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SUMMARY

On February 12-13, 1992, the National Institute for Occupational Safety and Health (NIOSH) conducted a Health Hazard Evaluation (HHE) at the Inland Steel Company's No. 3 Cold Strip - East Mill in East Chicago, Indiana. This evaluation was made in response to a joint request from Inland Steel and the United Steelworkers of America, Local 1010. The request involved the assessment of potential employee exposures in specific areas of the cold strip mill that were identified by a newly established joint union/management safety committee.

On February 11, 1992, an opening conference was held between NIOSH, management, and union representatives to discuss the specific areas that were outlined in the request. These areas included the 80" Tandem Mill/basement, #5 Pickle Line, #29 Temper Mill, Side trim/Inspection lines (Rewind), #6 Anneal Furnaces, Roll Building, and Shipping Department-East. On February 12-13, 1992, air sampling and a noise survey were conducted. During the environmental evaluation, the union requested that the Pico Roll Shop be included in the HHE.

Personal breathing zone (PBZ) and general area air samples were collected for oil mist, naphtha, acid mist, metals, and hydrocarbons throughout the facility. Airborne oil mist concentrations ranged from non-detected to 0.29 milligrams per cubic meter (mg/m^3) of air. All the oil mist concentrations were well below the NIOSH Recommended Exposure Limit (REL), the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV), and the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 5 mg/m^3. The samples for naphtha indicated airborne concentrations ranging from non-detected to 43 mg/m^3. The NIOSH REL, ACGIH TLV, and OSHA PEL for naphtha are 350, 525, and 1600 mg/m^3, respectively. Both hydrochloric and sulfuric acids were detected on the acid mist samples at concentrations below the evaluation criteria of 7 mg/m^3 (ceiling) of air and 1 mg/m^3, respectively. Hydrochloric acid concentrations ranged from non-detected to 0.18 mg/m^3, while sulfuric acid concentrations ranged from 0.01 to 0.04 mg/m^3. Four relatively non-toxic metals (calcium, iron, magnesium, zinc) were detected during a welding operation. An airborne iron concentration of 0.06 mg/m^3 on one sample was the highest level measured. However, the evaluation criteria for iron oxide, dust or fume, is 5 mg/m^3. The hydrocarbon samples were used to qualitatively identify the presence of potential contaminants produced as emissions from the heated oils. This analysis identified several contaminants with the major components being branched alkanes (C_9-C_{11}), nonane, decane, and undecane. Minor chromatographic peaks were also identified for benzene and toluene. Bulk samples collected for qualitative analysis indicated that the rust preventative contained mostly long chain hydrocarbons and the cleaning solution from the Pico Roll Shop consisted of triethyl borate and boron nitrilotriethoxide. When the cleaning solution was heated to simulate its use on the hot rollers from the tandem mill, propylene glycol was detected.

The noise evaluation consisted of both personal samples (measured with dosimeters) and area samples (measured with a sound level meter). The time-weighted averages for these samples ranged from 83.0 to 95.8 decibels, A-weighted scale (dB[A]). Five of the 17 dosimeter samples exceeded the OSHA PEL for noise. However, of the 12 surveyed employees who had noise exposures less than 90 dB(A), only four of these were also less than 85 dB(A), the OSHA action level and the NIOSH REL for noise. Thus, 13 of the 17 noise dosimeter samples exceeded OSHA noise levels for either hearing conservation regulations or possible engineering controls. Nearly all of these employees were observed wearing some type of hearing protection during the

sampling period. The area samples had noise levels ranging from 68 to 124 dB(A). Noise levels using the C-weighted scale were also collected in most of the areas and ranged from 76 to 110 dB(C). Many of these samples were used to determine the noise attenuation of protective booths.

The environmental air samples collected during this investigation do not indicate excessive exposure to oil mist, naphtha, acid mist, or metals. However, these results may not be indicative of typical exposures due to low production requirements and other difficulties encountered during this investigation. The noise survey indicates that employee noise exposures exceeded OSHA PELs or action levels in several areas. The presence of several employees in the No. 3 Cold Strip - East Mill with hearing loss as well as hearing threshold shifts over a four year period implies that the Inland Steel Company's Hearing Conservation Program is not completely effective and needs further improvement.

KEYWORDS: SIC 3316 (Steel Works, Blast Furnaces, and Rolling and Finishing Mills) oil mist, naphtha, hydrochloric and sulfuric acid, metals, noise, hearing loss, threshold shift, cold rolling.

INTRODUCTION

On February 12, 1991, the National Institute for Occupational Safety and Health (NIOSH) received a joint request for a Health Hazard Evaluation (HHE) from representatives of the Inland Steel Company and the United Steelworkers of America, Local 1010. This request was submitted as a follow-up to a previous HHE (HETA 90-325) where a NIOSH walk-through investigation was performed in response to a joint initiative by the operating management and union officials of the #3 Cold Strip Intermediate Products Department. The joint initiative introduced a new safety program, and requested the assistance of NIOSH in evaluating potential employee exposures. At that time, NIOSH determined that there were no specific health complaints and that the request was beyond the scope of the HHE program. As a result, management and union officials identified specific areas of greatest concern and resubmitted the current HHE request outlining these areas.

On February 11-13, 1992, investigators from NIOSH visited the Inland Steel Company to conduct environmental sampling in the No. 3 Cold Strip - East Mill. On February 11, 1992, an opening conference was held with management and union representatives to discuss the specific areas outlined in the request. After the meeting, a walk-through of these areas was conducted to familiarize the NIOSH investigators with the processes and employee classifications. The areas listed in the request included the 80" Tandem Mill/basement, #5 Pickle Line, #29 Temper Mill, Side trim/Inspection lines (Rewind), and Shipping Department-East.

