
  Poster, Exhibit Hall, Wednesday 8:00 AM

- **Smith, D.S., Diamond, R., Tait, T., Santore, R., Wood. C.M.** Method Comparisons for Copper Speciation in Salt Water and Implications for Bioavailability Model Development.
  Platform, Ballroom C, Thursday 11:05 AM

- **Tellis, M., Alsop, D.E., Wood, C.M.** Endocrine Disruption or Adaptation? Loss of an acute cortisol stress response with chronic copper exposure in rainbow trout.

Poster, Exhibit Hall, Thursday 8:00 AM

- **Zimmer, A.M., Barcarolli, I.F., Wood, C.M., Bianchini, A.** Evaluating the effects of sub-lethal copper exposure on ammonia excretion in the euryhaline guppy, *Poecilia vivipara*. Poster, Exhibit Hall, Wednesday 8:00 AM

Business Meetings:

There's a **Metals Advisory Group Meeting and Reception** on Monday in Room 200, 6-9 PM. Furthermore, don't forget about the **Marine Metals NSERC CRD Update Meeting** on Wednesday in Room 305, 3-4:30 PM (for additional information contact Scott Smith: ssmith@wlu.ca).

Other presentations (2010-2011):

- **Al-Reasi, H., Smith, D.S., Wood, C.M.** (2010). Ameliorative effect of natural organic matter (NOM) on metal toxicity to aquatic organisms: Evaluating the influence of NOM quality. 37th Annual Aquatic Toxicity Workshop, October 2010. Toronto, Ontario.

- **Al-Reasi, H., Smith, D.S., Wood, C.M.** (2011). The influence of natural organic matter (NOM) on sodium transport in freshwater organisms. 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **Alsop, D., Wood, C.M.** (2011). Sodium loss is the acute toxic mechanism of diverse contaminants in zebrafish: Implications for additive toxicity. 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **Banerjee, U., Leonard, E., Wood, C.M.** (2011). Chronic Ni exposure to round gobies fed Ni contaminated Lumbriculus- assessing subcellular distribution of Ni in prey and predator. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Chan, K., Livingstone, K., McGeer, J.C.** (2011). Influence of natural organic matter and Ca on the acute toxicity of Cu and Ni in *H. azteca*. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Costa, E-J., McGeer, J.C.** (2010). The Effect of Metal-Oxide Nanoparticles on Daphnia pulex and Hydra Attenuata. 31st Society for Environmental Toxicology and Chemistry Conference, November 2010. Portland, Oregon.
  *****Won the best undergraduate oral presentation!!!*****

- **Costa, E-J., McGeer, J.C.** (2011). Determining the mechanisms of Ag nanoparticle toxicity. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Costa, E-J., McGeer, J.C.** (2011). Nano-silver toxicity in Daphnia pulex: determining the role of ionic silver. 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **Costa, E-J., McGeer, J.C.** (2011). Approaches to understanding the acute and chronic toxicity of metal containing nanoparticles. 38th Annual Aquatic Toxicity Workshop, October 2011. Winnipeg, Manitoba.

- **Cunningham, J., McGeer, J.C. (**2010). The effects of chronic cadmium exposure on the repeat swimming performance in three species of salmonids. 31st Society for Environmental Toxicology and Chemistry Conference, November 2010. Portland, Oregon.

- **Cunningham, J., McGeer, J.C.** (2011). The effect of cadmium exposure on the repeat swimming ability and metabolic activity of three species of salmonids. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Cunningham, J., McGeer, J.C.** (2011). The effects of Cd exposure on performance and capacity to recover from repeat swimming in rainbow trout (*Oncorhynchus mykiss*). 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **Diamond, R.L., Tellis, M., Wood, C.M., Smith, D.S.** (2011). Fluorescence quenching method to determine copper, lead, zinc and nickel binding to organic matter in saltwater. Canadian Society of Chemistry, June 2011. Montreal, Quebec.
  ***** Won a best student poster award!!! *****

- **Ellis, J., Fernandes, E., Cunningham, J., McGeer, J.C.** (2011). Effect of sublethal Ni exposure on sustained swimming ability and stress response in rainbow trout. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Ellis, J., McGeer, J.C.** (2011). The effect of chronic nickel exposure on the sustained swimming ability of rainbow trout (*Oncorhynchus mykiss*). 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **Ellis, J., McGeer, J.C.** (2011). The effect of chronic nickel exposure on swim performance and bioaccumulation in rainbow trout (*Oncorhynchus mykiss*). 38th Annual Aquatic Toxicity Workshop, October 2011. Winnipeg, Manitoba.

- **Eyckmans, M., Lardon, I., Wood, C.M. and DeBoeck, G.** (2010). Physiological effects of waterborne lead exposure in the spiny dogfish (*Squalus acanthias*). Annual Meeting of the SEB, June/July 2010. Prague, Czech Republic.

