Marcellus Shale Drilling and the Effects on Aquatic Life

Marcellus Shale drilling is of the hydraulic fracturing (hydrofracturing) type of drilling involving a gel like substance containing sand and a number of various chemicals. This gel like substance breaks down leaving the sand to hold open the fractured shale. This water, brine or "product water" is then removed and the gas extracted. This brine or product water contains not only the fracturing chemicals but also sodium, chloride, bromide, arsenic and barium. This water is disposed of in three major ways. First, the water is transported to municipal waste treatment plants, which are often not equipped to handle the amount of organic solids and heavy metals. Second the water is pumped into deeper formations below the shale, which are not aquifers. Although the EPA has determined that fracturing chemicals are injected directly into USDW's (aquifers).[i]. Third, the water is placed in open tanks to evaporate and the solids transported to waste systems for disposal.[ii]

> According to the Interstate Oil and Gas Compact Commission, 90 percent of oil and gas
> wells in the U.S. undergo fracturing to stimulate production.[1] Despite the widespread use of the practice, and the risks hydraulic fracturing poses to human health and safe drinking
> water supplies, the U.S. Environmental Protection Agency ("EPA") does not currently
> regulate the injection of fracturing fluids under the *Safe Drinking Water Act*. The oil and
> gas industry is the only industry in America that is allowed by EPA to inject hazardous
> materials –unchecked– directly into or adjacent to underground drinking water supplies.[iii]

With this background this literature review focuses on the most hazardous of chemicals used in hydraulic fracturing associated with Marcellus Shale gas drilling and the knowledge of how these chemicals can affect aquatic life. This search utilized major databases of research information from peer reviewed journals, books and dissertations. They are: PubMed, CINAL, OVID, AGRICOLA, EMBASE.com, Google Scholar, the website of the U.S. Environmental Protection Agency, and the website for the Agency for Toxic Substances Database Registry.. Initially these searches included terms associated with aquatic life and Marcellus shale drilling. These included: Ecology, Ecological, Ecotoxicology, Aquatic, Fish, Bird, Dafnia (water flea), Shrimp, and Marcrinvertebrates. Search terms used were ecotoxicology AND speciality chemicals OR aquatic OR Aquatic Life. Ecotoxicology AND Aquatic Life; Marcellus Shale Drilling AND Ecotoxicology AND Aquatic Life. There were no

studies associated with the above search terms in any of the databases presented previously

At this point, the search was expanded to include names of chemicals used in the fracturing process along with the search terms used above such as: specialty chemicals OR aquatic OR Aquatic Life. Many of the chemicals in the list of fracturing chemicals were not found at all in the literature related to toxicity and aquatic life, some were not found with the other search terms used simultaneously, and others were found with those terms but deemed irrelevant. What follow is the information found in the literature related to specific fracturing chemicals but with no application to Marcellus Shale drilling. This is due to the unknown concentration of each chemical that is used in the fracking fluid as well as resulting product water.

Important abbreviations to note are:

> LC50 - lethal concentration for 50% mortality
> EC50 - effective concentration for 50% mortality
> NOEC no observed effect concentration
> PAH - Polycyclic Aromatic Hydrocarbons which form a large group of organic compounds, characterized by the presence of two or more condensed aromatic/benzene rings

What follows is a report of literature related to the most hazardous of the fracturing chemicals used in Marcellus Shale drilling.

Linear alkylbenzene sulfonates (LAS) are a well-known group of surfactants that can be present in coastal marine waters (Christoffersen et al., 2003). Commercial LAS is a mixture of homologues, most of them with chain lengths of between 10 and 13 carbon atoms, to which a benzene ring with a sulfonate group is attached. Each of these homologues consists of a varying number of positional isomers depending on the position of the benzene ring (Leo´n et al., 2000). Coastal ecosystems receive large quantities of surfactants from urban wastewaters, which are discharged either treated or untreated, into receiving waters (Leo'n et al., 2002). Lamellar gill epithelia hypertrophied and swimming capacity were reduced when Rainbow Trout fry were chronically exposed (54 days) to 0.2 mg/l of LAS (CI) even though this was the NOEC. (Hofer and Bucher 1995).