On February 12-13, 1992, the environmental sampling was conducted. Environmental air samples and bulk samples for potential contaminants were collected from employees and areas in the following locations: #5 Pickle Line, #29 Temper Mill, 80" Tandem Mill, Rewind Area, and Shipping Dept.-East. At the request of the union, the Pico Roll Shop was also included in the scope of the HHE. Previous environmental sampling and other pertinent data collected by the company were requested for review. Personal noise measurements were collected with noise dosimeters over the two days in the following locations: #5 Pickle Line, #6 Anneal Furnaces, #29 Temper Mill, 80" Tandem Mill, and Roll Building. Additional area noise measurements were made in various locations in the Cold Strip Mill for comparison to the company's noise measurements that were provided to NIOSH. Finally, audiometric data for employees in the Cold Strip Mill, given to NIOSH investigators by the Environmental, Health, and Safety Office of Inland Steel Company, were analyzed. Some of the personal samples are less than full-shift duration because of employees' work schedules or because of production difficulties.

BACKGROUND

The No. 3 Cold Strip - East Mill at Inland Steel cold rolls steel for use in auto bodies, refrigerators, and other familiar products. The cold-reduced steel is made by cold rolling previously hot-rolled steel which is in long, thin sheets wrapped into a coil. The coils of steel are received from a Hot Strip Mill after cooling and fed onto the #5 Pickle Line. During the pickling process, oxides and scale are chemically removed from the surface of the steel by the action of water solutions of inorganic acids.(1) After the pickling, the coils are fed to the 80" Tandem Mill which rolls the steel under great pressure to precision thicknesses. This process generates considerable heat and not only raises the temperature of the steel but also that of the rolls applying the pressure. The heat is dissipated by a system of flood lubrication in which a mixture of oils is directed in small streams or jets against the roll bodies and the surface of the steel. The resultant steel temperatures generally range between 150˚ and 250˚F.(1) Cold-rolling substantially reduces the thickness of the steel to fine tolerances. As a result of the cold rolling, the material is hardened, which is an undesirable effect. The steel is then softened by reheating the coils in the

#6 Box Annealing Furnaces. The furnaces slowly raise the temperature of the steel to a specified level, which is then maintained for several hours. This process restores the ductility lost during the cold reduction. After the coils are cooled, the steel is further cold reduced in the #29 Temper Mill. This rolling imparts the desired surface finish to the steel, produces an acceptable flatness, and develops the desired mechanical properties.(1) Lubricating oils are also used during this cold rolling process to dissipate the heat, and a coating of a rust preventative may also be applied. The steel coils are then prepared for shipment in the Rewind area where surface treatments, rust preventative, or wrappings may be applied. The coils are then loaded onto rail cars in the Shipping East Area. Additional applications of the rust preventative may be applied before shipment.

METHODS

Personal breathing zone (PBZ) and general area air samples were collected from various areas throughout the facility. These included samples for oil mists, naphtha, acid mists, metals, and hydrocarbons. Bulk samples of the various lubricating and rolling oils used in these areas were collected for use as standards during laboratory analysis. Bulk samples of a rust inhibitor (NALCO 6292) used in various areas and a cleaning solution (MW5200) used in the Pico Roll Shop were also collected. Personal noise measurements were collected with noise dosimeters from the same areas as the air samples, as well as areas near the #6 Anneal Furnaces and Roll Building. Area noise measurements were made in various locations in the Cold Strip Mill for comparison to the company's noise measurements. Other pertinent records from the Cold Strip Mill were also reviewed during this investigation. Included were employee audiometric data, the hearing conservation program, the Occupational Safety and Health Administration (OSHA) 200 logs, and previous environmental sampling data.

The samples for oil mist were collected using 37 millimeter (mm), mixed cellulose ester membrane (MCE) filters with an 8 micron (µm) pore size. These filters were attached via Tygon® tubing to Gilian®, Model No. HFS 513A, hi-flow personal sampling pumps calibrated at a flow rate of 2.0 liters per minute (lpm). These filters were then analyzed for oil mist by infrared spectrophotometry following NIOSH Method 5026.(2) Each filter was transferred with tweezers into a scintillation vial and extracted with 10.0 milliliters (ml) of Freon 113. These samples were analyzed, against standards prepared from the liquid oil bulk samples, at an absorbance of 2940 reciprocal centimeters (cm^{-1}) to determine oil mist concentrations.

The air samples for naphtha were collected using standard 150 milligram (mg) activated charcoal tubes. These sorbent tubes were attached via Tygon® tubing to Gilian®, Model No. LFS 113 DC, low-flow personal sampling pumps calibrated at a flow rate of 200 ml per minute (ml/min). These sorbent tubes were then analyzed by gas chromatography according to NIOSH Method 1550.(2) The samples were desorbed for 30 minutes in 1.0 ml of carbon disulfide. Aliquots of the resulting solution were analyzed with a Hewlett-Packard, Model 5890A, gas chromatograph equipped with a flame ionization detector (GC/FID). Standards prepared from the bulk sample of the rust inhibitor were used to determine the naphtha concentrations.

The acid mist samples were collected using 600 mg, ORBO™ 53 washed silica gel sorbent tubes in the same manner as the naphtha samples. These samples were analyzed for fluoride, chloride, nitrate, bromide, phosphate, and sulfate concentrations by ion chromatography according to NIOSH Method 7903.(2) The samples were desorbed in 10.0 ml of a 0.675 millimolar (mM) sodium bicarbonate and 1.98 mM sodium carbonate solution and heated in a boiling water bath for ten minutes. An aliquot of each sample was analyzed by a Dionex 2010i ion chromatograph equipped with a WISP 710B autosampler.

The air samples for metals were collected in the same manner as the oil mist samples using the 37 mm MCE filters. These samples were then analyzed for 30 metals following NIOSH Method 7300.[2] The filters were digested in 4 ml of concentrated nitric acid and 1 ml of concentrated perchloric acid. Samples were diluted to 10 ml after digestion and analyzed using a Thermo Jarrell Ash ICAP 61 simultaneous scanning inductively coupled plasma emission spectrometer controlled by a NEC Personal Computer-AT.

The air samples for hydrocarbons (hydrocarbon screen) were collected using activated charcoal tubes in the same manner as the naphtha samples. These samples were desorbed with 1 ml of carbon disulfide and screened by GC/FID, using a 30 meter DB-1 fused silica capillary column (splitless mode). The resulting chromatograms were compared, and one representative sample was then further analyzed by GC equipped with a mass selective detector (MSD) to qualitatively identify the hydrocarbons present.