- **Fernandes, E., McGeer, J.C.** (2011). Physiological effects of chronic sublethal waterborne Ni exposure in rainbow trout (*Oncorhynchus mykiss*). Ontario Biology Day Annual Conference, March 2011. Waterloo, Ontario.

- **Gheorghiu, C., Smith, D.S., Kara, Y., Wilkie, M. P.** (2010). Source of nom differently affects metal-gill binding in rainbow trout (*Oncorhynchus mykiss*) exposed to Pb-Cd mixture. Canadian Society of Zoology, May 2010. Vancouver, British Columbia.

- **Jorge, M.B., Bianchini, A., Wood, C.M.** (2011). Copper toxicity to glochidia larvae (*Lampsilis cardium*): accumulation and effects. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Klinck, J.S., Wood, C.M.** (2011). Comparing calcium and cadmium uptake along the gastrointestinal tract of freshwater and seawater acclimated steelhead trout. 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **Kozlova, T., Wood, C.M., McGeer, J.C.** (2010). Chronic toxicity of dietary nickel to *Daphnia pulex* in soft water. Laurentian SETAC 15th Annual Conference, June 2010. Niagara-on-the-lake, Ontario.

- **Leonard, E.M., Wood, C.M.** (2011). Bioaccumulation and ionoregulatory disruption in four invertebrate species following acute (48h-96h) waterborne exposures to nickel in hard and soft water. 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **Livingstone, K., McGeer. J.C.** (2011). Examining the effect of source of natural organic matter on the acute toxicity of copper to *Hyalella azteca*. Ontario Biology Day Annual Conference, March 2011. Waterloo, Ontario.

- **Malhi, G., McGeer, J.C**. (2011). The effects of metal oxide nanoparticles on *Hyalella azteca*. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Malhi, G., McGeer, J.C**. (2011). The chronic effects of titanium dioxide nanoparticles on *Hyalella azteca*. 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **McGeer, J.C., Milne, J., Mancini, A.** (2010). Bioaccumulation and physiological effect of chronic sublethal Cd exposure in rainbow trout. 37th Annual Aquatic Toxicity Workshop, October 2010. Toronto, Ontario.

- **McGeer, J.C., Milne, J., Mancini, A.** (2010). Bioaccumulation and physiological effect of chronic sublethal Cd exposure in rainbow trout. 31st Society for Environmental Toxicology and Chemistry Conference, November 2010. Portland, Oregon.

- **McGeer, J.C., Pais, N., Costa, E-J., Straus, A.** (2010). Bioaccumulation of Cd in *Lumbriculus vaiegatus*, *Lymnaea stagnalis* and *Hyalella azteca* and development of a novel tissue residue approach. 31st Society for Environmental Toxicology and Chemistry Conference, November 2010. Portland, Oregon.

- **McGeer, J.C., Smith, D.S., McClelland, G.C., Wood. C.M.** (2010). Towards marine/estuarine biotic ligand models for Cu, Pb, Zn and Ni: chemical and biological aspects. International Copper Association, Health and Environment Program Advisory Committee, August 2010. Phoenix, Arizona.

- **Norgueira, L., Bianchini, A., Wood, C.M.** (2011). Physiological effects of high NaCl exposure on the freshwater larvae L. fasciola. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Pais, N., McGeer. J.C.** (2011). Using bioaccumulation as an indicator of chronic impact for Cd: a novel approach using resistant and sensitive organisms. 20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Pais, N., McGeer. J.C.** (2011). Linking the chronic effects of waterborne cadmium on *Lymnaea stagnalis* and *Hyalella azteca*. 50th Annual Meeting of the Canadian Society of Zoology, May 2011. Ottawa, Ontario.

- **Pais, N., Costa, E-J., Straus, A., McGeer, J.C.** (2010). Acute and Chronic Effects of Bioaccumulated Cd on *Lumbriculus variegatus, Lymnaea stagnalis, Hyalella azteca* and *Daphnia pulex*. 37th Annual Aquatic Toxicity Workshop, October 2010. Toronto, Ontario.

- **Sandhu, N., McGeer, J.C., Vijayan, M.** (2010). Cadmium impacts the cortisol stress axis in rainbow trout. 31st Society for Environmental Toxicology and Chemistry Conference, November 2010. Portland, Oregon.

- **Smith, D.S.** (2011). Electrochemical method comparison for copper speciation in salt water and implications for bioavailability models. Canadian Society of Chemistry, June 2011. Montreal, Quebec.

- **Smith, D.S.** (2011). Research driven by regulatory needs: metals in aquatic systems including the Grand River. Rotary Club Lunchtime Seminars, January 2011. Fergus, Ontario.

- **Tellis, M., Wood, C.M.** (2011). Effects of Pb and Zn on marine invertebrates-interactions of dissolved organic carbon and salinity20th Annual Comparative Physiology and Biochemistry Workshop, Elmhirst's Resort, February 2011. Keene, Ontario.