5-chloro-2-methyl-4-isothiazolin-3-1 - There is negligible risk to aquatic life due to the chemicals rapid metabolism into less toxic products. (Williams and Jacobsen).

Benzene (PAH)

A number of PAHs are considered hazardous to aquatic organisms. (Connell and Miller 1981a; 1981 b: Miller and Connell 1980; Miller 1982). Polycyclic aromatic hydrocarbons

(PAHs) are nearly ubiquitous trace contaminants of freshwater and marine sediments worldwide. They are being recognized with increasing frequency as major contributors to the hazard to aquatic life of contaminated sediments, particularly near areas of intense human activity (Neff, et al, 2005; Neff 1979, 2002). Polycyclic aromatic hydrocarbons are composed of two or more fused benzene (aromatic) rings (Neff 1979) Because of hydrocarbons high stability they tend to be preserved in fish. (Grimmer 1983) In contrast to its homologues (toluene and xylenes) benzene is extremely resistant to biological oxidation and tends to accumulate in living organisms, thus being a very toxic cumulative poison (Henderson et al. 1989; Medinsky et al. 1989). It is important to note that there are clear differences between fish species in their response to PAHs (Aas et al., 2001; Eggens et al., 1996; Ploch et al., 1998). Results from one species can therefore not be directly extrapolated to another (Hylland 2006). Benzene is an emerging and less known contaminant which is believed to pose a new threat to our environment.

 Benzene has been found to be present in wild yellow eel in Belgium (Roose et al. 2003) (Akaishi et. al 2004). In addition, according to Birtwell *et al.* (1999), exposure to benzene, can result in decreasing chemosensory reception with probable consequences to homing, feeding behavior, and avoidance of predators (Babcock 1985). Nine months after an oil spill when natural waters contained neither benzene nor its derivatives at that time, benzene derivatives were identified in the fish, and also in sturgeon species (Huso dauricus, Acipenser schrenckii) and bivalves (Sinanodonta likharevi, Cristaria herculea) which were collected near the spill site. (Levshina et. al 2009)

Nitrobenzene compounds with an additional substituted group in the *p* position were extremely toxic to daphnia and carp (HungYen et. al 2002). Among the dinitro- and trinitrotoluenes and benzenes, toxicity tended to increase with the level of nitrogenation (Nipper et. al 2001).v Styrene is a catalytic product of Benzene and that the major types of environmental processes for Styrene's conversion include photo oxidation, volatilization, and biotransformation. The effect of styrene after chronic exposure has not been investigated for aquatic organisms or amphibians. However a few studies were mentioned that have studies other effects. Styrene and styrene oxide alter the development of sea urchin embryos. The toxicity (24-hr LC50 values) of styrene for rainbow trout (Oncorhynchus mykiss) and the marine sheep head minnow (Cypronodon variegatus) were determined to be 2.5 mg/L and 9.1 mg/L respectively. Five other species of fish have also been studied to obtain 24- to 96-hr LC50 values. They include goldfish (Carassius auratus) at 25 mg/L and guppy (Poecilia reticulata) at 74.83 mg/L. For aquatic invertebrates the value where no effect was observed was less than 6.8 mg/L and the value for 48-hr LC50 was 23 mg/L for daphnids. When the amphipod (Pontoporeia affinis) was exposed to styrene at concentrations from 35 to 45 mg/L, swimming stopped and lasted several days (Gibbs and Mulligan 1997). Aminophenol is said to be the metabolite of

nitrobenzene as well as other xenobiotics and that they caused death and DNA damage of Zebra fish depending on concentration used and life stage of the fish (Sun, et al 2004).

Inhibition of acetylcholinesterase (AChE) can result in death (Soliman *et al.* 1995). AChE effects, together with changes to the gill morphology, can cause several alterations in fish physiology and behavior, including locomotion, feeding, and defense (Silva *et al.* 1993).