The bulk samples of the rust inhibitor (NALCO 6292) and cleaning solution (Pico Roll Shop) were analyzed to determine their constituents. An aliquot of the rust inhibitor was injected directly into a VG Trio-1 gas chromatograph/mass spectrometer. The cleaning solution sample was analyzed using a Perkin-Elmer ATD 400 automatic thermal desorber interfaced directly to a HP5890A gas chromatograph and HP5790 mass selective detector (TD-GC-MSD). The bulk sample was thermally desorbed at 50˚C to simulate the use of this solution to clean the hot rolls from the Tandem Mill and to identify the potential contaminants that are vaporized. This bulk solution was also diluted with ethanol and carbon disulfide and analyzed by GC/MSD to identify its major components.

The noise dosimeters used in the survey were Metrosonics Model dB301/26 Metrologgers, a small noise level recording device which is worn on the waist of the employee with a 1/4 inch microphone attached to the shoulder of the worker's shirt. This dosimeter is designed to measure noise in decibels, A-weighted levels (dB[A]) four times per second. The noise measurements are integrated according to the OSHA noise regulation (see Evaluation Criteria section of this report) for an entire minute and stored separately in the Metrologger for later analysis and final storage. Each dosimeter was calibrated according to the manufacturer's instructions before being placed on the worker. After the recording period was completed, the dosimeter was removed from the worker and placed in the standby mode of operation. The data were later transferred to a Metrosonics Model dt-390 Metroreader/Data Collector following the noise sampling. Prior to turning off the dosimeter, it was again calibrated to assure that the device had not changed during the sampling period. The dosimeter information was finally transferred to a personal computer with supporting Metrosonics Metrosoft computer software for permanent data storage and later analysis.

Area noise samples were made with a Quest Electronics Model 2400 Type 2 Sound Level Meter. A-weighted and C-weighted measurements were made with the meter in the maximum hold mode in each of the areas that were surveyed. During the measurement period, the digital display was monitored by the investigator to assure that the value was not the result of extraneous noise or a unique event.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to ten hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Recommended Exposure Limits (RELs),[3] 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs),[4] and 3) the U.S. Department of Labor, OSHA Permissible Exposure Limits (PELs).[5] The OSHA PELs may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH RELs, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in the report, it should be noted that the most stringent standard was used; however, industry is legally required to meet those levels specified by the OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a chemical substance during a normal 8- to 10-hour workday. In the case of noise exposures, a TWA refers to a normal 8-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

A. Oil Mists

The evaluation criteria for oil mists are primarily based on studies conducted with a petroleum based, white mineral oil with no additives.[6,7] Mineral oils, as well as other lubricating or cutting oils, can contain a complex mixture of aromatic, naphthenic, and straight- or branched-chain paraffinic hydrocarbons. The composition of a given oil depends upon the way in which the oil was processed, and the degree to which it was processed. Many mineral oils in use today vary in composition, and can contain various additives and impurities.

Mineral oil mist is of low toxicity.[8] Inhalation of mineral oil mist in high concentrations may cause pulmonary effects, although this has rarely been reported. A single case of lipoid pneumonitis suspected to have been caused by exposure to very high concentrations of oil mist was reported in 1950; this occurred in a cash register serviceman whose heavy exposure occurred over 17 years of employment.[9] Early epidemiological studies linked cancers of the skin and scrotum with exposure to mineral oils.[10] These effects have been attributed to contaminants such as polycyclic aromatic hydrocarbons (PAHs) and/or additives with carcinogenic properties present in the oil. The International Agency for Research on Cancer (IARC) determined that there is sufficient evidence for carcinogenicity to humans, based on epidemiologic studies of uncharacterized mineral oils containing additives and impurities; there is inadequate evidence for carcinogenicity to humans for highly refined oils.[11] Prolonged exposure to mineral oil mist may also cause dermatitis. Persons with pre-existing skin disorders may be more susceptible to these effects.

Environmental evaluation criteria for mineral oil mist have been established by ACGIH and OSHA, at 5 milligrams per cubic meter (mg/m^3) of air as an eight-hour TWA. This criterion was established to minimize respiratory irritation and pulmonary effects. The NIOSH REL for oil mist is also 5 mg/m^3, with a STEL of 10 mg/m^3. However, since the role of additives and oil fume from partial heat-decomposition have yet to be completely evaluated experimentally, NIOSH suggests that these criteria may not be applicable to all forms of oil mists.(6)

B. Petroleum Distillates (Naphtha)

Petroleum naphtha is comprised mainly of aliphatic hydrocarbons.(12) Effects from exposure to these solvents are primarily acute, unless significant amounts of substances that have chronic toxicity are present, such as benzene or glycol ethers. Epidemiologic studies have shown that exposure to similarly refined petroleum solvents (i.e., mineral spirits, Stoddard solvent) can cause dry throat, burning or tearing of the eyes, mild headaches, dizziness, respiratory irritation, and dermatitis.(13) Some of these refined petroleum solvents have also been shown to cause transient central nervous system depression and that chronic intoxication may lead to polyneuropathy. The onset of these symptoms can be associated with the presence of C_5-C_8 alkanes and their isomers.(6,14)

Petroleum naphtha appears to have weak skin cancer causing potential in laboratory mice.(15) IARC has determined that there is only limited evidence implicating petroleum naphtha as a carcinogen in animals and insufficient evidence associating exposure to petroleum naphtha and the development of cancer in humans.(16) However, depending upon the manufacturing process, petroleum naphtha may sometimes contain varying amounts of aromatic hydrocarbons such as benzene. Benzene is classified by IARC as a known human carcinogen and has been associated with the development of leukemia and some lymphomas in humans.(16)

Since naphthas are mixtures of aliphatic hydrocarbons, the evaluation criteria are based upon the most commonly available varieties (petroleum ether, rubber solvent, varnish makers' and painters' naphtha, mineral spirits, and Stoddard solvent). The NIOSH REL for petroleum distillates (naphtha) is 350 mg/m^3 as a TWA exposure. In addition, a ceiling concentration limit (15 minutes duration) of 1800 mg/m^3 is stipulated. The OSHA PEL for petroleum distillates (naphtha) is 1600 mg/m^3 TWA, while the PEL for Stoddard solvents is 525 mg/m^3. The ACGIH has established a TLV of 525 mg/m^3 for Stoddard solvent. The NIOSH REL for benzene is 0.1 ppm of air and classifies it as a human carcinogen; the OSHA PEL is 1 ppm; and the current ACGIH TLV is 10 ppm as a suspected human carcinogen. ACGIH has proposed to lower the TLV to 0.1 ppm and classify it as a proven human carcinogen.(3)

