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PERCHLORATE ASSESSMENT OF THE NAKDONG AND YEONGSAN WATERSHEDS, REPUBLIC OF KOREA

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Abstract—The objective of the present study was to conduct a preliminary assessment for perchlorate in surface water, drinking water, and wastewater treatment plant effluent samples obtained from the Nakdong and Yeongsan watersheds in the Republic of Korea. Samples were analyzed for perchlorate using ion chromatography with suppressed conductivity detection (IC-CD) and/or liquid chromatography with tandem mass spectrometry detection (LC-MS/MS). Method reporting limits were 5.0 μg/L for IC-CD and 0.05 μg/L for LC-MS/MS analysis. At perchlorate levels above 5.0 μg/L, IC-CD and LC-MS/MS provided comparable results. The levels of perchlorate detected in the samples procured from the Yeongsan watershed were <5.0 μg/L in each case. However, Nakdong watershed samples contained perchlorate at levels up to 60 μg/L. The highest concentrations of perchlorate were found in surface water samples, although drinking water contained perchlorate at concentrations up to 35 μg/L. In a subset of samples analyzed by LC-MS/MS, chlorate and bromate also were detected at concentrations ranging from <0.10 to 44 μg/L and <0.10 to 2.6 μg/L, respectively. To the best of the authors' knowledge, this is the first perchlorate assessment reported for water sources in the Republic of Korea.

Keywords—Perchlorate Surface water Analysis Korea

INTRODUCTION

Perchlorate salts serve as oxidizing agents in the manufacturing of solid rocket propellants, explosives, fireworks, signal flares, matches, and automotive air bag inflators. As such, they are used worldwide in the chemical, aerospace, and defense industries [1,2]. Additionally, naturally occurring perchlorate deposits have been reported in Chile [3,4], Texas (USA), and New Mexico (USA) [5]. In West Texas, the pervasive presence of perchlorate in groundwater has been attributed to atmospheric production and/or surface oxidative weathering [4,6]. Perchlorate is practically unreactive in dilute solutions under typical environmental conditions [7] and has poor adsorption to minerals [8], making it highly mobile and persistent in groundwater [9]. Additionally, the stability of the perchlorate ion in water over time has been well established [10]. Throughout the United States, perchlorate has been detected, primarily in groundwater, in more than 100 sites in 30 states [11]. In drinking water sources, perchlorate contamination has been particularly well documented in the southwestern United States, often attributed to manufacturing and/or ballistics [12,13]. Whether the source is natural or anthropogenic, perchlorate also has been found in dietary supplements and flavor enhancers [14], dairy products and human breast milk [15], plants [16,17], fish [18], and blood from exposed cattle [19]. Low, yet consistent, concentrations of perchlorate also have been found in urine [20], cow's milk [15], and natural and bottled waters [21] from origins where there are no explicit governmental, industrial, or agricultural sources, thus suggesting significant levels of naturally occurring perchlorate.

Water contamination of perchlorate has become a major environmental and health concern in recent years as toxicological associations of perchlorate to abnormal endocrine functions have emerged. Perchlorate has been linked with inhibited larval development and metamorphosis in amphibians [22,23] and has been recognized as a disruptor of iodide accumulation in lamprey [24]. Recently, hermaphroditism in fish has been attributed to perchlorate contamination [25]. In mammals it has been shown that perchlorate is a competitive inhibitor of thyroidal iodide uptake [26,27] and drinking water perchlorate contamination has been associated with abnormal newborn human thyroid function [28]. Reference doses for safe human consumption in the United States amount to a drinking water equivalent level of 24.5 μg/L ([29]; www.nap.edu), although regulations set maximum contaminant levels as low as 2.0 μg/L (www.mass.gov/dep/water/drinking/percinfo.htm).

The chlorate anion exhibits the same mechanism of action on the thyroid as perchlorate, albeit with lower potency [30]. It is produced during onsite generation of hypochlorite used in drinking water treatment and is a byproduct of oxidative treatment of drinking water with chlorine dioxide [21]. In the United States, chlorate has been shown to occur in bottled water and municipal drinking water at levels up to 270 μg/L [21]. The state of California (USA) has set an action level for chlorate in drinking water at 800 μg/L (www.dhs.ca.gov/ps/ddwem/chemicals/AL/notificationlevels.htm) and action levels as low as 200 μg/L have been suggested (www.oehha.ca.gov/water/pals/chlorate.html).

Bromate, another disinfection byproduct, is found in some finished drinking waters as the result of ozonation disinfection processes [31]. Bromate in drinking water primarily is asso-

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