“brine” - What is in it?

Dan Volz,PhD, excerpt below (*fractracker wastewater volz 3 11 11*) is discussing disposal into rivers, streams - and saying in this paper that eventual mixing does dilute the materials once mixed, but three factors are evident:
- there are plumes of high concentration in the waterbodies,
- there is bioaccumulation of TENORM, technically enhanced radioactivity,and other contaminants, in fish and other aquatic resources
- many of the contaminants have health consequences at low concentrations when humans ingest these materials disolved in their drinking water, especially over a period of time.

In the case of “brine” spreading on roads there is no dilution.

This below starts on page 12 of *fractracker wastewater volz 3 11 11*:

The Devil’s Details about Radioisotopes and Other Toxic Contaminants in Marcellus Shale Flowback Fluids and Their Appearance in Surface Water Sources and Threats to Recreationalists, Private Well Water Users, and Municipal Water Supplies
By, Conrad Dan Volz, DrPH, MPH

Appendix 1, Background Information

Hydraulic fracturing (HF) of shale gas deposits uses considerable masses of chemicals, for a variety of purposes to open and keep open pathways through which natural gas, oil and other production gases and liquids can flow to the well head. HF, also known as slick-water fracturing, introduces large volumes of amended water at high pressure into the gas bearing shale where it is in close contact with formation materials that are enriched in organic compounds, heavy metals and other elements, salts and radionuclides. Typically, about 1 million gallons and from 3-5 million gallons of amended water are needed to fracture a vertical well and horizontal well, respectively (Hayes, T; 2009, Vidic, R.; 2011). Fluids recovered from these wells can represent from 25% to 100% of the injected amended water solution (Vidic R., 2011) and are called “flowback” or “produced” water depending on the time period of their return.

Flowback and produced water contain high levels of total dissolved solids, chloride, heavy metals and elements as well as enriched levels of organic chemicals, bromide and radionuclides – in addition to the frac chemicals used to make the water slick-water. Levels of contaminants in flowback water generally increase with increasing time in contact with formation materials. There is abundant evidence that fluids recovered from this operation have high levels of total dissolved solids, barium and strontium, chlorides and bromides.

While there is at present considerable scientific inquiry and even controversy regarding the potential of vertical or horizontal fracturing of shale gas reservoirs to contaminate shallow or confined groundwater aquifers (thus exposing municipal or private well water users to chemicals used in the hydrofracturing process and/or toxic elements, organic compounds, and **radionuclides** that exist in the formation materials); disposal of oil and gas wastewater/ Marcellus shale brine water in sewage treatment plants or inefficient brine wastewater treatment facilities is a direct exposure threat to public health through ingestion, inhalation and dermal (skin) absorption exposure pathways.

ALSO http://www.nytimes.com/2011/02/27/us/27gas.html?pagewanted=all&_r=0

look in this section **Overwhelmed, Underprepared**

BELOW FROM Volz's Senate Congressional hearing Testimony http://www.epw.senate.gov/public/index.cfm/hearings?Id=270378F4-802A-23AD-4D07-C6B1FD44510B&Statement_id=A74A298A-85A2-4431-A75C-482061876FF5

The third problem public health and environmental policy area to be addressed is the disposal of gas extraction flowback fluids, carrying a plethora of toxic elements and chemicals, in inefficient "brine" treatment facilities and Publicly Owned Treatment Works (POTW's) [commonly called sewage treatment plants], which discharge effluent into surface water sources. Studies of the effluent from a commercial facility in Pennsylvania that treats fluids only from gas and oil operations shows discharge of 9 pollutants in excess of nationally recognized human and/or aquatic health standards into a nearby stream. The contaminants include:

- **Barium**, found in effluent over 8 times its minimum risk level (MRL) in drinking water to children and 27 times its EPA consumption concentrations for fish and "fish plus water".

- Stable **Strontium**, found in effluent 43.29, 51.68 and 97.90 times the drinking water MRL's for intermediate exposures for adult men, adult women, and children, respectively. Strontium levels found in effluent were 29,811 times the reporting limit in the plants NPDES permit.

