the Rain events

SPECIAL EDITION

UNDERSTANDING

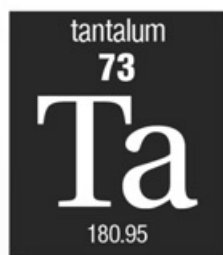| phosphorus	oxygen	lutetium	tantalum	nitrogen	tennessine
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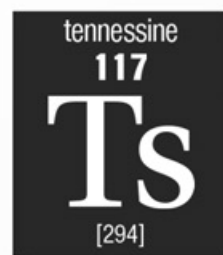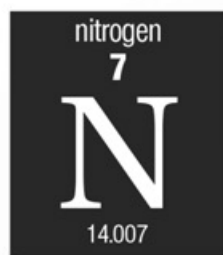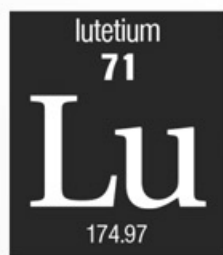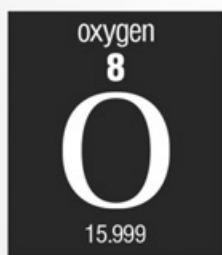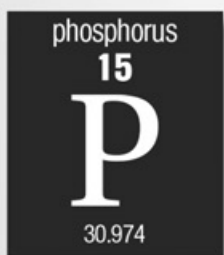
The working professional's resource for understanding common storm water pollutants.

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The *Understanding Pollutants* series was originally published in **The Rain Events** newsletter, starting in January 2017, and finishing in October 2018. In this special edition, we've compiled all twelve articles into one easy-reference publication.

Letter from the editor

Chemistry is daunting. All those formulas, calculations, and experiments have a way of giving most normal people a headache. But hiding behind the numbers is some information that's actually useful and practical.

In the past twelve editions of **The Rain Events**, we've attempted to take these chemistry concepts and distill them into something that the average person can readily understand. We received tons of positive comments about this series of newsletters. (Apparently, we weren't the only ones scratching our heads about chemistry.) So, our staff put together a compilation of the *Understanding Pollutants* series, creating what we hope is not only a beautiful special issue, but a useful reference for the working storm water professional.

In this resource, you will find twelve chapters covering some of the most common industrial pollutants. Each chapter gives a brief but easily understandable chemistry lesson and provides some little-known facts about each pollutant. We'll also try to identify potential industrial activities that may be a source for these pollutants and we discuss best management practices and treatment control measures to prevent, reduce, or remove the pollutant from storm water discharges.

Feel free to share this resource with your storm water colleagues and clients and continue to check out our monthly **The Rain Events** newsletter for more helpful information to assist you and your facility in its compliance with the Industrial General Permit.

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pH

Instantaneous NALs = below 6.0, above 9.0
Annual Average NAL = N/A

We're going back to the basics. Or, more specifically, back to the bases and acids. If you have been around storm water testing for any amount of time, you've probably had to test for pH. While most of us know that pH has to do with how acidic or basic the water is; we may be unsure of what pH is actually measuring and how the changes in pH affect storm water.

The term "pH" stands for "Potential of Hydrogen," and measures the concentration of hydrogen ions. The International Encyclopedia of Chemical Science defines it as a *"specific property of many diverse materials that possess some acidic or basic [alkaline] character."* A solution with a pH of 7 is considered neutral; pH readings less than 7 are acidic, and readings higher than 7 are basic or alkaline.

Pure water has a pH of 7, which is considered neutral. Surprisingly, rain water typically has a slightly acidic pH of 5.6, due to the carbon dioxide gas in the atmosphere. The normal pH of a stream is between 6.0 and 8.0. The pH of seawater is about 8.1. Though we commonly refer to water as H_2O, pure water is actually made up of equal parts of hydronium ions (H_3O^+) and hydroxide ions (OH^-). The more hydronium ions, the more acidic (lower pH) the water is. Conversely, a greater amount of hydroxide ions will turn the water basic (higher pH). When chemicals or pollutants are mixed with water, the chemical reaction changes the hydronium/hydroxide ratio, and the water becomes either acidic or basic – for instance, storm water that comes into contact with lime (calcium **hydroxide**) or freshly poured cement can have a pH as high as 10 or 11.

The pH scale is logarithmic, which means that each whole step in pH values is 10 times more acidic or basic. For instance, a pH of 5 is ten times more acidic than a pH of 6, and a hundred times more acidic than a pH of 7. Similarly, a pH of 8 is ten times more basic than a pH of 7.

So, you've got a pH problem at your facility – what to do? Well, one of the best ways to control pH is to prevent exposure of pH-affecting materials in the first place. This is called source control,

and some of our frequent readers are probably getting tired of us talking about it. But for pollutants that are hard to treat, like pH, the best way to make sure you don't have NAL exceedances is to keep those industrial pollutants inside enclosed buildings, or at least under cover. Many pH-affecting materials are in powder or liquid form (concrete, lime, or liquid acids/bases), so make sure your buildings are sealed as much as possible to prevent those materials from escaping and mixing with rain water. Say you've done all the source control possible. Now, don't forget the next most important part of your BMP arsenal – good housekeeping. Possibly the most effective thing you can do to improve your storm water numbers is to run a clean shop. Keep your yard area spotless, and make sure your employees clean up after themselves. Keep things neat and tidy. It's much cheaper than paying for treatment BMPs, and in many cases, it works better.

The reason for all this emphasis on source control and good housekeeping is this – you don't want to try to treat for high or low pH. It's labor intensive, requires a lot of coordination with your Regional Water Board, and it's not going to be cheap. Basically, the only way you can neutralize pH is by adding a chemical to push the pH in the opposite direction. So, if your water has a high pH, you add an acid (or a buffer) to bring the pH back to neutral. But be careful! You can't just start adding random chemicals to your storm water runoff – that's a sure way to get yourself in trouble. It's much easier to prevent pH-affecting materials from coming in contact with storm water than to try to correct pH problems after the fact.

