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Sensors for Environmental Monitoring and Long-Term Environmental Stewardship

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Sensors for Environmental Monitoring and Long-Term Environmental Stewardship

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Abstract

This report surveys the needs associated with environmental monitoring and long-term environmental stewardship. Emerging sensor technologies are reviewed to identify compatible technologies for various environmental monitoring applications. The contaminants that are considered in this report are grouped into the following categories: (1) metals, (2) radioisotopes, (3) volatile organic compounds, and (4) biological contaminants. Regulatory drivers are evaluated for different applications (e.g., drinking water, storm water, pretreatment, and air emissions), and sensor requirements are derived from these regulatory metrics. Sensor capabilities are then summarized according to contaminant type, and the applicability of the different sensors to various environmental monitoring applications is discussed.

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1. Introduction

Environmental monitoring is required to protect the public and the environment from toxic contaminants and pathogens that can be released into a variety of media including air, soil, and water. Air pollutants include sulfur dioxide, carbon monoxide, nitrogen dioxide, and volatile organic compounds, which originate from sources such as vehicle emissions, power plants, refineries, and industrial and laboratory processes. Soil and water contaminants can be classified as microbiological (e.g., coliform), radioactive (e.g., tritium), inorganic (e.g., arsenic), synthetic organic (e.g., pesticides), and volatile organic compounds (e.g., benzene). Pesticide and herbicides are applied directly to plants and soils, and incidental releases of other contaminants can originate from spills, leaking pipes, underground storage tanks, waste dumps, and waste repositories. Some of these contaminants can persist for many years and migrate through large regions of soil until they reach water resources, where they may present an ecological or human-health threat.

The United States Environmental Protection Agency (U.S. EPA) has imposed strict regulations on the concentrations of many environmental contaminants in air and water. However, current monitoring methods are costly and time-intensive, and limitations in sampling and analytical techniques exist. For example, Looney and Falta (2000, Ch. 4) report that the Department of Energy (DOE) Savannah River Site requires manual collection of nearly 40,000 groundwater samples per year, which can cost between \$100 to \$1,000 per sample for off-site analysis. Wilson et al. (1995, Ch. 36) report that as much as 80% of the costs associated with site characterization and cleanup of a Superfund site can be attributed to laboratory analyses. In addition, the integrity of the off-site laboratory analyses can be compromised during sample collection, transport, storage, and analysis, which can span several days or more. Clearly, a need exists for accurate, inexpensive, long-term monitoring of environmental contaminants using sensors that can be operated on site or *in situ*. However, the ability to deploy and use emerging sensors for these applications is uncertain due to both cultural and technological barriers.

The purpose of this report is to assess the needs of long-term environmental monitoring applications and to summarize the capabilities of emerging sensor technologies (with an emphasis on Sandia-developed sensor technologies). A market survey is presented that elucidates the costs, drivers, and potential benefits of using in-situ sensors for long-term environmental monitoring. Regulatory metrics for different environmental monitoring applications are then presented to provide requirements for the sensor technologies. Emerging sensor technologies are then evaluated that can be used to monitor environmental contaminants, particularly for long-term environmental stewardship. We limit our focus to four categories of contaminants: (1) metals, (2) radioisotopes, (3) volatile organic compounds, and (4) biological contaminants. For each contaminant, we seek portable sensors that can provide rapid responses (relative to current methods and technologies), ease of operation (for field use), and sufficient detection limits.

2. Market Survey

In 2001, U.S. companies generated \$213 billion in environmental industry revenue, with a growth of 2.1% and exports representing 11% of this figure (US DOE, 2002). Overall, the

environmental industry is in a state of evolution. The U.S. environmental remediation/industrial services markets have topped out and are projected to decline. A decline in hazardous waste management funding continues with a trend that began in 1993. Returns on investment in hazardous waste remediation technologies have been low for some time and the DOE continues to be the largest funding source within the U.S. for the site remediation market.

A 15% growth in the overall environmental industry is forecasted as the combination of two major groups. The first group is comprised of energy and water that is projected to experience growth ranging from 19% to over 250% during the first decade of the 21st century (US DOE, 2002). The second group consists of compliance, remediation and waste management that are projected to decline 13% to 49% during the same timeframe. The first group is driven by economics and basic human needs while the second group is driven by regulations and enforcement.

The two best performing environmental industry segments are also the best performers over the past decade: clean energy systems/power (+16%) and process/pollution prevention technology (+9%). Clean energy systems/power (\$10.0 b) accounted for 65% of the overall market growth in dollars. Process and pollution prevention technology have annual revenues of \$1.3 billion. Continued growth of clean energy/power and process/pollution prevention technologies are projected.

Instrument technology is a \$3.8 billion dollar industry and has experienced an annual growth rate of approximately 4%. The U.S. water industry – made up of water utilities (\$30.9 b), wastewater treatment works (\$28.8 b), and water equipment/chemicals (\$20.3 b) accounts for 38% of the environmental industry revenues. Solid waste management (\$40.8 b), air pollution control equipment (\$18.3 b) and consulting/engineering (\$18.0 b) are also major contributors to the environmental industry revenue stream.

In the present DOE Environmental Management (EM) market, technology investments are not occurring on a scale that is likely to make major cost and schedule differences. EM is focusing its resources on actual clean-ups and site closures and not on technology innovations. Low interest in technologies increases the difficulty in finding willing investors. Investors are likely to be wary of any growth potential in a market that has an environmental connotation. However, technologies that have a specific need that saves money can be successful. Technological improvements in excavation, transportation, disposal, analytical services, robotics, sample preparation, field sampling, and monitoring are examples of areas where technological improvements could be successful (Stetter, 2001).

Data Quality Objectives (DQOs) must be considered as part of technology development and a focus should be made on the most urgent problems, such as situations where contaminants are in contact with groundwater. Regulator involvement in new technology development and acceptance of technologies is also very important (Stetter, 2001).

Science and technology needs include methods of detection, analysis, remote sensing, and data transmission. A technology-needs analysis determined that the most important needs for analytical capabilities were the use of fieldable instrumentation for organic compounds in water/soil/air and for Resource Conservation and Recovery Act (RCRA) metals in water/soil

(Stetter, 2001). It was further noted that a leap in technology would occur when the performance of the field instruments more closely approaches that of laboratory-based instruments. A potential application in long-term monitoring and stewardship is in the area of performance monitoring of water to address current technical uncertainties (US DOE, 1999). Additionally, information is needed to determine if ambient conditions change significantly enough over the long term to diminish the effectiveness of the remedy.

Based on information gathered in equipment user surveys, an analysis of the market for environmental field instrumentation determined that field instrumentation has been expanding due to cost savings from on-site analysis and improved regulatory and customer acceptance of on-site methods (US DOE, 1996). The environmental field instrument market is expected to enjoy an average growth of 7% annually for the foreseeable future. The market will expand with technology developments and increasing regulatory acceptance. However, given the current regulatory environment, field instruments may never completely replace laboratory analysis, and therefore never realize its maximum market potential.

Remediation opportunities will wane and be replaced with smaller, longer-term opportunities related to post-closure monitoring and long-term stewardship. This should open doors to new instruments and measurement technologies and remote information management systems. The market consists of many niche applications, which are met by a number of different technologies. The long-term nature of post-closure monitoring and surveillance will be required at a wide variety of nuclear sites, uranium mill tailing sites, low-level and mixed-waste burial grounds, and hazardous waste sites that may create new areas for application. This market overlaps with other markets, such as for chemical industry process monitoring. Technology developments that can crosscut multiple areas within the environmental industry have a greater potential for success within the industry.

Long-term stewardship is not unique to the DOE. The EPA is currently determining its stewardship responsibilities through its Federal Facilities Restoration and Reuse Office. Both EPA Region IV and X have released policy documents on the use of institutional controls at Federal facilities. However, the specific ways in which long-term institutional control issues are implemented vary considerably at state and local offices. The Department of Defense (DoD) conducts cleanup activities at more than 10,000 sites, nearly 2,000 military installations and more than 9,000 formerly used defense properties. The Department of Interior (DoI) is responsible for overseeing approximately 13,000 former mining sites, some of which have been abandoned by the original owners. The nation's commitment is also not limited to federal properties. For example, sanitary and hazardous landfills, industrial facilities, and former waste management operations likely require long-term monitoring that will be funded by state and local governments.

The DOE conducts its stewardship activities in compliance with applicable laws, regulations, and inter-agency agreements. In general the DOE is required to implement some land-use controls at waste disposal facilities in perpetuity. Groundwater-monitoring timeframes are expected to be 30 years or greater. Costs of post-cleanup stewardship activities are currently unknown. However, a DOE Office of Inspector General audit found that the "DOE groundwater monitoring activities were not being conducted economically as they could have been since some sites had not adopted innovative technologies and approaches to well installations, sampling operations,

and laboratory analysis.” The report concluded that in part this occurred because innovative groundwater monitoring techniques were either unavailable or had not been effectively disseminated, evaluated for applicability at other sites and implemented” (IG-0461). In summary, the development of sensors for long-term groundwater monitoring may fill a niche that could have a wide-ranging application for long-term environmental monitoring.

3. Regulatory Requirements, Standards, and Policies

3.1 Drinking Water

National Primary Drinking Water Regulations apply to public water systems and are legally enforceable standards. These primary standards are intended to protect public health by limiting the levels of contaminants that can be found in drinking water. Although these standards are applicable to public water systems (i.e., at the tap), they are often applied by remediation regulators in the aquifer (i.e., at the monitoring wellhead). The following tables summarize the drinking water standards imposed by the U.S. Environmental Protection Agency (EPA). Additional information regarding potential health impacts and sources of contamination can also be found at their web site (<http://www.epa.gov/safewater/mcl.html>).

Table 1. EPA national primary drinking water standards for microorganisms.

Contaminant	Maximum Contaminant Level Goal (mg/L)	Maximum Contaminant Level (mg/L)
Cryptosporidium	zero	See footnote*
Giardia lamblia	zero	See footnote*
Heterotrophic plate count	n/a	See footnote*
Legionella	zero	See footnote*
Total Coliforms (including fecal coliform and E. Coli)	zero	5.0%**
Turbidity	n/a	See footnote*
Viruses (enteric)	zero	See footnote*

*EPA's surface water treatment rules require systems using surface water or ground water under the direct influence of surface water to (1) disinfect their water, and (2) filter their water or meet criteria for avoiding filtration so that the following contaminants are controlled at the following levels:

- Cryptosporidium (as of 1/1/02 for systems serving >10,000 and 1/14/05 for systems serving <10,000) 99% removal.
- *Giardia lamblia*: 99.9% removal/inactivation
- Viruses: 99.99% removal/inactivation
- *Legionella*: No limit, but EPA believes that if *Giardia* and viruses are removed/inactivated, *Legionella* will also be controlled.
- Turbidity: At no time can turbidity (cloudiness of water) go above 5 nephelometric turbidity units (NTU); systems that filter must ensure that the turbidity go no higher than 1 NTU (0.5 NTU for conventional or direct filtration) in at least 95% of the daily samples in any month. As of January 1, 2002, turbidity may never exceed 1 NTU, and must not exceed 0.3 NTU in 95% of daily samples in any month.
- HPC: No more than 500 bacterial colonies per milliliter.
- Long Term 1 Enhanced Surface Water Treatment (Effective Date: January 14, 2005); Surface water systems or (GWUDI) systems serving fewer than 10,000 people must comply with the applicable Long Term 1 Enhanced Surface Water Treatment Rule provisions (e.g. turbidity standards, individual filter monitoring, Cryptosporidium removal requirements, updated watershed control requirements for unfiltered systems).

- Filter Backwash Recycling; The Filter Backwash Recycling Rule requires systems that recycle to return specific recycle flows through all processes of the system's existing conventional or direct filtration system or at an alternate location approved by the state.

**more than 5.0% samples total coliform-positive in a month. (For water systems that collect fewer than 40 routine samples per month, no more than one sample can be total coliform-positive per month.) Every sample that has total coliform must be analyzed for either fecal coliforms or *E. coli* if two consecutive TC-positive samples, and one is also positive for *E. coli* fecal coliforms, system has an acute MCL violation.

Table 2. EPA national primary drinking water standards for disinfectants.