- **Bromide**, which forms mixed chloro-bromo byproducts in water treatment facilities that have been linked to cancer and other health problems were found in effluent at 10,688 times the levels generally found acceptable as a background in surface water.

- **Benzene**, a known carcinogen, is present in effluent water at over 2 times its drinking water standard, over 6 times its EPA consumption criteria, and 1.5 times the drinking water MRL for chronic exposure for children.

- **2-butoxyethanol (2-BE)**, a glycol ether and used as an antifoaming and anti- corrosion agent in slick-water formulations for Marcellus Shale gas extraction was found in effluent water at 24.48, 29.21, and 55.14 times the drinking water MRL's for intermediate exposure to adult males, adult females, and children, respectively –based on hepatic health effects.

- **Chlorides**, the concentration of chlorides in the effluent was 138 and 511 times the EPA maximum and continuous concentration criteria set for the health of aquatic organisms, respectively.
  Due to time constraints I will not cover impacts to air quality, although I wish to go on record that these impacts could be significant, due to release of hazardous air pollutants from 10's of thousands of projected natural gas wells, with the subsequent formation of ozone; areas of Maryland, Pennsylvania, Ohio, New York, and New Jersey are already in EPA nonattainment status for ozone exposure.

- [additional] chemicals including **antimony, radium, radionuclides**, **phenols** and derivatives, polynuclear aromatic hydrocarbons (PAH's), phthalates, and total petroleum hydrocarbons.

FROM Ron Bishop, PhD, Risk Assessment of Natural Gas Extraction

Flowback Fluids: pages 14 and on [he also means 'produced water' or "brine"]
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 very high levels of sodium chloride (83). 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 operator.

Because of to 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 (83) are discussed below: barium, lead, arsenic, chromium, benzene and technologically enhanced naturally occurring radioactive materials.

Barium (Ba):
Barium is a toxic heavy metal commonly found in Marcellus shale well flowback fluids (85). 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 (86). Further, barite (barium sulfate), used as a weighting agent in drilling muds, reacts with radium salts in shale, forming radioactive scale on metal parts which then are subsequently brought to the surface (57); 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 (87).

Arsenic (As):
Arsenic, another component of black shale (83), 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 (88). Arsenic is harmful below one part per trillion (ppt) in water, and is a confirmed carcinogen.

Chromium (Cr):
Chromium, also found in Marcellus shale (89), may be an essential nutrient required in extremely small known. Exposure to elevated doses by inhalation, ingestion, skin or eye contact may lead to respiratory, gastrointestinal, reproductive, developmental and neurological symptoms (90). 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) (91), the major hazard posed by chromium is as a carcinogen, especially in stomach and lung tissues (90).

Benzene:
Benzene, a known shale constituent (83), 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 (92).

Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM): oil and gas production have been shown to mobilize naturally occurring radioactive materials, including uranium- 238, radium-226 and radon-222 (93). This has been identified as one of the greatest challenges facing the American gas industry today (94). Of these, radon is of special concern because as a gas it is extremely mobile, and it is intensely radioactive (94). Exposure by inhalation or ingestion typically results in migration to the lungs, which are susceptible to damage from its nuclear decay; exposure to radon is considered the second leading cause of lung cancer after tobacco smoking (95).

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) (96). This is one of the most potent carcinogens known, particularly for inducing cancer of the mouth (97). 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 (96).

Biological Contamination: from page 18

Rock strata beneath the earth's surface are populated by microscopic organisms, and the advent of air-lubricated drilling (without biocides) has introduced a risk of contaminating surface (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*, a facultative anaerobe that thrives in fresh water where some sulfate (such as is present in pyrite or hematite) is available (101), (Figure 2) (102).

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 (103). There they produce hydrogen sulfide (H_2 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 (104).

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

NOTE - best to read all of Professor Bishop's paper Can be found here: http://66.147.244.96/~damascu5/wp-content/uploads/2012/01/chem_bio_risk_assess_ny_bishop_2011.pdf

This compilation prepared by
Damascus Citizens for Sustainability
DamascusCitizens.org