

# **Illicit and Legal Drugs in Oregon Wastewaters**

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# The 'Other'

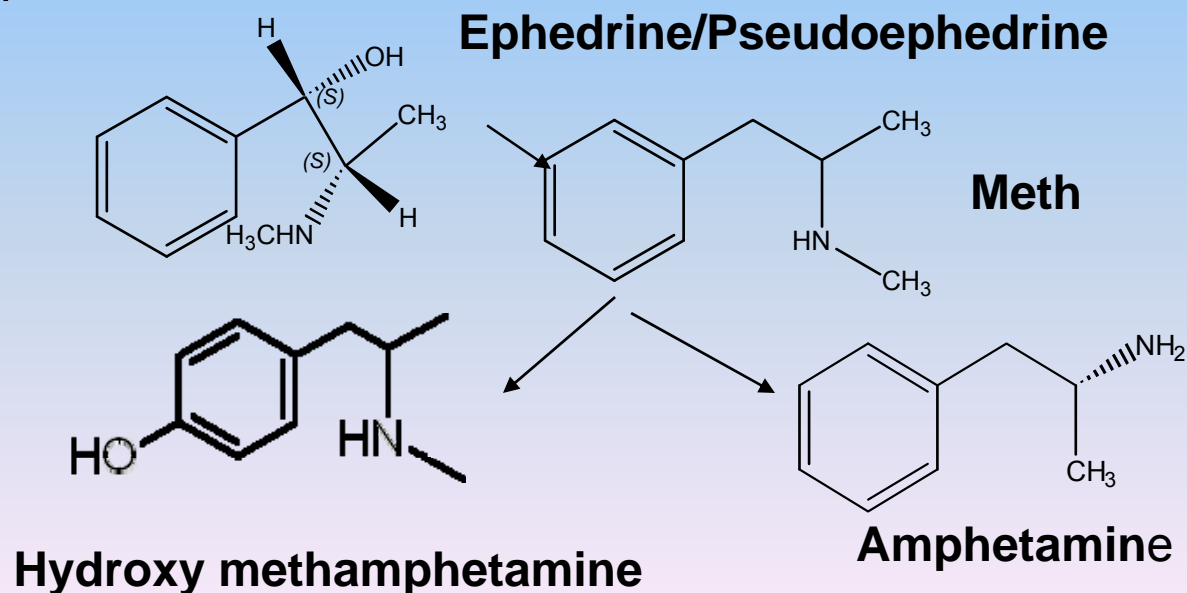
## Pharmaceuticals...Illicit Drugs

- No sales data- only rough estimates
- Taken in mg quantities per dose
- 'Designed' for biological effects
- Acute and chronic effects known for humans, not known for aquatic and other organisms