Contaminant	Maximum Contaminant Level Goal (mg/L)	Maximum Contaminant Level (mg/L)
Chloramines (as Cl₂)	MRDLG=4*	MRDL=4.0**
Chlorine (as Cl₂)	MRDLG=4*	MRDL=4.0**
Chlorine dioxide (as ClO₂)	MRDLG=0.8*	MRDL=0.8**

*Maximum Residual Disinfectant Level Goal (MRDLG) - The level of a drinking water disinfectant below which there is no known or expected risk to health. MRDLGs do not reflect the benefits of the use of disinfectants to control microbial contaminants.

**Maximum Residual Disinfectant Level (MRDL) - The highest level of a disinfectant allowed in drinking water. There is convincing evidence that addition of a disinfectant is necessary for control of microbial contaminants.

Table 3. EPA national primary drinking water standards for disinfection byproducts.

Contaminant	Maximum Contaminant Level Goal (mg/L)	Maximum Contaminant Level (mg/L)
Chlorite	0.8	1.0
Haloacetic acids (HAA5)	n/a*	0.060
Total Trihalomethanes (TTHMs)	n/a*	.08

*Although there is no collective MCLG for this contaminant group, there are individual MCLGs for some of the individual contaminants:

- Trihalomethanes: bromodichloromethane (zero); bromoform (zero); dibromochloromethane (0.06 mg/L). Chloroform is regulated with this group but has no MCLG.
- Haloacetic acids: dichloroacetic acid (zero); trichloroacetic acid (0.3 mg/L). Monochloroacetic acid, bromoacetic acid, and dibromoacetic acid are regulated with this group but have no MCLGs.

Table 4. EPA national primary drinking water standards for inorganic chemicals.

Contaminant	Maximum Contaminant Level Goal (mg/L)	Maximum Contaminant Level (mg/L)
Antimony	0.006	0.006
Arsenic	0*	0.010 (as of 01/23/06)
Asbestos (fiber >10 micrometers)	7 million fibers per liter	7 million fibers per liter
Barium	2	2
Beryllium	0.004	0.004
Cadmium	0.005	0.005
Chromium (total)	0.1	0.1
Copper	1.3	Action Level=1.3**
Cyanide (as free cyanide)	0.2	0.2
Fluoride	4.0	4.0
Lead	zero	Action Level=1.3**
Mercury (inorganic)	0.002	0.002
Nitrate (measured as Nitrogen)	10	10
Nitrite (measured as Nitrogen)	1	1
Selenium	0.05	0.05
Thallium	0.0005	0.002

*MCLGs were not established before the 1986 Amendments to the Safe Drinking Water Act. Therefore, there is no MCLG for this contaminant.

**Lead and copper are regulated by a Treatment Technique that requires systems to control the corrosiveness of their water. If more than 10% of tap water samples exceed the action level, water systems must take additional steps. For copper, the action level is 1.3 mg/L, and for lead is 0.015 mg/L.

Table 5. EPA national primary drinking water standards for organic chemicals.

Contaminant	Maximum Contaminant Level Goal (mg/L)	Maximum Contaminant Level (mg/L)
Acrylamide	zero	Treatment Technology*
Alachlor	zero	0.002
Atrazine	0.003	0.003
Benzene	zero	0.005
Benzo(a)pyrene (PAHs)	zero	0.0002
Carbofuran	0.04	0.04
Carbon tetrachloride	zero	0.005
Chlordane	zero	0.002
Chlorobenzene	0.1	0.1
2,4-D	0.07	0.07
Dalapon	0.2	0.2
1,2-Dibromo-3-chloropropane (DBCP)	zero	0.0002
o-Dichlorobenzene	0.6	0.6
p-Dichlorobenzene	0.075	0.075
1,2-Dichloroethane	zero	0.005
1,1-Dichloroethylene	0.007	0.007
cis-1,2-Dichloroethylene	0.07	0.07
trans-1,2-Dichloroethylene	0.1	0.1
Dichloromethane	zero	0.005
1,2-Dichloropropane	zero	0.005
Di(2-ethylhexyl) adipate	0.4	0.4
Di(2-ethylhexyl) phthalate	zero	0.006
Dinoseb	0.007	0.007
Dioxin (2,3,7,8-TCDD)	zero	0.00000003
Diquat	0.02	0.02
Endothall	0.1	0.1
Endrin	0.002	0.002
Epichlorohydrin	zero	Treatment Technology*
Ethylbenzene	0.7	0.7
Ethylene dibromide	zero	0.00005
Glyphosate	0.7	0.7
Heptachlor	zero	0.0004
Heptachlor epoxide	zero	0.0002
Hexachlorobenzene	zero	0.001
Hexachlorocyclopentadiene	0.05	0.05
Lindane	0.0002	0.0002
Methoxychlor	0.04	0.04
Oxamyl (Vydate)	0.2	0.2

Contaminant	Maximum Contaminant Level Goal (mg/L)	Maximum Contaminant Level (mg/L)
Polychlorinated biphenyls (PCBs)	zero	0.0005
Pentachlorophenol	zero	0.001
Picloram	0.5	0.5
Simazine	0.004	0.004
Styrene	0.1	0.1
Tetrachloroethylene	zero	0.005
Toluene	1	1
Toxaphene	zero	0.003
2,4,5-TP (Silvex)	0.05	0.05
1,2,4-Trichlorobenzene	0.07	0.07
1,1,1-Trichloroethane	0.20	0.2
1,1,2-Trichloroethane	0.003	0.005
Trichloroethylene	zero	0.005
Vinyl chloride	zero	0.002
Xylenes (total)	10	10

*Each water system must certify, in writing, to the state (using third-party or manufacturer's certification) that when acrylamide and epichlorohydrin are used in drinking water systems, the combination (or product) of dose and monomer level does not exceed the levels specified, as follows:

- Acrylamide = 0.05% dosed at 1 mg/L (or equivalent)
- Epichlorohydrin = 0.01% dosed at 20 mg/L (or equivalent)

Table 6. EPA national primary drinking water standards for radionuclides.

Contaminant	Maximum Contaminant Level Goal	Maximum Contaminant Level
Alpha particles	zero	15 picocuries per Liter (pCi/L)
Beta particles and photon emitters	zero	4 millirems per year
Radium 226 and Radium 228 (combined)	zero	5 pCi/L
Tritium	zero	20,000 pCi/L
Uranium	zero	30 ug/L (as of 12/08/03)

3.2 Storm Water Monitoring

Under the National Pollutant Discharge Elimination System (NPDES) regulations, all facilities which discharge pollutants from any point source into waters of the United States (US) are required to obtain a permit. The NPDES storm water regulations cover the following classes of storm water dischargers: operators of municipal separate storm sewer systems (MS4s); industrial

facilities in any of eleven identified categories that discharge to an MS4 or to a water of the US; and operators of certain construction activities. Storm water regulations are implemented by the EPA or authorized states.

NPDES permits may be issued as individual or general permits. In either case, NPDES permits generally require the development of a storm water pollution prevention plan, implementation of best management practices, and monitoring and reporting of storm water discharge data. Most industrial facilities elect coverage under a general permit because the permitting process is designed to be more efficient.

EPA has developed a multi-sector general permit (MSGP) for storm water dischargers, providing both general requirements and sector-specific requirements. The specific requirements apply to each of 30 industrial sectors and their associated subsectors. The current MSGP was published in the Federal Register on October 30, 2000 (65 FR 64746). Authorized states may use alternative permits and/or may impose additional requirements.

Three types of monitoring may be required under the MSGP: visual examination, analytical monitoring, and compliance monitoring. Visual examinations are intended to provide a simple, inexpensive evaluation of storm water quality. Analytical monitoring is required for only specified subsectors, those which EPA has determined have a high potential to discharge a pollutant at concentrations of concern. For each of the identified subsectors, EPA has defined the parameters to be monitored and has established benchmark concentrations for each parameter. Analytical monitoring is required on a quarterly basis in year two of the permit; if these results exceed a benchmark value, a second round of analytical monitoring is required in year. Any time a benchmark concentration is exceeded, the facility must review their storm water pollution prevention plan to reduce pollutant loads.

Compliance monitoring is performed on an annual basis for certain storm water discharges subject to effluent guidelines. Some EPA regions require quarterly monitoring. The applicability of compliance monitoring is limited to the following discharges: landfill discharges; coal pile runoff; contaminated runoff from phosphate fertilizer manufacturing facilities; runoff from asphalt paving and roofing emulsion production areas; material storage pile runoff from cement manufacturing facilities; and mine dewatering discharges from crushed stone, construction sand and gravel, and industrial sand mines.

Specific storm water monitoring requirements under the MSGP are identified in Tables A-1 through AA-1 in the Appendices (Section 7.1). The MSGP analytical and compliance monitoring requirements are limited to discrete sampling events at specified intervals. Grab sampling is required. Authorized states may impose more extensive monitoring requirements.

3.3 National Pretreatment Program Monitoring

Under the NPDES permitting program, EPA established the National Pretreatment Program to address “indirect discharges” into waters of the United States. Indirect discharges are discharges from industrial facilities to publicly owned treatment works (POTWs). The National Pretreatment Program requires dischargers to treat or control pollutants in their wastewater prior

to discharge to the POTW. (The POTW is required to obtain an NPDES permit as a direct discharger.)

Under the General Pretreatment Regulations (40 CFR 403), all large POTWs, and some smaller POTWs with significant industrial discharges, must establish local pretreatment programs. The local pretreatment programs impose national pretreatment standards and requirements, as well as any more stringent local requirements.

EPA has established two general requirements for industrial dischargers prohibiting “interference” and “pass through.” These requirements are designed to prevent damage to the treatment works and environmental harm downstream. In addition, EPA controls the discharge of 126 “priority pollutants,” including metals and toxic organics.

Categorical pretreatment standards limit the discharge of specific pollutants; they are national standards for indirect dischargers in specific industrial categories. These standards are further categorized into pretreatment standards for existing sources (PSES) and pretreatment standards for new sources (PSNS). Currently, 32 industrial categories are subject to pretreatment standards. The standards may be expressed as concentration-based or mass-based, or both, depending upon the operational characteristics of the industry.

Significant industrial users (SIUs) are required to monitor, at a minimum, on a semi-annual basis. Confirmatory sampling by the regulatory authority is required annually. Depending upon factors such as effluent variability, effluent impacts, and compliance history, the SIU may be required to sample more frequently.

The type of industry regulated under the pretreatment program is wide-ranging, including grain mills, feedlots, electroplating facilities, iron and steel manufacturers, and fertilizer manufacturers. For many industries, the monitoring required is limited to several effluent characteristics, such as biological effluent demand, total suspended solids, and pH. For other industries, monitoring of a select set of priority pollutants, such as a specified subset of metals, is required. In a few instances, monitoring of all priority pollutants is required. Pretreatment standards for indirect discharges from manufacturers of organic chemicals, plastics, and synthetic fibers are provided in Table 7.

Table 7. Pretreatment standards for manufacturers of organic chemicals, plastics, and synthetic fibers (40 CFR Part 414).

Environmental Protection Agency

Effluent characteristics	BAT effluent limitations and NSPS ¹	
	Maximum for any one day	Maximum for monthly average
Anthracene	47	19
Benzene	134	57
Benzo(a)anthracene	47	19
3,4-Benzofluoranthene	48	20
Benzo(k)fluoranthene	47	19
Benzo(a)pyrene	48	20
Bis(2-ethylhexyl) phthalate	258	95
Carbon Tetrachloride	380	142
Chlorobenzene	380	142
Chloroethane	295	110
Chloroform	325	111
Chrysene	47	19
Di-n-butyl phthalate	43	20
1,2-Dichlorobenzene	794	196
1,3-Dichlorobenzene	380	142
1,4-Dichlorobenzene	380	142
1,1-Dichloroethane	59	22
1,2-Dichloroethane	574	180
1,1-Dichloroethylene	60	22
1,2-trans-Dichloroethylene	66	25
1,2-Dichloropropane	794	196
1,3-Dichloropropylene	794	196
Diethyl phthalate	113	46
2,4-Dimethylphenol	47	19
Dimethyl phthalate	47	19
4,6-Dinitro-o-cresol	277	78
2,4-Dinitrophenol	4,291	1,207
Ethylbenzene	380	142
Fluoranthene	54	22
Fluorene	47	19
Hexachlorobenzene	794	196
Hexachlorobutadiene	380	142
Hexachloroethane	794	196
Methyl Chloride	295	110
Methylene Chloride	170	36
Naphthalene	47	19
Nitrobenzene	6,402	2,237
2-Nitrophenol	231	65
4-Nitrophenol	576	162
Phenanthrene	47	19
Phenol	47	19
Pyrene	48	20
Tetrachloroethylene	164	52
Toluene	74	28
Total Chromium	2,770	1,110
Total Copper	3,380	1,450
Total Cyanide	1,200	420
Total Lead	690	320
Total Nickel	3,980	1,690
Total Zinc ²	2,610	1,050
1,2,4-Trichlorobenzene	794	196
1,1,1-Trichloroethane	59	22
1,1,2-Trichloroethane	127	32
Trichloroethylene	69	26
Vinyl Chloride	172	67

¹ All units are micrograms per liter.