- **Wilkie, M.P., Gheorghiu, C., Smith, D.S.** (2010). Metal-gill binding and toxicity in fish: the influence of NOM quality. 37th Annual Aquatic Toxicity Workshop, October 2010. Toronto, Ontario.

- **Wilkie, M.P., Gheorghiu, C., Kara, Y., Smith, D.S.** (2010). The influence of NOM quality on metal-gill binding in fish exposed to metals and metal mixtures. SEB Annual Main Meeting, June/July 2010. Prague, Czech Republic.

- **Wood, C.M.** (2010). The two faces of DOC. First @ Ryan's Camp Metals Symposium, Death Valley, California.

- **Wood, C.M.** (2010). Regulation and toxicity of metals in aquatic ecosystems. Annual Meeting of the SEB, June/July 2010. Prague, Czech Republic.

- **Wood, C.M.** (2010). Effects of waterborne silver in a marine teleost, the gulf toadfish (*Opsanus beta*): Effects of feeding and chronic exposure on bioaccumulation and physiological responses. Canadian Society of Zoology, May 2010. Vancouver, British Columbia.

The following peer reviewed papers were published by the Metals Bioavailability Group (2010-2011):

- **Adams, W.J., Blust, R., Borgmann, U., Brix, K.V., Deforest, D.K., Green, A.S., Meyer, J., McGeer, J.C., Paquin, P., Rainbow, P.S., Wood, C.M.** (2011). Utility of tissue residues for predicting effects of metals on aquatic organisms. Integr. Env. Assess. Man. 7:77-98.

- **Al-Reasi, H.A., Wood, C.M., Smith, D.S.** (2011). Physicochemical and spectroscopic properties of natural organic matter (NOM) from various sources and implications for ameliorative effects on metal toxicity to aquatic biota. Aquat. Toxicol. 103:179-190.

- **Alsop, D., Wood, C.M.** (2011). Metal uptake and acute toxicity in zebrafish: common mechanisms across multiple metals. Aquat. Toxicol. 105:385-393.

- **Arnold, W.R., Diamond, R.L., Smith, D.S.** (2010). The effects of salinity, pH, and dissolved organic matter on acute copper toxicity to the rotifer, *Brachionus plicatilis* (L strain). Archives of Environ. Contam. Toxicol. 59:225–234.

- **Arnold, W.R., Diamond, R.L., Smith, D.S.** (2010). The acute and multi-generation chronic toxicity of copper to the rotifer, *Brachionus plicatilis* ("L" strain). Archives of Environ. Contam. Toxicol. 60:250–260.

- **Arnold, W.R., Cotsifas, J.S., DePalma, S.G.S., Smith, D.S.** (2010). A comparison of the copper sensitivity of *Mytilus galloprovincialis*, *Crassostrea virginica*, *Dendraster excentricus*, and *Strongylocentrotus purpuratus* in ambient saltwater of varying dissolved organic matter concentrations. Environ. Toxicol. Chem. 29:311–319.

- **Caron, F., Sharp-King, K., Siemann, S., Smith, D.S.** (2010). Fluorescence characterization of the natural organic matter (NOM) in deep ground waters at Chalk River, Ontario, Canada. J. Radioanal. Nucl. Chem. 286:699–705.

- **Caron, F., Smith, D.S.** (2010). Fluorescence analysis of natural organic matter fractionated by ultrafiltration: contrasting between urban-impacted water, and radio-contaminated water from a near-pristine site. Water, Air & Soil Pollution 214:471–490.

- **Clifford, M., McGeer, J.C.** (2010). Development of a biotic ligand model to predict the acute toxicity of cadmium to *Daphnia pulex*. Aquat. Toxicol. 98:1-7.

- **Craig, P.M., Wood, C.M., McClelland, G.B.** (2010). Water chemistry alters gene expression and physiological endpoints of chronic waterborne Cu exposure in zebrafish *Danio rerio*. Env. Sci. Technol. 44:2156-2162.

- **DePalma, S.G.S., Arnold, W.R., McGeer, J.C., Dixon, D.G., Smith, D.S.** (2011). Variability in dissolved organic matter fluorescence & reduced sulphur concentration in coastal marine & estuarine environments. Appl. Geochem. 26:394–404.

- **DePalma, S.G.S., Arnold, W.R., McGeer, J.C., Dixon, D.G., Smith, D.S.** (2011). Effects of dissolved organic

matter and reduced sulphur on copper bioavailablity in coastal marine Environments. Ecotoxicol. Env. Safety 74:230–237.

- **Diamond, M., Adams, W., Atherton, J., Bhavsar, S., Bulle, C., Campbell, P., Dubreuil, A., Fairbrother, A., Farley, K., Gandhi, N., Green, A., Guinee, J., Hauschild, M., Humbert, S., Jensen, K., Jolliet, O., Margni, M., McGeer, J.C., Peijnenburg, M., Rosenbaum, R., Van de Meent, D., Vijver. M.** (2010). The Clearwater Consensus: the estimation of metal hazard in fresh water. Int. J. Life Cycle Assess. 15:143-147.