Among the aromatic compounds detected in process water are several toxicants of concern including benzene, toluene, phenol, and PAHs. Some authors suggested that PAHs detected in river sediments and water may contribute to endocrine disruption, which is supported by numerous studies on the physiological effects of PAH exposure on fish in other regions (e.g., Lintelmann, et al. 2003). Other studies have reported evidence of PAH exposure among fish populations in demonstration ponds (van den Heuvel et al. 1999*a*), and cited PAHs as potential stressors causing increased mortality and malformations in fish (Colavecchia, et al. 2004).

Boric Acid

There are concern about the effects of elevated concentrations of boron due to phytotoxicity, reproductive effects, and growth effects which have been observed in laboratory studies (Howe 1998; IPCS 1998) Boric acid and borates form very stable complexes with organic chemicals such as *a*-hydroxy carboxylic acids, potentially reducing the bioavailability of boron (Black et al. 1993) and indicating the possibility of decreased bioavailability and toxicity. Chronic studies with freshwater fish have generally reported no observed effect concentrations (NOECs) in the range of 1–25 mg B/L (Birge and Black 1977; Black et al. 1993; Butterwick et al. 1989). (Hamilton 1995) The most sensitive species and life stage in laboratory tests was determined to be embryo–larval rainbow trout, with a lowest observed effect concentration (LOEC) of 0.1 mg B/L (Birge and Black 1977). Subsequent studies conducted by these same researchers (Black et al. 1993) suggested that rainbow trout chronic toxicity might be reduced in natural waters; effect concentrations were reported between 0.75 and 1.0 mg B/L. Field observations have suggested that even this value might be conservative, given that healthy trout populations have been observed in waterways with B concentrations equaling or exceeding 1.0 mg/L (Goldstein et al. 2001; Howe 1998; Loewengart 2001). Laboratory studies on a limited number of freshwater invertebrates have reported NOECs in the range of 6–18 mg B/L (Gersich 1984; Gersich and Milazzo 1990; Hickey 1989; Howe 1998; Lewis and Valentine 1981; Maier and Knight 1991).

A study of boron and molybdenum show that they are relatively non-toxic (96-hr LC50s > 100 mg/L) to both life stages of both species Chinook and Coho Salmon. Only the swim-up fry of coho salmon were more sensitive than Chinook salmon to boron. (Hamilton and Buhl

1990) Comparison of 96-hr LC50 values with a Utah Creek, which receives irrigation drain water, revealed moderate hazard ratios for boron. (Table) (Hamilton 1995)

Acute 48-h median lethal concentrations (LC50) for the water flea, Daphnia magna, were 130 mg B/L as was a 24-h median effective concentration (EC50) for Ceriodaphnia dubia, which is often more sensitive than D. magna (Gersich 1984; Hickey 1989; Lewis and Valentine 1981; Maier and Knight 1991).

The 48- h LC50 for Chironomus decorus was much greater, 1376 mg B/L (Maier and Knight 1991). Representative species of other aquatic organisms, including plants and amphibians, usually tolerate chronic exposure of up to 10 mg B/L without adverse effects (Eisler 1990).

The rank order of 9 individual inorganics, from most to least toxic, ranked boron second least toxic. Comparison of 96-h LC50 values with reported environmental water concentrations from the San Juan River revealed low hazard ratios for boron. (Hamilton and Buhl, 1997) table

Representative species of aquatic organisms, including plants, invertebrates, fishes, and amphibians, usually tolerated up to 10 mg B/L of medium for extended periods without harm (Eisler 1990) Table. Data are limited for aquatic invertebrates and boron, although those data available suggest that the NOELs were 13.6 mg B/L for freshwater organisms and 37 mg B/L for marine biota (Table 7). (Eisler 1990)

DBNPA (2,2-Dibromo-3-nitrilopropionamide)

Table (Edwards 1996) Biocides can consist of highly toxic organic compounds, such as thiocyanates, isothiazolins, cyanobutane, dithiocarbamate and bromo compounds (Latorre et. al 2005).