But if you're left with no other choice than to treat for pH, you may want to look into a technique called *CO_2 sparging*. Instead of adding a mineral acid like sulfuric acid to lower pH, this technique bubbles CO_2 gas through the water, which forms carbonic acid (H_2CO_3), which further dissociates into a proton (H^+) and a bicarbonate anion (HCO_3^-). The carbonic acid is a weak acid that lowers pH. CO_2 sparging is safer than mineral acids for a couple reasons: 1) it's virtually non-toxic, and 2) it's actually a buffer, not an acid or a base. Because it is a buffer, it would be difficult to overdose the CO_2 and create harmfully low pH levels. But keep in mind that chemical-based treatment BMPs are subject to the requirements in IGP Section X.H.6 concerning design storm standards for treatment control BMPs. CO_2 sparging is a complicated and technical procedure, and should not be performed without proper engineering and equipment.

finding the S O Ur Ce S

- Sodium hydroxide (very common strong base; pH of 14)
- Hydrochloric acid (very common strong acid; pH <0)
- Sulfuric acid (strong acid; pH of 1)
- Ammonia (moderate base; pH of 12)
- Lime, quicklime, concrete, cement (moderate bases; pH of 12)

Oil and Grease

What comes to mind when you think about the Oil and Grease analysis? Probably a couple things – first, it's not a very scientific term, and second, Oil and Grease is a pretty broad category. Does it test for all oils and greases? Or just petroleum oils and greases? Why does my lab report call it HEM? These are all good questions, and in this month's edition of The Rain Events, we're going to try our best to answer them.

The first step in understanding the Oil and Grease analysis is understanding the analytical method. Table 2 in the Industrial General Permit specifies EPA Method 1664A for measuring oil and grease. If you look at the EPA's analytical method reference, the actual name for this test is n-Hexane Extractable Material, or HEM for short. The analytical procedure uses a solvent called n-hexane to isolate hexane-soluble materials from your storm water sample.

Well, you might ask, what materials are hexane-soluble? To answer this, we'll have to look at the chemistry concept of polarity. Without getting overly complicated, molecules can generally be divided into two groups – polar and nonpolar. This is important when it comes to dissolving a substance into another substance. The solvent (say, H_2o, or water) must be the same polarity as the solute (say, NaCl, or table salt). In this case, both water and table salt are polar molecules, so the salt dissolves in water. Why doesn't oil mix with water? You guessed it – oils are nonpolar molecules, which can't dissolve in a polar solvent. The answer to the question of which materials are hexane-soluble is simple: Hexane is a nonpolar solvent, which means that it will dissolve nonpolar molecules.

If you're paying close attention, you're probably thinking *"Wait. Oils and greases can't be the only nonpolar molecules, so is this analytical procedure picking up other things too?"* Good observation. Most organic (carbon-based) compounds are nonpolar – including hydrocarbons, polymers (plastics and rubbers), waxes, soaps, and fatty acids (like those found in animal and plant based oils). All of these substances can potentially be detected by the EPA 1664A test. So, it is possible that a high oil and grease result could be caused by something other than motor oil or hydraulic fluid.

That being said, the SMARTS data for the 2016-2017 storm water monitoring year seems to indicate two main sources of oil and grease – used petroleum oil and/or fuel, and animal-based fats. The top five sources of oil and grease in California are SIC codes **5093** (scrap and waste materials), **4212** (local trucking without storage), 5015 (used motor vehicle parts), **4953** (refuse systems), and **2013** (sausages and other prepared meats).

So, if you're struggling with your oil and grease numbers, what to do? Well as always, the best BMP strategy uses a combination of source control, good housekeeping, and treatment control. Keep oily parts and equipment stored under cover, and perform maintenance activi-ties indoors if possible. Keep your yard swept and clean, and do your best to run a tight ship. In most cases, a combination of good source control and good housekeeping is all you'll need to bring your oil and grease numbers under control. Remember, oil is nonpolar and water is polar – so grease isn't going

Instantaneous Max NAL = 25 mg/L
Annual Average NAL = 15 mg/L

to want to slough off into your storm water. But what if you've done everything possible to control your oil and grease numbers, but your numbers are still high? Well, do a thorough investigation to see if there are any unexpected oil sources on your site (don't forget to check those roof vents). If you can't find any sources of oil, check to see if there are other pollutants that are causing a "false positive" reading – other nonpolar compounds that are being extracted by the hexane test and being reported as oil and grease. Of special note is colloidal sulfur and thiosulfate – both of which are mentioned in the EPA 1664 method as known causes of false positive readings.

Extra Learning Resources

Here are a couple video resources to help you get a better grasp on organic chemistry. Warning - your brain might hurt!

- Motor oil and vehicle oils (petroleum oils)
- Heavier petroleum fuels (diesel, kerosene, fuel oil)
- Animal-based fats (lard, tallow, etc.)
- Plant-based fats (vegetable oils, olive oil, etc.)
- Waxes (paraffin wax, beeswax, carnauba wax)

Total Suspended Solids

Instantaneous Max NAL = 400 mg/L
Annual Average NAL = 100 mg/L

Which IGP Table 2 pollutant has the most NAL exceedances? Alright, alright. We'll tell you the answer – Total Suspended Solids, or TSS. During the 2016-2017 year, there were a total of 3,825 NAL exceedances for TSS. Judging by that number, it's safe to say that there are many California facilities who are struggling with TSS. Ironically, out of all the Table 2 pollutants, TSS is also the easiest one to treat in storm water runoff.

So, what is TSS? Is it the same as turbidity? To answer these questions, we need to look at how the analytical test is performed. According to Table 2 in the Industrial General Permit, the analytical method for Total Suspended Solids is Standard Method 2540 D (or SM 2540D). If you turn to section 2540 in the Standard Methods handbook, you'll find that this particular test is grouped with a bunch of other tests that measure the concentration of solids in water. Method 2540 D measures only suspended solids by passing water through a 2.0 μm filter, and measuring the weight difference of the filter. The analytical method contains steps to ensure that dissolved solids (like salts and minerals) are not reported through this test. Turbidity, while similar in some ways to TSS, is an optical test as opposed to a mechanical one. The difference between tests can be radical, specifically when it comes to colloidal clay suspensions. Colloids can pass right through a 2 μm filter, but will cause a very high turbidity number.

So, what is measured by TSS, and what isn't measured? Well, anything that doesn't pass through the 2 μm filter is potentially measured. That being said, the lab does not usually use the entire 1-liter sample to perform the test – and unless they are broken up and distributed when stirred, large floating particles, submerged agglomerates, and non-homogenous materials are typically excluded from the test as non-representative.

Most dissolved solids will pass through the filter, but before drying and weighing the sample, the lab will triple-rinse the filter with deionized water to remove any stubborn dissolved solids.

What causes high TSS numbers? The obvious culprit is sediment – but what may not be so obvious is the source of the sediment. Sediment could be coming from erosion, industrial activities (sawdust, concrete or lime dust, etc.), tracked in from off-site, or blown onto your facility from next door. We've had clients with paved parking lots experience very high TSS numbers, while other clients have gravel lots and somehow still stay under the NALs.