² Total Zinc for Rayon Fiber Manufacture that uses the viscose process and Acrylic Fibers Manufacture that uses the zinc chloride/solvent process is 6,796 µg/l and 3,325 µg/l for maximum for any one day and maximum for monthly average, respectively.

3.4 Ambient Air Quality

A number of substances are identified as hazardous air pollutants (now termed "toxic air pollutants" by EPA) under the Clean Air Act and are regulated under the National Emission Standards for Hazardous Air Pollutants program. The American Conference of Governmental Industrial Hygienists (ACGIH) established airborne concentration limits called Threshold Limit Values (TLV) of various hazardous air pollutants. The TLVs are believed to represent conditions under which nearly all workers could be exposed day after day without adverse health effects. The TLVs are based on information from industrial experience and experimental studies on humans and animals. Table 8 lists a few hazardous air pollutants (HAP) and the associated ACGIH TLVs. Additional information on these compounds can be found from the following web sites:

- www.epa.gov/ttn/atw/hlthef/benzene.html
- www.epa.gov/ttn/atw/hlthef/xylenes.html
- www.epa.gov/ttn/atw/hlthef/tri-ethy.html

Table 8. Threshold Limit Values for several hazardous air pollutants (ACGIH, 2000).

Hazardous Air Pollutant	Threshold Limit Value (ppm)	
	8-Hour Time Weighted Average	15-Minute Short-Term Exposure Limit
Benzene	0.5	2.5
Xylenes	100	150
Trichloroethylene	50	100

In 1998, the City of Albuquerque adopted a policy for regulating emissions from industries. An analysis for each relevant HAP at a site is performed to determine if the emissions from the stack result in an exceedance of the ACGIH TLV for any of the relevant substances. If the ACGIH TLV at the stack is exceeded, the concentration of that substance must be analyzed at the "fence line" (i.e., property boundary). The concentration at the fence line should not exceed 1/100th the ACGIH TLV. For any HAP that has uncontrolled emissions which result in an exceedance of the ACGIH TLV at the stack and 1/100th of the ACGIH TLV at the fence line, air-pollution controls will be required to reduce the concentrations to 1/100th the TLV at the fence line. An air quality permit will also be required to ensure proper operation of the control equipment.

Additional air quality standards have been compiled from 20.11.1 NMAC - Title 20, Environmental Protection - Chapter 11, Albuquerque/Bernalillo county Air Quality Control Board - Part 1 General Provisions (see Table 9).

Table 9. Enforceable standards for various air pollutants.

Pollutant	Goals	Enforceable Standards		
	Albuquerque	New Mexico State	Federal Primary	Federal Secondary
Carbon Monoxide (CO)				
8-hour average	---	8.7 ppm	9.0 ppm	9.0 ppm
1-hour average	13 ppm	13.1 ppm	35 ppm	35 ppm
Nitrogen Dioxide (NO₂)				
24-hour average	.062 ppm	10 ppm	---	---
Annual arithmetic mean	.053 ppm	.05 ppm	.053ppm	.053 ppm
Ozone (O₃)				
1-hour average	.120 ppm	---	.120 ppm	.120 ppm
Sulfur Dioxide (SO₂)				
24-hour average	.10 ppm	.10 ppm	---	.140 ppm
3-hour average	---	---	---	.5 ppm
Annual arithmetic mean	.004 ppm	.02 ppm	.03 ppm	---
Particulate Matter (PM₁₀)				
24-hour average	150 µg/m ³	---	150 µg/m ³	---
Annual arithmetic mean	---	---	---	50 µg/m ³
Lead (Pb)				
Quarterly arithmetic mean	1.5 µg/m ³	---	1.5 µg/m ³	1.5 µg/m ³
Hydrogen Sulfide				
1-hour average	.003 ppm	.010 ppm	---	---
Total Reduced Sulfur				
½ hour average	---	.003 ppm	---	---
1-hour average	.003 ppm	---	---	---
Particulate Matter (TSP)				
24-hour average	150 µg/m ³	150 µg/m ³	---	---
7-day average	---	110 µg/m ³	---	---
30-day average	---	90 µg/m ³	---	---
Annual geometric mean	60 µg/m ³	60 µg/m ³	---	---

4. Sensor Technologies for Environmental Monitoring

The purpose of this section is to identify and describe sensor technologies (with an emphasis on Sandia-developed technologies) that may be applicable to monitoring various contaminants described in the previous sections. The technologies are organized according to analyte, which

include trace metals, radioisotopes, volatile organic compounds, and biological pathogens. The sensor technologies are described briefly, and then tables summarizing features and specifications (e.g., sensitivity, size, speed, etc.) of each sensor technology are presented in Table 10 through Table 13 in Section 4.5.

4.1 Trace Metal Sensors

4.1.1 Nanoelectrode Array

Nanoelectrode arrays have been fabricated to identify and quantify dissolved metals (Horton, 2003; Ashby, 2002). Signals from the electrodes are obtained by monitoring current and voltage during application of an electrical potential. Approximately 1 million individual electrodes can be placed on a 1 square inch substrate using electron beam lithography or chemical vapor deposition. The sensing electrodes are integrated with the reference electrode, eliminating the need for buffers and permitting non-contaminating sensing in ultra-pure water. The small electrode size coupled with a very high density produces a signal with up to 10^3 times better signal to noise ratio than standard electrodes. Using multiple electrodes, coatings, and electrochemical techniques, target analytes can include toxic industrial chemicals and metals, such as trichloroethylene, methyl-t-butyl ether, arsenic, lead, and chromium.

4.1.2 Laser-Induced Breakdown Spectroscopy (LIBS)

As its name implies, LIBS uses a laser to rapidly heat a very small area (usually solid or liquid), generating a plasma from the atomic constituents present at the focal point. Radiative relaxation of the plasma is then observed using sensitive spectroscopic instrumentation. LIBS is also known as Laser Spark Spectroscopy (LASS).

LIBS can be used for rapid analysis of hazardous metals and other inorganic contaminants in water, soil, and mixed waste sites (Hahn et al., 1997; Matalucci, 1995, p. 95). It can be used to detect almost all elements, though certain metals exhibit orders of magnitude greater emission. Detection limits are a function of each specific metal, and the spectroscopic and detector hardware. Low ppb levels are typical. Contaminants targeted in Sandia projects include As, Be, Hg, Se, Pb, Cd, Cu, Zn, Ag, Cr, Fe, and Mn. Recently, a LIBS system was set up for measuring metal emissions in the waste streams of a thermal treatment facility (Blevins, 2003). Currently, a field deployable LIBS system is configured at Sandia-Livermore employing an image intensified CCD array, which provides sufficient signal intensity for single laser pulse LIBS. Delivery of the laser light to remote location via a fiber-optic cable has been performed. Spectral emission likewise can be readily be transported over hundreds of feet for analysis (Matalucci, 1995, p. 95). LIBS can be extended to biodetection by looking for rapid, temporal increases in the presence and/or ratios of Ca, Na, K.

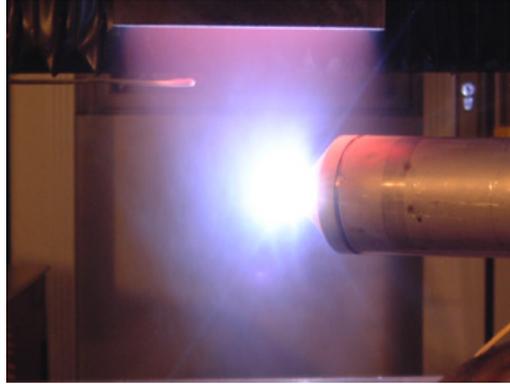


Figure 1. Stand-off LIBS probe head. Laser ablation energy and spectroscopic collection occurs through fiber optics.

4.1.3 Miniature Chemical Flow Probe Sensor

The miniature chemical flow-probe sensor can detect metals, especially copper. See “Miniature Chemical Flow Probe Sensor” in Section 4.3.3 below for details.

4.2 *Radioisotope Sensors*

4.2.1 RadFET (Radiation-Field Effect Transistor)

The RadFET concept for measuring gamma radiation dose has been around for many years. It is based on ionizing radiation permanently promoting high mobility electrons into low mobility holes. This creates an irreversible shift in the FET’s threshold voltage. Sandia has microfabricated miniature RadFETs (Moreno, 1997). Sensitivities depend in part upon fabrication structure, and range from 0.01 to 5 mV per rad. An energy spectrometer can be made by fabricating filters of varying threshold energies on RadFET arrays (Figure 2). With consideration of threshold barriers, RadFETs are universal ionizing radiation detectors. The sensitivity of RadFETs increases with application of increasing bias voltage. However Sandia has fabricated designs that are moderately sensitive with no voltage source.

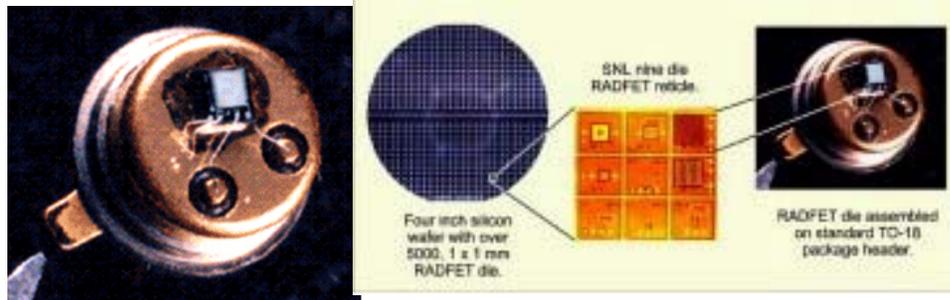


Figure 2. The 1 mm² RadFET element fits on a standard TO-18 package header. Over 5000 RadFETs can be microfabricated on a single 4 inch wafer.

4.2.2 Cadmium Zinc telluride (CZT) detectors

CZTs are semiconductor gamma and neutron radiation detectors, producing current flow under the influence of a gate voltage, upon exposure to high energy radiation. They can be fabricated in arrays to perform imaging or spectroscopy (Murray, 2000). While these are promising and sensitive sensors, their performance, and thus calibration, degrades with cumulative exposure. Long term performance is hard to track, as damage may be progressive with radiation energy levels (Doyle, 1999). Sandia performed experiments to improve the fabrication process for industry. Commercial sensors and spectrometers are available from EV Products or AmpTek.

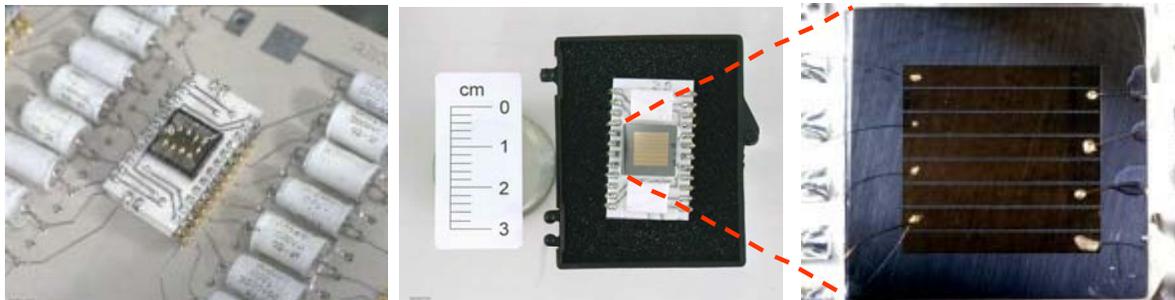


Figure 3. The 1 cm² CZT array sits on a dip package on a circuit board for a handheld gamma radiation spectrometer.

