Chemical and Biological Hazards Posed by Drilling Exploratory Shale Gas Wells in Pennsylvania's Delaware River Basin

Report for the Delaware River Basin Commission Exploratory Well Hearing

to

Delaware Riverkeeper Network

and

Damascus Citizens for Sustainability

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Summary:

Over the last decade, operators in the natural gas industry have developed highly sophisticated methods and materials for the exploration and production of methane from black shale. In spite of the technological advances made to date, these activities carried out on <u>any</u> <u>scale</u> pose significant chemical and biological hazards to human health and ecosystem stability. In brief:

- The probability that shale gas well projects will impact local groundwater ranges from 4.0 to 5.7% over the short term, *i.e.* while the wells are in development.
- The probability that shale gas wells will degrade local water quality over the long term (50 years) exceeds 16%; a project scope of as few as ten wells practically guarantees long-term groundwater contamination.
- Some chemicals in ubiquitous use for shale gas well drilling constitute human health and environmental hazards even where they are extremely diluted. For example, the biocide DBNPA is lethal to Chesapeake Bay oysters at parts-per-trillion concentrations, below its chemical detection limit.
- Some constituents of flowback fluids from shale gas wells are hazardous to human health at extreme dilutions; potential exposure effects include tissue poisoning and cancer.
- The risks of exposing workers and neighbors to toxic chemicals and harmful bacteria are exacerbated by certain common practices in Pennsylvania, such as air-lubricated drilling and the use of impoundments for flowback fluids; these are not regarded as best practices from a national perspective.

Overall, proceeding with any shale gas projects in the Delaware River Basin by current practices is highly likely to degrade surface water and groundwater quality, to harm humans, and to negatively impact aquatic ecosystems.

Background:

Natural gas production from hydrocarbon-rich shale formations is probably the most rapidly developing trend in onshore oil and gas exploration and production today. "In some areas, this has included bringing drilling and production to regions of the country that have seen little or no activity in the past. New oil and gas developments bring changes to the environmental and socio-economic landscape, particularly in those areas where gas development is a new activity. With these changes have come questions about the nature of shale gas development, the potential environmental impacts, and the ability of the current regulatory structure to deal with this development." (1)

The major features of shale gas development, which distinguish it from conventional gas extraction activity, are the use of horizontal drilling and high-volume hydraulic fracturing. While these technologies certainly lead to well projects which are larger than traditional gas wells by fifty-fold or more, and enable energy development companies to pursue projects in places which historically weren't commercially viable (such as the Delaware River Basin), gas exploration and production have never been free of risk. Toxics Targeting, Inc., using data compiled by the New York State Department of Environmental Conservation (NYS DEC), brought to light 270 gas drilling-related contamination incidents which had occurred in New York State since 1979 (2). This value, compared with a total of 6,680 active gas wells (3), points to a serious incident rate of 4.0%. These were in addition to incidents which were not reported to the DEC, such as the "wildcat" operation by which the U.S. Gypsum Company of Batavia, NY contaminated its own water well while drilling for natural gas on company property (4).

Data from Colorado indicated that 1549 spill incidents related to natural gas extraction activities occurred in the period from January 2003 to March 2008; the Congressional Sportsmen's Foundation estimated that 20% of these (310) impacted groundwater (5). The New Mexico Oil Conservation Division recorded 705 groundwater-contaminating incidents caused between 1990 and 2005 by the oil and gas industry (6). And the Pennsylvania Land Trust reported 1610 DEP violations in the Commonwealth between January 2008 nd late August 2010, 1052 of them likely to impact the environment (7). Compared with totals of 25,716, 40,157 and 55,631 producing gas wells in Colorado, New Mexico and Pennsylvania, respectively (3), these data suggest that natural gas development in a region degrades groundwater quality at a rate of 1.2 to 1.9 incidents per 100 gas wells. However, not all producing gas wells pose equal risk; new construction accounts for most spills and other mishaps. Interpreted in the context of new gas (and only gas) wells, (18,554 in Pennsylvania for the period January 2008 through August 2010 – mostly non-Marcellus projects) (8), the data suggest that we may reasonably anticipate a violations rate of 8.7% (one citation for every 11 – 12 gas wells) and a groundwater contamination rate of 5.7% (one incident for every 17 – 18 wells).