Fortunately, sediment is almost always visible, and can be cleaned up fairly easily. Interestingly, many other pollutant problems can be traced back to sediment too. For instance, many times we have noticed a direct link between metals and TSS – high TSS tends to correlate with high metals, and vice versa. So, staying on top of any loose sediment, dust, or dirt on your site can have the added advantage of keeping your other sampling parameters under control.

If your facility is permeable and sweeping isn't practical, there are other things you can do to control sediment. Gravel is very effective – a ring of gravel around drain inlets can drastically reduce TSS. If you can cover all of your permeable surfaces with gravel, even better!

Compost socks work wonders with sediment, but can cause flooding, especially with a heavy sediment load. Drain insert bags are minimally useful for TSS, because they don't capture fine particles. And don't install them where you collect a sample – disturbing the drain bag releases all sorts of trapped pollutants directly into the water that you're sampling.

To sum up, TSS comes – not surprisingly – from sediment. The bad news is that sediment is everywhere; but the good news is that it's pretty easy to control. A regular sweeping schedule can vastly improve high TSS numbers, and there are many relatively cheap and effective sediment BMP products on the market.

How turbid is it?

In most situations, a TSS concentration below 20 mg/L appears clear, while levels over 40 mg/L may begin to appear cloudy. In comparison, a turbidity reading below 5 NTU appears clear, while a reading of 55 NTU will start to look cloudy and a reading over 500 NTU will appear completely opaque. It is important to note that this is dependent on the size and nature of the suspended solids.

- Exposed soils, especially bare or eroding soil.
- Powdery industrial materials (sawdust, gypsum board dust, lime, sand/gravel, etc)
- Tracked-on sediment from vehicle tires
- Historical sediment in storm drain lines
- Wind-blown dust or dirt from adjoining property

Zinc

What do chain-link fences, sunblock, trombones, Van Gogh paintings, multivitamins, rat poison, and cigarette filters have in common? Well, about the only thing that could tie that odd list together is a bluish-white heavy metal called zinc. Zinc is a very abundant and useful element, and is an essential nutrient for humans, animals, plants, and microorganisms. However, too much zinc can cause toxicity problems (especially in plants and invertebrates), and due to its widespread occurrence, is one of the most prolific pollutants listed on Table 2 in the Industrial General Permit.

Zinc is most commonly used as either a metal or an oxide. In its pure metallic form, zinc is a bluish-white, lustrous, diamagnetic metal. Over 50% of the metallic zinc produced each year is used as an anti-corrosion agent, the most familiar form of which is galvanization – coating a corrosive metal such as iron or steel with a layer of zinc. Metallic zinc is also used in alloys such as brass (consisting of 33% zinc and 67% copper), nickel silver, and bronze.

The rubber industry is the largest consumer of zinc oxide, which is used as an activator during the vulcanization process, as a catalyst during manufacture, and also in the final product to disperse heat. Zinc oxide is also used in pigments, plastics, pharmaceuticals, and anti-corrosive paints and coatings for metals.

Zinc is the 24th most abundant element in Earth's crust, and is the 4th most commonly used metal. Soil concentrations range between 5 and 770 ppm, with an average concentration of 64 ppm. Most zinc is mined from China, Australia, Peru, and the United States.

OK, so on an average industrial facility, what might be some common sources of zinc? As mentioned above, the most common uses of zinc are galvanized metals and rubber products – and both of these materials can be found at probably every industrial facility in the State of California. Galvanized metal buildings, chain link fences, flashing, gutters, and hot-dipped steel pieces are all strong sources of zinc. Tires and other rubber materials contain zinc, and tire wear can be a significant source of zinc in storm water runoff. Many other common products could also contain zinc – such as brake pads, wheel weights, motor oil and lubricating oils, asphalt, pesticides, fungicides, and wood preservatives.

However, it's important to differentiate between industrial and non-industrial sources of zinc. Under the Industrial General Permit, facilities are not required to sample for non-industrial pollutants – so if your facility does not use any zinc-containing products as a part your industrial activities, then you do not need to sample for zinc (assuming zinc is not a required sampling parameter for your SIC code in Table 1 of the IGP). Check out the SWPPP Radio podcast (link opposite) with Laurel Warddrip of the State Water Board. Laurel gives some very insightful information about when zinc should be classified as an industrial or non-industrial pollutant. Regardless of whether your facility should have been sampling for zinc or not, if you reach Level 1 status for zinc, you have the responsibility to bring your zinc numbers back under control – and until then, you're stuck sampling for zinc.

Instantaneous Max NAL = N/A
Annual Average NAL = 0.26 mg/L

So, if you are required by Table 1 or your industrial activities to sample for zinc, what are some practical steps you can take to reduce the amount of zinc present in your storm water runoff? As we mentioned last month, the most effective BMP strategy involves a combination of source control, pollution prevention, and treatment. Unless you are a galvanizing plant or a rubber plant, try implementing some source control and see if there is a different product you could use that doesn't contain zinc. For pollution prevention, good housekeeping can go a long way toward minimizing zinc. Studies have shown that vacuum-assisted dry sweepers can remove a substantial amount of zinc by removing zinc-containing materials such as tire dust and other fines. When it comes to treatment, there are many different options on the market for reducing zinc concentrations – but ultimately, the effectiveness of any treatment solution depends on the effectiveness of your source control and pollution prevention strategy.

Podcast: The Science of Zinc

Podcast: Zinc. Industrial or not?

- Ceramic glaze and frit compounds
- Pharmaceutical ointments and creams, disinfectants
- Vitamin-enriched foods
- Paints, paper, and photocopiers using zinc white
- Methane reforming
- Metal working
- Manufacturing electroluminescent panels
- Manufacturing semiconductors
- Wood preservatives
- Fungicides

Copper

Instantaneous Max NAL = N/A
Annual Average NAL = 0.0332 mg/L

What does the Statue of Liberty have to do with storm water? Not much, except for a reddish-orange metal that makes up most of the iconic structure (the green color is caused by oxidation). Copper is one of the oldest metals used by mankind, and is listed as a constituent in Table 2 of the Industrial General Permit, with a notoriously low NAL of 0.0332 mg/L.

Copper is a malleable and ductile metal with very high thermal and electrical conductivity properties. A freshly exposed surface of pure copper reveals a reddish-orange color, which turns green as the metal oxidizes. Since copper is one of the few metals that naturally occurs in a usable metallic form, it was likely one of the first metals to be used by mankind. Copper was also the first metal to be purposefully alloyed with another metal – tin – to create bronze, circa 3500 BC. During the Roman empire, copper was mainly mined on the island of Cyprus, and was called *aes cyprium*. The name was corrupted to *cuprum*, from which our English word *copper* and the chemical symbol Cu are derived. Copper is an essential trace mineral for all living organisms, and is found naturally in foods such as oysters, lobster, beef and lamb liver, Brazil nuts, blackstrap molasses, cocoa, and even black pepper. But too much copper in water can harm marine and freshwater fish and mollusks by causing damage to the gills, liver, kidneys, and nervous system.

