Reminiscence of Forty Years of Environmental Chemistry

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Editor-in-Chief Comment Please take the time to read this interesting retrospective that highlights Dr. Vladimir Zitko's extensive career in the field of environmental chemistry. Note that nine of his papers referenced in this retrospective were published in BECT during the 1970s.

After working on blood anti-clotting substances from phospholipids in the R&D laboratories of Canada Packers Limited in Toronto in 1968, I accepted the position of a chemist at the Fisheries Research Board of Canada Biological Station in St. Andrews, New Brunswick. In water pollution research, the Station staff monitored copper and zinc concentrations in the Northwest Miramichi River and their effect on the movement of Atlantic salmon. I joined a team studying the movement of salmon through the estuary, started looking at dissolved organics and found pentachlorophenol in the effluent of a wood preserving plant (Zitko and Carson 1969a). In minor projects, the decomposition of thiosulfate was identified as the cause of a puzzling acidification of a New Brunswick river (Zitko and Carson 1969b), and lignosulfonates were found in the Mactaquac impoundment on the Saint John River (Zitko 1970a, b, c).

Then came four nondiscretionary projects. The 'red her-ring' episode in Placentia Bay, Newfoundland resulted in a study of the toxicity of yellow phosphorus to Atlantic herring (Zitko et al. 1970a, b). Yellow phosphorus is extremely lethal and causes subcutaneous bleeding, turning the herring red. A major residual oil spill in Chedabucto Bay prompted the development of a method to measure it in aquatic fauna (Zitko 1970a, b, c). The concentrations of the oil were around 100 µg/g. A concern about mercury in the

environment led to a survey of methyl mercury in aquatic fauna (Zitko et al. 1971). A widespread contamination was found. A method was devised for removal of methyl mercury from fish meal (Zitko 1971a, b). Forest spraying by fenitrothion provided an opportunity to test its effect on fish brain acetylcholine esterase (Zitko et al. 1970a, b). No significant effects were found.

Finally, I could start work of my own choice. Homogeneous solutions of PCBs were prepared by nonionic surfactants to determine the PCBs toxicity to juvenile salmon (Zitko 1970a, b, c). PCBs were not very acutely toxic and the surfactants did not prevent their accumulation in fish. The presence of PCBs was wide-spread in freshwater and marine fishes (Zitko 1971a, b). Unusually high concentrations of PCBs in hatchery-reared Atlantic salmon led to the discovery of 6.5% of the PCB preparation 'Aroclor 1254' in the antifouling paint of hatchery tanks (Zitko and Hutzinger 1972). Long-chain chlorinated paraffins (Zitko 1980a, b, c) replaced Aroclor 1254 in the paint. Their presence in reformulated paint was confirmed by dechlorination (Zitko 1974). They were less accumulated by fish, but further work had to wait for better instrumentation. In the meantime, all PCB congeners became available and a reference to individual congeners required consultation of long tables. A shorthand description was suggested (Zitko 1983), but is was not popular. Polychlorinated terphenyls (Zitko et al. 1972) were detected in herring gulls, but not in cormorants. Accordingly, it appeared that they may not be as widely spread in the environment as PCBs. Further work had to wait for better methods. Chloroalkylene 12, which, in addition to chlorine also contains isopropyl groups, was developed by the industry to soften the environmental effects of PCBs. It did (Zitko and Carson 1977), but has not become widely used. Further studies

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of organohalogen compounds of potential concern to fisheries included hexahlorobenzene and hexabromobenzene. The former was, but the latter was not accumulated by juvenile salmon (Zitko and Hutzinger 1976). Chlorinated diphenyl ethers (PDEs) behaviour was very similar to that of PCBs. The BDE congener profile in Atlantic herring was different from that in Baltic herring (Roots et al. 2009). Brominated toluenes were more persistent in fish than PDEs (Zitko and Carson 1977). Polybrominated biphenyls (PBBs) with six or fewer bromine atoms were taken up from water by the fish. All PBBs were taken up from food and some new less brominated congeners were found in the fish as well. (Zitko 1977). Mirex and Dechlorane 602 were taken up by salmon both from water and from food, while Dechloranes 603, 604 and Plus 25 only from food (Zitko 1980a, b, c).

With the advent of the mass spectrometer, nonachlor and chlordane were found in aquatic fauna (Zitko 1978). Interestingly, these were the only pesticides present at much higher concentrations in a 'sick' bluefin tuna. However, the tuna also contained components of toxaphene, not quantitated because of absence of standards (Zitko 1980a, b, c).

Additional work included a study of the release of heavy metals from sediments by nitrilotriacetic acid (Zitko and Carson 1972), of the effect of humic acid on the toxicity of copper and of season of the year on the toxicity of zinc to juvenile Atlantic salmon (Zitko et al. 1973; Zitko and Carson 1977), work on thallium (Zitko et al. 1975), on toxicity of pyrethroids to salmon (Zitko et al. 1977), and many other interesting projects, not mentioned here because of space limitations.

Little can be done about chemicals that are already in the environment, but one should avoid surprises by unexpected presence of potentially risky chemicals in various materials. One such surprise was nonylphenol, present as a component of the pesticide aminocarb used in forest spraying in New Brunswick. It is more toxic to juvenile Atlantic salmon than the pesticide (McLeese et al. 1980). Materials used in aquaculture require attention, Hexabromocyclododecane was found in expanded polystyrene beads from floats (Zitko 1993), 10,10'-oxybisphenoxarsine in plastic liners, decabromodiphenyl ether in fiberglass of fish tanks (Zitko 1999), and long chain alkyl phosphates in the plastic coating of lobster traps (Zitko 2001a). An unintentional formation of irritants by faulty plumbing and poor laboratory techniques was detected in a histological laboratory (Zitko 2001b).

For all these years, the Bulletin of Environmental Contamination and Toxicology was an excellent medium for sharing information. Unfortunately, environmental chemistry at the Biological Station attracted little attention in 'A Century of Maritime Science' (Hubbard et al. 2016).

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