- **Gheorghiu, C., Smith, D.S., Al-Reasi, H.A,, McGeer, J.C., Wilkie, M. P.** (2010). Influence of natural organic matter (NOM) quality on Cu-gill binding in the rainbow trout (*Oncorhynchus mykiss*). Aquat. Tox. 97:343–352.

- **Gillis, P.L., Mackie, G.L., McGeer, J.C., Wilkie M.P., Ackerman. J.D.** (2010). The effect of natural dissolved organic carbon on the acute toxicity of copper to larval freshwater mussels (*glochidia*) to acute copper exposure. Env. Toxicol. Chem. 29:2519-2528.

- **Green, W.W., Mirza, R.S., Wood, C.M., Pyle. G.G.** (2010). Copper binding dynamics and olfactory impairment in fathead minnows *Pimephales promelas*. Env. Sci. Technol. 44:1431-1437.

- **Klinck, J.S., Wood, C.M.** (2011). In vitro characterization of cadmium transport along the gastro-intestinal tract of freshwater rainbow trout (*Oncorhynchus mykiss*). Aquat. Toxicol. 102 : 58-72.

- **Leonard, E.M., Barcarolli, I., Silva, K.R., Wasielesky, W., Wood, C.M., Bianchini, A.** (2011). The effects of salinity on acute and chronic Ni toxicity and bioaccumulation in two euryhaline crustaceans: *Litopenaeus vannamei* and *Excirolana armata*. Comp. Biochem. Physiol. C. In Press.

- **Marentette, J.R., Gooderham, K.L., McMaster; M.E., Ng, T.Y.T., Parrot, J.L., Wilson, J.Y., Wood, C.M., Balshine, S.** (2010). Signatures of contamination in invasive round gobies (*Neogobius melanostomus*): A double strike for ecosystem health? Ecotox. Environ. Safety. 73: 1755-1764.

- **Martins, C.M., Barcarolli, I.F., Menezes, E.J., Giacomin, M.M., Wood, C.M., Bianchini, A.** (2011). Acute toxicity, accumulation and tissue distribution of copper in the blue crab *Callinectes sapidus* acclimated to different salinities: In vivo and in vitro studies. Aquat. Toxicol. 101:88-99.

- **McGeer, J.C., Ng T., Wood. C.M.** (2011). Using bioaccumulation models for predicting dissolved metal toxicity. pg 62-67. *in* Proceedings of the Environmental Effects Monitoring Investigation of Cause Workshop for Metal Mining. Dec 8-9, 2009. Gatineau.

- **Nadella, S.R., Hung, C.Y., Wood, C.M.** (2011). Mechanistic characterization of gastric copper transport in rainbow trout. J.Comp. Physiol. B. 181:27-41.

- **Ng, T.Y.T., Chowdhury, M.J., Wood, C.M.** (2010). Can the Biotic Ligand Model predict Cu toxicity across a range of pHs in softwater-acclimated rainbow trout? Env. Sci. Technol. 44: 6263-6268.

- **Ng, T.Y.T., Pais, N., Wood, C.M.** (2011). Mechanisms of waterborne Cu toxicity to the pond snail *Lymnaea stagnalis*: physiology and Cu bioavailability. Ecotoxicol. Environ. Safety. 74:1471-1479.

- **Ng, T.Y.T., Smith, D.S., Straus, A., McGeer. J.C.** (2011). Review of Aquatic Effects of Lanthanides & Other Uncommon Elements. Final Report for CNTC/Environment Canada Project. 42 pg. plus reference database.

- **Tellis M., Alsop, D., Wood, C.M.** (2011). Effects of copper on the acute cortisol response and associated physiology in rainbow trout. Comp. Biochem. Physiol. C. In Press.

- **Wood, C.M., Al-Reasi, H.A., Smith, D.S.** (2011). The two faces of DOC. Aquat. Toxicol. In Press.

- **Wood, C.M., Grosell, M., McDonald, D.M. Playle, R.C., Walsh, P.J.** (2010). Effects of waterborne silver in a

marine teleost, the gulf toadfish (*Opsanus beta*): Effects of feeding and chronic exposure on bioaccumulation and physiological responses. Aquat. Toxicol. 99: 138-148.

The following books and book chapters were published by the Metals Bioavailability Group (2010-2011):

- **Bury, N.R., Boyle. D., & Cooper, C.A.** (2011). Iron. In Fish Physiology, Vol. 31B: Homeostasis and Toxicology of Non-Essential Metals (C.M. Wood, A.P. Farrell & C.J. Brauner, editors). Academic Press, San Diego, pp. 201-251.