4.2.3 Low-Energy Pin Diodes Beta Spectrometer

A handheld low-energy beta spectrometer was assembled at Sandia for detecting tritium contamination using commercially available pin photodiodes from Hamamatsu (Wampler, 1994). The system works by measuring current pulses generated in the diode when beta particles strike. Electronic circuits convert each signal to a voltage pulse whose amplitude is proportional to the energy of the particle.

4.2.4 Thermoluminescent dosimeter (TLD)

A thermoluminescent dosimeter is a crystal that absorbs energy from radiological exposure, semi-permanently promoting electrons into semi-conductor holes. Upon heating the crystal, the trapped energy is released in the form of light. A TLD reader uses a photodetector to convert the signal into a radiation dose reading. Commonly used crystals are calcium fluoride-manganese and lithium fluoride. Sandia has fabricated TLDs with crystals implanted in Teflon to improve sensitivity (Schwank, 1997; Carlson, 1989). Thin crystals can be used to measure low energy radiation, while thick crystals measure total exposure. Filters and different crystal types can also be used for energy discrimination.

4.2.5 Isotope Identification Gamma Detector

An isotope identification gamma detector was developed in conjunction with the Defense Threat Reduction Agency, Northrup Grumman, Applied Research Associates, and DOE/NNSA laboratories. This was designed as a portal instrument to find and identify unconventionally transported nuclear weapons and radiological dispersal devices (Murphy, 2004).

4.2.6 Neutron Generator for Nuclear Material Detection

A small neutron generator is being developed for use in probing for the presence of nearby nuclear materials (Garcia, 2004). The meter-tall instrument interrogates nuclear material by "pinging" it with neutrons to incite the release of secondary particles. These particles, which are indicative of their atomic source, are then detected. The smaller prototype will be tested soon.

4.2.7 Non-Sandia Radiation Detectors

Commonly used gamma radiation detectors include high purity germanium (require liquid nitrogen), and scintillation crystals, such as thallium doped sodium iodide (low energy resolution). Geiger counters were one of the first radiation detectors available, and the first to provide quantitative measurements of radiation. They use very simple electronics and cover a wide radiation range, but they are bulky compared to some of the sensors described above.

Commercial Options: Radiation Experiments and Monitors (REM) makes a commercial radiation FET sensor with a sensitivity of -10 mV/rad when biased to +20V. TLDs can be purchased from Teledyne Isotopes. CZT detectors can be purchased from Mitsubishi Electric and Communication Electronics, Inc. (Ann Arbor, MI). Geiger counters can be purchased from Mineralab (Prescott, AZ).

4.3 Volatile Organic Compound Sensors

4.3.1 Evanescent Fiber-Optic Chemical Sensor

An evanescent wave is the energy that penetrates a dielectric interface when electromagnetic radiation undergoes total internal reflection. This wave can interact with matter within the penetration depth. By using specialized coatings as the fiber-optic cladding, chemical species can

be preferentially concentrated from a matrix into the evanescent interaction zone. Polymer optical wave guides have been used for sensing organic compounds in aqueous solutions at low ppm levels (Blair, 1997). Ph measurements can be made using sol-gel coatings. For sensing applications, near infrared (NIR) spectroscopy is used for quantitative measurements. With excellent light transmission in this region, sensing can be performed over great distances. However, the spectroscopic signal from mixtures must be deconvolved using multivariate analysis.

4.3.2 Grating Light Reflection Spectroelectrochemistry

Grating light reflection spectroscopy (GLRS) is a technique for spectroscopic analysis and sensing. A transmission diffraction grating is placed in contact with a liquid sample to be analyzed, and an incident light beam is directed onto the grating. At certain angles of incidence, some of the diffracted orders are transformed from traveling waves to evanescent waves. This occurs at a specific wavelength that is a function of the grating period and the complex index of refraction of the sample. The intensity of a diffracted order is also dependent upon the sample's complex index of refraction. The real part of the theoretical equations correspond to the speed of light in the material, and the imaginary part corresponds to light absorption. This technique was used at Sandia in combination with electrochemical modulation of a gold coated metallic spectroscopic grating for the detection of trace amounts of aromatic hydrocarbons (Zaidi, 2000). The grating was configured as the working electrode in an electrochemical cell containing water plus trace amounts of TNT and a dye. Cyclic electrochemical modulation produced lower limits of detection, 50 parts per million and 50 parts per billion, respectively.

4.3.3 Miniature Chemical Flow Probe Sensor

This down-hole probe is designed to measure organic analytes diffusing through a semi-permeable membrane (Matalucci 1995, p. 141). The analytes react with a reagent, forming spectrally distinct products. Absorption bands from a flash lamp are then observed with a spectrometer system, using fiber-optics to carry the light in both directions. Target analytes can be volatile organic compounds in air or water (particularly chlorinated halocarbons), or dissolved metals (copper gives particularly strong response).

4.3.4 SAW Chemical Sensor Arrays

An acoustic sensor is typically used by measuring a decrease in its active resonant frequency that is related to trace mass loading on the active surface (Figure 4). Polymers, sol-gels, and high surface area coatings are often applied to enhance mass absorption/adsorption, and to provide a degree of chemical class selectivity. Acoustic sensors used at Sandia include flexural plate wave (FPW) sensors, quartz crystal microbalances (QCM), and surface acoustic wave (SAW) sensors. By placing coatings of various chemical properties on a 6-SAW array, chemical speciation and quantification of vapors have been performed (Ricco, 1994). In one test the responses of these materials to each of 14 different analytes, representing the classes of saturated alkane, aromatic hydrocarbon, chlorinated hydrocarbon, alcohol, ketone, organophosphonate, and water, was evaluated. The results revealed a qualitative "chemical orthogonality" of the films useful for pattern recognition analysis. SAWs are the most sensitive of the above-mentioned acoustic

sensors, and a number of technological advances have been made to facilitate their use in other chemical systems. Perhaps the most important of these advances is an ASIC (application specific integrated circuit) that converts DC power to the required high frequency impulse, and a reverse conversion for monitoring the frequency shift as a proportional DC shift (Cernosek, 1994).

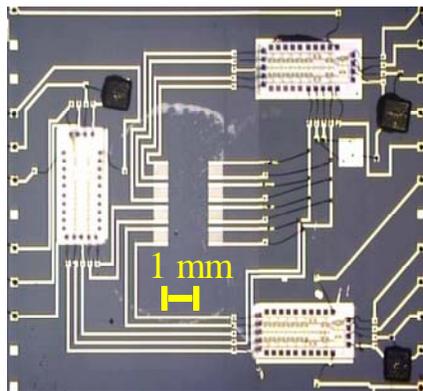


Figure 4. Four SAW sensor elements aligned vertically on an application specific integrated circuit. One delay line is left uncoated to compare frequency shifts of the other polymer or sol-gel coated lines.

4.3.5 MicroChemLab (gas phase)

The gas phase MicroChemLab is a miniature gas chromatography (GC) system originally designed for chemical warfare agent detection for national security needs. Due to the high versatility of GC it has widespread utility. The MicroChemLab can likewise be configured for a variety of applications, including quantification of organic compounds from natural gas to explosives to derivatized biological fatty acids. The main components typically consist of a microfabricated hotplate preconcentrator (PC), a micromachined silicon gas chromatography column (μ GC), and a surface acoustic wave (SAW) sensor array (Sandia, 2002). The PC uses absorbent sol-gels, polymers, or a high surface area adsorbent solid phase. The low heat capacity membrane is then heated to hundreds of degrees in milliseconds to desorb collected analyte. This serves as the injection mechanism for the μ GC. The μ GC separates the injected chemicals in elution time through differing retention capacities with the polymer coated wall or solid packing materials. The chemicals are then detected in order by the SAW sensor.

To address the different nature of the various applications, several variations in components exist. For highly volatile compounds (methane, carbon dioxide) an injection loop is commonly used. A Sandia microfabricated version does not yet exist. A variety of sensors are also in various stages of development, each with advantages and disadvantages. These include a thermal conductivity detector, micro-pellistor array, gold nanowire sensor, and a nitrogen-phosphorous detector (Manginell, 2002).

4.3.6 Gold Nanoparticle Chemiresistors

Gold nanoparticle chemiresistors rely on the general ohmic sensing principles behind other chemiresistors with a few differences. In this sensor, the gold nanoparticles are electrically connected through conductive polymer linkages. While the conduction system is structurally bound in a second, nonconductive polymer, polymer swell minimally affects the resistive measurement. A more stable, reproducible, and sensitive signal is obtained from the direct interaction of analytes with the polarizable polymer links. Thus, films can be significantly thinner and detect lesser concentrations. To date, the sensors have measured pH and other ion concentrations in liquids (Wheeler, 2004). Outside researchers have primarily focused on gas phase VOCs, which is the next target of the Sandia sensor.

4.3.7 Electrical Impedance of Tethered Lipid Bilayers on Planar Electrodes

This sensor consists of a very thin layer of lipid bilayers (Hughes, 2002). VOCs adsorbing or absorbing into the layer changes ion mobility in the structure. This may offer orders of magnitude increase in sensitivity over existing polyelectrolyte coated capacitive chemiresistors. The large increase in sensitivity arises from molecular recognition elements like antibodies that bind the analyte molecules.

4.3.8 MicroHound

The MicroHound is a complete analytical system consisting of a chemical preconcentration system and a miniature Ion Mobility Spectrometer (IMS) (Linker, 2003). Designed primarily for explosives, it can be modified for detecting semi-volatile organic compounds in air. The preconcentration system draws large volumes of air through a mesh screen that selectively adsorbs explosives. The screen is then rapidly heated to desorb the chemicals as a pulse into the inlet of the IMS. The IMS ionizes chemicals at the time-gated entrance of a drift tube. The ions are electrostatically driven against a counter-flowing inert gas to a sensing electrode. Ions are separated from each other in the drift tube according to size, with smaller chemicals arriving first. Identification and quantification are determined by drift time and peak size, respectively.

4.3.9 Hyperspectral Imaging

Multiple infrared images of the same location (microscopic or macroscopic) are obtained using different filters. Thus, a color spectrum of each pixel is obtained. These multidimensional images can be processed for quantitative species mapping (Koehler, 1999). This is a stand-off method and could be used from a UAV or satellite for surface soil monitoring. These methods have also been used for biological and biomedical applications (Timlin, 2003).

4.3.10 Chemiresistor Array

The chemiresistor sensor is a chemically sensitive resistor comprised of a conductive polymer film deposited on a micro-fabricated circuit (Ho et al., 2003). The chemically-sensitive insulating polymer is dissolved in a solvent and mixed with conductive carbon particles. The resulting ink is then deposited and dried onto thin-film, parallel, non-intersecting platinum traces

on a solid substrate (chip). When chemical vapors come into contact with the polymers, the chemicals absorb into the polymers, causing them to swell. The swelling changes the physical conformation of the conductive particles in the polymer film, thereby changing the electrical resistance across the platinum-trace electrodes, which can be measured and recorded using a data logger or an ohmmeter. The swelling is reversible if the chemical vapors are removed, but some hysteresis can occur at high concentration exposures. The amount of swelling corresponds to the concentration of the chemical vapor in contact with the chemiresistor, so these devices can be calibrated by exposing the chemiresistors to known concentrations of target analytes.

Figure 5 shows the architecture of the microsensor, which integrates an array of chemiresistors with a temperature sensor and heating elements (Hughes et al., 2000). The chemiresistor array has been shown to detect a variety of VOCs including aromatic hydrocarbons (e.g., benzene), chlorinated solvents (e.g., trichloroethylene (TCE), carbon tetrachloride), aliphatic hydrocarbons (e.g., hexane, iso-octane), alcohols, and ketones (e.g., acetone). The on-board temperature sensor comprised of a thin-film platinum trace can be used to not only monitor the in-situ temperature, but it can also be used in a temperature control system. A feedback control system between the temperature sensor and on-board heating elements can allow the chemiresistors to be maintained at a fairly constant temperature, which can aid in the processing of data when comparing the responses to calibrated training sets. In addition, the chemiresistors can be maintained at a temperature above the ambient to prevent condensation of water, which may be detrimental to the wires and surfaces of the chemiresistor.