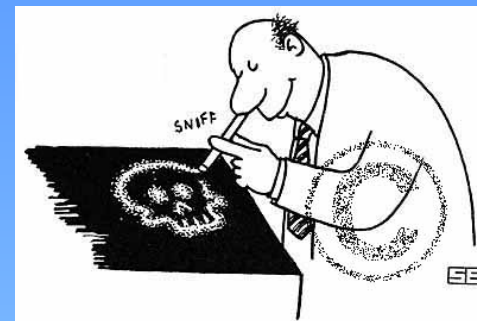
# Methamphetamine



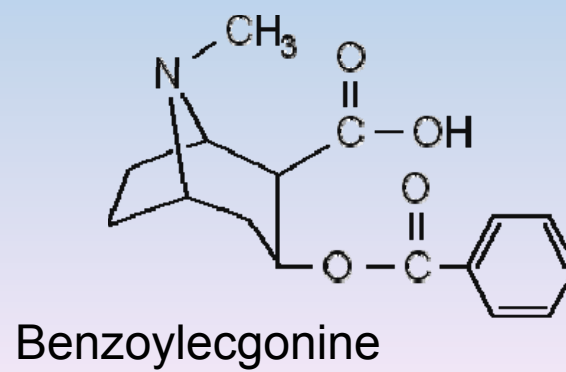
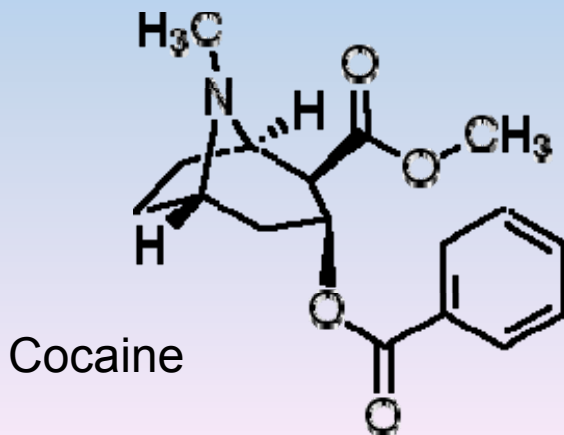
- synthesized in Japan in 1940s
- ‘mother’ of all dopamine releasers\* → illegal (+)-D/(-)-L legal in asthma inhalant and Parkinson’s disease
- More widely used than cocaine or heroin on west coast
- Clandestine manufacturing in US (80s and 90s) reduced by 2003 laws controlling ephedrine/pseudoephedrine
- largest source now importation from Mexico



# Cocaine



- One of the oldest drugs (> 100 yrs)
- > 200 deaths in Oregon and Washington
- More prevalent in urban and affluent areas
- Episodic or 'recreational' use
- Cocaine & metabolites excreted (45-60%)
  - Cocaine (1-3%)
  - Benzoyllecgonine (20-90%)



# Other Drugs on the Increase

## New(er)

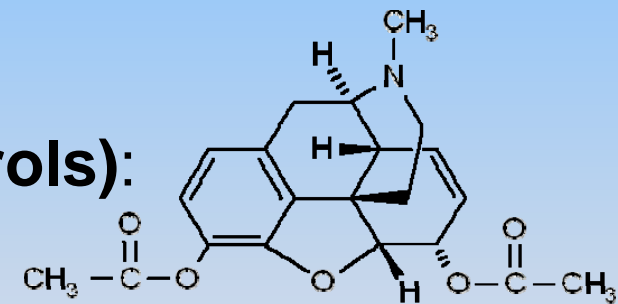
- Rave: MDMA (Ecstasy), MDA

## Old, Still Around, & Increasing

- Heroin
- PCP (Phencyclidine)
- LSD (2-oxo-hydroxy-LSD)
- Marijuana

## Prescription Opiates (Positive Controls):

- Hydrocodone
- Oxycodone
- Methadone: increase in deaths
  - 2/3 for pain control, 1/3 for heroin treatment



heroin

# Research on 2 Fronts

## 1. New tool for drug epidemiology<sup>a</sup>

- a) To provide quantitative 'hard' data (vs. street 'buys' and forensic data from mortality cases, workplace drug tests)
- b) To reduce bias
  - i. Mortality data – biased toward more lethal drugs & data lags behind entrance of drugs onto 'market'
  - ii. Emergency room reports – decline with time
  - iii. Poison control center calls - decline with time

## 2. Environmental fate and effects<sup>b</sup>

- a) Occurrence in surface/drinking waters, fate, biological effects, & treatability

<sup>a</sup> the focus of this talk

<sup>b</sup> work by others in literature

# Raw Wastewater Influent

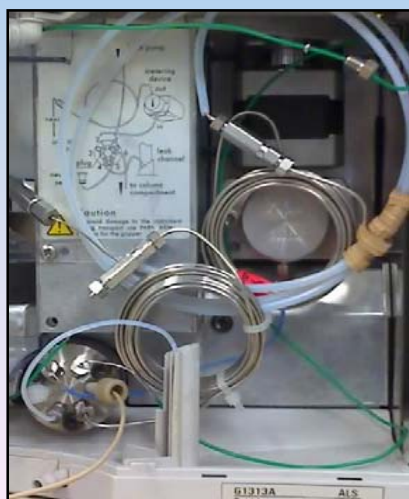
- Sampling site 'closest to the urinal or toilet'
- Conveniently 'focused' and sampled at a central location
- Least amount of degradation compared to effluent
- Others have found illicit drugs in municipal wastewaters<sup>a</sup>
- Preserves privacy of individuals (important in U.S.)
- Samples collected daily/monthly
- Known flows for calculation of loads