- **McGeer, J.C., Niyogi, S., & Smith, D.S.** (2011). Cadmium. In Fish Physiology, Vol. 31B: Homeostasis and Toxicology of Non-Essential Metals (C.M. Wood, A.P. Farrell & C.J. Brauner, editors). Academic Press, pp. 126–168.

- **McGeer, J.C., Clifford, M., Janssen C.R., & De Schamphelaere, K.A.C.** (2010). Modelling the toxicity of metals to aquatic biota using the biotic ligand approach. In Essential Reviews in Experimental Biology Vol. 2. Surface Chemistry, Bioavailability and Metal Homeostasis in Aquatic Organisms: an Integrated Approach (N.R. Bury, & R.D. Handy, editors). SEB Press. London UK, pp. 205-231.

- **McGeer, J.C., Smith, D.S., Brix K.V., & Adams, W.J.** (2011). The importance of metal speciation and its application in biotic ligand modelling to understand effects in aquatic biota. In Environmental Radioactivity and Ecotoxicology of Radioactive Substances, Vol XX of Encyclopedia of Sustainability Science and Technology (G. Bird, editor). Springer Science. *In Press*.

- **Wood, C.M.** (2011). An introduction to metals in fish physiology and toxicology: Basic principles. In Fish Physiology, Vol. 31A: Homeostasis and Toxicology of Essential Metals (C.M. Wood, A.P. Farrell & C.J. Brauner, editors). Academic Press, San Diego, pp. 1-51.

- **Wood, C.M.** (2011). Silver. In Fish Physiology, Vol. 31B: Homeostasis and Toxicology of Non-Essential Metals (C.M. Wood, A.P. Farrell & C.J. Brauner, editors). Academic Press, San Diego, pp. 1-65.

- **Wood, C.M., Farrell, A.P. & Brauner, C.J.** (2011). Homeostasis and Toxicology of Essential Metals. Fish Physiology Vol. 31A, Academic Press, San Diego. 497 p.

- **Wood, C.M., Farrell, A.P. & Brauner, C.J.** (2011). Homeostasis and Toxicology of Non-essential Metals. Fish Physiology Vol. 31B, Academic Press, San Diego. 507 p.

Research Highlights

This issue will highlight research conducted by Rachael Diamond who is a current M.Sc. student under the supervision of Scott Smith. This work is currently being written up for publication.

Characterizing Dissolved Organic Matter and Cu^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+} Binding in Seawater: Implications for Toxicity

Rachael L. Diamond[a], Sunita Nadella[b], Chris, M. Wood[b], D.Scott Smith[a]

[a] Wilfrid Laurier University, Department of Chemistry, Waterloo, Ontario, Canada
[b] McMaster University, Department of Biology, Hamilton, Ontario, Canada

Introduction

Trace amounts of metals are present as natural components of the environment and at low concentrations many metals are essential for life. Unfortunately, due to anthropogenic inputs, trace metal concentrations are increasing. This increase can result in potential toxicity to organisms and there is a need to monitor the levels and effects of these metals in aquatic systems. For freshwater systems the Biotic Ligand Model (BLM) has been successful in predicting metal toxicity as a function of water chemistry. The BLM has become an excellent tool for regulatory and risk assessment purposes. For saltwater systems, such as estuaries and ocean environments, BLMs have not been as extensively developed. A requirement for BLM development in salt water is an understanding of metal interactions (speciation) in saltwater environments.

Metal binding ligands can range from hydroxide, chloride and carbonate to complicated organic macromolecules of dissolved organic matter (DOM). DOM contains many potential binding sites for available metals in marine systems. Metals can bind to many functional groups present within NOM , with metal binding functional groups such as carboxyl (M-CO_2H), amino (M-NHR, [M-NH_2R]+, phenolic (M-OAr), metal sulfides or thiols (M-SH) (Smith et al., 2002).

Aquatic systems usually contain a mixture of terrigenous and autochthonous natural organic matter (McKnight et al. 2001). Terrigenous DOM is terrestrially derived and is comprised of organic matter from decomposition of plants (mostly lignin oxidation products), containing carboxylic and phenolic functional groups attached to aromatic rings. Autochthonous DOM is composed from the organic matter from microorganisms and bacteria and is generated within the water column, containing proteinaceous functional groups including amines. Sewage derived organic matter contains intermediate properties between terrigenous and autochthonous DOM.

The Biotic Ligand Model (BLM) has been adopted by the USEPA for prediction of metal toxicity for a number of dissolved metals in freshwaters. The BLM is based on equilibrium calculations of metal speciation and has a numerical scheme to predict toxic metal concentrations and establish site specific criteria for a given location depending on its water chemistry parameters (Santore et al., 2001). Although well developed for freshwater, there is a need for saltwater research for a marine BLM.

The purpose of this research is to characterize dissolved organic matter and its binding characteristics with divalent metal cations, Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2+} in marine systems using fluorescence spectroscopy and voltammetry. More specifically to: (i) Quantify binding capacity and logK values for Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2+} to different sources of

marine organic matter at environmentally relevant concentrations; (ii) test fluorescence quenching and voltammetric method for use in seawater conditions; (iii) compare predicted speciation parameters with toxicological observations in the same samples.