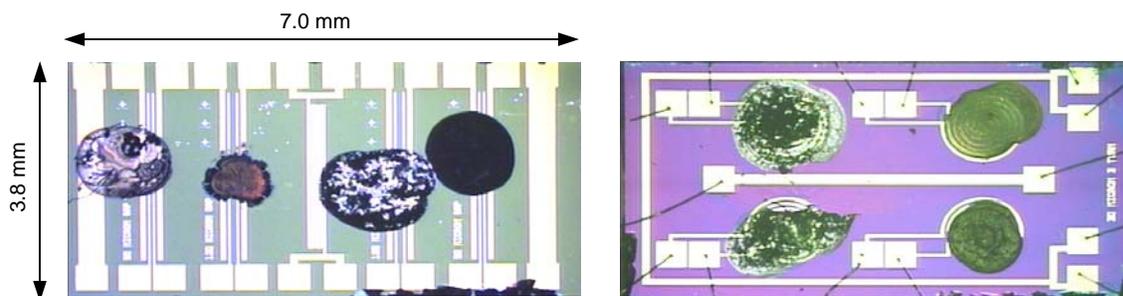


Figure 5. Chemiresistor arrays developed at Sandia with four conductive polymer films (black spots) deposited onto platinum wire traces on a silicon wafer substrate.

A robust package has been designed and fabricated to house the chemiresistor array (Ho and Hughes, 2002). This cylindrical package is small (~ 3 cm diameter) and is constructed of rugged, chemically-resistant material. Early designs have used PEEK (PolyEtherEtherKetone), a semi-crystalline, thermoplastic with excellent resistance to chemicals and fatigue. Newer package designs have been fabricated from stainless steel (Figure 6). The package design is modular and can be easily taken apart (unscrewed like a flashlight) to replace the chemiresistor sensor if desired. Fitted with Viton O-rings, the package is completely waterproof, but gas is allowed to diffuse through a GORE-TEX[®] membrane that covers a small window to the sensor. Like clothing made of GORE-TEX[®], the membrane prevents liquid water from passing through it, but the membrane “breathes,” allowing vapors to diffuse through. Even in water, dissolved VOCs can partition across the membrane into the gas-phase headspace next to the chemiresistors to allow detection of aqueous-phase contaminants. The aqueous concentrations can be determined from the measured gas-phase concentrations using Henry’s Law. Mechanical

protection is also provided via a perforated metal plate that covers the chemiresistors. The chemiresistors are situated on a 16-pin dual-in-line package that is connected to a weatherproof cable, which can be of any length because of the DC-resistance measurement. The cable can be connected to a hand-held multimeter for manual single-channel readings, or it can be connected to a multi-channel data logger for long-term, remote operation.

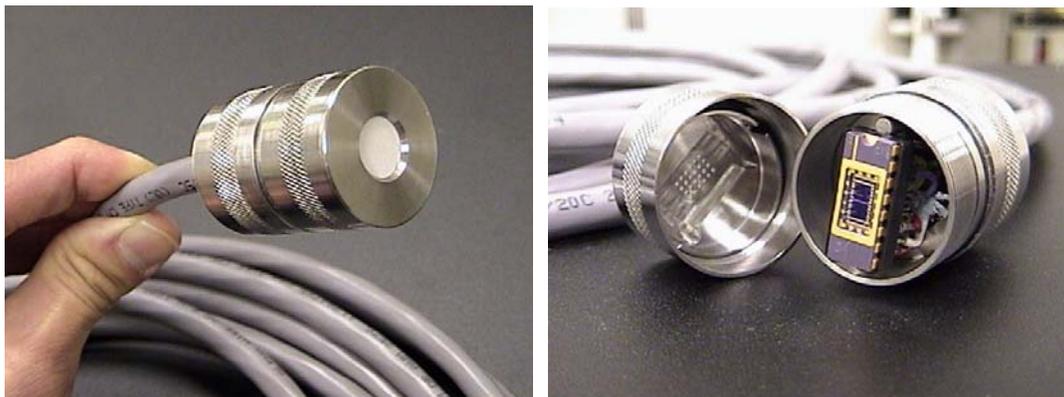


Figure 6. Stainless-steel waterproof package that houses the chemiresistor array. Left: GORE-TEX[®] membrane covers a small window over the chemiresistors. Right: Disassembled package exposing the 16-pin dual-in-line package and chemiresistor chip.

4.4 Biological Sensors

4.4.1 Fatty Acid Methyl Esters (FAME) Analyzer

This method uses microhotplates and micro-chromatography columns (μ GC) from the MicroChemLab to analyze whole biological cells (Mowry, 2002). A liquid sample is placed on the hotplate along with a methylating agent. When the hotplate is thermally ramped (to 500°C in tens of milliseconds) the cells are lysed with proteins in the lipid bilayer forming semi-volatile FAMES. This also served as the injection mechanism into a μ GC, where the FAMES were separated for identification and quantification. The ratios of the FAMES can be used to distinguish bacteria at the gram-type, genera, and even species level with high-resolution instrumentation. Sandia work aimed at miniaturizing half-million dollar bench scale instrumentation down to a handheld, battery-powered instrument with minimal sample preparation. Target analytes include biological warfare agents, food contaminants, and other toxic pathogens.

4.4.2 iDEP (insulator-based dielectrophoresis)

This technique uses an electric field applied across a microfabricated array of insulating posts (Murphy, 2004; Simmons, 2003). The polypropylene device selectively preconcentrates particles based on their polarizability and size (Figure 7). It can be used to preconcentrate proteins for analysis in the liquid MicroChemLab or other systems for fingerprint identification of pathogens.

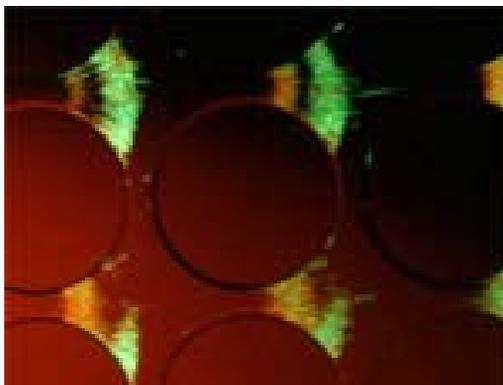


Figure 7. Electric field gradients created between microfabricated posts separate fluorescently tagged live and dead *E. coli* while dielectrophoretically concentrating them in zones.

4.4.3 Bio-SAW Sensor

Acoustic sensors are typically used by measuring a decrease in their resonant frequency that is related to mass loading. Biological detection can be performed by applying specific antibody coatings to the active surface of the acoustic device (Figure 8). Anthrax spores can be detected in a few minutes, and other biological threats can be detected using other antibody coatings (Brozik, 2002). An array of sensors with different coatings would provide increased versatility.

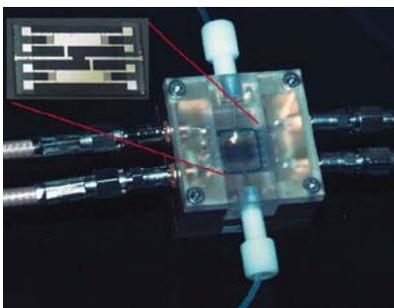


Figure 8. A miniaturized biosensor is shown consisting of a shear horizontal surface acoustic wave sensor coated with a molecular recognition layer. Highly specific coatings are used for biological warfare agent detection and medical diagnostics.

4.4.4 μ ProLab

This LDRD Grand Challenge system is being designed for preconcentration and analysis of proteins and peptides using MIMS (molecular integrated microsystems) (Napolitano, 2002). This architecture will take the advantages inherent in system miniaturization to a higher level of performance. At the same time, simplicity of production is sought. Successes to date include cast-in-place fluidic structures and coatings, and the ability to preconcentrate protein and peptide signatures 1000 fold using programmable switchable polymers and electrokinetic trapping.

4.4.5 MicroChemLab (Liquid)

The liquid MicroChemLab is the counterpart to the gas-phase MicroChemLab above (Nolan, 2004). It is a hand-portable, low-power instrument designed to detect a broad range of chemical and biological agents in less than five minutes. The detector uses capillary electrophoresis with three analysis trains: 1) DNA analysis to identify bacteria and viruses, 2) immunoassays to identify bacteria, viruses, toxins, and 3) protein signatures to identify toxins. Fluid handling is contained to micromachined channels on a single board, and driven by high voltage, but low power, electrokinetic forces. Sample preconcentration and injections occur through manipulation of the electrophoretic fields without the use of valves. Fluorescent detection occurs using a diode laser. The system has been designed to have manufacturable, replaceable modules with simplicity for a non-technical end-user.

4.5 Summary and Specifications of Sensor Technologies

The following tables summarize specifications for the sensor technologies described in the previous sections. In many cases, rigorous specifications are not available because of limited studies. In these cases, estimates are provided based on the judgment of the principal investigators.

Table 10. Summary of specifications for **trace metal** sensors.

Sensor Technology	Specifications								
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost	Contact
A) Nanoelectrode Array	low ppb	elemental in non-complex mixtures	long-term	seconds	1 square inch dip probe		personal computer	sensor:	W. Graham Yelton (1743) (505) 284-3925
B) Laser-Induced Breakdown Spectroscopy	low ppb	elemental	long-term	ms with intensified-CCD, minutes with scanning spectrometers or signal averaging	fiber-optics; lengths of 100+ meters possible	mW per pulse	personal computer	system: \$50-150K	Shane Sickafoose (8773) (925) 294-3526
C) see Miniature Chemical Flow Probe Sensor in Table 12									

Table 11. Summary of specifications for **radioisotope** sensors.

Sensor Technology	Specifications								
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost	Contact
A) RadFET	5 mV/rad	speciation with filters	> 1 year, 5% drift over 1000 hours after strong exposure	milliseconds, or cumulative expose can be read later	¼" with ASIC and dip	passive or mW bias	sensitive digital multimeter	< \$1 in volume	Mark Jenkins (1769) (505) 844-8688
B) Cadmium Zinc Telluride detectors (CZT)	0.8 mV/keV	very selective with spectroscopy	long-term	microseconds	3 mm ² plus electronics	< 1 Watt	hand held or personal computer	\$3000+ for system	Barney Doyle (1111) (505) 844-7568
C) Low-energy Pin Diodes Beta Spectrometer	single events > 1.4 keV. Above background noise, LOD is 0.1 disintegration s/cm ² /sec (3 rem/year)	very selective	long-term	20 ms	sensor: 13 mm ² , plus electronics	passive or mW bias	hand held or personal computer	\$1000+ for photodiode	Barney Doyle (1111) (505) 844-7568
D) Thermoluminescent Dosimeter (TLD)	1 micro-rad/hour	non-specific to radiation source, but can employ filters or different crystal thicknesses and types	long-term	cumulative dose; nanoseconds per event	5 mm ²	passive	TLD Reader	low dollars for crystals; \$1000+ for reader	James Schwank (17621) (505) 844-8376
E) Isotope Identification Gamma Detector	very high	very selective	long term	seconds	vehicle portal	110 AC	laptop		
F) Neutron Generator for Nuclear Material Detection	very high	very selective	long term	seconds	1 meter tall	110 AC	laptop		Jim Wang (8773) 925-294-2786

Table 12. Summary of specifications for **volatile organic compound (VOC)** sensors.