Diesel

Diesel represents acute toxic risk at the time of spill to fish and a sub acute hazard of a gradual mortality from anoxia, increased susceptibility to disease, and possibly endocrine disruption (Mos, et al 2008). Diesel fuels, home heating oils, and engine oils (crankcase oil; middle distillate fuels) may contain aromatic hydrocarbons from benzene through fluoranthene (four aromatic rings). Embryonic and larval stages of salmon and herring demonstrated both exposure and chronic toxicity in situ. The coincidence of spawning and oil deposition in spawning shoals resulted in CYP1A induction, blue sac disease of larvae, and recruitment failure, and effects were associated with exposure to the polycyclic aromatic hydrocarbon (PAH) fractions (Carls et al., 1999) (Schein et. al 2009). Petroleum hydrocarbon exposure relationship to hemolysis and/ or hemorrhage (Alkindi et al., 1996),

Gill and liver damage due to lesions (Simonato et. al 2008; Martinez et al., 2004; Khan 1998, 2003; Engelhardt et al., 1981; Myers et al., 1998) possibly leading to loss of homeostasis maintenance (Simonato et. al 2008). Acute exposure of P. lineatus to Diesel Water Soluble Fraction (DWSF) caused significant physiological stress. (Simonato, et. al 2006; Machala et al. 1997). Due to metabolism, tissue residues are generally low, but metabolites can be found in bile (Aas, 2000). A causality was indicated between exposure to petrogenic PAHs (from sediment) and (1) increased content of bile metabolites, (2) induced hepatic cytochrome P-4501A, (3) elevated concentrations of DNA adducts in liver, and (4) increased prevalence of neoplasia (cancer) in liver (Collier et al., 1992a, 1995, 1998; Johnson et al., 1998, 1999; Landahl et al., 1997; Myers et al., 1994, 1998a, 1998b; Stein et al., 1992).

Because PAHs tend to accumulate in sediments, benthic organisms may be continuously exposed to the contaminants. However, sediment-sorbed PAHs have only limited bioavailability to marine organisms, which greatly reduces their potential toxicity. (Salazar-Coria et. al 2007) reduction in plasma cortisol concentrations (Alkindi et al., 1996; Pacheco and Santos, 2001a, b), suggesting that the water-soluble fraction of petroleum derivatives might interfere in the fish stress response. (Simonato et. al 2008)

Dichlorodiphenyltrichloroethane (DDT)

These are chemicals with a long half-life values and a high solubility in lipids (fats, oils, or waxes) will tend to accumulate in fatty tissue. Such lipophilic chemicals easily move into cells and are sequestered in fat, where they become more persistent (Kasozi et. al 2006).

DDT and its metabolites (DDE/DDD) have demasculinizing effects in aquatic life (Foster et al. 2001b; Baatrup and Junge 2001; Bayley et al. 2002; Feist et. al 2005).

Ethoxylated octylphenol

Potency studies suggest that concentrations greater than 1 µg/l of octylphenol (OP) in receiving waters pose a danger of Endocrine Disruption (Johnson and Jürgens 2003).

Ethylene Glycol (EG)

Glycols have been shown to be relatively low risk for aquatic toxicity (Kent et. al 1999). These compounds do not bioaccumulate in the tissues of biota and generally are rapidly biodegraded in aquatic ecosystems (Sills and Blakeslee, 1990; Verschueren, 1983; Budavari et al., 1989; Howard, 1990; ATSDR, 1993).