Results and Discussion

Fluorescence quenching has been used to determine equilibrium constants and binding capacity with freshwater DOM (Smith and Kramer, 2000). Previous research in our group applied this spectroscopic technique to determiner copper, lead, nickel and zinc binding with a freshwater reverse osmosis (RO) isolate, Luther Marsh (LM), in artificial seawater (Diamond et al., 2011). Equilibrium constants and binding capacities for the complexation of these metals and LM were obtained and showed promise for this technique in seawater applications. The next step was to compare predicted speciation parameters with observed toxicity data.

For this purpose, fluorescence quenching of lead was tested with Nordic Reservoir DOM in artificial seawater. The purpose here is to compare binding capacities determined for DOM with measured EC50 values. The lead toxicity tests show that the DOM displays protection for lead but an increase in DOM does not show greater protection. A dissolved organic carbon (DOC) concentration of 2 mg C/L provides an EC50 of 738 nM relative to a control EC50 of 304 nM, while a concentration of 12 mg C/L has an EC50 of 757 nM (see Table 1). The EC50 values demonstrate that the Nordic Reservoir DOM is protective but displays no dose dependence in its protectivity.

Fluorescence quenching results contradict the EC50 observations (Table 1). Binding capacity determined from fluorescence quenching shows an increase in the DOC results in an increased binding capacity for lead by a factor of five. This would suggest that there should be dose dependence observed in the EC50 values as well. In addition, the observed lead binding capacities are much lower than the increased binding suggested by the increase in EC50 values. There is a 400 nM increase in EC50 in the presence of DOC but only a 6 nM binding capacity predicted from fluorescence quenching for the same concentration of carbon.

Table 1: Binding Capacity for Nordic Reservoir organic matter concentrations of low and high DOC with comparison to EC50 values for *Mytilus galloprovincialis* and *Mytilus trossolus* in seawater. 95% confidence values indicated by ranges of values.

Sample[a]	EC50 (nmol/L) *Mytilus galloprovincialis*	EC50 (nmol/L) *Mytilus trossolus*	FQ Binding Capacity (nM)	Voltammetry Binding Capacity (nM)
0 mg C/L	304 (173-453)	217 (106-347)	---	---
2 mg C/L	738 (680-796)	564 (372-757)	6.35	320 (206 - 434)
12 mg C/L	758 (680-830)	521 (401-641)	32.3	347 (279-415)

[a] Samples were all prepared at full strength seawater salinity with Nordic Reservoir DOM as the carbon source. Nominal DOC values are listed. Low/high DOC measured values were 2.0/8.4 and 3.1/11.3 mg C/L for EC50 determinations for *M. galloprovincialis* and *M. trossolus* respectively.

Anodic stripping voltammetry (ASV) was used as an alternate method for determination of lead speciation. Electrochemically labile lead was measured using square wave anodic stripping voltammetry (SWASV) with a deposition potential of -0.65 V, a deposition time of 30 seconds, equilibration time of 5 seconds, voltage scanning (-0.65 to -0.25V), amplitude of 25 mV, frequency of 25 Hz, and a scan increment of 2mV. This corresponds to the method of Sánchez-Marín et al. (2011).

The resultant current measurements at the peak potential versus lead added result in the typical low slope initial data followed by steeper slope linear response at higher total lead. The small slope initial response occurs because the DOM is binding the available lead while the steeper slope arises when the binding capacity for the DOM is exceeded. The method assumes that only inorganic complexes and free lead are detected at the electrode (so-called ASV labile fraction) and strong organic matter complexes are not detected. Extrapolation of the linear data at high lead allows for estimation of the binding capacity as the x-intercept of the regression line.

The lead speciation results for the Nordic Reservoir organic matter in synthetic seawater agrees more closely than fluorescence results with the observed lead toxicity in the same system (Table 1 and Figure 1). Voltammetry demonstrates that an increased amount of DOC does not bind significantly more lead. The 2 mg C/L Nordic Reservoir had a binding capacity of 320 nM while the 12 mg C/L had a binding capacity of 347 nM. This represents a binding capacity increase of a factor of 1.1. This supports the EC50 data indicating similar EC50 values resulting from similar binding capacities. The lead binding capacity determined for NR organic matter more closely matches the increase in EC50 (Table 1 and Figure 1). Figure 1 shows the increase in EC50 for DOC exposed samples over exposures without added DOC. The increase in EC50 values very closely matches the DOM binding capacity determined by ASV. The data in Figure 1 is normalized to DOC. The EC50 and ASV binding capacities are almost independent of DOC; thus, the higher DOC exposures show lower bars in the plot. This pattern is not observed for the fluorescence quenching determined binding capacities. The constant bar height of these data represent a dose dependence in binding capacity with a near-constant capacity per mg of carbon.