Sensor Technology	Specifications								
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost	Contact
A) Fiber Optic Chemical Sensor	low ppm for hydrophobic organics;	good selectivity with multivariate analysis in moderately complex environments. Coating is non-specific for hydrophobic compounds.	weekly calibration	20 minutes	fiber-optics; lengths up to kilometers possible	110 V, 5 amps	laptop	\$0.25/meter \$2500 for spectrometer	Dianna Blair (6926) (505) 845-8800
B) Grating Light Reflection Spectro-electrochemistry	ppm to ppb	multivariate analysis required for simple mixtures	long term	seconds to minutes	dip probe	5 Watts	laptop	<\$500	Dianna Blair (6926) (505) 845-8800
C) Miniature Chemical Flow Probe Sensor	low ppb to low ppm, depending on analyte	good selectivity in moderately complex matrix	flow cell and fresh reagents ensure high reproducibility	1-2 minutes	2" probe diameter, up to 150 feet long; spectrometer and PC in 2 suitcases	110 AC when built (1995)	laptop	\$10K for total system	George Laguna (2333) (505) 844-5273
D) SAW Chemical Sensor Arrays	ppm to ppb	good with multivariate analysis of mixtures that are not too complex	slow drift over time	tens of seconds	< 1 square inch sensor	mW	laptop or digital display	<\$500	Richard Cernosek (1764) (505) 845-8818
E) MicroChemLab (gas phase)	ppb	very good	slow drift over time	1-5 minutes	handheld	< 1 Watt	laptop or digital display	\$10-20K	Richard Cernosek (1764) (505) 845-8818
F) Gold Nanoparticle	ppb	may be tailored to chemical	TBD	seconds	< 1 square	mW	laptop or digital	<\$100	David Wheeler (1764)

Sensor Technology	Specifications								
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost	Contact
Chemiresistors		classes			inch sensor		display		(505) 844-6631
G) Electrical Impedance of Tethered Lipid Bilayers on Planar Electrodes	ppm to ppb	very high with antibody coatings; lower for non-specific receptors	weeks	minutes	cm ²	mW for sensor; 110 AC for whole instrument	laptop	<\$1 per sensor	Susan Brozik (1744) (505) 844-5105
H) MicroHound	ppb	fairly high	days to weeks	seconds	handheld	battery	laptop or digital display	<\$5K	Kevin Linker, (4148) (505) 844-6999
I) Hyperspectral Imaging	ppm to ppb	good with multivariate analysis of mixtures that are not too complex	long term	seconds to minutes	handheld		laptop	\$10K to \$100K	David Haaland (1812) (505) 855-5292
J) Chemiresistor Arrays	~typically tens to hundreds of ppm; 0.1% of saturated vapor pressure	arrays can discriminate different classes of VOCs	slow drift over time	seconds to minutes, depending on concentration	several mm; package is ~2.5 cm diameter x~6 cm long	mW; battery powered	laptop or computer	<\$100 for sensor array; package can be ~\$500	Cliff Ho (6115), (505) 844-2384

Table 13. Summary of specifications for **biological** sensors

Sensor Technology	Specifications								
	Sensitivity	Selectivity	Stability	Speed	Size	Power	User Interface	Cost	Contact
A) Fatty Acid Methyl Esters (FAME) Analyzer	low nanograms	highly selective	SAW sensor can irreversibly load	< 10 min.	handheld	< 5 Watts per analysis	syringe and keypad or laptop	potentially < \$10K	Curtis Mowry (1764) (505) 844-6271
B) iDEP (insulator-based dielectrophoresis)	preconcentration method for other sensors	non-selective	expected to be high	milliseconds	millimeters	< 1 W	Is a module for larger systems	< \$1	Blake Simmons (8762) 925-294-2288
C) Bio-SAW Sensor	picograms of proteins	highly selective	SAW can drift over time. Analyte binding can be irreversible	minutes	several square cm	mW	system display plus some liquid handling; laptop	<\$100 per sensor	Susan Brozik (1744) (505) 844-5105
D) μ ProLab	picograms	expected to be highly selective	acoustic sensors tend to drift with time; optical systems will be more stable	minutes	handheld	< 5 W	minimal fluid handling, system display or laptop	TBD	Jeff Brinker (1002) (505) 272-7627
E) MicroChemLab (Liquid)	depending on analyte: 10-100 ppb for chemicals; sub-toxic (picomoles) for biotoxins	very high	hours	< 5 minutes	handheld	5 Watts	LCD display or laptop	< \$10K	Art Pontau (8358) 925-294-3159

5. Summary and Recommendations

This report has identified regulatory standards, policies, and needs associated with monitoring environmental contaminants for drinking water, storm water, pretreatment, and ambient air quality (see Section 3). Table 14 presents a summary and relative comparison of the general requirements for different environmental monitoring applications. The required concentration limits, sampling frequency, sampling method, and sampling phase are listed in relative terms to provide metrics for evaluation of the sensor technologies.

Table 14. Summary and comparison of relative requirements for different environmental monitoring applications.

Requirements	Drinking Water	Storm Water	Pre-Treatment	Ambient Air
Concentration	Lowest concentrations (ppb to ppm in aqueous phase)	Higher concentrations than drinking water (e.g., arsenic is 160 ppb in storm water for wood preservers while drinking water is 10 ppb)	Concentration are higher than drinking water (e.g., TCE is 69 ppb (daily) compared to 5 ppb for drinking water); almost all biological except for a few industries that manufacture chemicals; INDUSTRY SPECIFIC	Air concentrations are typically in the ppm range
Sampling Frequency	Most frequent sampling of the three water applications (would like real time, continuous monitoring)	Only need to sample occasionally (during rain storms)	More frequent monitoring than for storm water but less than for drinking water	Continuous (current methods average over a period of time using continuous flow)
Sampling Method	On-line, continuous with remote telemetry	Can be hand-held for occasional sampling	On-line or hand-held	Continuous air monitoring with remote telemetry
Sample Phase	Aqueous	Aqueous	Aqueous	Gas

Sensor technologies have been identified that may be compatible with the needs of the various environmental monitoring applications (see Section 4). Based on these surveys, Table 15 lists some of the viable sensor technologies that appear to have the highest potential in addressing the needs of these environmental monitoring applications.

Table 15. Summary of potential sensor technologies that can address environmental monitoring needs.

Sensor Technology	Application	Analyte	Comments
LIBS	Drinking Water, Storm Water, Pretreatment	Trace Metals	The cost of the laser and spectrometer are high. Additional development needs to bring the price down and package it for use in water applications. Could potentially be used to simultaneously identify 9 RCRA metals plus arsenic. Sampling interval ranges from 1 s to ~1 minute (for signal averaging). Can be run continuously.
Nanoelectrode Array	Drinking Water, Storm Water, Pretreatment	Trace Metals	Less selective than LIBS. Commercial company in Washington. Sampling interval on the order of seconds. Still under development to discern among multiple target analytes present.
Miniature Chemical Flow Probe Sensor	Drinking Water, Storm Water, Pretreatment	VOCs, Trace Metals	Expensive because of spectrometry (like LIBS). Reagents need to be supplied. Need to acquire sample to introduce reagent in a side-stream.
RadFET	Drinking Water	Radioisotopes	Need to use filters to allow speciation. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
Low-energy Pin Diodes Beta Spectrometer	Drinking Water	Radioisotopes	Commercially available. May not need any additional development. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
Cadmium Zinc Telluride Detectors	Drinking Water	Radioisotopes	Commercially available. Sensitivity in water for alpha and beta emitters is questionable given the attenuation through water.
SAWs	Drinking Water, Storm Water, Pretreatment, Air	VOCs	Sensitivity can get down to ~ppm, but fluctuations in environmental parameters (e.g., humidity, temperature) can reduce the sensitivity and accuracy. Sensor signal drifts over time. Cannot analyze more than three contaminants at once.
Chemiresistors	Drinking Water, Storm Water, Pretreatment, Air	VOCs	Sensitivity is limited (hundreds of ppm). Needs preconcentration. These can also be used to monitor in-situ remediation activities (patent pending: SD-7097 Automated Monitoring and Remediation System for Volatile Subsurface Contaminants)
microHound/Ion Mobility Spectrometer (IMS)	Drinking Water, Storm Water, Pretreatment, Air	Semi-Volatile Organic Compounds	Gas-phase detection; need to develop a sampling system to introduce water samples to IMS. Should be able to detect semi-volatile chlorinated hydrocarbons (e.g., polychlorinated biphenyls (PCBs)). Can detect pesticides, organic nitrates.

microChemLab (gas)	Drinking Water, Storm Water, Pretreatment, Air	VOCs	MCL is manufacturing these for ~\$10K per unit. Additional development work is needed to adapt these systems for VOCs.
microChemLab (liquid)	Drinking Water	Biological	Cost is high.
FAME	Drinking Water	Biological	Sampling is currently done manually.

The list of sensors presented in Table 15 is culled even further to identify the most promising technologies for each analyte considered (i.e., trace metals, radioisotopes, VOCs, semi-volatiles, and biological pathogens). Table 16 provides a summary of the future development required for these technologies to be adapted for use in environmental monitoring applications.

Table 16. Summary of the most promising technologies for each analyte class that could benefit from further development.

Sensor	Analyte	Future Development Required
LIBS	Trace Metals	LIBS systems employ diffraction gratings that must be scanned to cover the spectral range of metal contaminants with sufficient resolution for positive identification and quantification. Speed could be increased through the use of Sandia's programmable diffraction grating. Simultaneous determination could be made through the computer-aided design of holographic diffraction gratings. Estimate: 2-3 years/\$3-400K.
CZT	Radioisotopes	These detectors are inexpensive and sensitive to regulated radiation levels. Commercial spectrometer systems are available. A low level effort could adapt the spectrometer for water monitoring. Alpha emitting contaminants in water can not be detected by radiation events as alpha radiation is nonpenetrating. Estimate: 1 year/\$75K.
MicroChemLab, gas phase	VOCs	Due to the wide variety of organic contaminants that can be present in air or water, separation is essential for analysis. The MicroChemLab can be adapted to collect and analyze in both air and water. Leveraging funding could direct development towards specific targets. Estimate: 2-3 years/ \$200-400K.
MicroHound/Ion Mobility Spectrometry	Semi-Volatiles	The ion mobility spectrometer behind this instrument can be used in positive mode for common semi-volatiles or negative mode for highly selective detection of pesticides and halogenated semivolatiles. The diffusion-based separation could benefit from a pre-separation using a chromatography column. Estimate: 2-3 years/\$300-500K.
Bio-SAW Sensor	Biological Pathogens	Sensors with bioreceptors are highly selective, providing detection amplification over background contaminants. Still, biofouling can occur. Further development is needed to array significant numbers of sensors into a small area for multi-pathogen monitoring. Estimate: 3-4 years/\$500-600K.

The advancement of the LIBS technology would be focused on developing a continuous LIBS sensor for water-monitoring applications. Ideally, the sensor would be able to simultaneously detect the nine RCRA metals plus arsenic at low ppb levels. The development of holographic diffraction gratings would increase the speed and efficiency of the LIBS ability to simultaneously detect these trace metals.

For the CZT sensors, a low-level effort is needed to adapt these sensors for water applications. A significant challenge will be to detect alpha-emitting contaminants since the radiation is attenuated rapidly. A continuous CZT sensor with spectrometry would need to be adapted for aqueous environments.

The MicroChemLab device requires additional development to detect VOCs in aqueous environments. Sampling, analysis, and parameter optimization (e.g., polymer selection) for target VOCs need to be pursued. With preconcentration, the sensitivity of these devices can be in the ppb range, but repeatability and drift are significant issues with MicroChemLab.

The ion mobility spectrometer implemented in the MicroHound shows promise for detecting semi-volatile compounds such as pesticides and halogenated contaminants at low concentrations. Sampling methods would need to be developed to introduce aqueous samples to the IMS. Separation is based on the different “drift” times of the different ions through the IMS tube, but additional separation could be obtained by adding a chromatography column at the inlet. A great deal of research invested in the MicroHound project can be leveraged for applications in water monitoring and ambient-air monitoring (e.g., new materials and designs for the IMS drift tube).

The Bio-Saw sensor, and other continuous, real-time biological sensors, still require significant research and development before they can be applied to environmental monitoring applications. Bio-assay test kits are available that can provide detection of biological agents, but these require manual operation and interfacing.

Of the sensors identified in Table 16, we believe that LIBS (for trace metals) and ion-mobility spectrometry (for semi-volatiles) show the most promise in terms of capabilities, adaptability, and potential impact. Both have the capability to detect concentrations at or below regulatory levels, and the ability to detect trace metals and semi-volatiles is needed in a number of environmental applications ranging from drinking-water to ambient-air monitoring.