Ethylene glycol is miscible in water and insoluble in benzene, chlorinated hydrocarbons, and oils (Budavari et al., 1989; ENVIRO TIPS, 1985). Propylene glycol and diethylene glycol are relatively nonvolatile and are miscible in water and are slightly more soluble than

ethylene glycol in most other solvents (Kent et. al 1999). Fathead minnows exposed to ethylene glycol based deicing fluids showed that gills and renal tissues were affected (Hartwell et al.1995). Kidney damage to fish has been reported (tessellated darters Etheostoma Olmstedi) and American eels (Anguilla Rostrata). (Evans-David 1974) Invertebrates such as Ceriodaphnia dubia are slightly more sensitive (reproduction/survival) to chronic ethylene glycol exposure than fish (Beak Consultants, 1995a; Pillard, 1995). EG has been reported to be estrogenic in rainbow trout (Ren et al. 1996) Fathead minnow (Pimephales promelas) IC25 value 65.45 ml/L EG (Pillard 1995) A hatching failure of 60% & 48% has been reported for EG & PG respectively at 10ml/L concentrations and a 100% hatching failure in 100 ml/L has been reported for EG & PG (Bass 2003). Organisms which died during exposure period without hatching exhibited developmental abnormalities including failure of eye and fin development and necrosis of head and tail regions (Bass 2003). Calculated EC50 values for EG and PG were 9.33 and 26.42 ml/L respectively (Bass 2003). Estimated no effect values (ENEV's) 2ml/L for EG and 5 ml/L for PG (Canadian Council of Ministers of the Environment 1999) Chronic LC50's for adult fish 28.7 to 44.9 ml/L for EG and <11.1 to 49.2 ml/L for PG. (Arco 1990; Pillard 1995)

2-Ethylhexanol

2-Theylhexanol is relatively hydrophobic and thus likely to partition into the sediments (Horn et. al 2004).

Ferrous sulfate Hepathydrate

Only one part of this chemical has been studied which is Fenton reagents, which are ferrous sulfates plus hydrogen peroxide. Fenton reagent induced oxidative stress and significantly reduced total glutathione (GSHT) on PLHC-1 (fish) cells. (Rau et. al 2004) Oxidative stress occurs when radical production exceeds the antioxidant capacity of a cell (Kohen and Nyska, 2002)

Formaldehyde

Formaldehyde treatment produces massive destruction of microalgae (Chiayvareesajja and Boyd 1993; Burridge et al. 1995) Cultures initially collapsed after exposure to 16 parts per million (ppm) formaldehyde. Microalgae tolerance to contaminated environments is relevant because these organisms are the principal primary producers of aquatic ecosystems (Lopez-Rodas et. al 2008). Owing to its solubility in water, formaldehyde can be absorbed via skin and gill – preferential targets for noxious agents in aquatic organisms-promoting local and systemic effects (WHO/Environmental Health, 1986). Significant morphological changes of skin and gill filamental epithelium have been reported when exhibiting a dose response pattern of exposure to formaldehyde. (Bueno-Guimaraes et. al 2001).

Glutaraldehyde (GA)

This is an important biocide. Glutaraldehyde is acutely toxic to aquatic organisms and is equally toxic to warm water and cold water fish, but is slightly more toxic to freshwater fish than salt water fish. The toxicity of GA is not appreciably increased with repeated long-term exposures. Results from environmental partitioning studies indicate that GA tends to remain in the aquatic compartment and has little tendency to bioaccumulate. Glutaraldehyde is readily biodegradable in the freshwater environment and has the potential to biodegrade in the marine environment. Reproduction inhibition of Daphnia magna at 4.25 mg/L of GA concentration has also been reported.(CCR, 1990).

Acute Toxicity of Glutaraldehyde to Freshwater Species

	Exposure condition	Guideline	LC_{50}[a,b]	NOEC[a]	Reference
Coho salmon (*Oncorhynchus kisutch*)	96 h flowthrough	—	3	—	SFU, 1993
Water flea (*Daphnia magna*)	48 h static	—	5	—	UCC, 1981a
Fathead minnow (*Pimephales promelas*)	96 h satic	—	5.4	2.6	UCC, 1996
Fathead minnow (*Pimephales promelas*)	96 h satic	ASTM	6	4	SLI, 1989
Bluegill sunfish (*Lepomis macrochirus*)	96 h static	—	9.4	2.5	UCC, 1977a
Bluegill sunfish (*Lepomis macrochirus*)	96 h static	—	11	5	UCC, 1978c
Rainbow trout (*Salmo gairdneri*)	96 h static	—	11	8	UCC, 1977b
Rainbow trout (*Salmo gairdneri*)	96 h static	—	12	9	UCC, 1978b

[a]In milligrams of active ingredient (glutaraldehyde) per liter.
[b]The median, arithmetic mean, and geometric mean are 7.7, 7.9, and 7.1 mg/L, respectively.