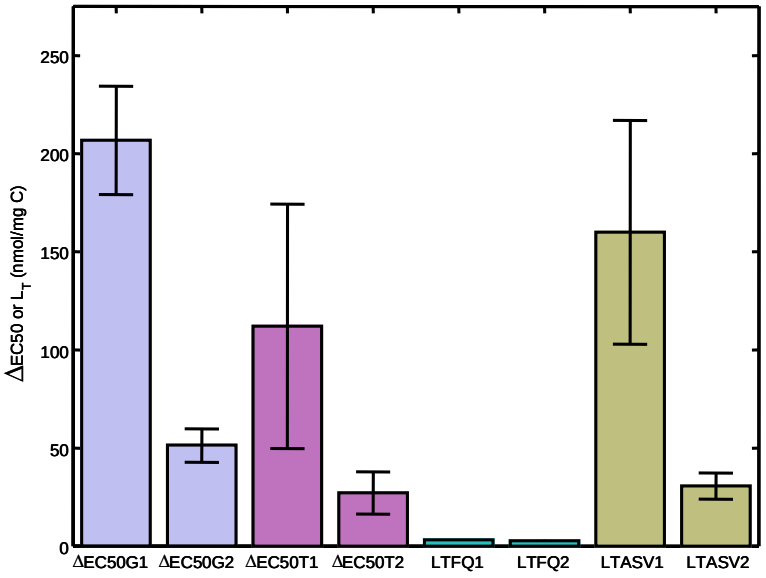


Figure 2: Increase in EC50 over DOC-free determinations and binding capacity values all normalized to DOC concentration. EC50 values for *M. galloprovincialis* at low (EC50G1) and high (EC50G2) DOC. EC50 values for *M. trossolus* at low (EC50T1) and high (EC50T2) DOC. Binding capacities determined by fluorescence quenching at low (LTFQ1) and high (LTFQ2) DOC values. Binding capacities determined by ASV at low (LTASV1) and high (LTASV2) DOC values. 95% confidence intervals are shown as error bars.

It is possible that the ionic strength effect of the seawater causes the lack of dose dependence of lead-DOM complexation and DOC protectivity. At low DOC concentrations, the ligand is free to interact with lead cations. As DOC concentrations are increased, DOC-DOC interactions predominate due to salting out effects and salt induced colloid formation

Thus, it seems for NR DOC in sea water the voltammetric method yields results more consistent with biological observations than fluorescence quenching. As a follow-up experiment, the fluorescence quenching method was tested in model systems where speciation can be calculated. Tryptophan (10 μM) was used as a model ligand in synthetic seawater, (seawater prepared according to OECD recommended recipe (OECD, 2001) and titrated with Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2+} (Figure 2). Fluorescence was measured at 275 nm excitation and emission range of 300 nm to 600nm. Fluorescence at each point in the titration is calculated by determining the speciation of the system using equilibrium constant values from NIST (Martell and Smith, 2001). With known calculated speciation the equation $F=k_{HTryp}[HTryp]$ can be used to calculated predicted fluorescence, where k_{HTryp} is a proportionality constant determined by the fluorescence response in the absence of metal (first data point).

Fluorescence quenching measurements for copper agree well with the theoretical model (Figure 2b). Lead, nickel and zinc data demonstrate excessive quenching compared to the predicted model. For the fluorescence quenching technique to work, the decrease in fluorescence is assumed to be a result of the formation of a less fluorescent metal-ligand complex (so-called static quenching). Alternatively fluorescence can be quenched by collisional deactivation in the excited state (so-called dynamic quenching). It appears that fluorescence quenching for lead, zinc and nickel is predominantly dynamic and thus the fluorescence quenching method, although it yields quenching curves, is not suitable for application in marine systems.