<sup>a</sup>Hummel (2006)  
Castiglioni (2006)  
Huerta-Fontela (2007)  
Bones (2007)  
Postigo (2008)



# Analytical Considerations

- 24 hr, flow-normalized (ideally) composites of raw WWTP influent
- HDPE bottles, ideally frozen immediately or acid preserved
- Centrifuge then large-volume, direct injection (1.8 mL)<sup>1</sup> – no SPE
- LC-MS/MS with matched stable-isotope labeled internal standards



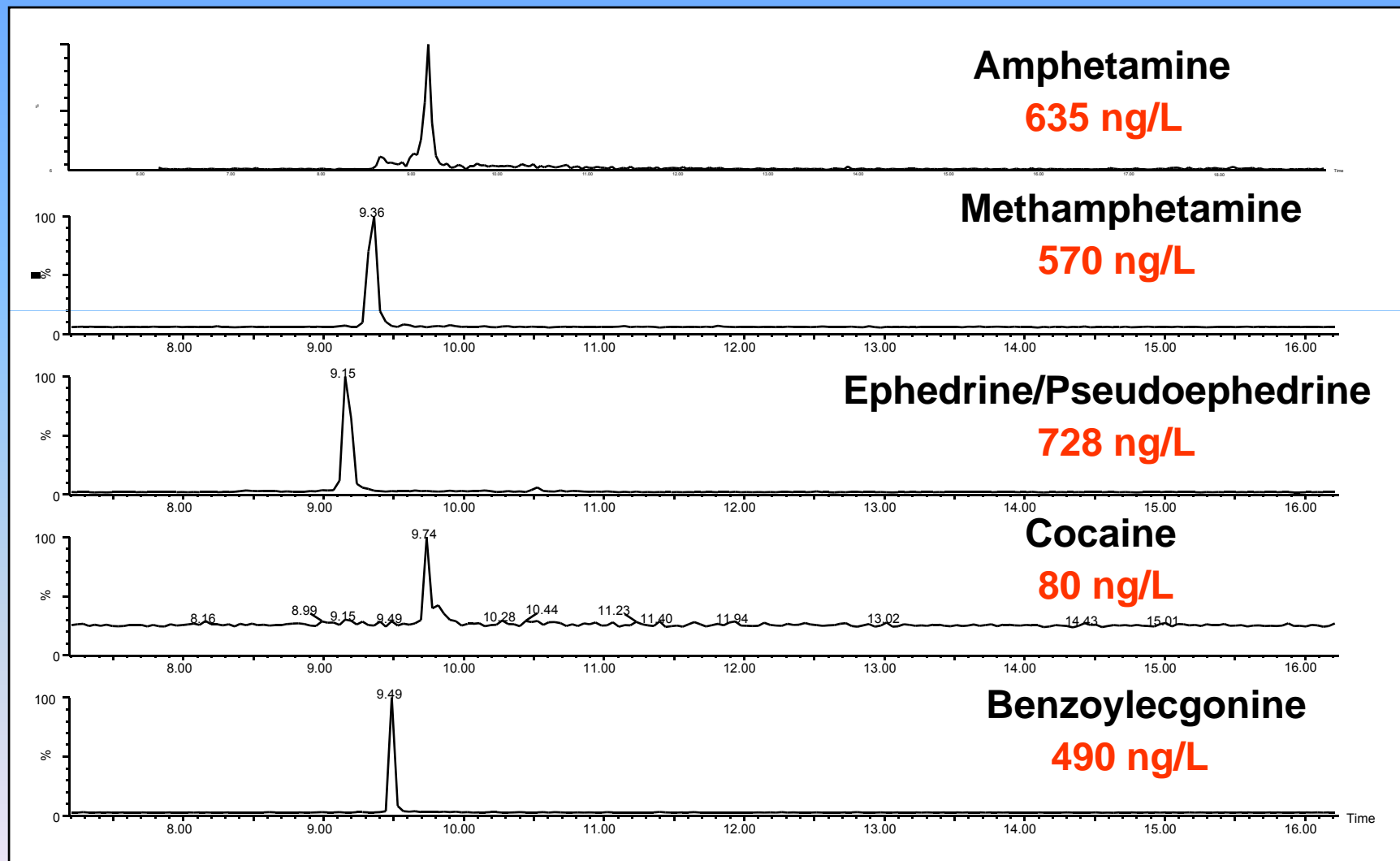
- LOQ = 5-20 ng/L
- Precision = < 10%
- Matrix effects addressed by internal standards