Acute Toxicity of Glutaraldehyde to Marine/Estuarine Species

	Exposure condition	Guideline	LC_{50}[a,b]	NOEC[a]	Reference
Calanoid copepod (*Acartia tonsa*)	48 h static	ISO TC147	0.11	0.029	SPL, 1997b
Mussel (*Mytilus edulis*)	5 days flowthrough	—	0.2[c]	—	SINTEF, 1991
Eastern oyster (*Crassostrea virginica*)	48 h static	—	0.55	—	UCC, 1975
Eastern oyster (*Crassostrea virginica*)	96 h flowthrough	FIFRA 72-3	0.78	0.16	SLI, 1993c
Mysid shrimp (*Mysidopsis bahia*)	96 h flowthrough	FIFRA 72-3	7.1	0.78	SLI, 1993b
Acorn barnacle (*Balanus improvisus*)	10 days static	—	7.5[c]	—	SINTEF, 1991
Sheepshead minnow (*Cyprinodon variegatus*)	96 h static	FIFRA 72-3	32	24	SLI, 1993a
Grass shrimp (*Palaemonetes vulgaris*)	96 h static	—	41	—	UCC, 1975
Green crab (*Carinus maenas*)	96 h static	—	465	—	UCC, 1975

[a]In milligrams of active ingredient (glutaraldehyde) per liter.
[b]The median, arithmetic mean, and geometric mean are 7.1, 61.6, and 4.1 mg/L, respectively.
[c]EC_{50} (growth rate).

The ability of Glutaraldehyde to inhibit the growth of aquatic organisms was studied in two species of freshwater alga.

Algal Growth Inhibition Studies with Glutaraldehyde

Alga	Guideline	Exposure (days)	EC$_{50}$ (mg a.i./L) Growth rate[a]	EC$_{50}$ (mg a.i./L) Biomass[b]	NOEC (mg/L)	Reference
Freshwater						
Scenedesmus subspicatus	OECD 201	4	—	0.97	0.31	RCC, 1990b
Selenastrum capricornutum	OECD 201	5	—	0.81	0.50	WIL, 1997
Marine						
Skeletonema costatum	—	3	0.17	—	—	SINTEF, 1991
Skeletonema costatum	ISO 10253	3	0.92	0.61	0.33	SPL, 1997c

[a]Growth rate was calculated from the linear portion of the growth curve.
[b]Biomass growth was calculated from the area under the growth curve.

Glutaraldehyde was tested in an early life-stage toxicity study with the fathead minnow (*Pimephales promelas*) see Table (WIL, 1999) (Boillot and Perrodin 2008) GA is acutely toxic to aquatic organisms at low doses (Table 1). Its toxicity does not increase appreciably with repeated long-term exposure (Leung, 2001) though data relating to the ecotoxicity of GA are rare (Leung, 2001; Sano et al., 2005).

Ecotoxicological data of GA

Species		Exposition	Effect (mg/l)	References
Alga	*Scenedesmus subcapitatus*	Growth inhibition 96h	EC50 = 1	NICNAS (1994)
Water flea	*Daphnia magna*	Acute toxicity 48h	LC50 = 16.3	NICNAS (1994)
Water flea	*Daphnia magna*	Reproduction effect 21 days	LOEC = 4.3	NICNAS (1994)
Water flea	*Ceriodaphnia dubia*	Acute toxicity 48h	LC50 = 4.7	Sano et al. (2005)
Water flea	*Ceriodaphnia dubia*	Reproduction effect 7 days	LOEC = 4.9	Sano et al. (2005)
Oligochaete	*Lumbriculus variegatus*	Acute toxicity 24h	LC50 = 11.1	Sano et al. (2003)
Amphipod	*Hyalella azteca*	Acute toxicity 24h	LC50 = 289	Sano et al. (2003)
Rainbow trout	*Oncorhynchus mykiss*	96h static	LC50 = 11	Leung (2001)
Coho salmon	*Oncorhynchus kisutch*	96h flowthrough	LC50 = 3	Leung (2001)
Bluegill sunfish	*Lepomis macrochirus*	96h static	LC50 = 11	Leung (2001)

Methanol

Fish liver and gill damage have been reported with exposure to methanol (Katsumiti et. al 2009).