Short-term collateral damage from gas well development is only part of this industry's hazard profile. In 1992, the US Environmental Protection Agency (EPA) estimated that of 1.2 million abandoned oil and gas wells in the U.S., 200,000 were leaking (9). This represents a 16.7% failure rate; one of every six abandoned wells is releasing its contents to the surrounding area, including the surface. A Canadian research team investigated the mechanisms for these failures, and determined that concrete shrinkage which leads to well casing fissures is essentially inevitable in a fifty-year time frame. They found that this cracking was especially severe at maximum depth, and exposure of steel casings to the hot (140 – 180 °F) brines there accelerated their breakdown, permitting subterranean gases and other fluids to re-pressurize the deteriorating wells (10). Wells in regions containing mobile geological faults (such as eastern Pennsylvania) are also subject to casing deformation and shear (11). Therefore, we may reasonably expect higher percentages of gas well casings to fail over time, especially longer than fifty years. The probability that a project scope of as few as ten gas wells will impact ground water within a century approaches 100%; ground water will be contaminated.

In view of the risks, summarized above, for gas wells to engender spills and leaks, a discussion of the chemicals involved with these projects is in order.

Drilling Additives:

Many chemical products are used in the development of a gas well. Some examples, along with their most common applications, are shown in **Table 1**. Individual additives are typically used in multiple stages of the drilling process ; most hydraulic fracturing additives are also used in drilling fluids (or "muds") (12). Two rare exceptions are bentonite and barium sulfate, which are used almost exclusively in drilling muds and packer slurries, and hemicellulase enzyme, used solely in post-fracturing fluids. Even the chemicals used for post-production purification may also be used as solvents in drilling muds.

The majority of chemical products used by the gas industry have not been fully tested for human or environmental toxicity (13, 14). Of those which have, a minority (*e.g.,* bentonite, guar gum, hemicellulase, citric acid, acetic acid, potassium carbonate, sodium chloride, limonene, polyethylene glycol and mineral oil) pose no significant hazards to humans or other organisms as utilized in gas extraction processes.

Table 1: Additive Functions in Shale Gas Extraction

Additive Type	Examples	Purpose	Used In
Friction Reducer	heavy naphtha, polymer microemulsion	lubricate drill head, penetrate fissures	drilling muds, fracturing fluids
Biocide	glutaraldehyde, DBNPA, dibromoacetonitrile	prevent biofilm formation	drilling muds, fracturing fluids
Scale Inhibitor	ethylene glycol, EDTA, citric acid	prevent scale buildup	drilling muds, fracturing fluids
Corrosion Inhibitor	propargyl alcohol, *N*,*N*-dimethylformamide	prevent corrosion of metal parts	drilling muds, fracturing fluids
Clay Stabilizer	tetramethylammonium chloride	prevent clay swelling	drilling muds, fracturing fluids
Gelling Agent	bentonite, guar gum, "gemini quat" amine	prevent slumping of solids	drilling muds, fracturing fluids
Conditioner	ammonium chloride, potassium carbonate, isopropyl alcohol	adjust pH, adjust additive solubility	drilling muds, fracturing fluids
Surfactant	2-butoxyethanol, ethoxylated octylphenol	promote fracture penetration	drilling fluids, fracturing fluids
Cross-Linker	sodium perborate, acetic anhydride	promote gelling	fracturing fluids
Breaker	hemicellulase, ammonium persulfate, quebracho	"breaks" gel to promote flow-back of fluid	post-fracturing fluids
Cleaner	hydrochloric acid	dissolve debris	stimulation fluid, pre-fracture fluid
Processor	ethylene glycol, propylene glycol	strip impurities from produced gas	post-production processing fluids

Several other additive chemicals, including ammonia, methanol, ethanol, 2-propanol, 1-butanol, thioglycolic acid, acetophenone, sodium perborate tetrahydrate, diammonium peroxydisulfate and hydrochloric acid, are moderately or acutely toxic to humans or aquatic organisms when encountered in concentrated forms (15 – 24), but as used by the natural gas industry, they end up greatly diluted, and so impose relatively modest hazards (13). More significant issues with these chemicals would be anticipated from storage sites, trucking accidents while they are being transported to remote well sites via rural roads, and stagingat well sites.