Table 1 in the Industrial General Permit requires sampling for copper for dischargers involved in wood preserving (SIC 2491), iron and steel foundries (332X), metal rolling, drawing and extruding (335X), and nonferrous foundries (336X). So unless your facility is involved in metalworking or wood preserving, you're not specifically required by the Industrial General Permit to sample for copper.

But the Permit also requires sampling for additional parameters that serve as indicators of the presence of industrial pollutants – so, if your facility uses copper or a copper-containing product as part of your industrial activities, you may need to include copper as a sampling parameter.

But be careful! Non-industrial sources of copper are very common, and it can be hard to tell if your elevated copper levels are from industrial or non-industrial activities. For instance: tire and brake dust from nearby roads can have heavy concentrations of copper, but would not be considered as industrial sources of copper. But if your facility has industrial sources of copper and brake dust is causing an NAL exceedance, you will have to continue sampling for copper regardless of whether it's from an industrial source or not. If this is the case, you may find yourself in a Level 2 ERA and need to do a non-industrial pollutant source demonstration.

Just as we have said in past articles in this series on industrial pollutants, the most effective BMP strategy involves a combination of source reduction, pollution prevention, and treatment. In the case of copper, source reduction may be a challenge, because many sources of copper on an industrial site are likely unavoidable. But effective pollution prevention and good housekeeping techniques can help keep your copper results under control. Since brake and tire dust are a big copper source, regular and thorough sweeping is essential. Treating for copper (either particulate or dissolved) can be done with an active or passive filtration unit, or with compost socks that have been specifically formulated for metals removal.

Copper in Brake Pads

Copper is commonly used in brake pads because it transfers heat efficiently, helps brake effectiveness in cold weather, and prevents squeaking and shuddering during braking. In the 1990s, it was found that 30-60% of copper in California's urban watershed runoff was from brake pads. In 2010, California and Washington passed laws that brake pads sold in each state must contain no more than 0.5% copper by weight. In California, the law will take effect on January 1, 2025. *Source: www.copper.org*

Podcast: Copper. Industrial or not?

Architectural Copper

Do you have any architectural copper on or near your industrial facility? Here's an interesting article written by the Copper Development Association, Inc., that talks about the impact of architectural copper on storm water toxicity.

finding the **S O Ur Ce S**

- Architectural copper
- Anti-biofouling paints and compounds (used to protect ships against barnacles and mussels). Keep in mind: this would count as an industrial activity for boatyards.
- Color stains in glassmaking and ceramic glazes
- Pyrotechnic manufacture
- Fungicides/herbicides/algicides

Magnesium

"Magnesium? I don't got any of that on my facility." If that was your first response when you read the title of this article, you're in for a surprise. Even our editors were surprised at how common this uncommon pollutant really is. Magnesium naturally occurs in vast quantities, has a large variety of uses (our video department's cameras are built out of magnesium), and is an essential mineral for virtually every living organism. And after doing some research, we found out it's not as toxic as you might think.

In its elemental form, magnesium is a shiny gray metal that is two-thirds the density of aluminum. It is the fourth most common element on Earth (after iron, oxygen, and silicon), making up 13% of our planet's mass, and a large fraction of our planet's mantle. It is also the third most common dissolved element in seawater after sodium and chlorine.

Magnesium is naturally occurring in large quantities, and can be found in deposits of magnesite, dolomite, and other minerals. The most common sources of elemental (metallic) magnesium are actually magnesium salts, which are extracted from sea water or other mineral-rich water. According to a 1912 US Geological Survey publication, the greatest concentration of magnesite in the United States is found in California – deposits are "widely distributed throughout the Coast Ranges and on the western slopes of the Sierra Nevada...a number of these deposits, especially in California, are of considerable size and yield magnesite of excellent quality." And according to the California Department of Conservation's website, magnesite can be found in 30 of California's 58 counties.

Magnesium is very widespread in terms of natural occurrence, but is even more so in terms of application. Metallic magnesium is the third most commonly used structural metal, following iron and aluminum. It is the lightest structural metal, but in the right alloy, can still be used in high-strength applications. Magnesium compounds are also widely used. Magnesium oxide has many industrial uses, including in Portland cement, as a water treatment additive, as fireproofing in wallboards, as a refractory material, and in pharmaceuticals and supplements. Magnesium chloride is used for dust control and road deicing, in fire extinguishers, as a fertilizer, in mineral supplements for animals, in the paper manufacturing process, and in cement manufacturing. Magnesium sulfate (Epsom salt) is also a common fertilizer/soil amendment, and is used as a brewing salt in beer production. Dolomite is used in concrete as an aggregate, and can be ground up for sale as dolomitic lime-stone.

In terms of toxicity, magnesium may not be as toxic as the NAL benchmark of 0.064 mg/L might lead you to believe. There have been relatively few studies on the effect of magnesium on fish, except to show the unhealthy effects of magnesium deficiency. One toxicity study on the effect of magnesium sulfate on freshwater fish showed the combined chronic inhibition concentration (IC_{50}) and acute lethal concentration (LC_{50}) ranging from 4 mg/L to 1,250 mg/L. For comparison, another fish toxicity study showed the LC_{50} of copper sulfate to be 58 mg/L.

Instantaneous Max NAL = N/A
Annual Average NAL = 0.0.64 mg/L

So, you may be wondering why the NAL for magnesium is so low – and we are too. It appears the Industrial General Permit NAL of 0.064 mg/L comes from the benchmark value for magnesium in the Multi-Sector General Permit (MSGP). According to the 2008 MSGP Fact Sheet, the benchmark levels for pollutants were based on the EPA's National Recommended Water Quality Criteria list. For pollutants that were not on the criteria list, the *"EPA instead used a value equal to 3.18 times the MDL [method detection limit] for that pollutant in lieu of the water quality criterion."* Interestingly, magnesium is not on the EPA's water criterion list. So, according to the Fact Sheet, the *"EPA used other sources of data to determine the appropriate benchmark value."* Which other sources of data? They don't say. And doesn't the MDL vary based on the sensitivity of laboratory equipment? Interestingly, the EPA's Region III freshwater screening benchmark for magnesium is 82 mg/L – over 1,200 times higher than the MSGP's and IGP's benchmark of 0.064 mg/L.