Methyl-4-isothiazolin

Isothiazolins are biocides with a broad spectrum antimicrobial used in a variety of industrial water treatment applications. In aquatic environments, these compounds rapidly biodegrade with half-lives significantly less than 24 hours. Like most biocides however these compound show a significant degree of toxicity to non-target aquatic organisms; however, their rapid metabolism results in compounds which are 4-5 orders of magnitude lower in toxicity. Both isothiazolins (methylchloro/methylisothiazolone (MCMI) and dichloro-n-octy lisothiazolone (DCOI) would be considered as acute but not chronic toxicants.(Williams and Jacobson 1993) Toxicity against non-target organisms was determined for freshwater algae, fish, and invertebrates and selected marine organisms. See Table (Shade et. al 1994)

Potassium Chloride or Potash

The toxicity of various dilutions of potash brine on Atlantic salmon (Salmo salar L.) eyed eggs, newly hatched alevins and newly feeding has been investigated and the influence of various dilutions on water hardening of salmon eggs and on early blastodisc formation. (Peterson et. al 1988). These brines consist primarily of the chlorides of potassium, sodium and calcium. Potassium chloride is the most toxic of these salts with threshold toxicities ranging from

750 mg/L (I0 mM) for pickerel (Stizostedion v. vitreum) to 10,368 mg/L (141 mM) for whitefish (Coregonus sp.) fry (Edmister and Gray 1948). The corresponding values for NaCI or CaCI$_2$ were 3859-16,500 mg/L (66-282 mM) and 12,060-22,080 mg/L (110-200 mM), respectively. It has been determined that 96 h TLm's of KCI and NaCI to bluegills to be 2054 mg/L (28 mM), and ca. 12,946 mg/L (221 mM), respectively (Trama, 1954). Also, Dowden and Bennett (1965) reported the 25 h T1 m of KCI to the same species to be 5,500 mg/L (75 mH) (Vijayavel and Balasubramanian 2007) Interaction of potash and decis in the ecophysiology of a freshwater fish, Oreochromis mossambicus, was studied. It was found that 300, 550 and 700mg L_1 of potash were sublethal (LC0), median lethal (LC50), and toxic (LC100) to O. mossambicus for 96 h exposure, respectively.

Propargyl Alcohol

Propargyl Alcohol is a form of the acetylenic alcohols found in some commercial acid inhibitor formulations. These may contain Mannich products or quaternary amines formulated with acetylenic alcohols t9 such as propargyl alcohol, hexynol (1-hexyl-3-ol), or ethyloctynol (4-ethyl-1-octyn-3-ol). Although these materials can produce excellent corrosion inhibitor products, the most effective acetylenic alcohols are quite toxic to mammals (Table 5). The lower molecular weight acetylenic alcohols, such as propargyl alcohol and hexynol, are very toxic by skin adsorption. For these reasons, there is a growing necessity to produce corrosion inhibitors that are less toxic to mammals as well as to marine environments than the current formulations. The acetylenic alcohols found most acceptable have a terminal acetylenic group but do not provide acceptable corrosion inhibition with current inhibitor technology

[i] Lisa Sumi (April 2005). OUR DRINKING WATER AT RISK: What EPA and the Oil And Gas Industry Don't Want Us to Know About Hydraulic Fracturing, Oil and Gas Accountability Project.
iiii Kappel, D. J. S. a. W. M. (May 2009). Water Resources and Natural Gas Production from the Marcellus Shale. U. S. G. Survey
iiiOp.cit, (Sumi, 2005)