A primary consideration that still remains to be addressed is the performance of these sensors in each of the field applications. Features such as sensitivity, stability, selectivity, speed, size, and cost need to be tested and evaluated under actual operating conditions. Harsh and fluctuating environmental conditions can degrade the performance of many of these sensors. Nevertheless, a market analysis presented in the beginning of this report (see Section 2) indicates that a wide-ranging (and commercially viable) need can be filled by the successful development and application of these sensors to environmental monitoring applications. The sensor technologies identified in Table 15 and Table 16 appear to be the strongest candidates that can be further developed and adapted to address these needs.

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7. Appendices

7.1 Appendix A: Storm Water Monitoring Requirements (from 65 FR 64746)

TABLE A-1.—SECTOR-SPECIFIC NUMERIC LIMITATIONS AND BENCHMARK MONITORING
[Sector of permit affected/supplemental requirements]

Subsector (Discharge may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cutoff concentration ¹	Numeric limitation ²
General Sawmills and Planing Mills (SIC 2421)	Chemical Oxygen Demand (COD).	120.0 mg/L.	6.0–9.0 s.u. No Discharge of debris that will not pass through a 2.54 cm (1") diameter round opening.
Wood Preserving (SIC 2491)	Total Suspended Solids (TSS).	100 mg/L.	
	Total Zinc	0.117 mg/L.	
Log Storage and Handling (SIC 2411)	Total Arsenic	0.16854 mg/L.	
	Total Copper	0.0636 mg/L.	
Wet Decking Discharges at Log Storage and Handling Areas (SIC 2411).	Total Suspended Solids (TSS).	100 mg/L.	
	pH	
Hardwood Dimension and Flooring Mills; Special Products Sawmills, not elsewhere classified; Millwork, Veneer, Plywood and Structural Wood; Wood Containers; Wood Buildings and Mobile Homes; Reconstituted Wood Products; and Wood Products Facilities not elsewhere classified (SIC Codes 2426, 2429, 2431–2439 (except 2434), 2448, 2449, 2451, 2452, 2593, and 2499).	Debris (woody material such as bark, twigs, branches, heartwood, or sapwood).	
	Chemical Oxygen Demand (COD).	120.0 mg/L.	
	Total Suspended Solids (TSS).	100.0 mg/L.	

¹ Monitor once/quarter for the year 2 and year 4 monitoring years.
² Monitor once per year for each monitoring year.

TABLE B-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring and cutoff concentration ¹	Numeric limitation
Part of Permit Affected/Supplemental Requirements			
Paperboard Mills (SIC Code 2631)	COD	120.0 mg/L.	

¹ Monitor once/quarter for the year 2 and year 4 monitoring years

TABLE C-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation ²
Part of Permit Affected/Supplemental Requirements			
Phosphate Subcategory of the Fertilizer Manufacturing Point Source Category (40 CFR §418.10)—applies to precipitation runoff, that during manufacturing or processing, comes into contact with any raw materials, intermediate product, finished product, by-products or waste product (SIC 2874).	Total Phosphorus (as P)	105.0 mg/L, daily max. 35 mg/L, 30-day avg.
	Fluoride	75.0 mg/L, daily max. 25.0 mg/L, 30-day avg.
Agricultural Chemicals (2873–2879)	Nitrate plus Nitrite Nitrogen	0.68 mg/L	Nitrate plus Nitrite Nitrogen
Industrial Inorganic Chemicals (2812–2819)	Total Recoverable Lead	0.0816 mg/L	
	Total Recoverable Iron	1.0 mg/L	
	Total Recoverable Zinc	0.117 mg/L	
	Phosphorus	2.0 mg/L	
Soaps, Detergents, Cosmetics, and Perfumes (SIC 2841–2844).	Total Recoverable Aluminum	0.75 mg/L	Nitrate plus Nitrite Nitrogen
	Total Recoverable Iron	1.0 mg/L	
Plastics, Synthetics, and Resins (SIC 2821–2824)	Nitrate plus Nitrite Nitrogen	0.68 mg/L	Nitrate plus Nitrite Nitrogen
	Total Recoverable Zinc	0.117 mg/L	
	Total Recoverable Zinc	0.117 mg/L	

¹ Monitor once/quarter for the year 2 and year 4 Monitoring Years.
² Monitor once/year for each Monitoring Year.

TABLE D-1.—SECTOR-SPECIFIC NUMERIC LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric Limitation ²
Sector of Permit Affected/Supplemental Requirements			
Asphalt Paving and Roofing Materials (SIC 2951, 2952)	Total Suspended Solids (TSS)	100mg/L	23.0 mg/L, daily max. 15.0 mg/L, 30-day avg.
Discharges from areas where production of asphalt paving and roofing emulsions occurs (SIC 2951, 2952).	TSS	
	Oil and Grease	
	pH	
			15.0 mg/L, daily max. 10mg/L, 30-day avg. 6.0–9.0

¹ Monitor once/quarter for the year 2 and year 4 monitoring years.
² Monitor once per year for each monitoring year.

TABLE E-1.—SECTOR-SPECIFIC NUMERIC LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation ²
Sector of Permit Affected/Supplemental Requirements			
Clay Product Manufacturers	Total Recoverable Aluminum	0.75 mg/L	6.0–9.0 S.U.
(SIC 3245–3259, 3261–3269)	TSS	100 mg/L	
Concrete and Gypsum Product Manufacturers (SIC 3271–3275).	Total Recoverable Iron	1.0 mg/L	
Cement Manufacturing Facility, Material Storage Runoff: Any discharge composed of runoff that derives from the storage of materials including raw materials, intermediate products, finished products, and waste materials that are used in or derived from the manufacture of cement.	Total Suspended Solids (TSS)	50 mg/L, daily max..	
	pH	

¹ Monitor once/quarter for the year 2 and year 4 monitoring years.
² Monitor once per year for each monitoring year.

TABLE F-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Sector of permit affected/supplemental requirements—			
Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cutoff concentration ¹	Numeric limitation
Steel Works, Blast Furnaces, and Rolling and Finishing Mills (SIC 3312–3317)	Total Recoverable Aluminum	0.75 mg/L	
	Total Recoverable Zinc	0.117 mg/L	
Iron and Steel Foundries (SIC 3321–3325)	Total Recoverable Aluminum	0.75 mg/L	
	Total Suspended Solids	100 mg/L	
Rolling, Drawing, and Extruding of Non-Ferrous Metals (SIC 3351–3357)	Total Recoverable Copper	0.0636 mg/L	
	Total Recoverable Iron	1.0 mg/L	
	Total Recoverable Zinc	0.117 mg/L	
	Total Recoverable Copper	0.0636 mg/L	
Non-Ferrous Foundries (SIC 3363–3369)	Total Recoverable Zinc	0.117 mg/L	
	Total Recoverable Copper	0.636 mg/L	

¹ Monitor once/quarter for the year 2 and year 4 Monitoring Years.

TABLE G-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING FOR COPPER ORE MINING AND DRESSING FACILITIES

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cutoff concentration ¹	Numeric limitation
Part of Permit Affected/Supplemental Requirements			
Copper Ore Mining and Dressing Facilities (SIC 1021)	Total Suspended Solids (TSS)	100 mg/L	
	Nitrate plus Nitrite Nitrogen	0.68 mg/L	
	Chemical Oxygen Demand (COD)	120 mg/L	

¹ Monitor once/quarter for the year 2 and year 4 Monitoring Years.

TABLE G-2.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING FOR DISCHARGES FROM WASTE ROCK AND OVERBURDEN PILES FROM ACTIVE ORE MINING OR DRESSING FACILITIES

Part of permit affected/supplemental requirements—			
Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cutoff concentration ¹	Numeric limitation
Iron Ores; Copper Ores; Lead and Zinc Ores; Gold and Silver Ores; Ferroalloy Ores Except Vanadium; Miscellaneous Metal Ores (SIC Codes 1011, 1021, 1031, 1041, 1044, 1061, 1081, 1094, 1099). See above, as applicable	Total Suspended Solids (TSS)	100 mg/L	
	Turbidity (NTUs)	5 NTUs above background.	
	pH	6.0–9.0 standard units.	
	Hardness (as CaCO ₃)	no benchmark value.	
	Antimony, Total	0.636 mg/L	
	Arsenic, Total	0.16854 mg/L	
	Beryllium, Total	0.13 mg/L	
	Cadmium, Total (hardness dependent)	0.0159 mg/L	
	Copper, Total (hardness dependent)	0.0636 mg/L	
	Iron, Total	1.0 mg/L	
	Lead, Total (hardness dependent)	0.0816 mg/L	
	Manganese, Total	1.0 mg/L	
	Mercury, Total	0.0024 mg/L	
	Nickel, Total (hardness dependent)	1.417 mg/L	
	Selenium, Total	0.2385 mg/L	
Silver, Total (hardness dependent)	0.318 mg/L		
Zinc, Total (hardness dependent)	0.117 mg/L		

¹ Monitor at least once during the first year of permit coverage, and twice annually thereafter for any parameter that exceeds the benchmark value. Facilities that monitored for the full list of Table G-2 parameters during the previous permit need not sample the entire list again, however they must continue twice annual monitoring for parameters that exceeded the benchmark values in the initial sampling event.

TABLE G-3.—ADDITIONAL MONITORING REQUIREMENTS FOR DISCHARGES FROM WASTE ROCK AND OVERBURDEN PILES FROM ACTIVE ORE MINING OR DRESSING FACILITIES

Supplemental requirements—			
Type of Ore mined	Pollutants of concern		
	Total suspended solids (TSS)	pH	Metals, total
Tungsten Ore	X	X	Arsenic, Cadmium (H), Copper (H), Lead (H), Zinc (H).
Nickel Ore	X	X	Arsenic, Cadmium (H), Copper (H), Lead (H), Zinc (H).
Aluminum Ore	X	X	Iron.
Mercury Ore	X	X	Nickel (H).
Iron Ore	X	X	Iron (Dissolved).
Platinum Ore			Cadmium (H), Copper (H), Mercury, Lead (H), Zinc (H).
Titanium Ore	X	X	Iron, Nickel (H), Zinc (H).
Vanadium Ore	X	X	Arsenic, Cadmium (H), Copper (H), Zinc (H).
Copper, Lead, Zinc, Gold, Silver and Molybdenum	X	X	Arsenic, Cadmium (H), Copper (H), Lead, Mercury, Zinc (H).
Uranium, Radium and Vanadium	X	X	Chemical Oxygen Demand, Arsenic, Radium (Dissolved and Total), Uranium, Zinc (H).

Note: (H) indicates that hardness must also be measured when this pollutant is measured.

TABLE H-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cutoff concentration ¹	Numeric limitation
Part of Permit Affected/Supplemental Requirements			
Coal Mines and Related Areas	Total Recoverable Aluminum	0.75 mg/L	
(SIC 1221-1241)	Total Recoverable Iron	1.0 mg/L	
	Total Suspended Solids	100 mg/L	

¹ Monitor once/quarter for the year 2 and year 4 Monitoring Years.

TABLE J-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cutoff concentration ¹	Numeric limitation ²
Part of Permit Affected/Supplemental Requirements			
Mine Dewatering Activities at Construction Sand and Gravel, Industrial Sand, and Crushed Stone Mining Facilities (SIC 1422-1429, 1442, 1446)	Total Suspended Solids ... pH	25 mg/L, monthly avg. 45 mg/L, daily max 6.0-9.0
Sand and Gravel Mining (SIC 1442, 1446)	Nitrate plus Nitrogen	0.68 mg/L	
	Total Suspended Solids	100 mg/L	
Dimension and Crushed Stone and Nonmetallic Minerals (except fuels) (SIC 1411, 1422-1429, 1481, 1499)	Total Suspended Solids ...	100 mg/L	

¹ Monitor once/quarter for the year 2 and year 4 Monitoring Years.

² Monitor once/year for Each Monitoring Year.