Now, say your analytical results show an exceedance for magnesium. What to do? Source control is about the only option. Since most industrial uses of magnesium are magnesium salts and compounds, attempting to remove magnesium from your storm water runoff would be as easy as trying to remove sodium chloride (table salt) from your water. But even with the best source control, you'll probably still have magnesium NAL issues. There are many natural sources of magnesium in California, and the likelihood of natural background sources or ambient deposition contributing to your magnesium levels is pretty high.

What's the takeaway? At The Rain Events, we recommend that you don't sample for magnesium if you don't have to. The only Table 1 industry required to sample for magnesium is hazardous waste facilities. If you have an industrial source of magnesium and you need to choose an activity assessment analyte, try to choose something other than Total Magnesium if possible – for instance, for magnesium chloride, try using Specific Conductivity for your activity assessment. It doesn't have an NAL value, and it will detect the presence of magnesium chloride (and other minerals/salts) without putting your facility into a Level 1 or Level 2 situation. At The Rain Events, we're looking forward to the Water Board re-evaluating the magnesium NAL level during the next IGP renewal.

Iron

Instantaneous Max NAL = N/A
Annual Average NAL = 1.0 mg/L

In a past edition of The Rain Events, we saw that zinc is the fourth most commonly used metal. In this month's edition, we're going to talk about the *most* **commonly used metal, and the most common element found on Earth – iron. Because of it's widespread occurrence, it's also one of the toughest pollutants to trace back to industrial activity. Elevated iron levels could be coming from any number of sources – exposed metal equipment, soil erosion, industrial products and additives, or even from cast iron storm drain grates!**

Iron is an essential element for almost all living things, and is found in the human body in the range of 3 to 415 ppm. In excess, iron can be toxic, and overconsumption of iron-containing supplements is one of the more common toxicological causes of death in children under the age of six. Iron deficiency is a much more common problem, though, and if left untreated will develop into anemia.

In terms of mass, iron is the most abundant single element on Earth, and is thought to be the main component of the Earth's inner and outer cores, which together comprise about 35% of the Earth's mass. In its pure form, iron is a relatively soft, lustrous silver-gray metal. Fresh iron surfaces will quickly oxidize in normal air to give hydrated iron oxides, or common rust. Since the iron oxides occupy more volume than the metal itself, the rust will flake off and expose a fresh surface to oxidation. Because of the quick oxidation process, most of the iron found on the Earth's crust is in iron oxide minerals such as hematite, magnetite, and siderite.

As a metal, iron has been used since antiquity, most notably during the Roman era. Though pure iron is a relatively soft metal, it can be considerably strengthened by impurities, such as carbon. Adding a small proportion of carbon (from 0.002% to 2.1%) produces steel, which can be up to 1000 times harder than pure iron. Today, iron is the most widely used metal, accounting for over 90% of metal production worldwide. Most iron is alloyed with other elements to make steel or other iron alloys.

So, where might iron be coming from on an average industrial facility? Well, because iron is such a commonly used and naturally occurring element on Earth, it could be coming from any number of places. One obvious source would be an iron alloy metal that is exposed to the weather – such as steel equipment and parts. But iron could also come from erosion and sediment problems. We've all seen the black sludge commonly caused by standing water and organic material – the black (or brown) color and pungent odor is usually from iron sulfide.

But maybe a more important topic is not the possible iron sources at your facility, but whether those iron sources should be considered as industrial or non-industrial sources. If your SIC code doesn't require you to sample for iron, then Laurel Warddrip's advice on zinc should also apply towards iron. That is, if your industrial facility could conceivably apply for NEC coverage regarding your use of iron, there's a good chance that your sources of iron are non-industrial. For instance – steel buildings and forklifts that are well maintained could very well be sources of iron, but would both be allowed under NEC permit coverage, and hence are non-industrial sources. But if your facility processes metal products or stores them outdoors, then you'll have to analyze for iron in your storm water. On the other hand, if you've determined that there are industrial sources of iron on your site, it becomes a bit of an interesting situation. Because iron has such a widespread occurance, there probably are many non-industrial sources of iron on your facility that can significantly contribute to your iron levels. For example – even the cast iron storm drain grate could introduce iron and rust flakes directly into your sample bottle if you're not careful. Because of this, it's in your best interest to design a BMP strategy that targets all sources of iron on your facility, industrial or not. Control iron sources by keeping exposed metal inside rain-proof structures. Prevent pollution by painting, powder coating, or covering metal that is used or stored outdoors. Since sediment can be an iron source, control erosion on your site with vegetation, hydroseeding, erosion control, or similar measures. Use filtration technologies to reduce pollutant loads – depending on your site and how many iron sources you have, it could entail installing some compost socks, or possibly a passive or active treatment system.

finding the SOUrCeS

- Flocculant in wastewater and drinking water applications
- Additive in animal feeds
- Copper etchant in producing circuit boards
- Manufacturing inks and pigments
- Manufacturing fortified foods and supplements
- Treated wood

Podcast: The Science of Iron

Aluminium

Aluminium (or aluminum) is the most abundant metal in the Earth's crust. Yet surprisingly, it was not discovered or isolated in its elemental form until 1824. Because of its high chemical reactivity, native aluminium is extremely rare on Earth, and the metal must be smelted from ores, such as bauxite. But today, aluminium is an ubiquitous metal, used in many applications ranging from food and drink containers, pharmaceuticals, under-arm deodorant, transportation vehicles, construction, and many more. And many industrial facilities in California will recognize aluminium as one of the notorious IGP Table 2 pollutants with a NAL.

Pure aluminium is a silvery-white lustrous metal with great reflectivity properties. It is soft, nonmagnetic, and ductile. Two highly-prized properties of aluminium are its low density and its resistance to corrosion. The addition of even a small amount of other minerals or metals can greatly increase the strength of the aluminium alloy, without significantly increasing the density of the metal. Aluminium resists corrosion because of a phenomenon called passivation – where a protective coating (in this case, aluminium oxide) forms on the outside of the metal, preventing the inner metal from being corroded. The main ore used to produce aluminium is bauxite, a sedimentary rock with large reserves in Guinea, Australia, Vietnam, Jamaica, and Brazil.

So on an industrial site, where do high aluminium storm water numbers come from? While aluminium metal is widespread, there is some doubt as to how much dissolved aluminium it contributes to storm water runoff. Several studies have shown that the high aluminium numbers in certain California creeks and rivers occur upstream of anthropologic influences, and are directly linked to the amount of suspended sediment. Aluminium is the most common metal in the Earth's crust (it's a component of clay, feldspar, granite, and many other common minerals), so it stands to reason that natural sources may be the biggest contributor to high levels of aluminium in storm water runoff. This does not exempt your industrial facility from analyzing for aluminium, if Table 1 requires you to do so – but, because of its widespread natural occurrence, it may not be the best Section XI.B.6.c "indicator parameter," if you have a choice. Talk to your storm water consultant to see what your options are.