<sup>1</sup>Chiaia et al., ES&T, 2008





# Illicit Drugs in Raw Influent



# Estimating Per Capita Loads

$$\left[ \frac{\text{ng drug}}{\text{L}} \right] \times \text{total flow influent} \left[ \frac{\text{L}}{\text{day}} \right] \times \left[ \frac{1}{\text{population}} \right] = \left[ \frac{\text{ng}}{\text{day} \bullet \text{person}} \right]$$

- Total flow available from WWTP
- Assumes constant (static) population
- Attempts to back calculate number of users assumes steady state conditions
  - excretion, fraction of drug excreted, mass of individual doses, purity, and number of doses<sup>a,b</sup>

<sup>a</sup>Rieckermann, J. 2008, 11<sup>th</sup> Intl Conf. Urban Drainage, Edinburgh Scotland

<sup>b</sup>Winker et al., 2008, Sci. Tot. Environ.

# Limited Illicit Drug Data for US<sup>a</sup>

	Wastewater Treatment Plant						
	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6	Plant 7
Region Located	South	West	North East	North East	South	West	Midwest
Population	350,000	841,000	27,300	39,800	48,953	54,890	650,000
Average Flow (L/d)	1.87E+08	7.08E+14	1.70E+07	2.15E+07	3.78E+07	4.96E+07	1.87E+14
<b>Analyte</b>	<b>Index Load</b>	<b>Index Load</b>	<b>Index Load</b>	<b>Index Load</b>	<b>Index Load</b>	<b>Index Load</b>	<b>Index Load</b>
Methamphetamine	0.49 ± 0.04	0.80 ± 0.10	NR	0.0050 ± 0.0004	0.71 ± 0.06	0.13 ± 0.01	NR
Amphetamine	0.12 ± 0.02	0.20 ± 0.03	0.050 ± 0.01	0.06 ± 0.01	0.19 ± 0.03	0.08 ± 0.01	0.06 ± 0.01
Ephedrine	1.80 ± 0.20	2.90 ± 0.40	0.80 ± .10	0.80 ± 0.1	2.08 ± 0.25	0.52 ± 0.06	0.60 ± 0.08
Cocaine	0.19 ± 0.02	0.10 ± 0.01	0.040 ± 0.004	0.040 ± 0.004	0.06 ± 0.01	0.009 ± 0.001	0.40 ± 0.04
Benzoylcegonine	1.50 ± 0.20	0.90 ± 0.10	0.20 ± 0.03	0.30 ± 0.04	0.32 ± 0.04	0.10 ± 0.013	0.80 ± 0.10
Norcocaine	0.008 ± 0.002	0.004 ± 0.001	NR	NR	0.003 ± 0.001	NR	0.026 ± 0.007
Norbenzoylcegonine	0.09 ± 0.01	0.07 ± 0.01	0.008 ± 0.001	0.010 ± 0.002	0.013 ± 0.002	NR	0.028 ± 0.004
Hydrocodone	0.070 ± 0.010	0.090 ± 0.020	0.008 ± 0.002	0.007 ± 0.001	0.057 ± 0.01	0.012 ± 0.002	0.015 ± 0.003
Oxycodone	0.040 ± 0.010	0.090 ± 0.010	0.040 ± 0.005	0.008 ± 0.001	0.17 ± 0.02	0.026 ± 0.003	0.040 ± 0.005
Methadone	0.018 ± 0.001	0.030 ± 0.002	0.0030 ± 0.0002	0.0090 ± 0.0007	0.048 ± 0.004	0.012 ± 0.001	0.023 ± 0.002
MDA	0.003 ± 0.001	0.0010 ± 0.0002	0.005 ± 0.001	NR	NR	NR	NR
MDMA	0.040 ± 0.010	0.012 ± 0.002	0.0020 ± 0.0002	NR	0.007 ± 0.001	ND	0.0017 ± 0.0002
MDEA	NR	NR	NR	NR	NR	NR	NR
MBDB	NR	NR	NR	NR	NR	NR	NR
Ketamine	NR	0.007 ± 0.001	NR	NR	NR	NR	NR
Norketamine	NR	NR	NR	NR	NR	NR	NR
2-Oxo-3-hydroxy-LSD	NR	NR	NR	NR	NR	NR	NR
LSD	NR	NR	NR	NR	NR	NR	NR
PCP	0.0020 ± 0.0004	NR	NR	NR	NR	NR	NR
Flunitrazepam	NR	NR	NR	NR	NR	NR	NR
Cotinine	1.03 ± 0.10	1.10 ± 0.10	0.08 ± 0.01	0.20 ± 0.02	1.7 ± 0.17	0.16 ± 0.02	0.60 ± 0.06
Caffeine	31 ± 2	50 ± 3	24 ± 2	22 ± 1	29 ± 1.74	10 ± 1	15 ± 1
Creatinine	120 ± 11	620 ± 30	460 ± 40	590 ± 50	180 ± 16.2	337 ± 30	240 ± 20