However, a few chemical products in widespread use, including in exploratory wells, pose significant hazards to humans or other organisms, because they remain dangerous even at concentrations near or below their chemical detection limits. These include the biocides glutaraldehyde, 2,2-dibromo-3-nitrilopropionamide (DBNPA) and 2,2-dibromoacetonitrile (DBAN), the corrosion inhibitor propargyl alcohol, the surfactant 2-butoxyethanol (2-BE), and lubricants containing heavy naphtha. (Note: CAS No. refers to a unique identifier assigned to every known substance by the Chemical Abstracts Service Registry.)

Glutaraldehyde:

Glutaraldehyde (CAS No. 111-30-8) is a biocide used widely in drilling and fracturing fluids. Along with its antimicrobial effects, it is a potent respiratory toxin effective at parts-per-billion (ppb) concentrations (24); a sensitizer in susceptible people, it has induced occupational asthma and/or contact dermatitis in workers exposed to it, and is a known mutagen (i.e., a substance that may induce or increase the frequency of genetic mutations) (25, 26). It is readily inhaled or absorbed through the skin. In the environment, algae, zooplankton and steelhead trout were found to be dramatically harmed by glutaraldehyde at very low (1 – 5 ppb) concentrations (27).

DBNPA:

2,2-Dibromo-3-nitrilopropionamide (DBNPA) (CAS No. 10222-01-2) is a biocide finding increasing use in drilling and fracturing fluids. It is a sensitizer, respiratory and skin toxin, and is especially corrosive to the eyes (28). In the environment, it is very toxic to a wide variety of freshwater, estuarine and marine organisms, where it induces developmental defects throughout the life cycle. In particular, it is lethal to "water fleas" (*Daphnia magna*), rainbow trout and mysid shrimp at low (40 to 50 ppb) concentrations, and is especially dangerous to Eastern oysters (29). Chesapeake Bay oysters are killed by extremely low (parts-per-trillion, ppt) concentrations of DBNPA, well below the limit at which this chemical can be detected.

DBAN:

Dibromoacetonitrile (DBAN) (CAS No. 3252-43-5) is a biocide often used in combination with DBNPA, from which it is a metabolic product (with the release of cyanide). Its human and environmental toxicity profiles are similar to that of DBNPA, except that DBAN is also carcinogenic (30). DBNPA and DBAN appear to work synergistically. In combination, the doses at which these biocides become toxic are significantly lower than when they are used separately. In other words, it takes much less of these chemicals to exert toxic effects when they are used together.

Propargyl Alcohol:

Propargyl alcohol (CAS No. 107-19-7) is a corrosion inhibitor that is very commonly used in gas well construction and completion. This chemical causes burns to tissues in skin, eyes, nose, mouth, esophagus and stomach; in humans it is selectively toxic to the liver and kidneys (31). Propargyl alcohol is a sensitizer in susceptible individuals, who may experience chronic effects months to years after exposure, including rare multi-organ failure (32). It is harmful to a variety of aquatic organisms, especially fathead minnows, which are killed by doses near 1 ppm (33).

2-BE:

2-Butoxyethanol (2-BE), also known as ethylene glycol monobutyl ether (EGBE) (CAS No. 111-76-2), is a surfactant used in many phases of gas exploration and extraction. It comprises a considerable percentage of Airfoam HD, which Newfield is using to drill some of the wells grandfathered by the SEDD (34). Easily absorbed through the skin, this chemical has long been known to be selectively toxic to red blood cells; it causes them to rupture, leading to hemorrhaging (35). More recently, the ability of EGBE at extremely low levels (ppt) to cause endocrine disruption, with effects on ovaries and adrenal glands, is emerging in the medical literature (36). This chemical is only moderately toxic to aquatic organisms, with harm to algae and test fish observed with doses over 500 ppm (35).