But if you have no choice in the matter and you're having aluminum issues, what to do? Well, we have a couple ideas. As mentioned earlier, there is a strong correlation between sediment load and aluminium levels. So, the first step in bringing your aluminium back under control should be to minimize your Total Suspended Solids, or TSS. This can be done by a variety of ways, but first and foremost by good housekeeping. A clean yard typically doesn't have high TSS numbers, which lowers your chance of high aluminium numbers. Also, any aluminium that actually comes from industrial sources is probably in some sort of particulate stage (aluminium grindings, clay dust, etc.), which can be controlled by sweeping.

But as we say at The Rain Events, the best BMP strategy is the one that uses a combination of source control, good housekeeping,

Instantaneous Max NAL = N/A
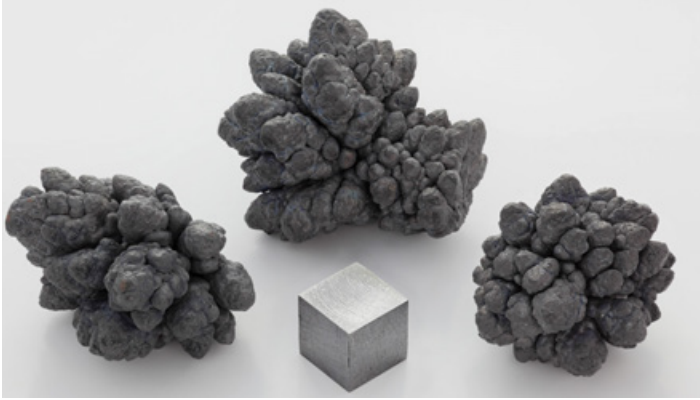### Annual Average NAL = 0.75 mg/L

and treatment. Sweeping is good, but for the best results, make sure you're hitting the other two points as well. Keep any industrial aluminium sources under cover (source control), and use some treatment BMPs. Treatment BMPs don't have to be expensive active treatment systems; remember, the majority of aluminium could be coming from natural sources, so focus your efforts on removing sediment from your storm water runoff. Use compost socks, vegetated swales, or erosion control BMPs first. If those don't work, then maybe it's time to look into a more aggressive treatment option.

Is pollution directly linked to industrial activity?

If you take a look at Table 2 in the Industrial General Permit, you'll notice that none of the elements listed are "man made," or synthetic chemicals. Is it possible that these elements could be causing pollution in rivers and streams without any input from anthropological sources? Well, yes and no. Yes, in that many of these elements are naturally occurring, and pollution due to natural occurrence is not only possible, but probable, as we saw with aluminium. Also, background concentrations of many of these pollutants have not been widely studied or documented, and the public tends to blame the most visible industry when an environmental problem crops up – so it's hard to say how much pollution is being contributed by industry as opposed to occurring naturally. But also no, in that by handling these pollutants as part of industrial operations, industry does contribute to pollution by upsetting the natural distribution of the elements. After all, what is pollution other than an imbalance in the distribution of naturally occurring elements? Petroleum in the form of crude oil is a natural occurrence underground – but when it ends up on the beach because of a spill, it's an imbalance in the natural distribution. Whether that imbalance is caused by man-made or natural sources, it still has the same devastating effect on Earth's delicate ecosystems.

Finding the Sources
- Aluminosilicates – kaolinites (clay soil, pottery, ceramics, etc) and zeolites (often used for water treatment)
- Aluminium Oxide (used in plastics, cosmetics, glassmaking, as an abrasive, in paint, and more)
- Aluminium Sulfates (used as a filler in paper, in fire extinguishers, and as a food additive)
- Aluminum chloride (petroleum refining, rubber facilities)

Lead

Instantaneous Max NAL = N/A
Annual Average NAL = 0.262 mg/L

We could call it the "assassin" pollutant. This very common element has had a hand in the demise of Ludwig von Beethoven, the Italian painter Michelangelo Caravaggio, Pope Clement II, and possibly even the Roman Empire itself. Lead, because of its relative softness and low melting point, has been widely used since antiquity – even as a sweetener in the form of lead acetate, which was popular during the Roman Empire.

Lead is a heavy metal that is denser than most common materials. It is soft and malleable, and has a relatively low melting point. In its untarnished state, lead is a silvery metal with a hint of blue, but quickly tarnishes to a familiar dull gray color. These properties, along with its relative abundance and low cost, resulted in a widespread use in plumbing, bullets and shot, weights, metal alloys, paint, and even gasoline.

Lead is a poisonous metal with no known biological role, but nonetheless is the third most prevalent heavy metal in the human body, behind iron and zinc. Unlike other elements which are easily excreted from the body, lead bioaccumulates in soft tissues and bones, and is particularly dangerous to children.

So on an industrial site, where would lead be coming from? Well, an examination of the public storm water data on SMARTs reveals that the SIC code group with the highest numbers is 5093 and 5015 – scrap and waste materials, and wrecking yards, respectively. Makes sense. But other sources of lead could be facilities that manufacture or handle batteries, marine and boat yards, and metal foundries. Facilities listed in Table 1 of the IGP that are required to sample for lead include fertilizer and pesticide facilities (SIC 287X), hazardous waste facilities (SIC 4953), water transportation (SIC 44XX), dismantling and wrecking yards (SIC 5015), and scrap and waste material facilities (SIC 5093). It's pretty obvious that lead could be coming from scrap or wrecking activities, but fertilizer and pesticides? Well, some of the materials that are used to make the fertilizer could be contaminated with lead – like the steel mill flue dust used to supply iron in some fertilizers. Lead is also used in marine operations and watercraft – like lead ballast weights, or red lead and white lead marine primer. Another potential source of lead

to keep in mind are mining facilities, or industries that use mining byproducts such as "chat."

OK, so if a facility has an issue with high lead numbers, what can be done to bring the results back under the NALs? As always, the best way to keep lead out of storm water is to, well, keep it out of storm water. This is source control – preventing exposure, keeping lead-containing materials under cover, and containing any contaminated dust. Also, don't forget your good housekeeping! But most people who have high lead numbers are likely beyond the help of source control and good housekeeping. Maybe there are high background levels of lead in the soil, or leftover from past industrial activity. So, what are the options for removing lead from storm water runoff? Fortunately, lead tends to precipitate out of solution, so dissolved lead in storm water isn't very common. A couple effective ways to remove lead from storm water runoff include using active or passive treatment systems that have been specifically engineered to remove heavy metals, and bioswales planted with lead-tolerant hyperaccumulator varieties. Because lead is typically in particulate form, sediment control BMPs like compost filter socks can also be effective, especially for facilities that aren't fighting particularly high numbers.