C. Hydrochloric and Sulfuric Acid

Hydrochloric acid (HCl) is a strong irritant of the eyes, mucous membranes, and skin, while sulfuric acid is a severe irritant that can also affect the respiratory tract. In addition to the irritant effects, exposure to these acids can cause dental erosion. The major effects of acute exposure to HCl usually are limited to the upper respiratory tract and are sufficiently severe to encourage a subject's prompt withdrawal from a contaminated atmosphere.(18) Effects usually are limited to inflammation and occasionally to ulceration of the nose, throat, and larynx.(19) Acute exposures causing significant trauma are typically limited to people who are prevented from escaping; in such cases, laryngeal spasm or pulmonary edema may occur.[8] The effects from acute exposure to sulfuric acid are more severe than HCl because mists can penetrate deeply into the lungs. Inhalation can cause pulmonary fibrosis, residual bronchitis, pulmonary emphysema, tissue necrosis, and pulmonary edema. Exposure of the skin to high concentrations of HCl will cause burns; repeated or prolonged exposure to dilute solutions may cause dermatitis. Concentrated sulfuric acid destroys tissue as a result of its severe dehydrating action, whereas the dilute form acts as a milder irritant due to its acidic properties.[8] A number of studies have indicated that exposure to sulfuric acid or acid mist, in general, are associated with laryngeal cancer.[20-22] Nine cases of laryngeal cancer were identified (versus 3.92 expected) in steelworkers exposed to sulfuric acid mist for a minimum of six months prior to 1965.[21] Exposure levels averaged about 0.2 mg/m^3 and the average duration of exposure was 9.5 years. It is not known if sulfuric acid can act as a direct carcinogen, as a promoter, or in combination with other substances.[8] A promoter is a compound that does not directly cause cancer, but enhances the carcinogenic effects of other compounds.

Environmental evaluation criteria for hydrochloric acid have been established by NIOSH, ACGIH, and OSHA at 7 mg/m^3 as a ceiling limit. These agencies have also established evaluation criteria for sulfuric acid at 1 mg/m^3 as a TWA.

D. Noise

Occupational deafness was first documented among metalworkers in the sixteenth century.[23] Since then, it has been shown that workers have experienced excessive hearing loss in many occupations associated with noise. Noise-induced loss of hearing is an irreversible, sensorineural condition that progresses with exposure. Although hearing ability declines with age (presbycusis) in all populations, exposure to noise produces hearing loss greater than that resulting from the natural aging process. This noise-induced loss is caused by damage to nerve cells of the inner ear (cochlea) and, unlike some conductive hearing disorders, cannot be treated medically.[24]

While loss of hearing may result from a single exposure to a very brief impulse noise or explosion, such traumatic losses are rare. In most cases, noise-induced hearing loss is insidious. Typically, it begins to develop at 4000 or 6000 hertz (Hz) (the hearing range is 20 Hz to 20000 Hz) and spreads to lower and higher frequencies. Often, material impairment has occurred before the condition is clearly recognized. Such impairment is usually severe enough to permanently affect a person's ability to hear and understand speech under everyday conditions. Although the primary frequencies of human speech range from 200 Hz to 2000 Hz, research has shown that the consonant sounds, which enable people to distinguish words such as "fish" from "fist", have still higher frequency components.[25]

The OSHA standard for occupational exposure to noise (29 CFR 1910.95)[26] specifies a maximum PEL of 90 dB(A)-slow response for a duration of eight hours per day. The regulation, in calculating the PEL, uses a 5 dB time/intensity trading relationship. This means that in order for a person to be exposed to noise levels of 95 dB(A), the amount of time allowed at this exposure level must be cut in half to be within OSHA's PEL. Conversely, a person exposed to 85 dB(A) is allowed twice as much time at this level (16 hours) and is within his daily PEL. Both NIOSH, in its Criteria for a Recommended Standard,[27] and the ACGIH, in their TLVs,[4] propose an exposure limit of 85 dB(A) for eight hours, 5 dB less than the OSHA standard. Both of these latter two criteria also use a 5 dB time/intensity trading relationship in calculating exposure limits.

TWA noise limits as a function of exposure duration are as follows:

Duration of Exposure (hrs/day)	Sound Level (dB(A)) NIOSH/ACGIH	OSHA
16	80	85
8	85	90
4	90	95
2	95	100
1	100	105
1/2	105	110
1/4	110	115 *
1/8	115 *	-
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* No exposure to continuous or intermittent noise in excess of 115 dB(A).

** Exposure to impulsive or impact noise should not exceed 140 dB peak sound pressure level.

The OSHA regulation also specifies an action level (AL) of 85 dB(A) which stipulates that an employer shall administer a continuing, effective hearing conservation program when the TWA value exceeds the AL. The program must include monitoring, employee notification, observation, an audiometric testing program, hearing protectors, training programs, and recordkeeping requirements. All of these stipulations are included in 29 CFR 1910.95, paragraphs (c) through (o).

The OSHA noise standard also states that when workers are exposed to noise levels in excess of the OSHA PEL of 90 dB(A), feasible engineering or administrative controls shall be implemented to reduce the workers' exposure levels. Also, a continuing, effective hearing conservation program shall be implemented.

RESULTS AND DISCUSSION

Samples to determine airborne oil mist concentrations were collected throughout the #3 Cold Strip Mill. The results for oil mists are included in Table I. A total of 24 PBZ and general area samples were collected from six locations which included the Rewind Area, Shipping Dept.-East, #29 Temper Mill, Temper Mill Basement Areas, 80" Tandem Mill, and the Tandem Mill Basement Areas. Bulk samples of the lubricating and rolling oils were used during the laboratory analysis to quantitate the actual oil mist concentrations. Since the oils used by the Inland Steel Company varied for the different operations and locations, different bulk oil samples had to be used for quantitation. This meant that the analytical limits of detection (LOD) and limits of quantitation (LOQ) differed for samples collected from different locations. Both the LODs and LOQs are values determined by the analytical procedures used to analyze the field samples. They are not dependent on the amount of air volume collected during sampling. Minimum detectable concentrations (MDCs) and minimum quantifiable concentrations (MQCs), however, are dependent on sample air volume. They are determined by dividing respective LODs and LOQs by air sample volumes appropriate for a given set of field samples.