Heavy Naphtha:

Heavy naphtha (CAS No. 64741-68-0) refers to a mixture of petroleum products composed of, among other compounds, the aromatic molecules benzene, toluene, xylene, 1,2,4-trimethylbenzene and polycyclic aromatic hydrocarbons including naphthalene. It is used by the gas industry as a lubricant, especially in drilling muds. This material is hazardous to a host of microbes, plants and animals (37). Several of the mixture's components are known to cause or promote cancer. If released to soil or groundwater, several components are toxic to terrestrial and aquatic organisms, especially amphibians, in which it impedes air transport through the skin.

Flowback Fluids:

Irrespective of chemical additives used for drilling, Marcellus shale contains several toxic substances which can be mobilized by drilling. These include lead, arsenic, barium, chromium, uranium, radium, radon and benzene, along with high levels of sodium chloride (38). These components make flowback fluids hazardous without any added chemicals, and are often among the analytes most easily measured by potential waste fluid treatment plant operators (**Figure 1**).

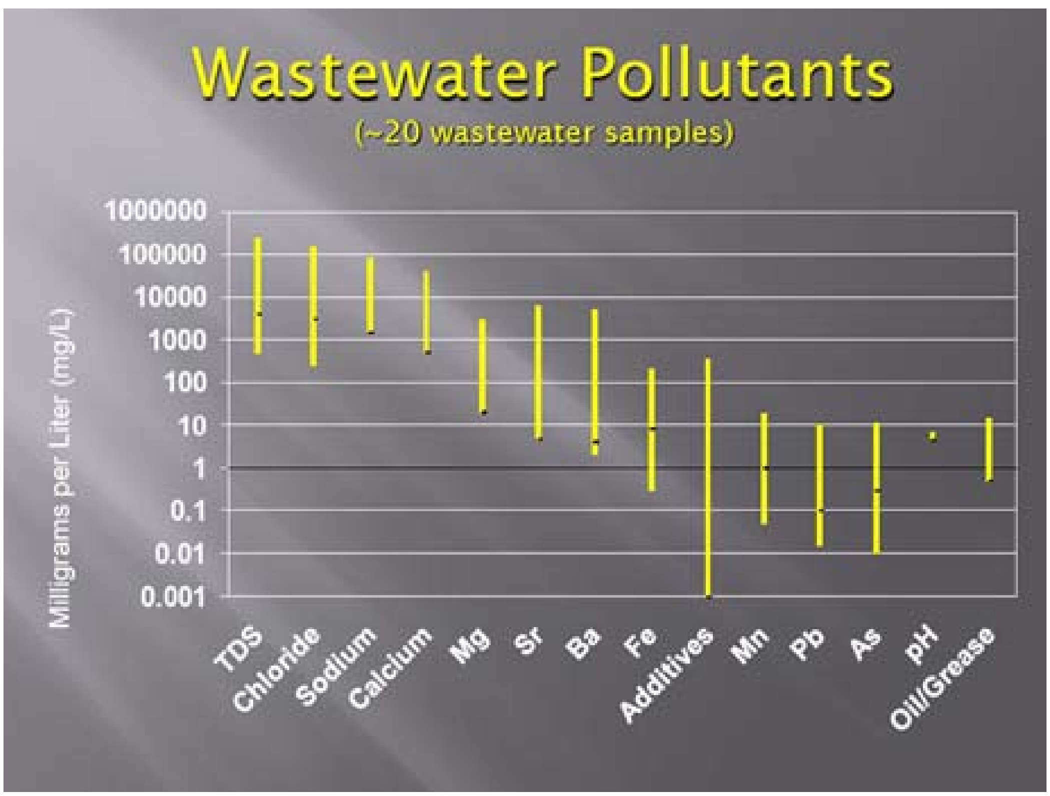

Figure 1: Wastewater Pollutants (39)