Hyperaccumulators. What are they?

We've all heard of bioswales and bioaccumulation – using plants and microbes to emove or reduce pollutants in an environmentally friendly way. But hyperaccumulators take bioswales to the next level. There are specific species of plants that have the ability to grow in soils with very high concentrations of heavy metals, and absorb extremely large amounts of metals. Compared to non-hyperaccumulating species, hyperaccumulator roots extract metals from the soil at a higher rate, transfer it more quickly to their shots, and store large amounts in their leaves and roots. Some of these species are so efficient at extracting metals that they can be used in phytomining – mining metals from soil by harvesting the hyperaccumulating plants. A list of hyperaccumulators can be found here:

https://en.wikipedia.org/wiki/List_of_hyperaccumulators

- Ammunition and bullet manufacturing
- Weights and ballast
- Architectural lead, such as in sound proofing sheets
- Lead-acid batteries
- Shielding applications to protect from radiation
- Solder for electronics
- As a component in PVC coatings (electrical cords, etc)
- Lead glass

BOD and COD

While there might be many pollutants on the IGP Table 2 list that aren't well understood, BOD and COD take the cake. They both measure the demand for oxygen, right? So what's the difference? Does it matter which one you use? And when the laboratory results come back high, how can you lower your numbers? These are complicated questions, but we're going to attempt to give some answers.

First, is there actually a real-world difference between COD and BOD? COD stands for chemical oxygen demand, and BOD for biochemical oxygen demand (sometimes also called biological oxygen demand). BOD is a measurement of the amount of oxygen required by bacteria while stabilizing decomposable organic matter in water under aerobic conditions. COD is the measurement of the total quantity of oxygen needed to completely oxidize all organic matter in the water to carbon dioxide and water. Both of these parameters report the same thing – the amount of oxygen (expressed in milligrams per liter) that is consumed in the sample during the analytical procedure. Higher amounts of organic materials will require more oxygen to oxidize, and will result in a higher analytical result. But even though we're discussing BOD and COD in our industrial pollutant series, it's important to know that BOD and COD are not pollutants – they are indicators of the presence of pollutants.

The difference between BOD and COD is the analytical procedure. The BOD test involves introducing a bacteria culture into the sample, and measuring the amount of oxygen consumed by organic compounds as they are oxidized by the bacteria. The BOD analytical procedure takes 5 days. COD uses a strong oxidizer (usually potassium dichromate) to oxidize all of the organic compounds in a sample, while recording the amount of oxygen consumed during the oxidation process. The analytical process for COD is much shorter than BOD, usually lasting around three hours. Because potassium dichromate is a faster and more aggressive oxidizer than bacteria, the COD analysis will return higher numbers than the BOD analysis, especially where there are higher levels of biologically-resistant compounds.

So, which test is more applicable for your facility? It all depends on what pollutants and compounds you are testing for. If the expected pollutants are good food sources for bacteria (i.e., oils, compost, food waste, sewage), then the BOD analysis would be a good fit. The COD analysis should be used when the main expected pollutants are toxic to or are not as easily oxidized by bacteria (i.e., volatile organic compounds, lignans, tannins, etc.)

What could cause elevated BOD and COD levels on a typical industrial facility, and how can you prevent elevated BOD and COD levels? Remember, oxidizing organic materials sap the dissolved oxygen out of your storm water. If there are any foreign materials in your storm water runoff, you're probably going to have high BOD or COD results. But beware – some elements can give a false positive. For instance, ammonia and phosphates can feed bacteria and cause a high BOD result. Of course, ammonia and phosphorous have their own analytical methods – so if your industrial processes involve

Annual Average NAL for BOD = 30 mg/L
Annual Average NAL for COD = 120 mg/L

either of those chemicals, use the specific analytical method to test for that chemical, not BOD or COD. And keep in mind that while a high sediment load can increase oxygen demand, BOD and COD are not necessarily linked to TSS. We've seen outfalls with TSS numbers in the 40s-50s that have COD results over 400.

The best way to prevent high BOD or COD numbers is to prevent your industrial materials from coming in contact with your storm water runoff. Practice good housekeeping, and store materials and equipment under cover wherever possible. Make sure any spills are promptly cleaned up. Treatment techniques will vary depending on what pollutant is causing your elevated numbers, but trying to lower BOD and COD numbers by treatment can be tricky. Most of the time, it's best to focus on keeping the pollutants out of your storm water, rather than trying to remove it once it's already been introduced. But, there are a few advanced treatment systems that can help reduce BOD and COD numbers.

Helpful Tip

The BOD and COD analytical tests detect the presence of organic matter in your sample – which, as you may have gathered from the other articles, includes a huge range of chemicals and materials. So, before specifying COD or BOD as an "activity assessment" test in keeping with IGP Section XI.B.6.c, make sure there is not a more specific test you can use. For instance, instead of using BOD to test for antifreeze, try using the ethylene glycol analysis (EPA Method 8015.B). And it's always a good idea to contact your lab for advice.

- Green waste
- Garbage and recyclable materials
- Petroleum products
- Vehicle fluids (ethylene glycol, hydraulic fluid, etc.)
- Sugars and alcohols

Ammonia

Instantaneous Max NAL = N/A
Annual Average NAL = 2.14 mg/L

You probably recognize the smell – the acrid tingle of smelling salts, or the bracing stench of a vault toilet in need of servicing. That familiar smell is ammonia, a toxic but necessary component of the food cycle. Without ammonia, plants wouldn't grow; and without plants, well, you get the idea. But, ammonia is also toxic to mammals and especially aquatic organisms, and an overabundance of ammonia in one's bloodstream can be fatal. In this edition of The Rain Events, we're going to take a step back from the "common" storm water pollutants, and look at a pollutant which may be a little less common.

Ammonia is a compound of nitrogen and hydrogen with the formula of NH_3. It is a colorless gas with a recognizable pungent smell. Although very common in nature as a waste product and widely used as a chemical, ammonia is both caustic and hazardous in concentrated form. Ammonia gas is very soluble in water, and aqueous solutions of ammonia are commonly used for household cleaning tasks. However, the largest use of ammonia (up to 88% in 2014) is in fertilizers – either in salt form, solutions, or anhydrously. Roughly a third of agricultural nitrogen applied in the United States is in the form of anhydrous (literally: "without water") ammonia.