One representative bulk oil sample was used for samples collected from the Rewind Area, Shipping Dept.-East, #29 Temper Mill and Basement locations; another bulk oil was used for the

80" Tandem Mill and Basement. Only two of the 15 samples collected from the Rewind Area, Shipping Dept.-East, and Temper Mill locations had detectable concentrations of oil mist. An area sample collected from a Rewind Area winder control panel had a concentration of 0.14 mg/m^3, while a PBZ sample from a roller operator working on the Temper Mill had a concentration of 0.29 mg/m^3. However, the amount of oil mist found on both of these samples was below the LOQ. This means that the concentration is only a reasonable estimate. The LOD for these samples was 80 micrograms (µg), which equates to a MDC of 0.11 mg/m^3; while the LOQ was 280 µg, which equates to a MQC of 0.38 mg/m^3. Both the MDC and MQC were determined by assuming a sampling volume of 733 liters. The samples collected from the Tandem Mill and Basement had oil mist concentrations ranging from non-detected to 0.11 mg/m^3, with an average of 0.07 mg/m^3. Three samples collected from Tandem Mill Stand Operators had consistent, and some of the highest, oil mist concentrations (0.08, 0.10, and 0.11 mg/m^3). A sample from the Tandem Mill Assistant Operator also had a concentration of 0.08 mg/m^3, while a sample from an area near a roll coolant tank in the Tandem Basement had a concentration of 0.10 mg/m^3. Also, three samples were below the LOQ; therefore, these concentrations were below the MQC. The LOD for these samples was 20 µg, which equates to a MDC of 0.03 mg/m^3; while the LOQ was 63 µg, which equates to a MQC of 0.08 mg/m^3. The MDC and MQC were determined assuming a sampling volume of 769 liters. All of the samples collected for oil mist had concentrations well below the evaluation criterion of 5 mg/m^3. These oil mist concentrations seem to be consistent with the results of recent monitoring performed by the Inland Steel Company. However, previous company monitoring found oil concentrations above 5 mg/m^3 at the 80" Tandem Mill.

Samples to determine airborne naphtha concentrations were collected in areas where the rust inhibitor (NALCO 6292) was applied to the steel coils. This product was primarily used in the Rewind Area, Shipping Dept.-East, and Temper Mill areas. The measured naphtha concentrations are included in Table II. A total of six PBZ and four general area samples were collected during the survey. The airborne naphtha concentrations determined from these samples ranged from non-detected to 43 mg/m^3, with an average concentration of 26 mg/m^3. The LOD for these samples was 0.1 mg, which equates to an MDC of 9 mg/m^3, assuming a sampling volume of 11.2 liters. The one sample that was non-detected was collected from an area near the Temper Mill wrapper; however, the sample volume was only 11.2 liters because the sampling pump faulted. Therefore, this may not be an accurate determination of the naphtha concentration. The highest naphtha concentrations were determined from samples collected from employees and areas in the Rewind area. The naphtha concentrations for these seven samples ranged from 21 to 43 mg/m^3, with an average of 31 mg/m^3. The remaining samples were collected from the Temper Mill (non-detected and 19 mg/m^3) and a wrapper/laborer in the Shipping East area (21 mg/m^3). Although all these samples were well below the most stringent criterion (NIOSH REL of 350 mg/m^3), they may not be representative of a typical day. During discussions with various employees, it was determined that the Rewind area usually processes 40 to 50 steel coils per shift, which means the operation runs at approximately 2000 feet per minute. On the day that sampling was performed, it was estimated that only 25 coils were processed and that the operation was running at approximately 500 feet per minute. During the shift that sampling was conducted on the Temper Mill, most of the production orders for steel did not require the application of the rust inhibitor. Therefore, the amount of rust inhibitor used during these operations was much lower than normal. As a result, airborne naphtha concentrations measured during this investigation are likely to be lower than when production levels are more typical.

Samples to determine airborne acid mist concentrations were collected from employees and areas on the #5 Pickle Line and two areas in the 80" Tandem Mill Basement. A total of four PBZ and five general area samples were collected, and the results are included in Table III. Both hydrochloric and sulfuric acid were detected on these samples. Hydrochloric acid concentrations ranged from non-detected to 0.18 mg/m^3, while sulfuric acid concentrations ranged from 0.01 to 0.04 mg/m^3. However, the amounts of acid detected on many of these samples were between the LOD and LOQ, including all of the sulfuric acid detected. The LOD for hydrochloric acid was 2 µg, which equates to a MDC of 0.03 mg/m^3; while the LOQ was 5.7 µg, which equates to a MQC of 0.07 mg/m^3. Sulfuric acid had a LOD and LOQ of 1 and 3.1 µg, respectively. These equate to a MDC of 0.01 mg/m^3 and a MQC of 0.04 mg/m^3. The MDC and MQC for both these acids were determined assuming a sampling volume of 70 liters. Only three general area samples collected from the Pickle Mill had acid concentrations (0.11, 0.13, and 0.18 mg/m^3 hydrochloric acid) above the MQC. These samples were collected from the acid tanks, ringer rolls, and the cascade pumps. The two area samples collected from the Tandem Basement had concentrations for both acids that were between the MDC and MQC. All of the airborne acid concentrations were well below the evaluation criteria for both acids. However, production difficulties on the Pickle Line limited the actual run time to 1 hour, 45 minutes which would reduce the potential for acid mist generation. The acid mist concentrations for this operation may be higher during normal operation. However, previous monitoring for hydrogen chloride, conducted by the Inland Steel Company, determined that concentrations were typically non-detectable.