Because of their significant toxicity at low (ppb) concentrations, and the fact that drill cuttings are often not removed, but rather are buried on-site, several of these flowback fluid and cuttings components (40) are discussed below, including barium, lead, arsenic, chromium and benzene:

Barium (Ba):

Barium is a toxic heavy metal commonly found in Marcellus shale well flowback fluids (39). Exposure to soluble salts (not the sulfate), which may occur by ingestion, absorption or inhalation, may induce drops in tissue potassium levels, and by this mechanism it is selectively toxic to the heart and kidneys (41). Further, barite (barium sulfate), used as a weighting agent in drilling muds, reacts with radium salts in shale, forming radioactive scale on metal parts (such as the drill "string") which then are subsequently brought to the surface (13); in these reactions, barite is converted to more soluble (i.e. more toxic) barium salts.

Lead (Pb):

The poisonous nature of lead has been known for centuries, but its ability to impair neurological development in children at very low (1 ppb) concentrations makes it a toxicant of special concern. The most sensitive targets for lead toxicity are the developing nervous system, the blood and cardiovascular systems, and the kidney. However, due to the multiple modes of action of lead in biological systems, and its tendency to bio-accumulate, it could potentially affect any system or organs in the body. It has also been associated with high blood pressure (42).

Arsenic (As):

Arsenic, another component of black shale (38), has also been known as a poison for hundreds if not thousands of years. The most sensitive target tissue appears to be skin, but arsenic produces adverse effects in every tissue against which it has been tested, especially brain, heart, lung, the peripheral vascular system, and kidney (43). Arsenic is harmful below one part per trillion (ppt) in water, and is a confirmed carcinogen.

Chromium (Cr):

Chromium, also found in Marcellus shale (44), may be an essential nutrient required in extremely small doses (µg per day), but the biological system it supports is not currently known. Exposure to elevated doses by inhalation, ingestion, skin or eye contact may lead to respiratory, gastrointestinal, reproductive, developmental and neurological symptoms (45). Sensitization-induced asthma and allergy have also been reported. However, at very low concentrations, particularly of potassium dichromate or strontium chromate (the hexavalent form, as found in shale rock) (46), the major hazard posed by chromium is as a carcinogen, especially in stomach and lung tissues (45).

Benzene:

Benzene, a known shale constituent (38), was briefly considered above as a component of heavy naphtha. In ppb concentrations, the primary hazard from this compound is due to its proven ability to cause acute non-lymphocytic leukemia (47).

4-NQO:

In addition to the above shale constituents, one chemical compound was consistently encountered in flowback fluids from Marcellus gas wells in Pennsylvania and West Virginia: 4-nitroquinoline-1-oxide (4-NQO) (48). This is one of the most potent carcinogens known, particularly for inducing cancer of the mouth (49). It is not used as a drilling additive and is not known to occur naturally in black shale; no studies have been published to date with respect to what chemical interactions account for its consistent presence in flowback fluids. However, it is dangerous at parts-per-trillion (ppt) concentrations, well below its levels reported in gas well flowback fluids (48).

Biological Contamination:

Rock strata beneath the earth's surface are populated by bacteria, and the advent of air-lubricated drilling (without biocides) has introduced a risk of contaminatingsurface (fresh) water zones with bacteria and other microbes from deeper (brine) layers, where they often flourish. Of particular concern are sulfate-reducing bacteria, especially *Desulfovibrio desulfuricans*, an organism that thrives in fresh water where some sulfate (such as is present in pyrite or hematite) is available (50), (**Figure 2)** (51). In fact, these bacteria are especially prevalent and aggressive in oil and gas producing regions, where they avidly form living black, sticky films in water wells and other structures (52). There they produce hydrogen sulfide (H_2S), characterized by a "rotten eggs" smell. Rock strata rich in gas are often also rich in this bacterium, and exposure to hydrogen sulfide along with methane raises significant health concerns –neurological syndromes in humans and, in livestock, elevated birth defect rates and diminished herd health. At high concentrations, hydrogen sulfate is lethal (53).