However, in this edition of our Understanding Pollutants series, we're going to do something we haven't done yet – talk about a different chemical that can change into ammonia. Because ammonia is so toxic, our liver automatically converts it into a safer substance – urea. Urea is an organic compound with the formula $CO(NH_2)_2$. Urea is formed by the liver when two ammonia molecules are combined with a carbon dioxide molecule. The urea is eventually excreted by the kidneys in urine, and once outside the body, bacteria breaks the urea back down into ammonia (hence the smell).

But aside from a sewer leak, where might ammonia come from on an industrial facility? Table 1 in the Industrial General Permit only lists two industries that are required to sample for ammonia – hazardous waste facilities, and air transportation facilities (potentially; see footnote 16 on page 42 of the IGP). It's probably not a surprise that there could be ammonia at a hazardous waste facility, but an airport? Well, that's where our second chemical comes in. Up until very recently, urea was used as a pavement deicer at many airports. However, because of its propensity to decompose into ammonia, the EPA has prohibited the use of urea at most airports in the United States.

The largest use of ammonia and urea is in fertilizer, but there are many other potential sources of ammonia at an industrial facility – look for ammonia and urea to be used in laboratories, in cleaning chemicals, in refrigeration systems, in automotive systems (as Diesel Exhaust Fluid), and in pharmaceuticals.

So, how can ammonia be removed from storm water runoff? Surprisingly, it may not be as hard as you think. Of course, as we say in every issue, the best way to remove a pollutant from storm water is to not let it come in contact with storm water in the first place – use good housekeeping and containment to keep your industrial materials and waste out of your storm water runoff. But when it comes to treatment, there are a variety of ways to effectively remove ammonia from storm water runoff: amended compost socks, active treatment systems, passive treatment systems, bioswales, and more.

To sum it up, ammonia and urea are not among the most commonly used chemicals in the industrial world, but ammonia is listed in Table 2 with a Numeric Action Level. There are only two industries required by Table 1 to sample for ammonia, but remember, if your facility uses ammonia or urea products, you'll probably have to add ammonia to your list of industrial activity indicator parameters.

- In manufacturing plywood – urea-formaldehyde resins
- In explosives – urea nitrate, and in nitrocellulose explosives
- In automobiles as Diesel Exhaust Fluid
- In the laboratory – virtually all synthetic nitrogen compounds are derived from ammonia, including nitric acid, nitric oxide, phenol, and urea.
- In pharmaceuticals (urea containing creams, tooth whitening products)
- In food (baker's ammonia, urea for browning pretzels)
- As a cleanser – ammonium hydroxide.
- As a refrigerant in industrial refrigeration and hockey rinks (usually anhydrous ammonia)
- In woodworking (ammonia fuming)

Nitrates and Nitrites. If you're like us, you probably reread that first sentence thinking we wrote the same word twice. Besides an "a" and an "i", what is the difference between nitrates and nitrites, and why are they tested as "N"?

So first, let's find out what this pollutant is. "Nitrite" refers to the nitrite ion, which has the chemical formula NO_2. One of its more common forms is sodium nitrite, or $NaNO_2$. Sodium nitrite is a salt that is commonly used in the food industry to preserve foods and prevent botulism. When dissolved in water, nitrites will rapidly convert into nitrates. "Nitrate" also refers to an ion, and has the chemical formula NO_3. Nitrates are also commonly found in salt form, the most common of which being potassium nitrate, or saltpeter. When analyzing for nitrogen in storm water runoff, the results for both nitrate and nitrite ions are added together and reported as Nitrogen - hence the name Nitrate + Nitrite Nitrogen, or N+N as N.

OK, so we know what nitrates and nitrites are. But most industrial facilities won't be using sodium nitrite or potassium nitrate – so where do high N+N numbers come from? Nitrates and nitrites are both commonly found in fertilizers, wastewater, and waste from animal feedlots. So, if your industrial facility handles any of those materials, your storm water could potentially contain traces of nitrates or nitrites.

Nitrates can also be used as an oxidizing agent, and is sometimes used in glass, metal, and plastic production. And remember that even if nitrites or nitrates are used indoors, they can still impact storm water by escaping through roof vents in particle (such as fertilizer dust) or gas (such as fumes from oxidizing reactions) forms.

Assuming that your facility has nitrate or nitrite sources on-site, what are some ways that you can prevent them from getting into your storm water runoff? Well, a good BMP strategy uses a combination of source reduction, pollution prevention, and treatment. Since nitrates and nitrites are not easy to remove from storm water runoff, the best approach is to keep it out of the storm water in the first place. The first thing you'll want to consider is whether the nitrate-containing materials at your facility are necessary. Is there another non-nitrate based material you can use that will have the same effect? This is source reduction. But in some cases, such as animal feedlots, nitrates are inescapable since they occur naturally in the waste products. Secondly, practice good pollution prevention strategies, such as good housekeeping bioretention pond, and try to minimize your storm water discharges as much as possible. Make sure fertilizers are applied correctly and your irrigation program is not creating a nitrate-charged runoff situation. Keep in mind that neglecting source reduction and pollution prevention strategies will create a problem that is not easily treatable. However, if you have reduced your pollutant source as much as possible and have good pollution prevention measures in place, treatment BMPs can help lower your numbers even further. Most treatment options will not completely remove nitrates from your storm water – depending on

Instantaneous Max NAL = N/A
Annual Average NAL = 0.68 mg/L as N

how much money you spend, you should only expect between 25-90% reduction. The more expensive treatment systems may be more towards the 90% side of the spectrum, while less expensive options may remove less than 50% of the pollutant.

To sum up, nitrates and nitrites are pollutants that primarily come from fertilizers and animal feedlots, though they can also be produced by a few other industrial activities. Nitrates are difficult to remove from storm water runoff, so your best strategy is to keep nitrate- or nitrite-containing materials away from storm water.

Treatment Options

1. The most cost-effective treatment option would be a drain insert or compost sock that has been formulated to remove nutrients (phosphates and nitrates/nitrites). Expect less than 50% removal rate.

2. Engineered wetlands or bio retention ponds are probably the most effective treatment strategy, but can be cost and space prohibitive. Expect up to 90% removal.

3. Floating treatment wetlands are a great alternative to Option #2. These rubber "islands" grow native plants hydroponically in your retention basin, and the plant roots effectively remove pollutants. Expect up to 90% removal.

finding the S O Ur Ce S

- Using or producing fertilizers
- Animal feedlot operations
- Using or producing explosives
- Wastewater treatment plants
- Metal finishing
- Concrete manufacturing
- Wood finishing
- Leather tanning

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Ammonia

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