One PBZ and two general area air samples for metals were collected from the welding operation located at the beginning of the Pickle Line. The PBZ sample was collected from the welder operator, while the area samples were collected at a point near the operator during welding, and inside the isolation booth. This booth was used when the operator was not performing the actual welding operation. Four metals (calcium, iron, magnesium, and zinc), which are considered to be relatively non-toxic, were detected on these samples at concentrations well below any of the pertinent evaluation criteria. Sodium was also detected; however, due to high sample blank levels, its presence was considered a sampling artifact. Of these four metals, the iron concentration (0.06 mg/m^3) on one sample was the highest. Calcium has the lowest evaluation criterion, which is 2 mg/m^3 as calcium oxide. As with the acid mist samples from the Pickle Line, these concentrations may not be representative of normal operations. Approximately 45 welds were made during this environmental sampling period, when 90 welds are routinely made during normal production. The LODs and MDCs for all the metals included in the laboratory analysis are listed in the appendix.

Eight samples for hydrocarbons (hydrocarbon screen) were collected from the 80" Tandem Mill and Basement to determine if any volatiles are released from the oils and lubricants during the milling process. However, three of these samples were not analyzed due to sorbent tube damage. The remaining five PBZ samples were submitted for laboratory analysis. Four of these samples were collected from employees working in the Tandem Mill area, while one sample was collected from a laborer in the Tandem Basement. Since the chromatograms from these samples appeared to be the same, a sample from a Tandem Mill stand operator was chosen as representative and used to identify contaminants. This analysis identified several contaminants with the major components being branched alkanes (C_9-C_{11}), nonane, decane, and undecane. These long chain hydrocarbons are commonly present in many refined petroleum oils. Minor chromatographic peaks were also identified for benzene and toluene. The chromatogram for the Tandem Mill stand operator sample is included in the appendix.

Two bulk samples of the rust inhibitor (NALCO 6292) and the cleaning solution (Pico Roll Shop, MW-5200) were analyzed to determine their major constituents. The rust inhibitor was found to contain mostly long chain hydrocarbons. It was found to consist of C_9-C_{16} hydrocarbons (63.7%) and C_{17}-C_{35} hydrocarbon alkanes (15.6%). Decane (1.1%), undecane (2.9%), dodecane

(3.6%), tridecane (6.0%), tetradecane (3.8%), and pentadecane (1.5%) were identified as being a majority of the remaining constituents. One percent of 2,6-di-tert-butyl *p*-cresol (BHT) was also found to be present. These compounds are common components of refined petroleum solvents. The bulk sample of cleaning solution was found to consist of two compounds, triethyl borate ($C_6H_{15}BO_3$, M.W.146) and boron nitrilotriethoxide ($C_6H_{12}BNO_3$, M.W.157). When this bulk was heated to 50˚C (144˚F) to simulate its application on the hot rollers from the Tandem Mill, one compound was found. This compound was identified as propylene glycol, which can be an irritant to certain susceptible individuals. Also, the material safety data sheet (MSDS) for the cleaning product states that skin contact or inhalation of the mist may cause irritation.

Personal noise monitoring was conducted in the following departments: five employees on the #5 Pickle Line, three employees in Roll Building, two employees on the #29 Temper Mill, five employees on the 80" Tandem Mill, and two employees in the #6 Anneal Furnaces. The results of the noise survey are given in Table IV. Nearly all of the surveyed employees were observed wearing some type of hearing protection device during the period that they were monitored. There were, however, other employees in the work area who were observed not wearing hearing protection devices while in high noise areas.

Five of the 17 dosimeter samples exceeded the OSHA PEL for noise exposure. The location of the five samples in the Cold Strip Mill were areas where one would expect the greatest noise exposures. Employees who were required to work near mill operations, that is, the Tandem and Temper Mill operators and the scaleman, as well as the welder on the Pickle Line and the floorman for the Anneal Furnaces, had the highest recorded TWAs for the sample period. Employees who had work responsibilities that allowed them to move in and out of the noise areas, and employees who spent part of the day in noise-attenuating chambers (cranemen and mechanics), had noise exposures that were less than the OSHA PEL of 90 dB(A) for an 8-hour TWA. However, of the 12 surveyed employees who had noise exposures less than 90 dB(A), only four of these were also less than 85 dB(A), the OSHA AL for the hearing conservation amendment and its requirements. Thus, 13 of the noise dosimeter samples exceeded OSHA noise levels for either hearing conservation regulations or possible engineering controls for noise reduction in the Cold Strip Mill.

Production difficulties on the #5 Pickle Line delayed operation of the line for approximately three hours on the first day of the survey. The difficulties also affected the total daily run time of the line, reducing the time recorded on a cumulative time clock in the control room to 1 hour, 45 minutes on the first survey day. On the second day of the survey, the total run time improved to 4 hours, 30 minutes on the same clock. The reduced production time influenced the noise on the Pickle Line as well as adjacent work areas, such as Roll Building. The limited production time would necessarily reduce worker noise exposure since fewer rolls of steel were processed on the day of the noise survey.

The area noise samples obtained by NIOSH investigators in various work areas of the Cold Strip Mill are given in Table V. Employees working in the area of the #6 Anneal Furnaces were exposed to noise levels between 92 dB(A) and 95 dB(A) whenever they were on the work floor. The noise levels measured by NIOSH are approximately 5 dB(A) higher than the levels referenced in the Inland Steel Company's Hearing Conservation Program outline provided to NIOSH investigators February 19, 1992. It is not obvious why there are differences in the two sets of data. The values reported by the Inland Steel Company in the outline agree with the values obtained in this HHE for the #5 Pickle Line and the 80" Tandem Mill. The data collected at the #5 Pickle Line comparing the noise values inside and outside the acoustic booths located on the line, show that the booths are effective in reducing the worker's noise exposure as long as he or she is in the booth with the door closed. The mean decrease in noise level was calculated to be 20 dB(A).

Audiometric test results for 12 employees from the #3 Cold Strip - East Mill, who had an annual audiogram in 1990, indicated that they had a significant threshold shift (STS).[26] The shift occurred over a time span of no more than four years. Nine of the STSs were in a direction that indicated that the employee's hearing had deteriorated between the baseline audiogram and the 1990 annual audiogram. The other three employees showed improved hearing from the baseline to annual hearing test of an amount equal or greater than a STS.