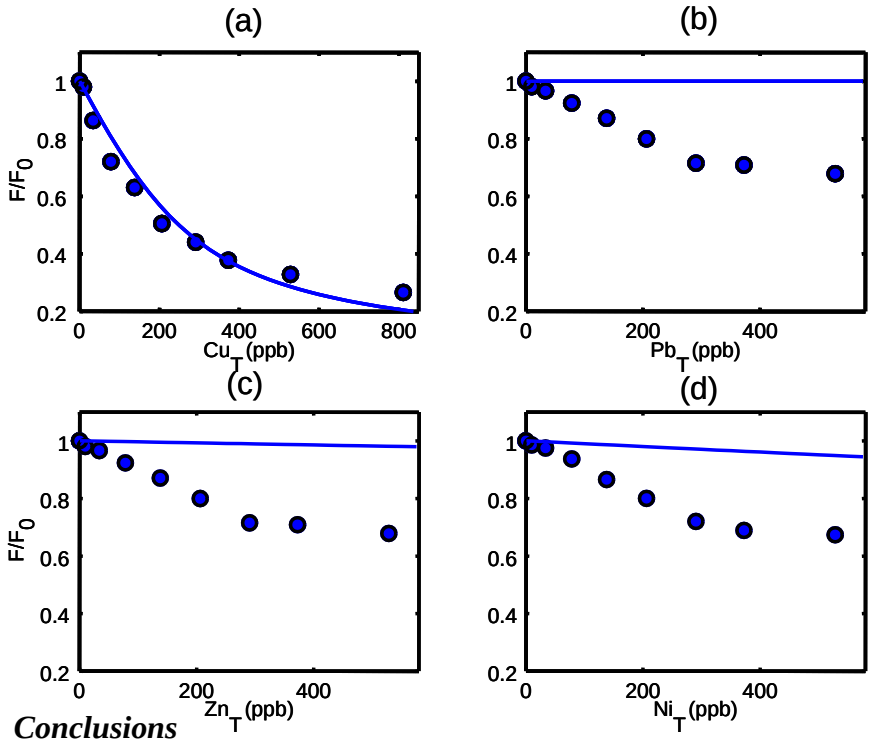


Figure 2: Model ligand tryptophan in synthetic seawater with metals (a) lead (b) copper (c) zinc (d) nickel. Data points are measured fluorescence quenching and lines are theoretical fluorescence quenching model based on NIST equilibrium constants and calculated speciation.

Conclusions

Lead speciation results for NR DOM determined by ASV qualitatively agree with the observed lead toxicity results. Both EC50 values and binding capacities show little variation when DOC is increased. Fluorescence quenching results do not agree with either EC50 or ASV results and in fact show an increased predicted binding capacity as DOC is increased.

Fluorescence quenching measurements for copper agree with predictions in a model system but lead, nickel and zinc display excessive quenching and disagreed with the theoretical model. Thus, fluorescence quenching seems to be a viable technique for copper speciation in marine systems but not for the other metal cations tested.

Acknowledgements

This research is supported by ILZRO, IZA, CDA, ICA, Tech Resources Inc., Vale Canada, Xstrata Zinc, NiPERA and NSERC.

References

Diamond, R. L., Tellis, M., Wood, C. M., and Smith, D. S. Fluorescence quenching method to determine copper, lead, zinc and nickel binding to organic matter in saltwater. Canadian Society of Chemistry, June 2011. Montreal, QC, Canada.

Martell, A., Smith, R., (2001). Critically selected stability constants of metal complexes, NIST Database 46 version 6. NIST, Gaithersburg, MD 20899.

McKnight, D.M., Boyer, E.W., Westeroff, P.K., Doran, P.T., Kulbe T., Anderson, D.T. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic materials and aromaticity. Limnol. Oceanogr. 46, 38-48. (2001).

Nadella, S.R., Fitzpatrick, J.L., Franklin, N., Bucking, C.P., Smith, S., Wood, C.M. Toxicity of dissolved Cu, Zn, Ni and Cu to developing embryos of the blue mussel (*mytilus trossolus*) and the protective effect of dissolved organic carbon. Comp. Biochem. Physiol. Part C. 149, 340-348. (2009).

OECD Environment, Health and Safety Publications Series on Testing and Assessment. No. 29 "Guidance Document on Transformation/Dissolution of Metals and Metal Compounds in Aqueous Media" ENV/JM/MONO(2001)9. April (2001).

Sanchez-Marin, P., Bellas, J., Mubiana, V.K., Lorenzo, J.I., Blust, R., Beiras, R. Pb Uptake by the marine mussel *Mytilus* sp. Interactions with dissolved organic matter. Aqua. Tox. 102. 48-57. (2011).

Santore, R.C., Di Toro, D.M., Paquin, P.R., Allen, H.E., Meyer, J.S. Biotic Ligand Model of the Acute Toxicity of Metals. 2. Application to Acute Copper Toxicity in Freshwater Fish and Daphnia. Environ. Toxic. And Chem. 20, 10, 2391-2402. (2001).

Smith, D.S., Bell, R.A., Kramer, J.R. Review: Metal Speciation in Natural Waters with Emphasis on Reduced Sulfur groups as Strong Binding Sites. Comparative Biochem.and Phys. Part C. 133, 65-74. (2002).

Smith, D.S., Kramer, J.R. Multisite Metal Binding to Fulvic Acid Determined Using Multiresponse Fluorescence. Anal. Chim. Acta. 416, 211–222. (2000).

Editor's Desk: This newsletter is distributed by the Metals Bioavailability Group, Wilfrid-Laurier and McMaster University. If you know of others who would enjoy this newsletter, or if you no longer wish to receive it yourself, please contact:

Chris Cooper, Department of Chemistry, Wilfrid-Laurier University, 75 University Ave. West, Waterloo, Ontario N2L 3C5, Canada. Tel.: 519-884-0710 ext. 2794; e-mail:ccooper@wlu.ca

An amoeba with a flashlight: *.

And one with a baker's hat on: !