<sup>a</sup>Chiaia et al., Environ. Sci. Technol., 2008, 42, 8841

Regions as defined on website maintained by the United States Drug Enforcement Administration

NR = not reported because either not detected or concentrations less than the lower limits of quantification

# Spatial Trends at Regional Scale

- Single-day 'snapshot' campaign to map drug excretion (use) in the State of Oregon
- Single 24 hr composite\* samples collected mid-week in March\*\* during low flow period \*\*\* across Oregon
- Acid preserved, overnight shipment
- 96 out of 130 'invited' wastewater treatment facilities participated and covers ~66% of state population potentially captured
- Voluntary participation – some known areas with meth did not participate (form of bias)
- GIS used to create maps of drug excretion (use) and to examine spatial relations and relations to conventional drug indicators (in progress)

\* >90% flow-proportional, 10% time-weighted

\*\* avoided 'elk' season

\*\*\* first attempt to sample = flooding featured on national news

# Implications: Surface Water

- Most observations of illicit drugs in Europe
- Illicit drug removal during wastewater treatment varies by drug and treatment regime<sup>a</sup>
  - 50 to 93% for cotinine to 80-90% for cocaine/benzoylecgonine
  - 38 to 50% for MDMA and Meth
- Surface water concentrations typically  $\ll$  1000 ng/L with many reported values  $<$  50 ng/L<sup>b</sup>
- Acute risk to aquatic organisms likely low but behavioral/developmental toxicity?

<sup>a</sup>Postigo et al., 2008; Huerta-Fontela et al., 2007

<sup>b</sup>Zuccato et al., 2008

# Implications for Drinking Water<sup>a</sup>

- Removal during drinking water treatment
  - Prechlorination, flocculation, and sand filtration removed amphetamine stimulants
  - Ozone removed 76% caffeine
  - GAC removed cocaine (100%), MDMA (88%), benzoylecgonine (72%), and cotinine (63%)
  - Postchlorination eliminated nicotine
  - Only caffeine (90% removal), cotinine (74% removal), and benzoylecgonine (90% removal) persisted through drinking water treatment

<sup>a</sup>Huerta-Fontela et al. (2008)

# Perspective on Risk from Drinking Water

- Benzoylecgonine (BZE, metabolite) 30 x less toxic than cocaine
- Drinking water concentrations 45-130 ng/L over 70 yrs & 2 L/day = 6 mg BZE
- = 20 x lower than single street dose (100 mg) cocaine

# Conclusions

- Raw wastewater analyses indicates occurrence of cocaine and meth entering wastewater treatment facilities across the state
- Loads of illicit drugs (mg/person/day) used to estimate no. of users, temporal and spatial trends
- Literature data indicates range of removal during wastewater treatment (50-90+%)
- Limited data from literature indicates 100% removal of most substances except benzoylecgonine, caffeine, and cotinine
- Acute toxicity likely low for aquatic organisms but developmental/behavioral toxicity should be investigated
- Risk to human from residues in drinking water likely low



# Acknowledgments

- Oregon Health Sciences University Medical Research Fund
- Doug Martin (Agilent)
- Greg Witkop (Waters)
- Guy Allen (WWTP Operator)
- Alsea Geospatial Inc.