Although the total number of employees in the No. 3 Cold Strip - East Mill who had audiometric tests done during this time period was not supplied to NIOSH investigators, to allow for a calculation of the percentage of employees who have exhibited a STS over the time period reported in the Inland Steel Company audiometric data, 12 employees suffering a STS over a short four-year time period seems excessive. Because nine of the 12 tested employees had hearing losses in four years or less implies that the Hearing Conservation Program is not completely effective. New methods of audiometric database analysis are being developed to determine the effectiveness of hearing conservation programs.[28-31] An American National Standards Institute (ANSI) working group (ANSI S12.12) has prepared a draft consensus standard for an audiometric database analysis techniques.[32]

CONCLUSIONS

The environmental sampling data collected during this investigation do not indicate excessive exposure to oil mist, naphtha, acid mist, or metals. However, these results may not be indicative of typical exposures due to unusually low production requirements and other difficulties encountered during this investigation. Typical exposures may be somewhat higher than those presented here. The noise evaluation indicated that employee noise exposures exceeded OSHA limits for either hearing conservation regulations or possible engineering controls for noise reduction in several areas. The presence of several employees in the No. 3 Cold Strip - East Mill with hearing loss as well as hearing threshold shifts over a four year period implies that the Inland Steel Company's Hearing Conservation Program is not completely effective and needs improvement.

RECOMMENDATIONS

The following recommendations are based on the environmental sampling results and observations made during the investigation.

1. Further environmental sampling should be conducted in both the Tandem and Temper Mill Basements, especially during heavy maintenance activities. Observations made during this investigation suggest that the potential exists for intermittent heavy exposures to the lubricating and cooling oils. Further sampling for acid mists at the Pickle Line should also be conducted during maintenance activities.

2. An industrial hygiene evaluation should be conducted in the Pico Roll Shop during the cleaning of the tandem rolls. This evaluation should investigate the potential for dermal as well as inhalation exposures to both propylene glycol and the original constituents (triethyl borate and boron nitrilotriethoxide) of the cleaning solution.

3. Efforts should be made to reduce residual oils on surfaces where employees walk. To reduce the potential for slip and fall injuries, processes involving the application of oils should be guarded to prevent spraying or splashing, especially in the Rewind Area. General maintenance and cleaning operations could be improved to reduce this potential. Alternative floor surfaces which provide better traction should be investigated.

4. Dermal exposures to picking acids, rust inhibitors, lubricating and cooling oils, and their potential to produce dermatitis should also be investigated. The use of current personal protective equipment (PPE) should be evaluated. Gloves made from nitrile rubber or polyvinyl alcohol may provide appropriate protection from the oils used, while butyl rubber gloves would be appropriate for protection from the acids in the Pickle Line. Cut resistant gloves treated with these types of materials may also be appropriate in many circumstances. The use of protective suits (i.e. Tyvek®, etc.) in the Tandem and Temper Mill Basements should also be investigated.

5. The hearing conservation program at the Inland Steel Company needs to be evaluated for its effectiveness in reducing worker hearing loss. The limited audiometric data from the No. 3 Cold Strip - East Mill furnished to NIOSH investigators revealed that the program is not adequately protecting workers' hearing. The use of new audiometric database analysis techniques(32) is one method to evaluate the program's effectiveness.

6. Hearing protection devices (HPDs) were readily available to employees in the Cold Strip Mill. A variety of styles and sizes were offered to employees. However, total compliance by employees in the use of the HPDs was not observed during the evaluation. There were several instances where the HPDs were observed hanging from the strap at the back of workers' hard hats, but not in the worker's ears. Supervisory reinforcement for the mandatory wearing of the HPDs is necessary to maintain compliance with the use of the devices.

7. Workers were able to choose the type and size of protectors they wished to wear. This practice can lead to the issuance of improperly sized ear plugs. Generally, workers will choose ear plugs that are too small because they are comfortable. However, they may fail to deliver the stated attenuation values if they do not properly fit in the worker's ear canal. Ear plugs that come in various sizes need to be individually fit to employees and dispensed by the medical or industrial hygiene department.

8. The noise attenuating booths in the Cold Strip Mill are effective in reducing worker noise exposures. The practice of using these booths should be continued and expanded to other work areas where feasible.

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3. OSHA, Region V

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table I
Airborne Oil Mist Concentrations
Inland Steel Flat Products Company
East Chicago, Indiana
HETA 91-115
February 12-13, 1992

Location	Description	Date	Sample Volume (Liters)	Oil Mist (mg/m^3)
Rewind	Feeder Operator Helper	2/12/92	812	ND
"	Winder/Sprays Oil	"	826	ND
"	Wrapper	"	786	ND
"	Helper	"	742	ND
"	Crane Operator	"	666	ND
"	Area on Winder Controls	"	740	(0.14)
"	Area near Winder	"	832	ND
Shipping East	Wrapper/Inspector	"	758	ND
"	Wrapper/Laborer	"	766	ND
"	Crane Operator	"	708	ND
"	Area on Oil Cart	"	778	ND
Temper Mill	Coiler	2/13/92	706	ND
"	Roller	"	696	(0.29)
Temper Basement	Mechanic	"	588	ND
"	Area near Oil Tanks	"	584	ND
Tandem Mill*	Feeder	"	812	(0.07)
"	Stand Operator	"	848	0.11
"	"	"	848	0.10
"	"	"	880	0.08
"	Crane Operator	"	852	(0.05)
"	Assistant Operator	"	814	0.08
Tandem Basement*	Laborer	"	376	ND
"	Mechanic	"	732	(0.04)
"	Area near Roll Coolant Tank	"	706	0.10
Evaluation Criteria		NIOSH REL,ACGIH TLV, & OSHA PEL		5

ND - Not Detected, ( ) - detected value was between the minimum detectable concentration (MDC) and minimum quantifiable concentration (MQC) of 0.11 and 0.38 mg/m^3, respectively, based on an air sampling volume of 733 liters.

* The MDC and MQC for samples from the Tandem Mill and Basement were 0.03 and 0.08 mg/m^3, respectively, based on an air sampling volume of 769 liters.