TABLE K-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK AND COMPLIANCE MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cutoff concentration ¹	Numeric limitation ²
Part of Permit Affected/Supplemental Requirements			
ALL—Industrial Activity Code "HZ" (Note: permit coverage limited in some States)	Ammonia	19.0 mg/L	
	Total Recoverable Magnesium	0.0636 mg/L	
	Chemical Oxygen Demand (COD)	120.0 mg/L	
	Total Recoverable Arsenic	0.16854 mg/L	
	Total Recoverable Cadmium	0.0159 mg/L	
	Total Cyanide	0.0636 mg/L	
	Total Recoverable Lead	0.0816 mg/L	
	Total Recoverable Mercury	0.0024 mg/L	
	Total Recoverable Selenium	0.2385 mg/L	
	Total Recoverable Silver	0.0318 mg/L	
ALL—Industrial Activity Code "HZ" Subject to the Provisions of 40 CFR Part 445 Subpart A.	BOD5		220 mg/l, daily max. 56 mg/l, monthly avg. maximum.
	TSS		88 mg/l, daily max. 27 mg/l, monthly avg. maximum.
	Ammonia		10 mg/l, daily maximum. 4.9 mg/l, monthly avg. maximum.
	Alpha Terpineol		0.042 mg/l, daily max. 0.019 mg/l, monthly avg. maximum.
	Aniline		0.024 mg/l, daily max. 0.015 mg/l, monthly avg. maximum.
	Benzic Acid		0.119 mg/l, daily max. 0.073 mg/l, monthly avg. maximum.
	Naphthalene		0.059 mg/l, daily max. 0.022 mg/l, monthly avg. maximum.
	p-Cresol		0.024 mg/l, daily max. 0.015 mg/l, monthly avg. maximum.
	Phenol		0.048 mg/l, daily max. 0.029 mg/l, monthly avg. maximum.
	Pyridine		0.072 mg/l, daily max. 0.025 mg/l, monthly avg. maximum.
	Arsenic (Total)		1.1 mg/l, daily maximum. 0.54 mg/l, monthly avg. maximum.
	Chromium (Total)		1.1 mg/l, daily maximum. 0.46 mg/l, monthly avg. maximum.
	Zinc (Total)		0.535 mg/l, daily max. 0.296 mg/l, monthly avg. maximum.
	pH		Within the range of 6-9 pH units.

¹ These benchmark monitoring cutoff concentrations apply to storm water discharges associated with industrial activity other than contaminated storm water discharges from landfills subject to the numeric effluent limitations set forth in Table K-1. Monitor once/quarter for the year 2 and year 4 monitoring years.

² As set forth at 40 CFR Part 445 Subpart A, these numeric limitations apply to contaminated storm water discharges from hazardous waste landfills subject to the provisions of RCRA Subtitle C at 40 CFR Parts 264 (Subpart N) and 265 (Subpart N) except for any of the facilities described below:

(a) Landfills operated in conjunction with other industrial or commercial operations when the landfill only receives wastes generated by the industrial or commercial operation directly associated with the landfill;

(b) Landfills operated in conjunction with other industrial or commercial operations when the landfill receives wastes generated by the industrial or commercial operation directly associated with the landfill and also receives other wastes provided the other wastes received for disposal are generated by a facility that is subject to the same provisions in 40 CFR Subchapter N as the industrial or commercial operation or the other wastes received are of similar nature to the wastes generated by the industrial or commercial operation;

(c) Landfills operated in conjunction with Centralized Waste Treatment (CWT) facilities subject to 40 CFR Part 437 so long as the CWT facility commingles the landfill wastewater with other non-landfill wastewater for discharge. A landfill directly associated with a CWT facility is subject to this part if the CWT facility discharges landfill wastewater separately from other CWT wastewater or commingles the wastewater from its landfill only with wastewater from other landfills; or

(d) Landfills operated in conjunction with other industrial or commercial operations when the landfill receives wastes from public service activities so long as the company owning the landfill does not receive a fee or other remuneration for the disposal service.

TABLE L-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK AND COMPLIANCE MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation ²
Sector of Permit Affected/Supplemental Requirements			
All Landfills, Land Application Sites and Open Dumps (Industrial Activity Code "LF"). All Landfills, Land Application Sites and Open Dumps, Except Municipal Solid Waste Landfills (MSWLF) Areas Closed in Accordance with 40 CFR 258.60 (Industrial Activity Code "LF"). All Landfills Which are Subject to the Requirements of 40 CFR Part 445 Subpart B (Industrial Activity Code "LF").	Total Suspended Solids (TSS)	100 mg/L	
	Total Recoverable Iron	1.0mg/L	
	BOD5		140 mg/l, daily max. 37 mg/l, monthly ave maximum
	TSS		88 mg/l, daily max. 27 mg/l, monthly ave maximum
	Ammonia		10 mg/l, daily max. 4.9 mg/l, monthly ave maximum
	Alpha Terpineol		0.033 mg/l, daily max. 0.016 mg/l, monthly ave maximum
	Benzic Acid		0.12 mg/l, daily max. 0.071 mg/l, monthly ave maximum
	p-Cresol		0.025 mg/l, daily max. 0.014 mg/l, monthly ave maximum
	Phenol		0.026 mg/l, daily max. 0.015 mg/l, monthly ave maximum
	Zinc (Total)		0.20 mg/l, daily max. 0.11 mg/l, monthly ave maximum
pH		Within the range of 6-9 pH units.	

¹ These benchmark monitoring cutoff concentrations apply to storm water discharges associated with industrial activity other than contaminated storm water discharges from landfills subject to the numeric effluent limitations set forth in Table L-1. Monitor once/quarter for the year 2 and year 4 monitoring years.

² As set forth at 40 CFR Part 445 Subpart B, these numeric limitations apply to contaminated storm water discharges from MSWLFs which have not been closed in accordance with 40 CFR 258.60, and contaminated storm water discharges from those landfills which are subject to the provisions of 40 CFR Part 257 except for discharges from any of facilities described in (a) through (d) below:

- (a) landfills operated in conjunction with other industrial or commercial operations when the landfill only receives wastes generated by the industrial or commercial operation directly associated with the landfill;
- (b) landfills operated in conjunction with other industrial or commercial operations when the landfill receives wastes generated by the industrial or commercial operation directly associated with the landfill and also receives other wastes provided the other wastes received for disposal are generated by a facility that is subject to the same provisions in 40 CFR Subchapter N as the industrial or commercial operation or the other wastes received are of similar nature to the wastes generated by the industrial or commercial operation;
- (c) landfills operated in conjunction with Centralized Waste Treatment (CWT) facilities subject to 40 CFR Part 437 so long as the CWT facility commingles the landfill wastewater with other non-landfill wastewater for discharge. A landfill directly associated with a CWT facility is subject to this part if the CWT facility discharges landfill wastewater separately from other CWT wastewater or commingles the wastewater from its landfill only with wastewater from other landfills; or
- (d) landfills operated in conjunction with other industrial or commercial operations when the landfill receives wastes from public service activities so long as the company owning the landfill does not receive a fee or other remuneration for the disposal service.

TABLE M-1.—SECTOR-SPECIFIC NUMERIC LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation
Sector of Permit Affected/Supplemental Requirements			
Automobile Salvage Yards (SIC 5015)	Total Suspended Solids (TSS)	100.0 mg/L	
	Total Recoverable Aluminum	0.75 mg/L	
	Total Recoverable Iron	1.0 mg/L	
	Total Recoverable Lead	0.0816 mg/L	

¹ Monitor once/quarter for the year 2 and year 4 monitoring years.

TABLE N-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation
Part of Permit Affected/Supplemental Requirements			
Scrap Recycling Facility (SIC 5093)	Chemical Oxygen Demand (COD). Total Suspended Solids (TSS). Total Recoverable Aluminum. Total Recoverable Copper Total Recoverable Iron Total Recoverable Lead Total Recoverable Zinc	120 mg/L. 100 mg/L. 0.75 mg/L. 0.0836 mg/L. 1.0 mg/L. 0.0816 mg/L. 0.117 mg/L.	

¹Monitor once/quarter for the year 2 and year 4 Monitoring Years.

TABLE O-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation ²
Part of Permit Affected/Supplemental Requirements			
Steam Electric Generating Facilities (Industrial Activity Code "SE").	Total Recoverable Iron	1.0 mg/L.	

¹Monitor once/quarter for the year 2 and year 4 Monitoring Years.

²Note that the numeric effluent limitation guidelines for coal pile runoff at steam electric generating facilities have been adopted as a standard numeric limits for all coal pile runoff. See Part 5.1.3.

TABLE Q-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation
Part of Permit Affected/Supplemental Requirements			
Water Transportation Facilities (SIC 4412-4499)	Total Recoverable Aluminum. Total Recoverable Iron. Total Recoverable Lead. Total Recoverable Zinc.	0.75 mg/L 1.0 mg/L 0.0816 mg/L 0.117 mg/L	

¹Monitor once/quarter for the year 2 and year 4 Monitoring Years.

TABLE S-1.—SECTOR-SPECIFIC NUMERIC LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation
Sector of Permit Affected/Supplemental Requirements			
Facilities at airports that use more than 100,000 gallons of glycol-based deicing/anti-icing chemicals and/or 100 tons or more of urea on an average annual basis; monitor ONLY those outfalls from the airport facility that collect runoff from areas where deicing/anti-icing activities occur (SIC 45XX).	Biochemical Oxygen Demand (BOD ₅).	30 mg/L Chemical Oxygen Demand (COD).	120.0mg/L. Ammonia 19 mg/L. pH 8.0 to 9 s.u

¹Monitor once/quarter for the year 2 and year 4 monitoring years.

TABLE U-1. SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one Sector/Subsector)	Parameter	Benchmark monitoring cut-off concentration ¹	Numeric limitation
Part of Permit Affected/Supplemental Requirements			
Grain Mill Products (SIC 2041-2048)	Total Suspended Solids (TSS).	100 mg/L.	
Fats and Oils Products (SIC 2074-2079)	Biochemical Oxygen Demand (BOD ₅). Chemical Oxygen Demand (COD). Nitrate plus Nitrate Nitrogen. Total Suspended Solids (TSS).	30 mg/L. 120 mg/L. 0.68 mg/L. 100 mg/L.	

¹Monitor once/quarter for the year 2 and year 4 Monitoring Years.

TABLE Y-1.—SECTOR-SPECIFIC NUMERIC EFFLUENT LIMITATIONS AND BENCHMARK MONITORING

Subsector	Parameter	Benchmark monitoring cutoff concentration	Numeric Limitations
Part of Permit Affected/Supplemental Requirements			
Tires and Inner Tubes; Rubber Footwear; Gaskets, Packing and Sealing Devices; Rubber Hose and Belting; and Fabricated Rubber Products, Not Elsewhere Classified (SIC 3011–3069, rubber).	Total Recoverable Zinc	0.117 mg/L	

¹Monitor once/quarter for the year 2 and year 4 Monitoring Years.

TABLE AA-1.—SECTOR-SPECIFIC NUMERIC LIMITATIONS AND BENCHMARK MONITORING

Subsector (Discharges may be subject to requirements for more than one sector/subsector)	Parameter	Benchmark monitoring cutoff concentration ¹	Numeric Limitation
Part of Permit Affected/Supplemental Requirements			
Fabricated Metal Products Except Coating (SIC 3411–3471, 3482–3499, 3911–3915).	Total Recoverable Aluminum	0.75 mg/L	
	Total Recoverable Iron	1.0 mg/L	
	Total Recoverable Zinc	0.117 mg/L	
	Nitrate plus Nitrite Nitrogen	0.68 mg/L	
	Nitrate plus Nitrite Nitrogen	0.68 mg/L	
Fabricated Metal Coating and Engraving (SIC 3479)	Total Recoverable Zinc	0.117 mg/L	
	Nitrate plus Nitrite Nitrogen	0.68 mg/L	

¹Monitor once/quarter for the year 2 and year 4 Monitoring Years

Distribution

Internal

1	MS-1079	M. Scott, 1700
1	MS-1425	S. Martin, 1707
1	MS-1425	S. Casalnuovo, 1744
1	MS-0892	R. Cernosek, 1764
1	MS-0892	A. Robinson, 1764
1	MS-0701	P. Davies, 6100
1	MS-0701	J. Merson, 6100
1	MS-0735	R. Finley, 6115
1	MS-0735	C. Ho, 6115
1	MS-0750	D. Borns, 6116
1	MS-0751	L. Costin, 6117
1	MS-0750	T. Hinkebein, 6118
1	MS-1088	D. Miller, 6134
1	MS-1088	S. Collins, 6134
1	MS-1089	D. Fate, 6135
1	MS-1089	M.J. Davis, 6135
1	MS-0755	W. Einfeld, 6233
1	MS-9018	Central Technical Files, 8945-1
2	MS-0899	Technical Library, 9616