The now-common use of air-lubrication (without biocides) while drilling the top one- to three thousand feet of gas wells (54) risks contaminating fresh water aquifers with sulfate-reducing bacteria from the deeper strata, but there is no clear evidence that this well-fouling mechanism is recognized by Pennsylvania DEP regulators.

Figure 2: Biofilm of *Desulfovibrio desulfuricans* Growing on a Hematite Surface

Cumulative Effects:

Hazards that accompany the above chemicals and microbes have to this point been considered individually. It is clear that they don't occur individually. No investigations of interactions among these materials have been reported to date. However, the author has been contacted by officials with the National Institute of Safety and Occupational Health, Centers for Disease Control (NIOSH/CDC), who requested any information that might shed light on a group of symptoms presented by clinical patients in southwestern Pennsylvania and the state of West Virginia which is tentatively identified as "downwinder's syndrome" (55). These symptoms, including irritated eyes, sore throat, frequent headaches and nosebleeds, skin rashes, peripheral neuropathy, lethargy, nausea, reduced appetite and mental confusion, were also reported in a Texas gas-field study conducted by Wilma Subra (56). These disparate observations are supported by a literature review of potential human health effects from gas drilling activities (57).

The practice in Pennsylvania of using open impoundments for capture of flowback fluids from gas wells may exacerbate the risk of this syndrome. Although most additives are greatly diluted in the drilling process, organic compounds (with the exceptions of DBNPA and DBAN) tend to be lighter than water; therefore they float to the surface of holding pits, where they concentrate to essentially 100% of the surface. From there they volatilize or aerosolize into the air, from which they may be inhaled by neighbors and on-site industry workers. Partly for this reason, the states of Colorado (58) and New Mexico (59) have prohibited the use of impoundments for flowback fluids.

As a case in point, at 7:00 AM on September 5, 2010, Greg Swartz and Tannis Kowalchuk, who live 0.3 miles from the Woodland Management Partners 11 exploratory gas well in Damascus Township, Wayne County, PA (developed by Newfield Appalachia PA, LLC), smelled a "chemical sulfuric odor". They put up with this odor for three days before the flowback fluids pit (evidently the source of the chemical smell) was pumped out and the odor subsided. Neither the fire department chief nor the DEP inspector indicated concern about the hydrogen sulfide being generated by bacteria living in the pit. However, Mr. Swartz and Ms. Kowalchuk were concerned, particularly for the health of their 2-year-old son (60).

The DEP inspection summary indicated that on September 2, three days prior to the sulfur odor complaint, workers were observed skimming an "oil sheen" from the pit fluids, and the odors detected then were typical of "drilling fluids and/or cuttings". On September 8, the hydrogen sulfide exposure grew worse for several hours, because the pit's contents were stirred as they were pumped out. Finally, the inspector noted that the sub-contractor planned to solidify the residual pit contents, fold them into the plastic liner and bury them in place (60).

Well permit data indicate that 2-butoxyethanol (2-BE) was used in the drilling fluids (61). Results from early ("tophole") analysis of the pit's contents (62) indicated the presence of high levels of barium, lead, arsenic and chromium (discussed above). No test for 4-nitroquinoline-1-oxide (4-NQO) was performed. However, a very high concentration of lithium (more than 600 times the reporting limit) was present. This is significant because lithium is psychoactive in humans at concentrations down to 1 part per billion (ppb) (63).

Therefore, the neighbors to this gas well were subjected to fumes from drilling fluids and cuttings, whether or not they identified those odors as nuisances. Then they were exposed to nuisance (and possibly greater) levels of hydrogen sulfide, which DEP reports to be common with gas drilling operations (60). Now, this family lives less than 600 yards from a buried repository of toxic solid waste, for which no long-term monitoring is planned (54). They were potentially exposed to chemicals known to cause disorders of the skin, eyes, mucous membranes, the gastrointestinal tract, kidneys, heart and brain. Threshold doses for some of these adverse health effects were realistically achievable, given the extreme potency of the agents involved. A slightly elevated risk of cancer for these people cannot be ruled out.