Table II
Airborne Naphtha Concentrations
Inland Steel Flat Products Company
East Chicago, Indiana
HETA 91-115
February 12-13, 1992

Location	Description	Date	Sample Volume (Liters)	Naphtha (mg/m³)
Rewind	Winder/Sprays Oil	2/12/92	82.6	21
"	Feeder/Operator Helper	"	81.2	30
"	Helper	"	74.2	35
"	Wrapper	"	78.6	27
"	Wrapper/Inspection Line	"	75.8	22
"	Area on Winder Controls	"	83.3	43
"	"	"	74.0	39
Shipping East	Wrapper/Laborer	"	76.6	21
Temper Mill	Area near Wrapper	2/13/92	11.2	ND
"	Area near Nalco Tanks	"	64.2	19
Evaluation Criteria		NIOSH REL ACGIH TLV OSHA PEL		350 525 1600

ND - Not Detected: The minimum detectable concentration for this sample was 9 mg/m³, based on the air sampling volume of 11.2 liters.

Table III
Airborne Acid Concentrations
Airborne Inland Steel Flat Products Company
East Chicago, Indiana
HETA 91-115
February 12-13, 1992

Location	Description	Date	Sample Volume (Liters)	Hydrochloric Acid (mg/m^3)	Sulfuric Acid (mg/m^3)
Pickle Mill	Crane Operator	2/12/92	86.6	(0.04)	(0.01)
"	Crane Cab	"	85.6	(0.03)	(0.01)
"	Fireman	"	41.6	ND	(0.02)
"	Utility Man	"	43.2	(0.07)	(0.02)
"	Area near Acid Tanks	"	56.6	0.18	(0.02)
"	Area near Ringer Rolls	"	56.0	0.13	(0.02)
"	Area near Cascade Pumps	"	55.0	0.11	(0.02)
Tandem Basement	Area near Acid Tank	2/13/92	79.4	(0.04)	(0.02)
"	Area near Roll Coolant Tanks	"	70.6	(0.07)	(0.04)
Evaluation Criteria		NIOSH REL, ACGIH TLV, & OSHA PEL		7 Ceiling Limit	1

ND - Not Detected, ( ) - detected value was between the minimum detectable concentration (MDC) and minimum quantifiable concentration (MQC): Hydrochloric acid had an MDC and MQC of 0.03 and 0.07 mg/m^3, respectively, while the respective MDC and MQC for sulfuric acid were 0.01 and 0.04 mg/m^3. These concentrations were based on an air sampling volume of 70 liters.

Table IV

Personal Noise Dosimeter Results
Inland Steel Company
HETA 91-115
February 12-13, 1992

LOCATION	SAMPLE TIME [Minutes]	1-Min. MAXIMUM LEVEL [dB(A)]	TWA [dB(A)]
#5 Pickle Line			
Welder	435	110	93.8
Cropman	426	101	83.3
Feeder/Helper - Entry End	395	103	88.4
#21 Crane Operator	429	93	83.0
Utilityman - Delivery End	392	101	88.9
Roll Building			
Mechanic (A)	450	108	86.9
Mechanic (B)	408	101	87.3
#26 Crane Operator	309	99	83.7
#6 Anneal Furnaces			
Furnaceman	334	106	87.9
Floorman	330	97	91.8
#29 Temper Mill			
Roller	347	108	95.8
Mechanic	295	99	86.3
80" Tandem Mill			
Laborer - Basement	203	97	88.2
Stand Operator	425	105	94.2
Scaleman	422	102	94.4
#26 Crane Operator	427	96	85.3
Mechanic - Basement	370	103	84.8

Table V

Area Noise Results
Inland Steel Company
HETA 91-115
February 12-13, 1992

LOCATION		A-WEIGHTED SOUND LEVEL [dB(A)]	C-WEIGHTED SOUND LEVEL [dB(C)]
#5 Pickle Line			
Welder's Station - outside booth during welding operation		104	103
Welder's Station - inside booth during welding operation		74	76
Welder's Station - outside booth while steel strip passes		108	110
Bridle Station - outside booth		88	92
Bridle Station - inside booth		72	82
Bander - outside booth		85	89
Bander - inside booth		68	82
#6 Anneal Furnaces			
Between Furnace #3 & #4		92	98
Aisleway at Furnace #4		93	99
Aisleway at Furnace #6		92	97
Between Furnace #7 & #12		94	99
Aisleway at Furnace #9		93	98
Aisleway at Furnace #15		93	98
Aisleway at Furnace #17		95	101
80" Tandem Mill			
Entry Operator	- metal rolling	90	95
	- warning bell	98	---
	- communications	108	---
1st Stand Operator	- metal rolling	96	98
	- end of roll	103	---
	- communications	124	---
	- air noise	96	---
3rd Stand Operator		97	98
Scale Operator		94	98

APPENDIX

#1 Limits of Detection and Minimum Detectable Concentrations for elemental (metals) analysis.

#2 Sample chromatogram from hydrocarbon screen.

Elemental Limits of Detection and Minimum Detectable Concentrations

Analyte	Limit of Detection (micrograms per sample)	Minimum Detectable Concentration* (milligrams per cubic meter)
Aluminum	5.0	0.01
Arsenic	2.0	0.004
Barium	0.2	0.0004
Beryllium	0.1	0.0002
Calcium	5.0	0.01
Cadmium	0.2	0.0004
Cobalt	0.5	0.001
Chromium	0.5	0.001
Copper	1.0	0.002
Iron	1.0	0.002
Lithium	0.5	0.001
Magnesium	1.0	0.002
Manganese	0.5	0.001
Molybdenum	0.5	0.001
Nickel	0.5	0.001
Lead	1.0	0.002
Phosphorus	5.0	0.01
Platinum	2.0	0.004
Selenium	2.0	0.004
Silver	0.5	0.001
Sodium	5.0	0.01
Tin	2.0	0.004
Tellurium	3.0	0.006
Thallium	3.0	0.006
Titanium	0.2	0.0004
Tungsten	3.0	0.006
Vanadium	0.5	0.001
Yttrium	0.2	0.0004
Zinc	0.5	0.001
Zirconium	0.5	0.001

The Minimum Detectable Concentrations were calculated assuming a sampling volume of 468 liters.

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