All this was the outcome of just one nearby "exploratory" gas well project where, from developers' and regulators' perspectives, nothing unusual happened.

If a spill, pit overflow, seepage from a defective plastic liner, or a tank leak had occurred, this family's exposures to noxious chemicals would have increased, possibly without their knowledge. Further, harm to sensitive environmental receptors, such as amphibians and aquatic organisms, would also have ensued. As discussed above, such incidents are unavoidable where any gas wells – including exploratory projects – are developed on a broad scale. When allowed to contaminate groundwater, the toxins and/or bacteria discussed above can persist at hazardous levels for years. Therefore, inevitable environmental damage extends to wherever gas well projects are developed, including the Delaware River Basin.

The opinions expressed in this report are stated to a reasonable degree of scientific and professional certainty.

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58. *Final Rule, Practice and Procedure* 2 CCR 404-1, *Eff. 09/30/2007;* Colorado Department of Natural Resources, Oil and Gas Conservation Comission.

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61. C*omponent of LE SUPERMUL, Appendix E;* DEP Permit No. 37-127-20017-00 to Newfield Appalachia PA, LLC (May 27,2010)

62. *Analytical Report, DRBC Well Smp, Wayne County PA;* Steve Moyer, Tetra Tech NUS, Inc., TestAmerica Laboratories, Inc. (August 18, 2010)

63. *Lithium Levels in Drinking Water and Risk of Suicide*; Hirochika Ohgami, Takeshi Terao, Ippei Shiotsuki, Nobuyoshi Ishii and Noboru Iwata (2009), British Journal of Psychiatry **194:** 464 – 465

Record of Pennsylvania Gas Industry Inspections, Violations and Enforcements

Exhibits for the Delaware River Basin Commission Exploratory Well Hearing

Ronald E. Bishop, Ph.D., CHO

To:

Delaware Riverkeeper Network

And

Damascus Citizens for Sustainability

Responding to Act 15, signed into law by Governor Rendell in March, 2010 (1), Pennsylvania's Department of Environmental Protection developed the DEP Oil and Gas Electronic Reporting website (2). Having obtained the records from that site, I am submitting a series of spreadsheets which summarize the Inspections, Violations and Enforcements related to natural gas extraction from (a) all target formations and (b) Marcellus shale. These official documents support a stance that gas industry operators in the Commonwealth have accumulated a poor safety record from 2008 to the present.

I summarize the official data in the following table:

Year	Formation	Inspections	Violations	Enforcements
2008	All	937	1447	662
	Marcellus	130	179	122
2009	All	1801	3159	693
	Marcellus	314	639	190
2010	All	1193	2193	590
	Marcellus	496	970	254
Total	All	3931	6799	1945
	Marcellus	940	1788	566

These records indicate that total violations and serious violations (enforcements) correlate well with the numbers of inspections, but Marcellus projects tend to generate violations and enforcements at rates that increase with the passing of time. Overall, out of 19,473 total new gas well projects reported in this period (3), these data indicate a serious (potentially groundwater-impacting) violations rate of 10%. Put another way, approximately one of every ten new gas well projects in Pennsylvania has run into serious trouble.

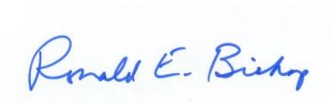
Footnotes:

1. DEP Oil & Gas Reporting Website – Welcome; http://www.marcellusreporting.state.pa.us/OGREReports/Modules/Welcome/Welcome.aspx

2. Oil & Gas Inspections - Violations – Enforcements, Division of Oil and Gas Management; http://www.dep.state.pa.us/dep/deputate/minres/oilgas/OGInspectionsViolations/OGInspviol.htm

3. 2010 Permit and Rig Activity Report, Division of Oil and Gas Management; http://www.dep.state.pa.us/dep/deputate/minres/oilgas/RIG10.htm

Respectfully submitted,



Dr. Ronald E. Bishop